

Article

Yield, Composition, and Property of Biochar Obtained from the Two-Step Pyrolysis of Rice Husk Impregnated with Boric Acid

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Abstract: Adding catalysts such as boric acid into biomass is a flexible method to achieve high biochar yield with low carbon emission levels. This work is directed towards investigating the effects of boric acid content on biochar yield, composition, and property through a two-step pyrolysis of rice husk. The results showed that biochar yields, compositions, and properties were associated with the amounts of boric acid impregnated. Yield, C content, and calorific value of biochar were improved by adding 2.0 wt % of boric acid into rice husk, and those values were 46.4 wt %, 59.3 wt %, and 22.6 MJ/kg, respectively. However, the fixed-carbon content of biochar was around 55.4 wt % and was barely affected by the changes in the amounts of boric acid absorbed. Therefore, the optimized boric acid content of rice husk was 2.0 wt % when biochar was applied to the fields of carbon storage and solid fuel. Meanwhile, the specific surface area of biochar continuously decreased with increasing boric acid content of rice husk, indicating that the boric acid had a negative influence on the pore structure of biochar. Thus, the addition of boric acid is not recommended when preparing a biochar to be used as an absorbent.

Keywords: boric acid; rice husk; biochar yield; composition; property

1. Introduction

Biomass is a promising energy source worldwide. In many countries, most of the biomass resources have been treated through traditional methods such as burning or burying. These treatments are not suitable to process biomass, as burning would generate a considerable amount of fine particles into the air and burying may pollute the soil due to the nitrogen containing compounds [1]. Therefore, an effective utilizing route satisfying both biomass disposal and energy conversion is required. More and more studies are focusing on biomass pyrolysis, since it is recognized as the most promising way [2]. Typically, pyrolysis can be divided into three categories including slow, fast, and flash pyrolysis, depending on the heating rate. Generally, slow pyrolysis yields the highest amount of solid residues (biochar) [3]. Biochar can be applied to many fields due to its variable properties and thus has attracted much attention [4–8]. However, biochar yield is often low due to the emission of large amounts of carbon during pyrolysis, even at a very slow heating rate. How to increase biochar yield has become a big issue. Numerous efforts have been made to address this challenge, including adjusting pyrolysis parameters and adding catalysts [9–12]. Between these two pathways, adding catalyst into biomass has been proven to be an efficient method to improve biochar yield. As one such catalyst, boric acid has a long history of treating lignocellulosic biomass and attracts much attention. Some researchers have investigated the pyrolysis characteristics of biomass in the presence of boric acid [13,14]. The results show that biochar yield is improved due to the dehydration reactions and

the formation of a polymeric structure catalyzed by boric acid as well as the formation of a coating or protective layer on the biomass [15]. Di Blasi et al. [16] investigate the flame retarding property of biochar obtained from the pyrolysis of woods treated with and without boric acid. Their results show that boric acid treatment of wood reduces the oxidation rates of the resulting biochar in air. However, most of the works have mainly focused on the catalytic mechanism during biomass pyrolysis or the fire-retardant property of the obtained biochar. The effect of boric acid on the composition and property of biochar is much less understood.

Millions of tons of rice husk are produced per year in China, and most of it is not properly used [17]. The effective utilization of rice husk remains a challenge. To the best of our knowledge, no research has been published investigating the yield, composition, and property of biochar obtained from the pyrolysis of rice husk impregnated with boric acid. In this work, a series of biochar samples was produced through a two-step pyrolysis of rice husks with different boric acid contents. The biochar yields, compositions, and properties were characterized. From these data, the effects of boric acid content on biochar yield, composition, and property were illustrated. This understanding is useful for biochar production and application from rice husk.

2. Materials and Methods

2.1. Materials

Rice husk was purchased from Shanghai Dingwang mill factory (China) and was dried at 90 °C for 24 h before use. Table 1 shows the composition of rice husk used.

Table 1. Composition of rice husk.

