Preparation and Characteristics of Biomass Char

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Rice husk and sawdust were selected as the raw materials for a study of biomass char yield in the range of 600 to 900 °C. It was found that temperature was the primary factor affecting the biomass char yield. The yield of the rice husk and sawdust chars decreased significantly with increasing temperature. As the residence time increased, the biomass char yield decreased. The smaller the size of the biomass particles, the higher the char yield. When the temperature exceeded 800 °C, the difference in the char yield was only slight. Given this finding, the surface morphologies of rice husk, sawdust, and their respective chars were investigated under various conditions *via* scanning electron microscopy. The effects of temperature on the pore structures were investigated by the Accelerated Surface Area and Porosimetry System. There were more holes in the biomass char, and the specific surface area was increased significantly as the temperature increased. The specific surface areas of rice husk and sawdust chars prepared at 900 °C were 320 and 1140 m^2/g, respectively.

Keywords: Biomass char; Yield; Surface morphology; Pore structure

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INTRODUCTION

Biomass char is a solid product from the pyrolysis of biomass under a reducing atmosphere condition. Since biomass contains large amounts of volatiles, a porous structure is formed inside and on the surface of pyrolyzed biomass (Yan *et al*. 2010; Xu *et al*. 2011). Compared to those of biomass, the volatiles and oxygen content in biomass char are much smaller and the fixed carbon composition is larger (Chaudhari *et al*. 2003; Klein *et al*. 2008). Biomass char has high reactivity with lower nitrogen and sulfur levels than coal, resulting in less pollution than coal char and making it a good-quality gasification material. However, the high tar content in biomass gasification gas is a major problem with current biomass gasification technology. One potential way to effectively remove or reduce the tar content is to separate pyrolysis and gasification at high temperatures, like in the Choren process (Basu 2013). The authors proposed a two-stage biomass cyclone pyrolysis and gasification process scheme adopting the design that separate pyrolysis zone from gasification zone using the cyclone furnace combustion principle (Zhang *et al*. 2013). In order to validate the scheme, the characteristics of biomass char in the pyrolysis zone need to be determined.

The surface structure, internal structure, and composition of biomass char formed under different pyrolysis conditions vary, which plays a significant role in gasification characteristics. Research on the characteristics of biomass char made at relatively high temperatures is helpful for further understanding its high-temperature gasification characteristics (Luo *et al*. 2007). The decomposition temperatures for lignocellulosic biomass components are roughly 220 °C for hemicellulose, 280 °C for cellulose, and 200 to 500 °C for lignin (Demirbas 2002). Raveendran *et al.* (1995) studied 13 types of biomass, finding that de-ashing increased the volatile yield, initial decomposition temperature, and rate of pyrolysis, but that some types of biomass, such as rice husk, exhibited an increase in char yield following de-ashing due to their high lignin, potassium, and zinc contents (Raveendran *et al.* 1995). Sharma *et al*. (2004) characterized lignin char prepared by pyrolyzing lignin at atmospheric pressure and temperatures ranging from 150 to 550 °C. The char yield decreased rapidly with increases in temperature to 400 °C. The surface area of the char was low, a maximum of 5 m^2/g. SEM analysis indicated that the pore structures decomposed rapidly at higher temperatures. For example, straw char has the largest surface area and pore volume at 800 °C because sintering occurs at higher temperatures (Wang *et al.* 2011; Wang *et al.* 2013). However, the reactivity of the char obtained was strongly influenced by the treatment conditions and may have been significantly increased by rapid pyrolysis and the small particle size of the biomass achieved at higher temperatures (Zanzi *et al*. 1996).

The yield and reactivity of char are determined by pyrolysis conditions such as temperature, heating rate, residence time, and particle size. However, most studies pertain to relatively low temperatures (below 600 °C) and short residence times. In the present study, a muffle furnace was used to produce rice husk and sawdust chars to study the effects of high temperatures, particle size, and long residence time on the char yield. The surface topography and structural properties of the rice husk and sawdust chars were investigated and analyzed with reference to the preparation of biomass char and its gasification conditions for our two-stage biomass cyclone pyrolysis and gasification process scheme.

