Effect of Residence Time on Hydrothermal Carbonization of Corn Cob Residual

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Hydrothermal carbonization is a promising technique for conversion of industrial waste into valuable products. Producing hydrochar from corn cob residual (CCR) in a cost-effective way is key, from an economic standpoint. For this purpose, the effect of residence time in the range of 0.5 to 6 h was studied under the optimal temperature of 250 °C. Results showed that the higher heating value (HHV) of hydrochar increased approximately 40% in comparison to that of the raw material; however, prolonging the residence time beyond 0.5 h had a negligible effect on the HHV increase. Chemical compositions and H/C and O/C ratios of hydrochars revealed a minimal effect of longer residence time. Furthermore, thermogravimetric and derivative thermogravimetric analysis (TG/DTG), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analysis of hydrochars also verified that the pyrolysis behavior and chemical structure of hydrochars with various residence times were similar.

Keywords: Residence time; Hydrothermal carbonization; Corn cob residues; Hydrochar

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INTRODUCTION

Utilization of renewable lignocellulose to produce fuel, heat, and electrical power is an alternative way to alleviate the rapid depletion of conventional fossil-based fuels (Yang *et al*. 2012; Shen *et al*. 2013; Luterbacher *et al*. 2014). Corn cob residual (CCR) is a type of industrial waste that is generated from the furfural production process in large quantities (Zhang *et al*. 2014). Approximately 23 million tons of CCR are produced annually in China (Bu *et al*. 2012). The exploitation of CCR to create valuable products fits well into the strategy of sustainable and environmentally friendly development.

Typically, the lignocellulose conversion process includes biological and thermochemical treatments; the former focuses on an effective pretreatment process for de-constructing the compact cell wall, by way of inhibitors such as acetic acid and furfural, and the latter treatment is much more flexible because of the short processing time and high product yield (Liu *et al*. 2013; Yang *et al*. 2013a,b; Liu *et al*. 2014). For high-efficiency conversions, hydrothermal carbonization is a suitable choice because the CO emissions decrease and the energy density increases during combustion of lignocellulose (Parshetti *et al*. 2013).

Hydrothermal carbonization simulates the coalification process to produce hydrochar with a high energy density through the omission of the energy-intensive drying process. In addition to the liquid and gaseous products from hydrothermal treatment, the solid product (hydrochar) is a valuable source for various applications (Kieseler *et al*. 2013; Kruse *et al*. 2013; Wang *et al*. 2014a). For example, the unique physicochemical properties of hydrochar generated from hydrothermal treatment of glucose and cellulose have been applied in products, *e.g.*, carbon precursors (Falco *et al*. 2013). Xiao *et al*. (2012) reported that the higher heating value (HHV) of hydrochar from corn stalk and *Tamarix ramosissima* was increased by 66.8% and 58.3%, respectively, from that of the raw material under the conditions of 250 °C for 4 h. Liu *et al*. (2013) reported that HHVs of 29.4 and 28.7 kJ/mol can be obtained for coconut fiber and eucalyptus leaves, respectively, under conditions of 300 °C for 0.5 h. However, there is a debate on the effect of residence time on hydrothermal carbonization process. For example, He *et al.* (2000) reported that longer residence time would favor the solid residue production due to the repolymerization of heavy oil. An opposite view was reported by Román *et al.* (2012), that a very slight decrease on the solid yield was determined for hydrothermal carbonization of walnut shell and sunflower stem. In our previous study, the effect of temperature on hydrothermal carbonization of CCR was investigated, and the results showed that the HHV increased 48% from that of the raw material, which can be achieved under the conditions of 250 °C for 1.5 h (Zhang *et al*. 2015).

Because hydrothermal carbonization is an energy-intensive process, residence time is critical for hydrochar production in a cost-effective manner. This study focused on the effect of residence time for the production of hydrochar in terms of HHV. The thermal stability and chemical structure of hydrochar were also analyzed based on thermogravimetric and derivative thermogravimetric (TG/DTG) analysis, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

Industrially produced CCR was collected from a furfural production mill that was located in Shandong, China. The CCR was milled into particle sizes of 100 mesh after air-drying.

Methods

Hydrothermal carbonization

A laboratory-scale 250-mL Parr stirred pressure reactor (4576A, Parr Instrument Company, USA) was used for hydrothermal carbonization. It was equipped with a temperature controller and pressure indicator. Initially, 5 g of CCR (equivalent to oven-dried weight) was weighed and loaded with 50 mL of distilled water into the reactor. Then, the reactor was sealed and flushed with nitrogen gas three times. After this, the reactor was heated to 250 °C and maintained at this temperature for time intervals from 0.5 to 6 h at a stirring rate of 150 ppm. Upon completion of the reaction, the reactor was rapidly cooled down to room temperature using cold tap water. Finally, the hydrochar was recovered by filtration using a sand core funnel and oven-dried (105 °C for 24 h) according to the procedures in Zhang *et al*. (2015).

