ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Wet Torrefaction of Bamboo in Hydrochloric Acid Solution by Microwave Heating

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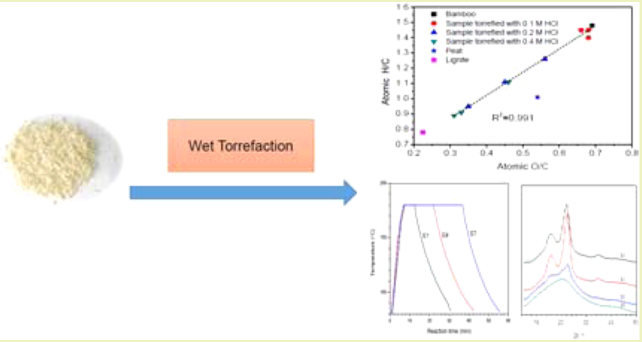
ABSTRACT: Bamboo was hydrothermally torrefied in hydrochloric acid solution assisted by microwave heating at 180 °C for 5−30 min. For bamboo torrefied in water, the yield of the torrefied bamboo decreased slightly from 96.15% to 85.83% and the hemicellulose content decreased from 31.78% to 25.71% with increased torrefaction severity from 3.27 to 3.89. Whereas for bamboo torrefaction in acid solutions, the yield of the torrefied bamboo was below 51% and hemicellulose was completely removed as evidenced by the fact that the solid residue contained no hemicellulose. The carbon content of bamboo was 48.82% and it increased slightly after torrefaction in water. It raised largely up to 67.03% under torrefaction with 0.4 M HCl solution at 180 °C for 30 min. The atomic H/C and O/C ratios of bamboo were 1.479 and 0.694, and as bamboo was wet torrefied, they were in the range of 0.891−1.454 and 0.313−0.676, respectively. The higher heating value (HHV) of the torrefied bamboo increased by 45.20% after torrefaction at 0.2 M HCl for 30 min, which (24.86 MJ kg^{-1}) was higher than that of Converse School-Sub C coal (21.67 MJ kg^{-1}) and comparable with that of German Braunkohole lignite (25.10 MJ kg^{-1}). In addition, the structural modifications of bamboo during the torrefaction process were investigated by chemical component and elemental analyses, CP/MAS ^{13}C NMR, FTIR, XRD complemented with TG/DTA.



KEYWORDS: *Wet torrefaction, Bamboo, Hydrochloric acid, Structural modification, Higher heating value*

INTRODUCTION

Lignocellulose is an abundant, clean and renewable resource in nature, which can be converted into energy and chemicals. The utilization of lignocellulose can reduce our dependence on foreign oil, improve the quality of air and achieve a sustainable economy. Some properties of lignocellulose, such as high volatile substance, high oxygen content, low density, limit its utilization as an energy resource. Torrefaction is an effective thermochemical technology to convert lignocellulose into a solid residue. The torrefied lignocellulose has a higher energy content and is easy to grind, which is a more uniform product for further processing. Because of the good fuel properties, the torrefied products have been used as a replacement of coal and as a feedstock for the production of pellets and briquettes.[1,2]

Generally, there are two ways to torrefy lignocellulose: dry and hydrothermal technologies. Dry torrefaction is conducted in an inert gas atmosphere at 200−350 °C. Numerous works have been conducted for many lignocelluloses under different conditions.[3−7] In this process, over 80% of the energy and 70−90% of the mass of lignocellulose are retained in solid char.[8] Hydrothermal torrefaction is considered to be a new promising approach to increase the energetic value of lignocellulose, achieving a value-added utilization. The hydrothermal torrefaction in water refers to heat a suspension of lignocellulose and water at 180−250 °C under saturated pressure. The exothermic process results in three products: gases, aqueous chemicals and solid residue (hydrochar). It should be noted that because the heat released during the carbonization process was very small and the reactor was cooled by the surroundings, a heating system should be used to maintain the temperature for the reaction of carbonization. Although higher temperature produced hydrochar with higher fuel calorific value, heating the reaction system to a high temperature needs more power, thus the application of a medium to achieve carbonization in a low temperature is energy efficient. Many studies have been carried out on hydrothermal torrefaction with respect to various feedstocks including loblolly pine,[9] palm empty fruit bunches,[10] eucalyptus sawdust and barley straw,[11] digested maize silage,[12] walnut shell and sunflower stem,[13] grape pomace,[14] etc. Yan et al. studied the hydrothermal torrefaction of loblolly pine at 200−260 °C, and found that the hydrothermal torrefaction achieved a higher energy densification as compared to the dry torrefaction under nitrogen atmosphere.[9] In the torrefaction of loblolly pine with hot compressed water at 200−260 °C for 5 min, it was found that a higher temperature resulted in the hydrochar obtained

