Reduction the Oxygen Content of the Coconut Shell Char Produced by Using Simple Pyrolysis Method

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Abstract. Pyrolysis is known as a heating method which can decompose biomass to be the char in the absence of oxygen by providing carrier gas into the furnace. In practice, not all laboratories are equipped with carrier gas. Especially in large scale production, high cost production become the main problem. In this study, we propose simple pyrolysis method without carrier gas to produce coconut shell char as one of the biomass sources. The purpose of this research was to produce the coconut shell char using the simple pyrolysis method to obtain high purity carbon with low oxygen content. Experimental studies focused on the additional treatments complement to the pyrolysis process of the coconut shell. These treatments are proposed to minimize the oxygen content in the char. In this case, the oxygen bind to the carbon can reduce the carbon pore size. The produced coconut shell char were characterized by employing SEM-EDX, XRD, FTIR and Nitrogen Isotherm Physisorption. It was found that the treatments potential to reduce the oxygen content, contaminant and also increase the carbon yield.

1. Introduction

The use of biomass as renewable carbon source that is abundantly available in many country has been attractive for many industry such as purification, pharmaceutical, food industry, catalytic supports and energy devices [1-2]. In this case, the presence of low cost technology processing will be more advantageous, especially for large scale manufacturing. Here, we introduce a simple pyrolysis by means of conventional heating method using the muffle furnace with no carrier gas to decompose the biomass by burning off its chemical substance to be char for a longer time. The char can be converted to higher value products that can be used as activated carbon.

Coconut shell is one of the popular biomass with has high carbon yield and low ash [3-4]. Coconut shell has a higher volatile content that can produces carbon with large pore volume. Many literature report the experimental study of the coconut shell char by using pyrolysis with the carrier gas [5-8]. Unfortunately, according to our experience, the char produced with no carrier gas have low carbon yield and high oxygen content. To solve this problem, we propose the physicochemical treatments supplementary to the simple pyrolysis method. The physicochemical treatments consist of pre-treatment by microwave heating and acid (HCl) immersing and post treatment by acid (HCl re-immersing). As far as we know, we did not found similar treatment to reduce the oxygen content.
Meanwhile, highly oxygen content can reduce the char pore size and might degrade the char quality [9].

2. Experimental
2.1 Synthesis of coconut shell char
Coconut shell was taken from traditional market of Dayeuh Kolot, Bandung, Indonesia. The coconut shell were selected by the dark-shell color. The shell were cleaned by eliminate its fibrous and then crushed and sieve into equal size with range of 1-3 mm using hummer mill machine. After the preparation of coconut shell completed, all the sample were put into a muffle furnace (Carbolite, type 3216) and subsequently carbonized at 500°C with a heating rate of 10°C/min and held on for 2 hour. We varied four kind of the treatments as listed in Table 1.

Table 1. Physicochemical treatments to the coconut shell used in the simple pyrolysis.

| Sample | Pre-treatment | Post-treatment |
|--------|---------------|----------------|
| C-1    | -             | -              |
| C-2    | Microwave (1 kW) for 1 hour | - |
| C-3    | Immerse in HCl 1 M for 12 hour, heating at 120°C for 1 hour and microwave (1 kW) for 1 hour | - |
| C-4    | Immerse in HCl 1 M for 12 hour, heating at 120°C for 1 hour and microwave (1 kW) for 1 hour | Immerse in HCl 1 M for 12 hour and heating at 120°C for 1 hour |

2.2 Characterization of coconut shell char
The resulted coconut shell char were characterized by employing Hitachi SU-3500 Scanning Electron Microscopy (SEM) to observe its surface morphology. The elemental composition of the char are analyzed with similar apparatus by using Energy Dispersive X-ray (EDX) spectroscopy method. FTIR spectroscopy (Thermoscientific Nicolet iS-10) was carried out to characterize the functional chemical groups of the char. X-ray diffractogram were obtained by Rigaku Smartlab (CuKα, λ = 0.154 nm) to investigate the char structure. Porous analyzing was used Nitrogen Isotherm Physisorption method (Quantachrome Autosorb Automated Gas Sorption). The surface area (SBET) was determined from its Nitrogen Isotherm Physisorption data using Brunauer-Emmett-Teller (BET) method. Total pore volume (VT) was defined as the volume of adsorbed N2 at a relative pressure of P/P0 = 0.99 [10]. The micropore volume (Vμ) was determined with the Dubinine-Radushkevich (DR) equation and the mesopore volume (Vm) was calculated by subtracting micropore volume from the total pore volume [11]. The pore size distribution of the char were obtained from Barrett, Joyner and Halenda (BJH method).