EXPERIMENTAL

Materials

Two biomass materials typically found in Heilongjiang, China, rice husk and sawdust, were chosen as the raw materials. Rice husk, an agricultural biomass resource, is composed of fiber, lignin, extractives, and ash. Unlike other agricultural biomass sources, rice husk is easy to collect and use since it accumulates primarily in rice processing plants. When making char samples, rice husks are not crushed, but are instead screened, and husks of similar particle size are chosen. Sawdust, a standard processing residue of timber plants, is a typical lignocellulosic biomass resource. The major species of the sawdust in this paper was pine, which was crushed and screened into different particle sizes.

Table 1. Proximate Analysis of Rice Husk and Sawdust

	$Moisture_{ad*}$ (%)	$Volatile_{ad}$ (%)	Ash_{ad} (%)	Fixed $carbon_{ad}$ (%)
Rice Husk	5.08	63.05	14.98	16.89
Sawdust	4.68	80.49	2.16	12.67
*ad: air-dry basis.				

Table 2. Ultimate Analysis of Rice Husk and Sawdust

	C_{daf*} (%)	H_{daf} (%)	O_{daf} (%)	N_{daf} (%)	S_{daf} (%)
Rice Husk	46.18	6.08	45.02	2.62	0.10
Sawdust	53.01	6.00	40.70	0.15	0.14
*daf: dry, ash-free basis.					

The proximate analyses of rice husk and sawdust are shown in Table 1, and the ultimate analyses are shown in Table 2. The two materials had similar water content, nearly 5%. Volatiles accounted for about 80% of the dry mass of sawdust, greater than in rice husk. Sawdust's 2.16% ash content was significantly lower than that of rice husk, meaning that sawdust char contained more carbon. The oxygen contents in the two materials were as high as 40%, resulting in low heat values and significant tar formation during gasification. The sawdust contained more carbon and less oxygen than the rice husk.

Methods

Biomass char was produced under high temperatures and oxygen-free conditions. The raw material was put into a sealed crucible at ambient temperature and then heated in a muffle furnace. A temperature controller monitored the temperature. The heating rate was 10 °C/min and the heating time was about 1.5 to 2 h. The influences of three factors, temperature, particle size, and residence time, on biomass char yield were studied. The char yield in muffle furnace was compared with the thermogravimetric analysis of char preparation using a thermogravimetric analyzer (Metrohm, Switzerland). The surface morphologies of rice husk and sawdust and their char samples were studied using an S-570 scanning electron microscope (HITACHI, Japan). An ASAP2020 specific surface area analyzer (Micromeritics, USA) was used to analyze the specific surface area and pore size distribution of the biomass char. Absorption theories regarding solid-specific surface area include the Langmuir, Brunall-Emmett-Teller (BET), Yang, and Dubinin theories (Chen *et al*. 2003). Methods to determine the pore size distribution include the Barret-Joyner-Halenda method (BJH), Horvath-Kawazoe model (HK), and Jaroniec-Choma model (JC) (Zhang *et al*. 2006). In this paper, BET was used to determine the specific surface area and BJH was used to determine the pore size distribution.

RESULTS AND DISCUSSION

Effect of Temperature on Biomass Char Yield

Rice husk and sawdust with particle sizes greater than 1.2 mm were used to prepare char samples. Figure 1 shows the two materials' char yield at different final temperatures.

