

Hydrothermal Carbonization of Lignocellulosic biomass: Chemical and Structural Properties of the Carbonized Products

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Abstract

Hydrothermal carbonization (HTC) is a novel thermochemical conversion process to convert lignocellulosic biomass into value-added products. In this work, two different biomass materials: corn stalk and *Tamarix ramosissima* were used as feedstock. HTC processes were performed at the temperature of 250 °C for 4 h, using a batch reactor system. Chemical and structural characterization of the solid materials was carried out by elemental analysis, nitrogen adsorption, scanning electron microscopy, X-ray diffraction, and spectroscopic techniques including Fourier transform infrared, X-ray photoelectron, and Raman. The results indicated HTC treatment brought an increase of the higher heating value up to 29.2 and 28.4 MJ/Kg for corn stalk and *T. ramosissima*, respectively, corresponding to an increase of 66.8% and 58.3% as compared to the natural biomass. The surface area determined by Brunauer–Emmett–Teller analyses was 10.8 and 11.3 m²/g, which was 4.8 and 10.9 fold for the hydrochars of corn stalk and *T. ramosissima*, respectively. Additionally, liquid products extracted with ethyl acetate were analyzed by gas chromatography–mass spectrometry. The identified compounds were phenolic and furan derivatives, confirming the mechanisms of dehydration, decarboxylation, and demethanation reactions during the carbonization processes. Based on these results, HTC is considered to be a potential treatment in a lignocellulosic biomass refinery.

Keywords: Hydrothermal carbonization, biomass, SEM, FT-IR, raman, XPS, GC–MS

Introduction

Hydrothermal carbonization (HTC) is a novel thermochemical conversion process to convert lignocellulosic biomass into value-added products. Recently, HTC method has attracted a great deal of attention because it uses water which is inherently present in green biomass, non-toxic, environmentally benign, and inexpensive medium (Libra et al. 2011). Typical HTC of biomass is achieved in water at elevated temperatures (180–250 °C) under saturated pressures (2–10 MPa) for several hours (Funke and Ziegler 2010, Mumme et al. 2011). Some publications have reported on the chemical transformations of model compounds under pressure in HTC processes, particularly cellulose, pentoses/hexoses (glucose and xylose), starch, and phenolic compounds (Titirici et al. 2008, Sevilla and Fuertes 2009, Ryu et al. 2010). However, the majority focused on model compounds and establishing the reaction kinetics and reaction pathways of such compounds in hydrothermal medium. So far, literature on the hydrothermal treatment of real complex biomass provides a rather inconsistent picture, and only few reports have provided a detailed description on the chemical composition of the reaction products. Therefore, the main objective of this work was to gain insights into the underlying mechanisms during HTC. This study focused on the reaction of natural complex biomass, their chemical and structural properties of carbonaceous solids (hydrochars) as well as the degradation products.

Materials and Methods

Materials. The dried raw materials were firstly ground to pass a 40-mesh screen and Soxhlet-extracted with ethanol/benzene (1:2, v/v) for 8 h. The extractive-free samples were oven-dried at 60 °C for 16 h and stored in a desiccator for use. All chemicals used were of analytical grade purchased from Sigma-Aldrich Company (Beijing).

Experimental procedure. The hydrothermal processes were carried out using 10 g feedstock dispersed in 100 mL of distilled water in a 1-L Parr stirred pressure reactor (Parr Instrument Company, Moline, Illinois) which was heated up to 250 °C at a heating rate of around 4 °C min⁻¹ (pressure at 250 °C of around 580 psi). The reactor was maintained at this temperature for 4 h with an agitation speed of 150 rpm. The reaction mixture, consisting of a liquid solution and solid phase (hydrochar) was collected in a glass beaker for separation by filtration and the solid was washed thoroughly with hot distilled water and then dried in an oven at 60 °C overnight. The hydrochar samples obtained from the feedstocks of CS and TR were denoted as CS250 and TR250, respectively.