Analytical methods

The carbon (C), hydrogen (H), sulfur (S), oxygen (O), and nitrogen (N) elemental compounds (wt-%) in the samples were determined using a Vario EL III Element

Analyzer (Elementar, European Virtual Institute for Speciation Analysis, Germany). The ash content (wt-%) was weighed after the sample was burned, as described in Zhang *et al*. (2015). The higher heating value (HHV) was calculated using Eq. 1 (Channiwala and Parikh 2002):

$$\text{HHV}\ (\text{MJ}\cdot\text{Kg}^{-1}) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.021\text{A} \quad (1)$$

where C is carbon (wt-%), H is hydrogen (wt-%), S is sulfur (wt-%), O is oxygen (wt-%), N is nitrogen (wt-%), and A is ash content (wt-%).

Characterization method

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were conducted using a TGA Q50 (TA Instruments, New Castle, DE, USA) at a heating rate of 20 °C/ min and under a nitrogen atmosphere (Yang *et al*. 2013c). The reflectance infrared spectra was recorded in the wavenumber range of 500 to 4000 cm^{-1} on a Fourier transformed infrared (FTIR) spectrophotometer (IRPrestige-21, Shimadzu Co., Japan) using a potassium bromide (KBr) pellet containing about 1.0% sample (Wang *et al*. 2014b). X-ray diffraction (XRD) patterns were obtained using a D8-AVANCE X-ray diffractometer (Bruker-AXS, Karlsruhe, Germany) under Cu-Kα radiation at 10 kV.

RESULTS AND DISCUSSION

Chemical Composition

The results for the hydrothermal carbonization yield of CCR under residence time intervals of 0.0 to 6 h are shown in Table 1.

Table 1. Chemical Compositions of CCR and Hydrochar at 250 °C

Residual Time (h)	Yield (%)	C (%)	H (%)	O (%)	N (%)	S (%)	Ash (%)	HHV (MJ/Kg-1)
0.0	--	43.06±0.05	5.82±0.02	44.56±0.03	0.23±0.01	0.12±0.01	4.15±0.03	17.2
0.5	46.6	61.76±0.03	4.68±0.03	25.06±0.04	0.47±0.01	0.03±0.01	10.00±0.04	24.3
1	46.3	59.76±0.04	4.47±0.02	24.08±0.04	0.45±0.02	0.07±0.01	10.70±0.03	23.4
1.5	46.0	63.07±0.03	4.69±0.01	23.70±0.02	0.45±0.01	0.04±0.01	9.96±0.02	24.9
2	46.1	62.03±0.03	4.57±0.03	24.12±0.01	0.43±0.02	0.02±0.01	10.82±0.03	24.3
3	45.8	61.54±0.02	4.31±0.01	23.56±0.04	0.44±0.01	0.03±0.01	10.19±0.03	23.9
4	45.3	62.95±0.04	4.49±0.02	23.86±0.02	0.44±0.03	0.03±0.01	9.74±0.04	24.6
5	45.7	63.60±0.02	4.57±0.03	23.68±0.05	0.44±0.01	0.05±0.01	9.50±0.02	24.9
6	45.6	62.08±0.03	4.34±0.01	21.41±0.03	0.42±0.01	0.03±0.01	8.80±0.01	24.7

C: carbon; H: hydrogen; O: oxygen; N: nitrogen; S: sulfur; HHV: higher heating value

For CCR, the composition of carbon, ash, and nitrogen increased with increasing residence time, whereas oxygen, hydrogen, and sulfur decreased. These results confirmed that the elemental hydrogen and oxygen were transformed into liquid and gas, implying that an extensive dehydration reaction occurred. As a result, the HHV of hydrochar increased by approximately 40% over that of the raw material. On the other hand, the hydrochar yield ranged from 45.3% to 46.6%, and the chemical compositions were comparable under various residence times. Because the HHVs of hydrochars remained constant beyond 0.5 h, the effect of prolonging the residence time beyond 0.5 h was minimal. Minimal effects of residence time on HHV were also reported by Gao *et al.* (2013), who found, in their study on HTC of water hyacinth carried out at 240 °C, that there was an increase in HHV from 17.72 to 18.58 MJ/Kg^{-1} by increasing residence time from 2 to 6 h.