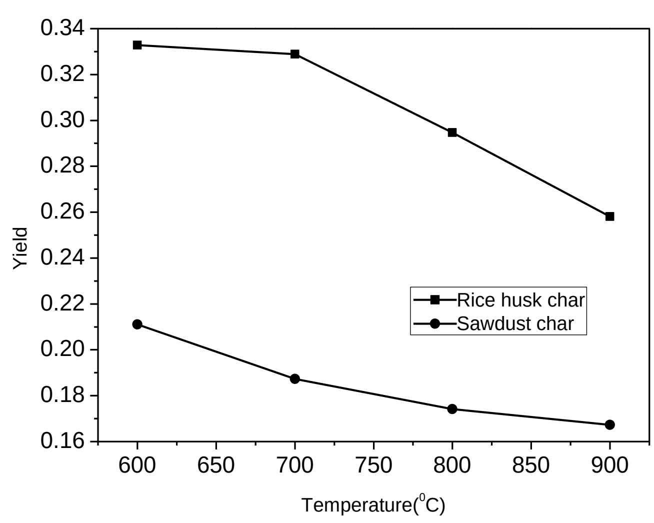
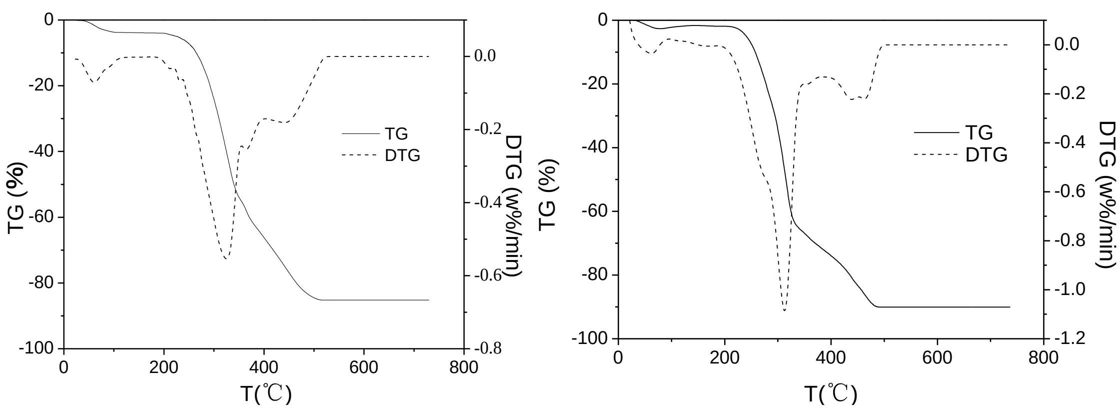


Fig. 1. Rice husk char and sawdust char yields with temperature

The yield was the fraction of mass of the residue to the mass of the raw material. Their yields exhibited the same trend. Increasing the temperature decreased the yield significantly. Rice husk char had 32 to 33% yield at 600 to 700 °C. However, when the temperature rose, the yield dropped sharply to 28.85 and 25.81% at 800 and 900 °C, respectively. Sawdust with particle sizes greater than 1.2 mm gave 21.11% char yield at 600 °C. As the temperature was increased, the sawdust char yield was decreased significantly. When the temperature rose to 900 °C, the yield dropped to 16.73% and stabilized. As temperature rose, volatiles in rice husk and sawdust precipitated out more thoroughly, decreasing char yield. The contrast between the char yields of the two biomass samples at different temperatures shows that rice husk has a better yield than sawdust, since the volatile content of rice husk is smaller than that of sawdust.

Figure 2 shows the two materials' TG/DTG curves under N_2 atmosphere. The yields of the chars exhibited the same trend, but they did not change when the temperature was over 500 °C and the final yields (14.8% for rice husk and 9.97% for sawdust) were much lower compared with that in muffle furnace. The reason is that in thermogravimetric analysis, all the volatiles emitted out and some of the ash was carried away from the char by N_2, but in muffle furnace, some of the volatiles like tar condensed on the char when it was cooled to ambient temperature.



a) Rice husk TG/DTG curves at 10℃/min b) sawdust TG/DTG curves at 10℃/min

Fig. 2. Thermogravimetric analysis of rice husk and sawdust

Effect of Particle Size on Biomass Char Yield

Sawdust screened to sizes of 0.7 to 1 mm, 1 to 1.2 mm, and over 1.2 mm in diameter was pyrolyzed at different temperatures for 40 min before preparation. The char sample yield was calculated to compare the effect of particle size on yield and the results are shown in Fig. 3.