Analysis	Content	Value
Proximate analysis (wt %)	Ash	15.0
	Volatiles	73.8
	Fixed-carbon	11.2
Elemental analysis (wt %)	C	42.5
	H	5.7
	O	36.4

2.2. Methods

2.2.1. Impregnation Process

The impregnation procedure was conducted as follows. Boric acid solutions were prepared by adding different amounts of boric acid to obtain the desired concentrations (0, 0.1 wt %, 0.5 wt %, 1.0 wt %, 2.0 wt %, and 3.0 wt %, respectively). Next, rice husk (20 g) was soaked in a boric acid aqueous solution (400 mL) for 24 h without stirring. After the soaking process, rice husk was collected by filtering and then was dried in an electric oven at 90 °C for 24 h. Finally, the dried sample was weighted to determine the amount of boric acid absorbed. The amounts of boric acid absorbed into rice husks by soaking at solution concentrations of 0, 0.1 wt %, 0.5 wt %, 1.0 wt %, 2.0 wt %, and 3.0 wt % were 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, respectively. The rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt % were referred to as R0, R1.0, R1.6, R2.0, R3.2, and R4.8, respectively.

2.2.2. Pyrolysis Procedure

The boric acid-treated rice husk was pyrolyzed using an electric furnace (50 × 700/10K-26C, Shanghai Yifeng Electrical Furnace Co., Ltd., Shanghai, China) in an inert atmosphere. The pyrolysis process was performed as follows: boric acid-treated rice husk was heated at 2 °C/min from room temperature to 300 °C with a holding time of 0.5 h, then from 300 °C to 500 °C at 10 °C/min with a holding time of 1 h. In a typical pyrolysis experiment, about 10 g of boric acid-treated rice husk was

used. Biochar obtained from the pyrolysis of rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, were labeled as R0, R1.0, R1.6, R2.0, R3.2, and R4.8, respectively. All yields were expressed as the average yields from at least three experiments, and were presented within the experimental error of ± 0.2 wt %.

2.3. Characterizations

The Chinese National Standards (CNS) method for the proximate analysis of solid biofuels (GB 28731-2012) was applied for the proximate analysis of the obtained biochar. In brief, ash content was characterized by the solid residue left after burning 1 g of dry biochar at 550 °C in air for 6 h. Volatiles content was determined by the mass loss of 1 g of dry biochar heating at 900 °C in a covered crucible for 7 min. Fixed-carbon content was calculated by the difference of ash and volatiles from the original dry biochar mass on a weight percent basis. Contents of carbon (C), hydrogen (H), and nitrogen (N) were determined through an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Hanau, Germany). Oxygen (O) (wt %) was calculated by subtracting C, H, N, and ash from 100. Calorific value (higher heating value) of biochar was measured with a calorimeter (SDACM3000, Hunan Sundy Science and Technology Co., Ltd., Hunan, China). Pore characteristics of biochar including specific surface area, average pore width, and pore volume were characterized by N₂ adsorption at -196 °C on the surface area analyzer (ASAP 2020, Micromeritics Instrument Corp., Atlanta, GA, USA). Morphology of biochar was observed by scanning electron microscopy (SEM) (Quanta-50, Thermo Fisher Scientific, Waltham, MA, USA) at 10 kV. All values were expressed the average values from at least three characterizations, and were presented within the error of ± 0.2 wt %.

3. Results and Discussion

3.1. Biochar Yield

Figure 1 shows the biochar yields from the pyrolysis of rice husks with different boric acid contents. It can be observed that the biochar yield dependence on the boric acid content showed two regions. In the first region (boric acid content below 2.0 wt %), biochar yields greatly increased from 38.1 to 46.4 wt % with increasing boric acid content. In the second region (boric acid content above 2.0 wt %), further increases of biochar yields were not obvious. The results showed that the presence of boric acid promoted char formation. This is because the boric acid catalyzes dehydration and oxygen-elimination reactions, as well as promotes the forming of aromatic structures during pyrolysis [13]. Moreover, the glassy coating formed from the decomposition products of boric acid inhibits release of volatiles, which also enhances char formation [15,16]. The results illustrate that there was an optimized content (2.0 wt %) of boric acid for increasing biochar yield.