Characterization of the hydrochars and liquors. The chemical compositions of the untreated and HTC treated biomass were determined using two-step acid hydrolysis and given in detail elsewhere (Xiao et al. 2011). Elemental analysis (C, H, N, and S; O content by difference) of the samples was performed in a vario MACRO cube (Elementar Analysensysteme GmbH, Germany). The surface area of the hydrochar sample was estimated by the standard Brunauer–Emmett–Teller (BET) method (nitrogen absorption isotherms). FT-IR spectra were recorded on an FT-IR spectrophotometer. Raman spectra

were recorded at ambient temperature on a Renishaw RM 2000 microspectrometer. Scanning electron microscopy (SEM) images were obtained with a Quanta 200F equipment (FEI, USA). X-ray photoelectron spectroscopy (XPS) were recorded performed using a Thermo Scientific Escalab 250Xi instrument equipped with Al K α radiation ($h\nu = 1486.6$ eV). Binding energies for the high-resolution spectra were calibrated by setting C 1s at 284.8 eV. The degradation products in the liquor fractions were analyzed by gas chromatography–mass spectrometry (GC–MS) (GC: GC 7890A; MS: Agilent MS 5975C). Agilent HP-5MS capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m) column and the NIST mass spectral library were used for the identification of compounds.

Results and Discussion

Yield and chemical characteristics of the hydrochars

The solid yield of biomass after HTC and its composition are presented in Table 1. As expected, the yields of hydrochars after the treatment were 35.5% and 38.1% for CS and TR, respectively, due to the high solubilization of components in hydrolysis liquors. On the other hand, the coal-like solid products were mainly composed of lignin, suggesting that there was a nearly complete hydrolysis of hemicelluloses and cellulose. Additionally, the fixed carbon contents in the both hydrochars were similar, ranging from 54.2% to 58.6%, indicating that a large fraction of the carbon in the lignocellulosic biomass was stored. The rest of the carbon (~41.4–45.8%) was mainly contained in the organic compounds that were dispersed in the aqueous phase, which will be discussed afterwards.

The elemental composition (C, O, and H) of the solid materials changed markedly as the result of HTC. The carbon content increased from 46.8% to 48.0% in the raw material to 71.4–72.1% in the hydrochar samples. Simultaneously, a reduction in the oxygen and hydrogen contents indicated that the hydrochar samples were less condensed (higher O/C and H/C atomic ratios). This was verified by the van Krevelen diagram (van Krevelen 1950) as illustrated in Figure 1, which allows for delineation of reaction pathways. In this diagram, the straight lines represent the dehydration, decarboxylation, and demethanation processes. The H/C–O/C atomic ratios for other substances (wood, cellulose, lignin, lignite coal, and bituminous coal) reported previously are also plotted in the same figure for comparison. The position of the hydrochars on this plot was similar to those associated with bituminous and lignite coals. Moreover, the energy contents of the raw materials and the corresponding hydrochars were also calculated and listed in Table 1. HTC processes brought an increase in the higher heating value (HHV) of the hydrochars up to 29.2 and 28.4 MJ/kg for CS and TR, respectively, which corresponded to an increase of 1.67- and 1.58-fold when compared with the raw materials.

The quantitative summary of surface area and pore volume is also listed in Table 1. A significant increase in the quantity of adsorbed nitrogen gas was observed for the carbonaceous hydrochars, indicating a higher specific surface area and a greater pore volume. The BET surface area increased from 2.3 to 10.8 m²/g and from 1.0 to 11.3 m²/g, which was 4.8 times and 10.9 times greater for the hydrochars of CS250 and TR250, respectively. Additionally, there was a 5.3-fold and 11.6-fold increase in the measured pore volume after HTC.

Table 1 Chemical characteristics and product yields of the raw materials and the hydrochars prepared from the HTC of CS and TA.

Sample	Elemental composition (%)			Atomic ratio		Yield (%)	Fixed carbon yield (%)	Klason lignin (%)	HHV (MJ/kg) ^a	BET	BJH
	C	H	O	O/C	H/C					surface	pore
										area	volume
										(m ² /g)	(cm ³ /g)
CS	46.84	6.26	40.70	0.652	1.591	—	—	20.96	17.51	2.26	0.01
CS250	71.36	5.60	16.27	0.171	0.935	35.48	54.21	96.50	29.21	10.79	0.03
TR	47.95	6.62	43.37	0.679	1.646	—	—	15.69	17.93	1.03	0.01
TR250	72.08	5.42	20.87	0.217	0.896	38.10	58.55	94.65	28.38	11.33	0.02

^a HHV, higher heating value. Evaluated using the Dulong's Formula: $\text{HHV} = 0.3383 \times \text{C} + 1.422 \times (\text{H} - \text{O}/8)$.