As the particles got larger, the sawdust char yield increased slightly. The differences were greater at low temperatures, because at lower temperatures, the larger particles had a temperature gradient on both of their sides, affecting heat and mass transfer. Meanwhile, the larger-sized particles had smaller specific surface area, not conducive to the precipitation of volatiles, resulting in higher char yield. Further, the rising temperature helped to improve reaction rate and heat transfer, and the temperature gradient on both sides of the particle was not obvious. Besides, the volatile in sawdust were easy to emit out at high temperatures due to the formation of extensive pore structures in any size of sawdust. Thus the particle size had little effect on the char yield.

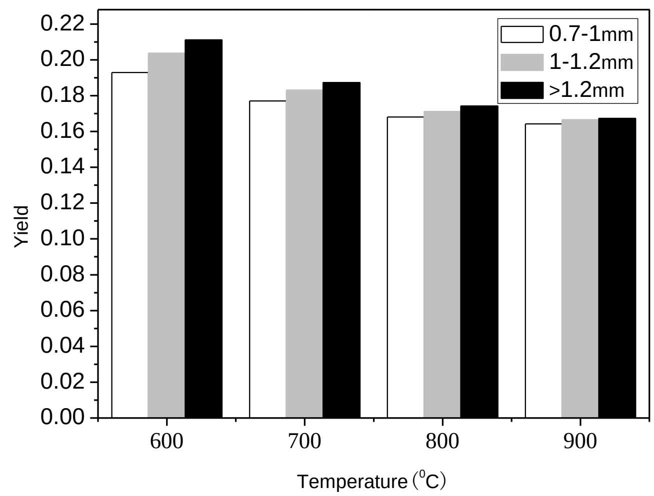


Fig. 3. Sawdust char yield with size of the particle at different temperatures

Effect of Residence Time on Biomass Char Yield

The rice husk and sawdust particles greater than 1.2 mm in size were incubated at different preparation temperatures for 20, 30, and 40 min to study the effects of different residence times on the char yield. The results are shown in Figs. 4. At constant temperature, increasing the residence time decreased the yields of rice husk and sawdust chars. Since the temperature rose during char preparation, volatiles in the biomass were not completely released to the atmosphere. As the residence time increased, the effect of heat and mass transfer were enhanced, resulting in further pyrolysis and gas precipitation. If the residence time was longer, more gas was emitted and the carbonization process was more thoroughly completed, resulting in a significant decline in the char yield.

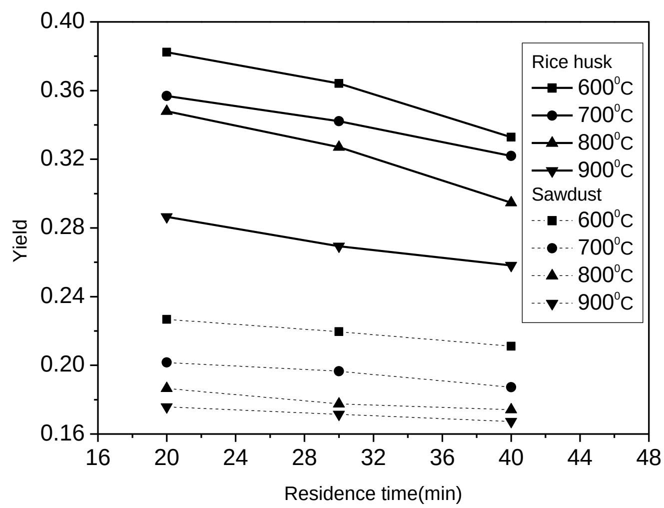
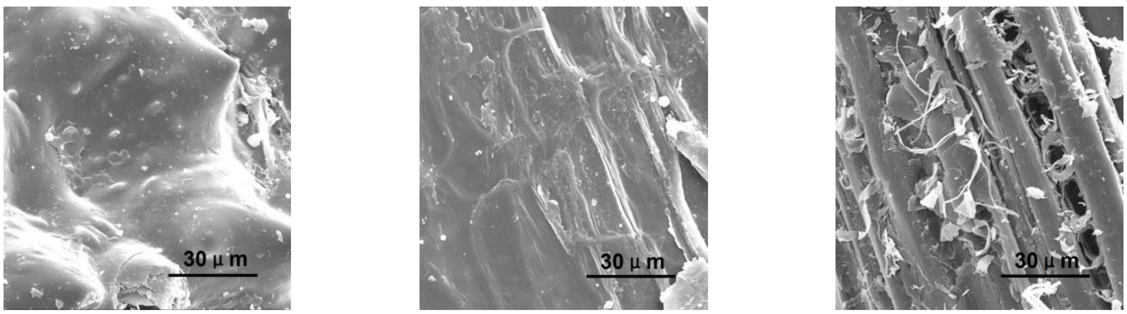