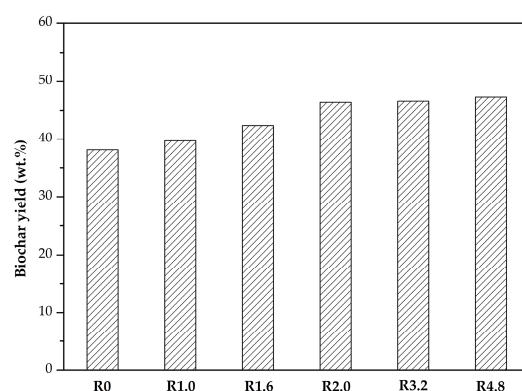


Figure 1. Biochar yields from the pyrolysis of rice husks with different boric acid contents. (R0, R1.0, R1.6, R2.0, R3.2, and R4.8 were rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, respectively.)

3.2. Biochar Composition

The compositions of biochar are shown in Table 2. The changes in ash and volatiles contents of biochar can be divided into two regions. In the first region (boric acid content below 2.0 wt %), the ash content decreased from 32.2 wt % (B0) to 29.9 wt % (B2.0), but the volatiles content increased from 12.5 wt % (B0) to 14.8 wt % (B2.0) with increasing boric acid content. In the second region (boric acid content above 2.0 wt %), the changes in ash and volatile contents were not significant. Ash originated from biomass is an inert ingredient and mostly remained in the biochar [18]. Meanwhile, the amount of solid deposits from boric acid decomposition slightly increased with increasing boric acid content. In the first region, increasing boric acid content resulted in the distinct improvement of biochar yield. Thus, the ash content of biochar decreased. In the second region, biochar yield did not show a significant further increase, which led to the indistinctive changes in the ash content of biochar. Increasing volatiles content in the first region was caused by the inhibition of volatiles release due to the glassy layers formed from solid deposits generated by the decomposition of boric acid [16]. In the second region, the insignificant change in the volatiles content was because high boric acid content mainly acted to increase the condensation of char and did not significantly affected the volatiles yield from fragmentation reactions during rice husk pyrolysis [19]. The fixed-carbon content of biochar seemed not to be affected by the changes in boric acid content. This result can be explained by the changes in ash and volatiles contents, since the fixed-carbon content was affected by both values. The total contents of ash and volatiles remained almost unchanged, which resulted in the nearly constant fixed-carbon content.

The changes in C and O contents of biochar also can be divided into two regions. In the first region (boric acid content below 2.0 wt %), C content increased from 55.2 wt % (B0) to 59.3 wt % (B2.0), but O content decreased from 9.9 wt % (B0) to 7.8 wt % (B2.0) with increasing boric acid content. In the second region (boric acid content above 2.0 wt %), both values remained almost unchanged. In the first region, the promotion of char formation accompanied with the release of oxygen containing compounds caused by the catalytic effect of boric acid during pyrolysis increased the C content and decreased the O content of biochar. In the second region, further increases of boric acid content had no significant effect on biochar production, which led to the indistinctive changes in the C and O contents of biochar. The results indicate that there was also an optimized content (2.0 wt %) of boric acid for increasing the C content of biochar.

Table 2. Compositions of biochar.

Composition	B0	B1.0	B1.6	B2.0	B3.2	B4.8
Proximate analysis (wt %)						
Ash	32.2	30.8	30.4	29.9	30.0	29.9
Volatiles	12.5	13.9	14.2	14.7	14.6	14.7
Fixed-carbon	55.3	55.3	55.4	55.4	55.4	55.4
Elemental analysis (wt %)						
C	55.2	57.5	58.7	59.3	59.4	59.5
O	9.9	8.7	8.5	7.8	7.7	7.7

3.3. Calorific Value and Specific Surface Area of Biochar

The calorific value is equivalent to its maximum value of energy available and is mainly correlated to the C and O contents of biochar. As shown in Figure 2, the changes in calorific values show a similar trend compared to the changes in the C content of biochar. When the boric acid content was lower than 2.0 wt %, the calorific value increased from 20.7 MJ/kg (B0) to 22.6 MJ/kg (B2.0) with increasing boric acid content. The catalytic effect of boric acid on biomass conversion resulted in a substantial increase of the C content and a decrease of the O content of biochar. This led to an increasing calorific value of biochar, since C-C bonds contain more energy than C-O bonds [20]. However, as boric acid content was above 2.0 wt %, calorific values of biochar showed no further increase. This was because

the changes in C and O contents of biochar were very slight in this region. The result demonstrated that 2.0 wt % of boric acid absorbed into rice husk was the optimized value for increasing the calorific value of biochar.

