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Carbonization process of Moso bamboo (*Phyllostachys pubescens*) charcoal and its governing thermodynamics

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ABSTRACT

The effect of a three-stage carbonization and activation process on the properties of a bamboo charcoal (BC), prepared from the 4- to 6-year-old Moso bamboo (*Phyllostachys pubescens*) planted in the Jhu-Shan of Nantou, Taiwan, was investigated. A process simulation, based on first principles thermodynamics, was conducted using a thermochemistry software package (FactSage). Our model not only reproduced the key experiments well, but also provided a detailed chemical reaction mechanism of the carbonization process involving multiple solids and multi-component gas phases. Three-stage process proposed herein consisted of first-stage carbonization process to prepare BC, second-stage activation process to activate BC, and third-stage activation process to refine activated BC. Measured changes in pH values of the BC were explained based on the chemistry of the gas products, and, accordingly, a theoretical maximum pH value for the BC was proposed. Furthermore, material properties like charcoal yield, ash content, pH level, elemental compositions, Brunauer–Emmett–Teller (BET) specific surface area, morphology, and Fourier transform infrared spectrum were measured. Interestingly, the observed maximum BET specific surface area (493.0 $m^2 g^{-1}$) of refined BC obtained through the above three-stage process was more than 2000 times larger than that of the sample fabricated at 400 °C in the first-stage carbonization process (0.2 $m^2 g^{-1}$), and this once again demonstrated the importance of process optimization. Our multi-stage process and new chemical reaction mechanism can be used to speed up the technology development of a general carbonization for a variety of bio-resources.

1. Introduction

Due to increasing concerns about global warming, the development of clean, accessible, and sustainable resources has received much attention. Bamboo, which is found in diverse climates from cold mountains to tropical or subtropical regions, is the most notable among biomass resources because it is one of the fastest-growing plants on Earth. According to the Annual Report of Forest (2006) published by The Forestry Bureau of Agriculture Council of Executive Yuan, ROC, bamboo groves in Taiwan occupy a total area of 152,300 ha, which is 7.2% of the total forest area in Taiwan (2,102,400 ha). If the cycle of its plantation is properly scheduled, bamboo can provide Taiwan a remarkably sustainable resource.

Through pyrolysis of bamboo in the absence of air, bamboo charcoal (BC) is obtained. Because it is usually used as an effective adsorbent for the removal of humidity and odors and as a convenient solid fuel [1], BC has attracted considerable interest. For example, Hsieh et al. presented the application of BC particles in blood purification [2]. Yang et al. investigated the antibacterial effect of BC/Ag composite on *Staphylococcus aureus* and *Pseudomonas aeruginosa* [1]. Chuang et al. prepared carbonized Moso bamboo powder modified with TiO_2 nano-particles to enhance its efficiency in the removal of harmful gases [3]. Yang et al. prepared BC/Ag by activation and chemical reduction, and the BC/Ag composites were characterized by silver particle size and distribution, silver ion (Ag+) release, and antibacterial properties [4]. Nitayaphat et al. prepared chitosan/BC composite films to provide more hydrophilic regions on the BC surface [5]. Lin et al. prepared a cell sorter with modified BC and indicated that the high surface area and porous structure of BC greatly increased cell density and protein production [6]. Yang et al. prepared functional fabrics of

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BC/Ag composite powder and evaluated its antibacterial efficacy [7]. Moreover, Zhu et al. prepared a biological activated BC and studied its use to remove quinoline from waste water [8].

Most of the cited studies are concerned with the applications of BC. However, research on the effect of multi-stage carbonization and activation process on the properties and adsorption capacities of BC has been less systematically studied. Moreover, Lan et al. prepared Moso BC using a one-stage carbonization process, and the maximum Brunauer–Emmett–Teller (BET) specific surface area of BC prepared at 600 °C was only 4.45 $m^2\,g^{-1}$ [9]. However, Pulido-Novicio et al. investigated the adsorption capacities and related characteristics of Sugi (*Cryptomeria japonica* D. Don) wood charcoals carbonized using a one-step or two-step process; they observed that the wood powder carbonized at 1000 °C with the two-step process showed higher capacity, but further heating up to 1400 °C drastically decreased the adsorption [10]. Aside from these, Sakuma et al. prepared BC by air oxidation following low temperature carbonization and found that the air oxidation treatment was effective in developing surface area and pore volume as well as surface functional groups [11].

Therefore, the multi-stage carbonization and activation process can be one of the promising methods to enhance the adsorption capacity of BC. In this study, a three-stage carbonization and activation process was used to prepare Moso bamboo (*Phyllostachys pubescens* Mazel) charcoal types, and their properties (such as: charcoal yield (CY), ash content, pH level, elemental composition, and BET specific surface area) were measured. Aside from these properties, the scanning electron microscope (SEM) micrographs and the Fourier transform infrared (FTIR) spectra of the Moso BCs were also obtained. The effect of the multi-stage carbonization and activation process on the above properties of BCs was also investigated. Interestingly, a commercial thermochemistry software package (FactSage), based on first principles thermodynamics, was used to simulate the carbonization process and to obtain a detailed chemical reaction mechanism of the carbonization process. Furthermore, this proposed three-stage process can be used to produce BC with higher BET specific surface area in some existed kilns, which do not have equipment for steam activation.