Fig. 4. Rice husk and sawdust char yield with residence time

Surface Morphology of Biomass and Its Char Samples

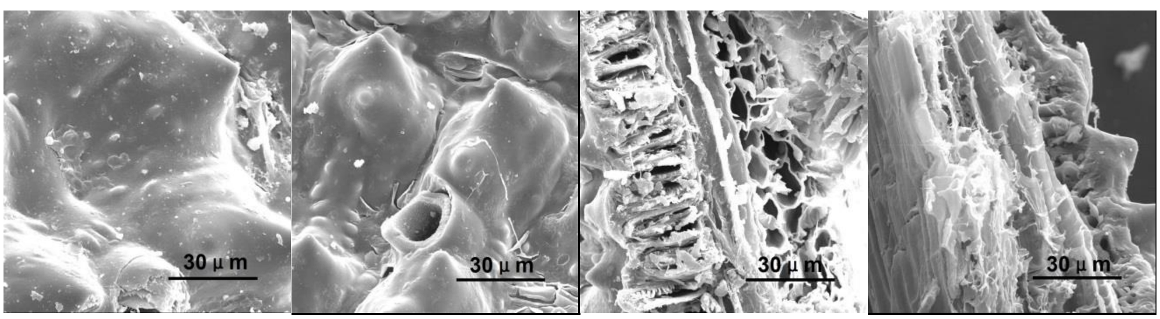
Figure 5 is an SEM comparison of rice husk and sawdust. The surfaces of the rice husk had erratic, rough serrations and no significant pore aperture. There was a narrow pore structure close to the outer surface of the rice husk and thin pores formed by material with flocculent structures close to the inner surface. The surface of sawdust was relatively smooth and without significant pore aperture. Sawdust was produced *via* crushing, and its surface had cracked, fibrous tissue relatively smooth compared to that of rice husk. Sawdust char also exhibited a significant pore aperture on its surface.

Figures 6 and 7 show the comparison of the materials and char samples of rice husk and sawdust, respectively. Compared with the rice husk raw material, its char surface had significant thermal etching traces, a convex surface, larger structures, and increased roughness and specific surface area. As can be seen in the cross-section, the flocculent matter in the narrow pores close to the outer surface of rice husk was burned and the pore structure was more obvious. The pores close to the inner wall surface were very thin and collapsed at high temperatures, forming a large number of micropores and increasing the specific surface area of the rice husk char pores.



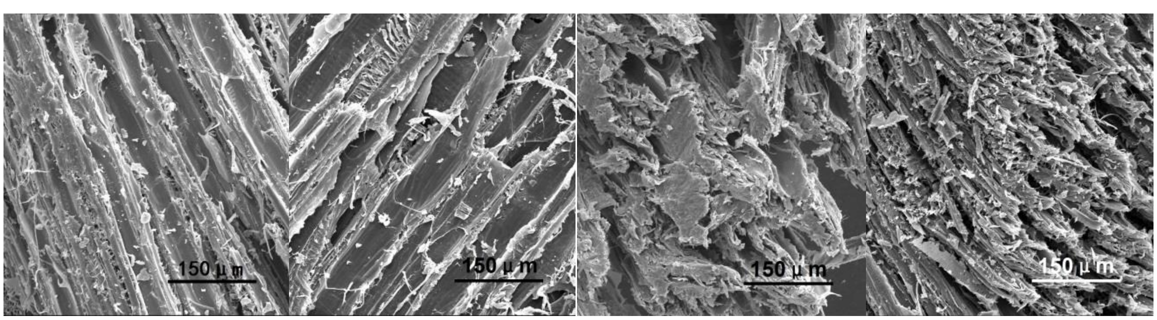
a) Outer surface of rice husk b) Inner surface of rice husk c) Sawdust