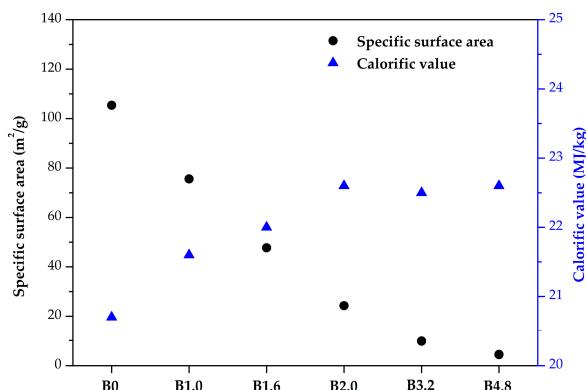


Figure 2. Calorific values and specific surface areas of biochar obtained from the pyrolysis of rice husks with different boric acid contents. (B0, B1.0, B1.6, B2.0, B3.2, and B4.8 were biochar samples prepared by the pyrolysis of rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, respectively.)

Specific surface area is an important property of biochar application. As depicted in Figure 2, the specific surface area of B0 was $105.4 \text{ m}^2/\text{g}$. As the boric acid content increases to 4.8 wt %, the specific surface area of biochar significantly reduced to $4.4 \text{ m}^2/\text{g}$ (B4.8). This result indicates that increasing content of boric acid had a strong negative effect on the specific surface area of biochar. The specific surface area of biochar is associated with its pore structure, which is affected by pore volume and average pore width. Generally, large pore volume and small average pore width results in a high specific surface area [21]. As presented in Figure 3, with increasing boric acid content, the pore volume of biochar sharply decreased from $0.026 \text{ cm}^3/\text{g}$ (B0) to $0.004 \text{ cm}^3/\text{g}$ (B4.8), and the average pore width increased from 3.2 nm (B0) to 5.8 nm (B4.8). These results showed that the presence of boric acid during pyrolysis led to pore blocking inside biochar. Boric acid decomposition in the pyrolysis process generates boron trioxides. The boron trioxides would melt before 500°C and form a glassy layer, which certainly block the open pores inside biochar [16]. Thus, increasing boric acid content caused a decrease of pore volume and an increase of average pore width, which led to the reduction in the specific surface area of biochar.

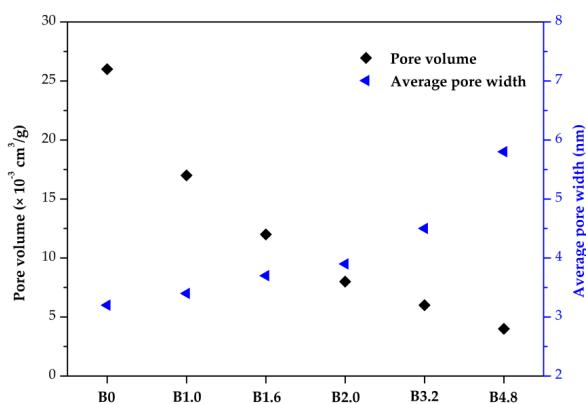


Figure 3. Pore volumes and average pore widths of biochar obtained from the pyrolysis of rice husks with different boric acid contents. (B0, B1.0, B1.6, B2.0, B3.2, and B4.8 were biochar samples prepared by the pyrolysis of rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, respectively.)

Figure 4 presents the cross-section morphologies of biochar samples. B0 shows a corrugated structure with few pores near the outer surface and relatively ordered honeycomb-like pores near the inner surface. Meanwhile, fewer pores near the outer surface of B1.0 existed compared to that of B0. The pores near the inner surface of B1.6 became poorly ordered and their sizes changed. Similar observations were made for B2.0. As for B3.2 and B4.8, pore blocking could be clearly observed for both sections near the outer and inner surfaces. As the boric acid content increased, the regular pattern of pore structure was continuously destroyed and the open pores were blocked due to the formation and melting of the solid deposits generated by the decomposition of boric acid. These results also explained the changes in the specific surface area of the obtained biochar samples mentioned above. The poorly arranged pore structure and lack of open pores resulted in the reduction in the specific surface area of biochar, which had a negative impact on the adsorption capacity of biochar.