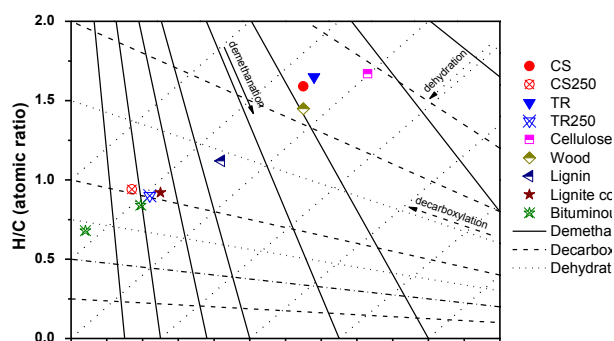


Figure 1. Atomic H/C versus O/C ratios (van Krevelen diagram) of the feedstocks and hydrochars prepared from the HTC of CS and TR. The atomic ratios of bituminous (two data points representing a range of H/C and O/C ratios), wood, cellulose, lignin, and lignite coals are included for comparison. The lines represent demethanation, dehydration, and decarboxylation pathways.

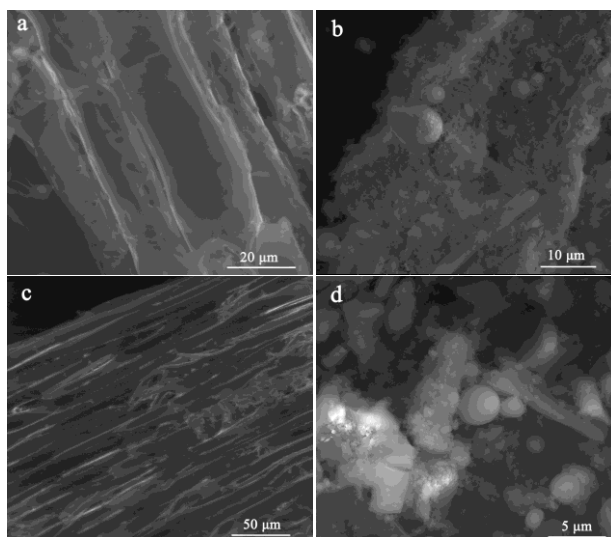


Figure 2. SEM images of CS (a) and the corresponding hydrochar CS250 (b); TR (c) and the corresponding hydrochar TR250 (d).

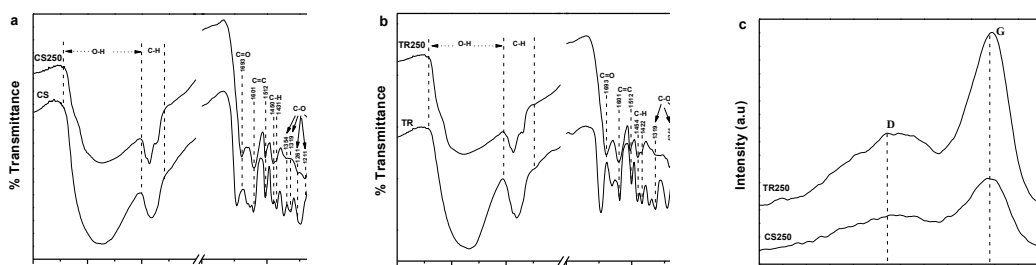


Figure 3. FT-IR and Raman spectra of feedstocks and hydrochars prepared by HTC at 250 °C for 4 h. (a) FT-IR spectra of CS and the corresponding hydrochar CS250; (b) FT-IR spectra of TR and the corresponding hydrochar TR250; (c) Raman spectra of hydrochars CS250 and TR250.

Structural prosperities of the carbonized hydrochars.

SEM images of the raw materials and the corresponding hydrochars are illustrated in Figure 2. A prominent change in the hydrochars was a more uneven and rougher surface morphology when compared to the pristine biomass.