2. Materials and methods

2.1. Preparation of BCs

The Moso bamboo (*Phyllostachys pubescens* Mazel) with age ranging from 4 to 6 years, which had been planted in the Jhu-Shan of Nantou County, Taiwan, was used to prepare BCs. The bamboo culm was cleaned and chopped into segments of 3 cm × 15 cm. The moisture content of these chopped bamboo segments was kept at 10% by air drying.

To fabricate BCs, a mechanical kiln was utilized to carbonize the chopped Moso bamboo segments in the first-stage process, and an activation kiln was then used to activate the carbonized bamboo segments in the second-stage and third-stage processes. The first-stage carbonization process is as follows: (1) the chopped bamboo segments were loaded into the mechanical kiln; (2) at nitrogen (N_2) atmosphere the chamber temperature was increased to the preset temperature with a rate of 100 °C/h; and (3) this temperature was retained for 1 h, and the BCs were then obtained. In Fig. 1, F-400, F-500, F-600, F-700, and F-800 represent the test pieces, whose final carbonization temperatures in the first stage are 400, 500, 600, 700, and 800 °C, respectively.

The second-stage activation process is as follows: (1) the BCs, which had been prepared at 40 °C in the first stage, were loaded into the activation kiln; (2) air was drawn from the chamber of the activation kiln using a vacuum pump; (3) nitrogen (N_2) was inputted into the chamber with a flow rate of 20 ml/min; (4) the temperature of chamber was increased to the preset temperature with a rate of 5 °C/min from room temperature; and (5) this temperature was retained for 1 h, and the activated bamboo charcoals (ABCs) were then obtained. In Fig. 1, S-500, S-600, S-700, S-800, and S-900 represent the test pieces, whose final activation temperatures in the second stage are 500, 600, 700, 800, and 900 °C, respectively.

The third-stage activation process is as follows: (1) the ABCs in tests S-500, S-600, S-700, S-800, and S-900 were respectively loaded into the activation kiln; (2) air was drawn from the chamber of the activation kiln using a vacuum pump; (3) nitrogen (N_2) was inputted into the chamber with a flow rate of 20 ml/min; (4) the temperature of chamber was increased to 1000 °C with a rate of 5 °C/min from room temperature; and (5) this temperature was retained for 1 h, and the refined bamboo charcoals (RBCs) were then obtained. In Fig. 1, T5-1000, T6-1000, T7-1000, T8-1000, and T9-1000 represent the test pieces, whose initial activation temperatures in the third stage are 500, 600, 700, 800, and 900 °C, respectively.

2.2. Characterization of BCs

The ash content and the pH level of the BC (ABC or RBC) were obtained according to CNS 5581 [12] and CNS 698 [13], respectively. The CY of the BC (ABC or RBC) is given by

$$\mathrm{CY}\quad(\%) = \frac{M_2}{M_1} \times 100 \tag{1}$$

where M_1 represents the mass of a Moso bamboo segment, which was dehydrated in a furnace at a temperature of 103 ± 2 °C, and M_2 represents the mass of this test piece after the carbonization (or activation) process.

An elemental analyzer (Heraeus CHNOS Rapid F002) and a FTIR spectrometer (Mattson Genesis^{TM} II) were utilized to obtain the weight percentage of elements and the surface functional groups of the ground BC (ABC or RBC) powder with a size of ≤100 mesh, respectively. A BET specific surface area analyzer (AF21023) was used to obtain the BET specific surface area of the ground BC (ABC or RBC) powder with a size of 6–8 mesh.

Aside from these property measurements, the SEM micrographs of the BC (ABC or RBC) were obtained by the following steps: (1) the BC (ABC or RBC) was broken into several pieces using a hammer; (2) these broken pieces were dehydrated in a furnace at a temperature of 103 ± 2 °C; (3) some of these broken pieces were attached to the stub, and an ion-sputter coater (Hitachi E-1010) with a vacuum level of 10^{-2} Torr was used to deposit a thin film of Au on the top of broken pieces of the BC (ABC or RBC); and (4) a SEM (TOPCON ABT-150S) was used to obtain the micrographs of the BC (ABC or RBC).

3. Results, discussion and modeling

3.1. CY and ash content

Fig. 2(a)–(c) shows variations in the CY and the ash content with the temperature in the first, second, and third stages, respectively. In the first-stage carbonization process, the CY of the BC decreased with increasing the final carbonization temperature (Fig. 2(a)). For example, as the final carbonization temperature increased from 400 to 800 °C, the CY of the BC decreased from 34.4% (in test F-400) to 27.7% (in test F-800). The ash content of the BC ranged from 1.39% (in test F-600) to 1.67% (in test F-400), and it did not significantly vary with the final carbonization temperature in the first stage (Fig. 2(a)). Matsunaga et al. carbonized Moso bamboo using the temperature ranging from 200 to 2500 °C and observed that the