Fig. 5. SEM images of rice husk and sawdust (1000× magnification)



a) Rice husk surface b) 600° C char surface c) Rice husk cross section d) 600 °C char cross section

Fig. 6. SEM images of rice husk and its char (1,000× magnification)



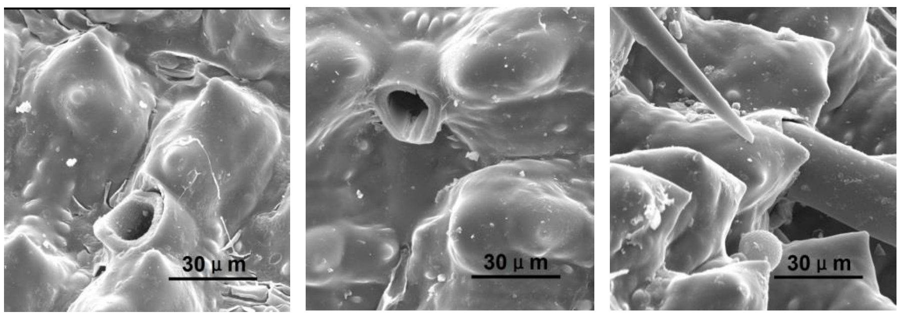
a) Sawdust surface b) 600° C char surface c) Sawdust cross section d) 600 °C char cross section

Fig. 7. SEM images of sawdust and its char (200× magnification)

Comparison of the electron microscopy patterns of the sawdust char and sawdust surfaces showed that the cracked fiber tissue on the surface of the sawdust was ablated. The original surface structure was enhanced and the specific surface area was increased.

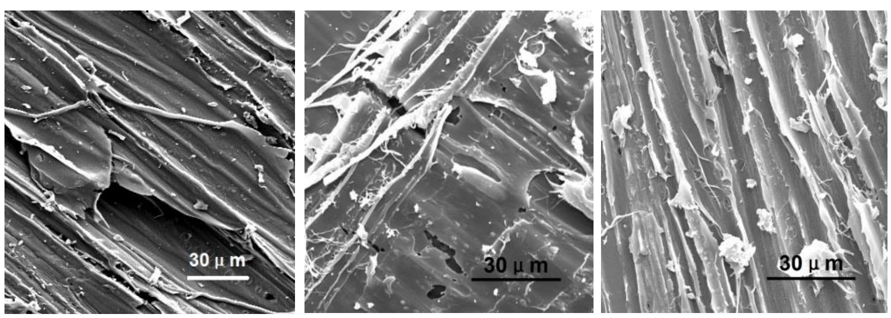
The original, macroporous structure shown in its cross-section was ablated and collapsed, forming a complex pore structure. New pores did not exist on the surfaces of rice husk or sawdust chars. Under slow heating conditions, volatiles in biomass were slowly volatilized from the original pores, and bubble generation and collapse did not occur on the surface so it retained its original form.

Figures 8 and 9 are electron microscope patterns of the rice husk and sawdust chars prepared at various temperatures and residence times. There was no significant difference in the surface morphologies of the rice husk and sawdust chars prepared at 600 and 800 °C. At different temperatures, the thermal etching phenomenon occurred on their surfaces. When the residence time increased, the rupture of fibrous tissue on the surface of sawdust caused more thorough thermal etching and the surface roughness and specific surface area experienced relative increases. The overall structure of the char did not fundamentally change.