Figure 3a and b shows the FT-IR spectra of the feedstocks and the corresponding hydrochars prepared by HTC at 250 °C for 4 h. The remarkable changes of the transmittance peaks mainly appeared in the range of 1800–750 cm⁻¹. It can be seen that the peaks at 1736 (C=O stretching), 1160 (C–O–C asymmetry stretching), and 899 cm⁻¹ (C–O–C stretching at β-glycosidic linkages) in the untreated feedstock spectra were absent in the hydrochar spectra, revealing that cellulose and hemicelluloses were thermally decomposed. Lignin, unlike cellulose and hemicelluloses, is aromatic and possesses olefinic carbon–carbon double bonds in cyclic structures and side chains. The peaks at 1512, 1427, and 1601 cm⁻¹ were well represented, suggesting that the aromatic nuclei of lignin were almost stable during the hydrothermal treatment. This result confirmed that the compact matrix of lignocellulosic material was significantly decomposed, and the remaining solid product was mainly composed of lignin, corroborating the aforementioned composition analyses in Table 1. Moreover, a new vibration band at 1693 cm⁻¹, corresponding to C=O groups, appears in the hydrochar material, indicating the aromatization of the samples. The intensities of the peaks at 1512, 1450, 1422, and 1261 cm⁻¹ were slightly decreased, suggesting the degradation of organic matter to some degree. In addition, an absorption band at 837 cm⁻¹ (aromatic out-of-plane C–H deformation and bending) was observed, which is attributed to the existence of phenolic compounds in the carbonaceous products, in accordance with the results reported by Ryu et al. (2010). A comparative analysis of the FT-IR spectra of the hydrochars and those of the raw materials of CS and TR suggested that dehydration and aromatization processes occurred during the HTC treatment, confirming the results deduced from the evolution of the O/C–H/C atomic ratios in the van Krevelen diagram (see Fig. 1).

The Raman spectra of the carbonaceous samples in the range of 1100–1800 cm^{-1} with $\lambda_0 = 514.5 \text{ nm}$ are presented in Figure 3c. All the curves exhibit two broad and overlapping peaks with intensity maximas at ~ 1370 and $\sim 1590 \text{ cm}^{-1}$, which correspond to the D and G bands of the disordered graphite, respectively (Cuesta et al. 1994). The vibration mode of the D peak is assigned to ring-breathing vibrations in benzene or condensed benzene rings in amorphous carbon films, whereas for the G peak involves the in-plane bond-stretching motion of pairs of C sp^2 atoms both in aromatic and olefin molecules. The G and D bands observed in the carbonaceous materials were relatively broad, indicating that the crystallite size of the carbon in the hydrochar samples was small. Therefore, both peaks revealed the presence of small aromatic clusters in the carbonaceous materials, corroborating the aromatization of the materials observed by FT-IR spectroscopy.

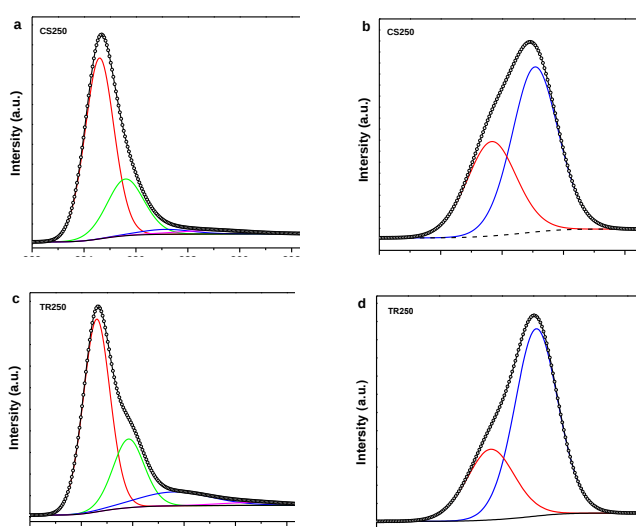


Figure 4. XPS spectra of C 1s (a: CS250, c: TR250) and O 1s (b: CS250, d: TR250) core-level spectra of the hydrochar samples.