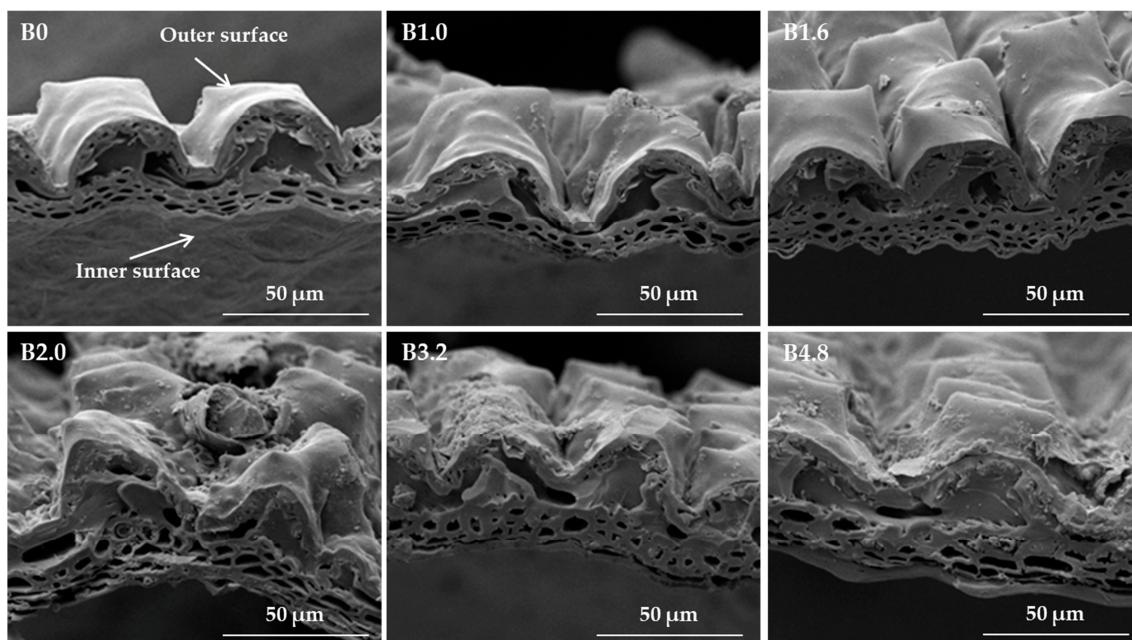


Figure 4. SEM images of biochar obtained from the pyrolysis of rice husks with different boric acid contents. (B0, B1.0, B1.6, B2.0, B3.2, and B4.8 were biochar samples prepared by the pyrolysis of rice husks with boric acid contents of 0, 1.0 wt %, 1.6 wt %, 2.0 wt %, 3.2 wt %, and 4.8 wt %, respectively.)

4. Conclusions

In this work, a series of biochar samples was produced through a two-step pyrolysis of rice husks with different boric acid contents and subsequently characterized. The results show that biochar yield was improved by the pyrolysis of rice husk impregnated with boric acid. An optimized content of boric acid for improving biochar yield was found to be 2.0 wt %. The impregnated boric acid had a significant influence on the ash, volatiles, C, and O contents of biochar, but it barely affected the fixed-carbon content of biochar. As for improving the calorific value of biochar, the optimized amount of boric acid absorbed was 2.0 wt %. Increasing the boric acid content of rice husk had a negative effect on the specific surface area of the resulting biochar. Above all, the optimum boric acid content of rice husk was 2.0 wt % to produce biochar for the applications of carbon storage and solid fuel. However, when preparing a biochar for use as an absorbent, adding boric acid is not recommended.

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Author Contributions: Xu Cheng designed and conducted the experiments; Xu Cheng and Biao Wang analyzed the data and wrote the paper. Both authors had read and approved this manuscript.

Conflicts of Interest: Both authors declare no conflict of interest.

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