3. Results
Figure 1 represent SEM images of the produced coconut shell char. The chemical composition of the SEM images were determined using EDX as shown in Table 2. The char with no additional treatment (sample C-1) contains small bright particles among the porous carbon as given in Figure 1.(a). These particles is came from the impurity of K atom about 25.2 % which is already exists in the as-received coconut shell (Table 2). Figure 1.(b) demonstrated the larger and more dense carbon particle of sample C-2 compared to the sample C-1. The more dense carbon particle is consistent to the lower oxygen content. The porous structure seen in the sample C-3, as illustrated in in Figure 1.(c) is more opened up than that in sample C-4 (Figure 1.(d)). From the Table 1, it clear evidenced that the acid pre-treatment of sample C-2 and C-3 are successfully eliminate the K atom, while the acid post-treated of the sample C-4 can increase the carbon content and simultaneously reduce the oxygen content. The mechanism of the K atom elimination in the sample C-2 and C-3 might be analogous to the dissolution process of the mineral in the acid solution. The K atom which is easily trapped in the cellulose or lignin of the coconut shell would react with acids to form the potassium salts and water. The sample
C-4 which is treated by microwave might have a homogeneous heating so that the carbon loss and oxidation process is decrease along the process.

![Figure 1](image1.png)

**Figure 1.** SEM images of coconut shell char: (a) sample C-1, (b) sample C-2, (c) sample C-3, and (d) sample C-4.

**Table 2.** Atomic composition of the coconut shell char determined using EDX.

| Sample | C (%) | O (%) | K (%) |
|--------|-------|-------|-------|
| C-1    | 49.3  | 25.5  | 25.2  |
| C-2    | 52.0  | 15.0  | 33.0  |
| C-3    | 78.0  | 22.0  | 0     |
| C-4    | 81    | 19    | 0     |
Figure 2. XRD analysis of coconut shell char: (a) sample C-1, (b) sample C-2, (c) sample C-3, and (d) sample C-4.

X-ray diffraction of the char are displayed in Figure 2. The resulted char have an amorphous structure with widened peaks reflection between 11° and 30°. These results show that the lignocellulose structure of the char are destroyed [12]. The sample C-3 (Figure 2.(c)) has the widest reflection, indicates the more amorphous structure. Unfortunately, the XRD curve contain many noise, so that Refinement of the XRD patterns is not done here.

Figure 3. FTIR spectra of coconut shell char: (a) sample C-1, (b) sample C-2, (c) sample C-3, and (d) sample C-4.

FTIR spectrum of the char is represented in Figure 3(a-d). Overall, there are two major peaks originated from C=O of carboxylic groups at 1708-1704 cm\(^{-1}\) and C=C bonds in aromatic at 1597-1618 cm\(^{-1}\) [8]. The C=O indicates the oxygen content in the char, whereas the C=C stretching attributed to the building block of carbon molecules of the char. The sample C-3 has the highest
intensity that show the highest density of carbon building block. This result is in line to that of EDX analysis (Table 2).

**Table 3. Porous Characteristics of the coconut shell char.**

| Sample | $S_{\text{BET}}$ (m$^2$/g) | $V_T$ (cc/g) | $V_{\mu}$ (cc/g) | $V_m$ (cc/g) | Average Pore Size (nm) |
|--------|-----------------|-------------|-----------------|-------------|-------------------|
| C-1    | 141             | 0.1         | 0.06            | 0.04        | 2.9               |
| C-2    | 116.4           | 0.09        | 0.046           | 0.044       | 3.0               |
| C-3    | 546.8           | 0.44        | 0.22            | 0.22        | 3.2               |
| C-4    | 259.7           | 0.15        | 0.12            | 0.03        | 2.3               |

The porous characteristics of the char are given in Table 3. The highest specific surface area and highest pore volume is resulted from sample C-3 ($S_{\text{BET}} = 546.8$ m$^2$/g). This $S_{\text{BET}}$ shows well pore development of the char which is comparable to the study reported in Ref 7. In contrary, the sample C-2 has lowest specific surface area of 116.4 m$^2$/g. This indicate that the acid pre-treatment can open up the char pore (micro- and meso pore). The higher $S_{\text{BET}}$ of the sample C-1 is derived from its small particle size as represent in SEM images of Figure 1.(a). The higher specific surface area is consistent to the higher micopore volume. This suggest that the all of the char exhibited a highly microporous materials with slit-like pores [13]. By acid post-treatment, sample C-4 show the low specific surface area and small average pore-size compared to the sample C-3. It need further study to investigate this unexpected result.

**Figure 4.** The BJH pore size distributions of the coconut shell char: (a) sample C-1, (b) sample C-2, (c) sample C-3, and (d) sample C-4.
The BJH pore size distributions of the char are demonstrated in Figure 4. The pores are distributed from micropores (with width less than 2 nm) and mesopores (with widths in the range of 2-50 nm width). All of the sample show the maximum pores is in the microporous range, except for sample C-3 has equal micro and mesopore volume. All of the sample have widely distributed pore in the range of 2-50 nm, except for sample C-3 which has limited pore-size in the range of 2-8 nm.

4. Conclusions
The coconut shell char have been manufactured by using simple pyrolysis method and comprehensively characterized. The SEM images shown the porous char structure as investigated from Nitrogen Isotherm Physisorption data and confirm by XRD with its amorphous structure. The acid and microwave heating treatments can increase the density of carbon in the char as shown by its SEM and EDX analyzing which is also supported from its FTIR spectra. Those results confirm that the higher carbon content is linear to the lower oxygen content. Therefore, the acid and microwave treatment can reduce the oxygen content of the coconut shell char.

5. References
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