XPS was used to characterize the oxygen functional groups at the outer surface of the hydrochar particles. The C 1s core level spectra obtained for the hydrochar samples, together with the peak-fitting of its envelope, are deposited in Figure 4. Each spectrum was resolved into four individual component peaks, namely: (1) aliphatic or aromatic carbon group (CH_x , C-C/C=C ; BE = 284.6 eV); (2) sp^3 hybridized carbon atoms (BE = 285.6 eV); (3) carbonyl groups ($>\text{C=O}$; BE = 287.6 eV); (4) carboxylic groups, esters or lactones ($>\text{COOR}$; BE = 290.7 eV) (Sevilla et al. 2011). On the other hand, the O 1s region in the XPS spectra of hydrochar materials exhibited two deconvoluted peaks at 533.1 and 531.7 eV, representing C=O and C-OH/C-O-C groups, respectively. These results indicated that the hydrochars obtained were enriched in oxygen-containing groups. Meanwhile, a comparison of the (O/C) atomic ratios determined by elemental analysis (see Table 1) with those calculated by XPS (0.169 and 0.230 for CS250 and TR250, respectively) confirmed that the (O/C) atomic ratios in the core and in the shell of the particles were quite similar, further demonstrating that there was also a high concentration of oxygen in the inner part of the hydrochar materials (Sevilla and Fuertes 2009).

Composition of hydrothermal liquors.

Figure 5 shows the results of GC–MS analysis of the ethyl acetate extracts of liquors from the HTC of CS and TR, respectively. The GC–MS analysis of the liquid products revealed that the main sugar-derived products were furfural, 2-ethyl-5-methyl-furan, and 2-hydroxy-3-methyl-2-cyclopenten-1-one. The amounts of these sugar-derived products from CS were lower than those of TR. It was found that the main phenol monomers of the ethyl acetate extracts from CS consisted mainly of 2,6-dimethoxyl, butyl 2-methylpropyl ester-1,2-benzenedicarboxylic acid, and 4-ethoxy-2,5-dimethoxybenzaldehyde. The results showed that these organic molecules ranged from C₈ to C₁₆. On the other hand, the major hydrocarbons of the lignin-derived compounds of TR were 2,6-dimethoxyphenol, 3-methoxy-1,2-benzenediol, *p*-xylene, and phenol, which were in the range of C₆–C₈. Compared to CS, TR produced more benzenediol and phenol derivatives. Additionally, the identified compounds were phenolic compounds and furan derivatives, confirming the mechanism of dehydration, decarboxylation, and demethanation reactions during the carbonization process, in well agreement with the results in the van Krevelen diagram aforementioned. Moreover, phenolic compounds from plant biomass are attractive renewable feedstock to produce phenolic precursors, polymer substitution, carbon fibers, and natural antioxidants as well as green aromatic-based compounds (Lavoie et al. 2011).

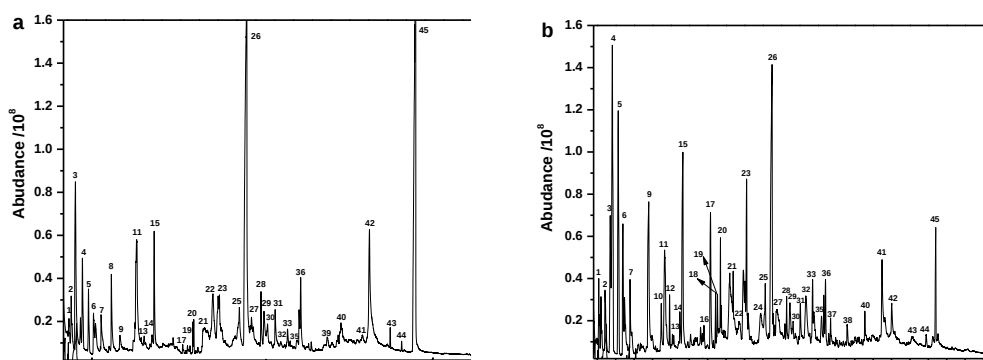


Figure 5. GC–MS chromatograms of the ethyl acetate extracts of the hydrolysates obtained by HTC of CS (a) and TR (b) with internal tetracosane standard (100 µg/mL).

Conclusions

Hydrothermal carbonization of lignocellulosic biomass completely broke down the plant cell wall and allowed rapid conversion of biomass into a carbon-rich and lignite-like product (hydrochar). The carbonized products were composed of water-soluble compounds and solid residues. The aqueous phase contained sugar and lignin derived compounds, which may be desirable feedstocks for biodiesel and chemical production. The resulting solid products consisted mainly of lignin with a high degree of aromatization and a large amount of oxygen-containing groups. Moreover, the hydrochar had a considerably higher heating value than that of the raw material. At last, we proposed a schematic representation of the possible formation process of hydrochars from lignocellulosic biomass via hydrothermal carbonization as shown below:

Acknowledgements

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