A Van Krevelen diagram is shown in Fig. 1 to express the hydrothermal carbonization of CCR. The atomic hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios were nearly identical for hydrochars produced with various residence time intervals. The atomic H/C and O/C ratios of hydrochar from CCR decreased from 1.62 and 0.78 to 0.9 and 0.3, respectively. The lower H/C and O/C ratios of hydrochars resulted from dehydration and decarboxylation reactions. As a result, the HHVs of hydrochars were higher than that of CCR. With extended hydrothermal treatment time, the H/C and O/C ratios only decreased slightly; thus, the HHVs of all hydrochars exhibited similar results (Table 1).

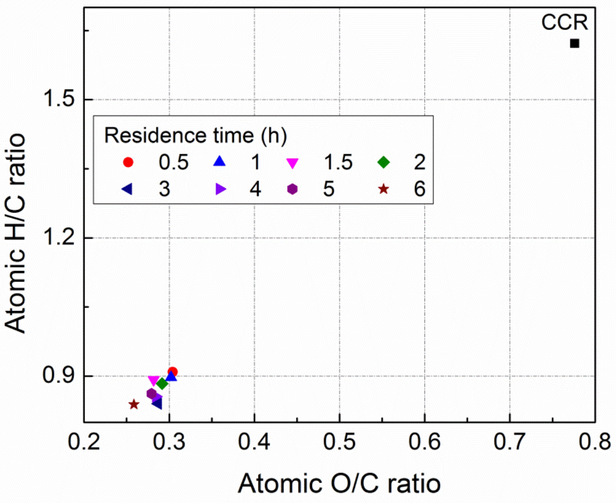

Fig. 1. Van Krevelen diagram (Van Krevelen 1950) for hydrochar samples

Thermal Stability

Figure 2 shows the thermogravimetric (TG) and divergent thermogravimetric (DGT) spectra of CCR and hydrochars at 2, 4, and 6 h. Results from the TG and DTG spectra showed that the hydrochar samples exhibited similar decomposition curves, which were visibly different from the decomposition curve of CCR. The increased residual weights of hydrochars at 700 °C implied that their thermal stability was improved, which favored the reduction of air pollution resulting from complete combustion. The sharp DTG peak of CCR at 300 °C was attributed to hemicellulose and cellulose decomposition (Wang *et al*. 2013), which was not apparent for hydrochar. Similar pyrolysis behavior in hydrochar produced at 6 and 24 h was also observed by Gao *et al*. (2013) when studying the hydrothermal carbonization of water hyacinth. The wide temperature of 430 to 620 ^{o}C may be attributed to lignin decomposition, as reported by Wang *et al*. (2013).

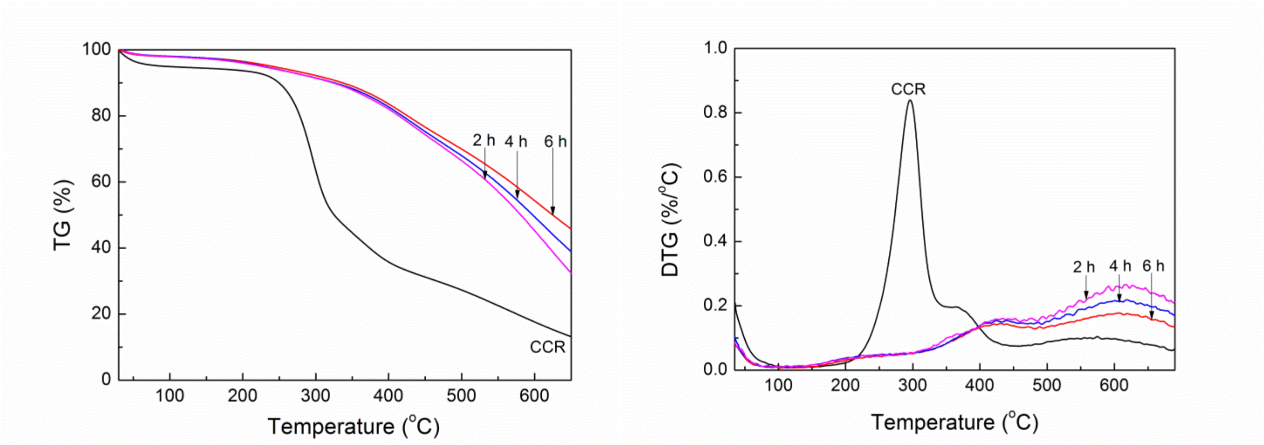

Fig. 2. Thermogravimetric and divergent thermogravimetric (TG and DTG) spectra of CCR and hydrochar at 250 °C