40 min at 600 °C 40 min at 800 °C 20 min at 800 °C

Fig. 8. SEM images of rice husk char at different char-making conditions (1,000× magnification)



40 min at 600 °C 40 min at 800 °C 20 min at 800 °C

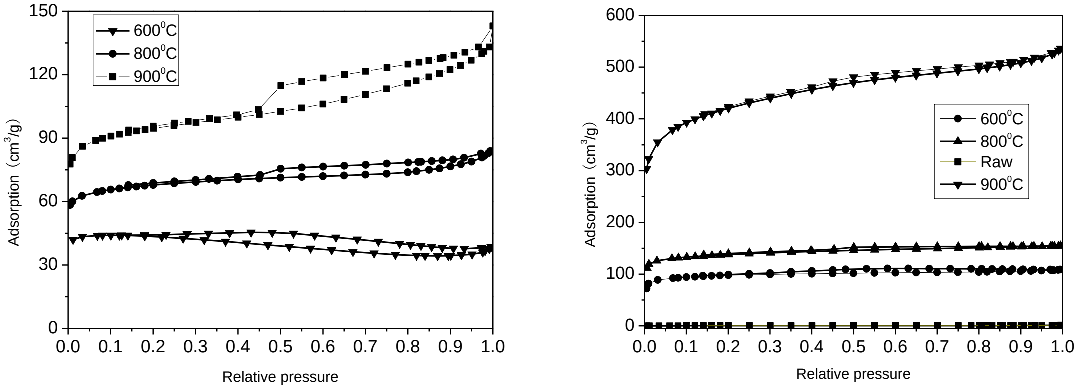
Fig. 9. SEM images of sawdust char at different char-making conditions (1,000× magnification)

Effect of Preparation Temperature on Specific Surface Area of Biomass Char

As shown in Fig. 5, rice husk has a relatively smooth surface with no significant pore structure, so its adsorption performance is poor. Figure 10 shows isothermal adsorption/desorption characteristics of rice husk and sawdust chars prepared under different temperatures.

The absorption curve of sawdust showed that it had better adsorption performance and a more extensive pore structure than rice husk. The adsorption curves of rice husk and sawdust chars have trended upwards and had convex shapes at relatively low pressure. When the relative pressure exceeded 0.8, the increase became more dramatic. The pore-filling phenomenon occurred mainly at low relative pressures and multilayer adsorption, capillary accumulation, and dispersion phenomena occurred at high relative pressures, indicating that the two biomass chars had continuous pore distribution structures.

Compared with the adsorption curves at 600, 800, and 900 °C, the char prepared at higher temperatures exhibited greater adsorption.



a) Rice husk char b) Sawdust char

Fig. 10. Isothermal adsorption/desorption curves for rice husk char and sawdust char

Table 3 displays the specific surface areas of the rice husk and sawdust chars prepared at different temperatures, as calculated using the BET theory. The specific surface area of the biomass materials was small.

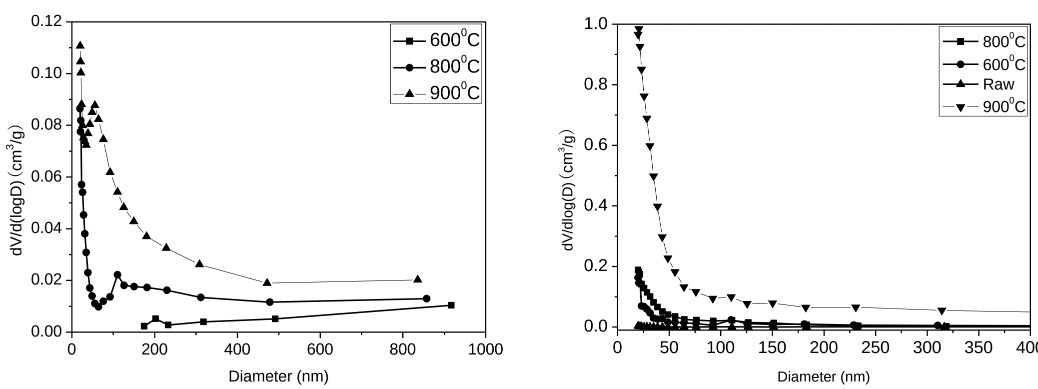
The specific surface area of char prepared at 900 °C was significantly higher than at 600 °C, so high preparation temperature was conducive to opening the inner pore structure of the biomass char and promoting the expansion of the pore structure to increase its specific surface area.