Fourier Transform Infrared Spectroscopy

The chemical structures of CCR and hydrochars are shown in Fig. 3. The three hydrochar samples exhibited similar transmittances from wavenumber 4000 to 500 cm^{-1}, suggesting that extending the residence time did not cause chemical structural changes. This is in agreement with the chemical compositions and HHVs, as shown in Table 1. When compared with CCR, there appeared to be a difference in the typical wavenumbers observed. The bands at 3500 to 3300 cm^{-1} belong to –OH stretching vibrations (Sevilla and Fuertes 2009), and they decreased after hydrothermal treatment; this was attributed to the dehydration reaction. The bands at 1710 cm^{-1} and 1000 to 1460 cm^{-1} can be attributed to C=O and C-O-C groups, respectively (Calucci *et al*. 2012). The decrease in these bands indicates carbon dioxide (CO_2) generation. The bands from 875 to 750 cm^{-1} represent aromatic C-H bending vibrations (Kim *et al*. 2014). The increase in these bands suggests that an aromatization process occurred during hydrothermal carbonization. Based on these results it can be inferred that the functional groups were converted during the decarboxylation reactions.

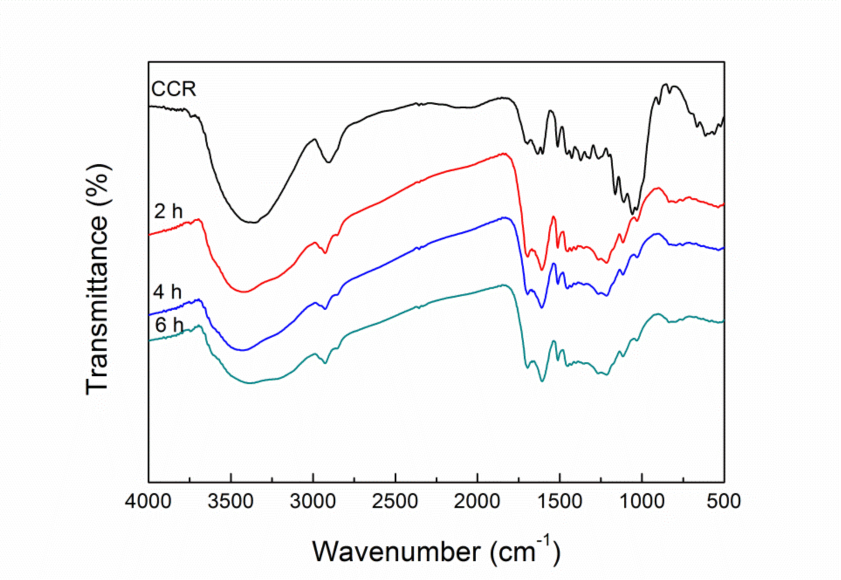

Fig. 3. Fourier transform infrared (FTIR) spectra of CCR and hydrochar at 250 °C

X-Ray Diffraction

Figure 4 shows the X-ray diffraction (XRD) spectra of CCR and hydrochars produced at 2, 4, and 6 h residence times. The three hydrochar samples exhibited similar XRD patterns, with different intensity patterns from that of CCR. For example, CCR exhibited two crystalline peaks, at 2θ values of 16° and 22.7°. The hydrothermal treatment caused the microcrystalline structure to disappear. This may be attributed to the decomposition of cellulose, which is in agreement with the pyrolysis behavior (Fig. 2). Kang *et al.* (2012) also observed the destroyed crystalline structure of hydrochar from XRD pattern when studying the hydrothermal carbonization of biomass.

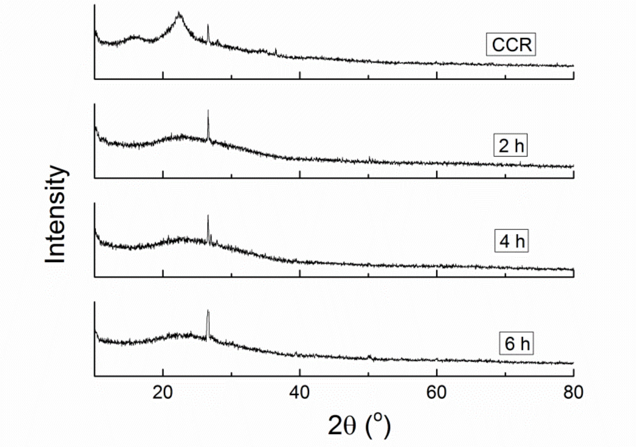

Fig. 4. The X-ray diffraction (XRD) spectra of CCR and hydrochar at 250 °C

CONCLUSIONS

1. Corn cob residual (CCR) was converted to hydrochar using a hydrothermal carbonization process at a temperature of 250 °C for 0.5 to 6 h.
2. Results from the hydrothermal carbonization showed that the higher heating value (HHV) of hydrochar increased by approximately 40% in comparison with that of the raw material, CCR. However, prolonging the residence time beyond 0.5 h had a negligible effect on the HHV increase.
3. The pyrolysis behavior, chemical structure, and crystalline structure were similar for hydrochars produced at various residence time intervals.

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