Table 3. BET Specific Surface Area of Rice Husk Char and Sawdust Char

BET (m^2/g)	Raw Material	600 °C Char	800 °C Char	900 °C Char
Rice Husk	0.105	139.22	228.35	319.46
Sawdust	1.39	330.14	464.53	1440.67

Effect of Preparation Temperature on Pore Distribution of Biomass Char

Figures 11 and 12 show the pore size distributions and pore areas of rice husk and sawdust chars as calculated using the BJH theory. Rice husk char apertures were concentrated at around 200 nm at 600 °C with an uneven distribution. Pores less than 20 nm in size were not measured.

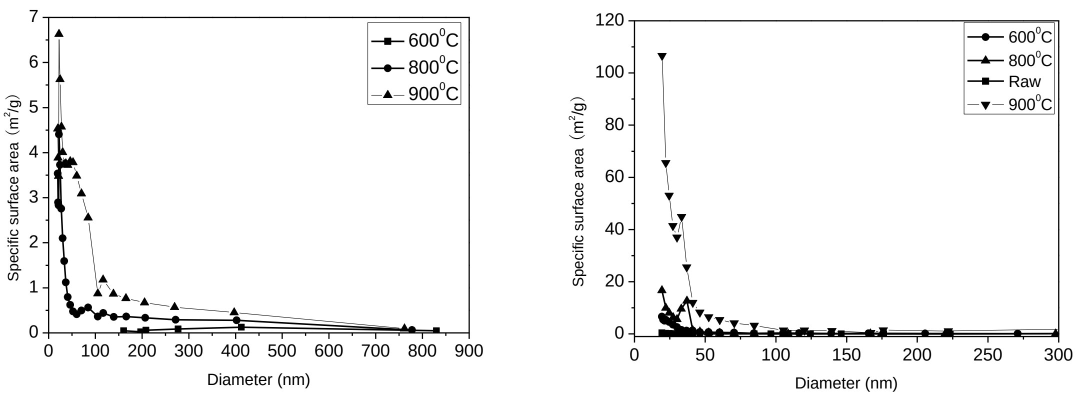


a) Rice husk char b) Sawdust char

Fig. 11. Pore size distributions of rice husk char and sawdust char

When the temperature rose to 900 °C, a peak appeared in the range of 20.6 to 92.7 nm, indicating that at this temperature, the holes that produce rice husk char were mainly concentrated in this pore size range. Compared with rice husk char, sawdust char had an extensive pore structure and the pore sizes of chars at 600 and 900 °C ranged from 19.8 to 64.4 nm and 20.6 to 43.4 nm, respectively.

As shown in Fig. 12, with decreases in the pore size, the specific pore surface area of the char increased, indicating that the specific surface area of the small-diameter pore played a significant role in the total specific surface area of the biomass char. Rice husk char, with pore diameters less than 50 nm, experienced a sharp increase in pore area at 800 and 900 °C, indicating that at high temperatures, the volatiles in rice husk precipitate out, and the internal pore structure opens further, and more small pore structures emerge. The average pore size of the biomass chars is reduced, and their distribution tends to be uniform. Pore areas of sawdust char at 900 °C were larger than chars at 600 °C, although they shared a similar average pore size, which indicated an increase in the number of apertures of sawdust char at high temperatures and increased the specific surface area of its aperture.



a) Rice husk char b) Sawdust char

Fig. 12. Specific surface area distributions of rice husk char and sawdust char

CONCLUSIONS

1. Temperature is the primary factor affecting the biomass char yield. The yield of the rice husk and sawdust char decreased significantly with increasing temperature. When the temperature exceeded 800 °C, further changes in the char yield were slight.
2. The longer the residence time, the lower the biomass char yield. The smaller the biomass particles, the higher char yield.
3. The surfaces of the rice husk and its char had erratic serrations and no significant pore aperture. Inside the char, the original macroporous structure collapsed and a complex microporous structure emerged.
4. The surface of the sawdust and its char sample were relatively smooth and without significant pore aperture.
5. The biomass material had a small specific surface area and poor adsorption characteristics. The specific surface areas of rice husk and sawdust chars at 900 ºC were 319.46 and 1440.67 m^2/g, respectively.

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