Received: April 11, 2015
Revised: June 10, 2015
Published: August 18, 2015

DOI: 10.1021/acssuschemeng.5b00296
ACS Sustainable Chem. Eng. 2015, 3, 2022−2029

Table 1. Reaction Condition, Yield and Chemical Component of Torrefied Bamboo Samples

						chemical component (%)				
entry	heating time (min)	concentration of HCl (M)	severity parameter	solid sample	yield (%)	cellulose	xylan	arabian	galactan	lignin
E1	5	0	3.27	S1	96.15 ± 1.05	40.66 ± 0.86	30.45 ± 1.02	1.02 ± 0.16	0.31 ± 0.06	23.74 ± 0.80
E2	15	0	3.61	S2	90.59 ± 1.24	41.83 ± 0.93	29.09 ± 1.21	0.73 ± 0.18	0.26 ± 0.09	25.92 ± 0.81
E3	30	0	3.89	S3	85.83 ± 0.85	42.61 ± 1.02	25.00 ± 0.03	0.53 ± 0.16	0.18 ± 0.06	23.18 ± 0.23
E4	5	0.2	3.27	S4	50.47 ± 0.93	51.54 ± 0.21	0	0	0	31.82 ± 0.81
E5	15	0.2	3.61	S5	41.36 ± 0.69	34.97 ± 0.13	0	0	0	33.94 ± 1.73
E6	30	0.2	3.89	S6	36.72 ± 1.02	13.96 ± 0.76	0	0	0	36.98 ± 1.15
E7	5	0.4	3.27	S7	40.46 ± 1.19	32.14 ± 0.21	0	0	0	27.00 ± 0.23
E8	15	0.4	3.61	S8	37.46 ± 0.69	5.76 ± 0.59	0	0	0	36.18 ± 1.96
E9	30	0.4	3.89	S9	36.01 ± 0.72	1.27 ± 0.62	0	0	0	34.99 ± 1.61
0				S0		41.98 ± 0.93	33.58 ± 0.43	1.21 ± 0.21	0.39 ± 0.19	24.20 ± 1.17

with a higher fuel calorific value and a lower mass yield.[15] To reduce the torrefaction temperature, the addition of acid is a feasible approach. The addition of acid in the hydrothermal carbonization process results in intensifying the degradation of hemicellulose. As compared to the carbonization in water, the carbonization with acid produced chars with higher HHV and fixed carbon, as well as less moisture and volatile material contents. The addition of sulfuric acid achieved the torrefaction of sugarcane bagasse at a low temperature of 180 °C with a solid concentration of 0.2 g mL^{-1}, yielding hydrochar with better properties. The carbonization with 0.1 mol L^{-1} H_2SO_4 produced a char with less moisture content and volatile material content of 2.1% and 77.8%, as compared to 3.5% and 89.6% of the char prepared by carbonization in water, respectively; whereas the fixed carbon content and HHV were 20.2% and 18.86 MJ kg^{-1}, increment up to 119.6% and 11.1%, respectively, as compared to those prepared by torrefaction in water.[16] When loblolly pine was torrefied at 230 °C for 5 min, the addition of acetic acid and/or lithium chloride was found to increase the energy density of the solid product.[17] The addition of acetic acid also led to the enhancement of the degradation of hemicellulose as well as the HHV. In addition, volatile acid was easy to recycle for treating new batches.

In most cases, the hydrothermal torrefaction was practiced via conductive and convective heating. Microwave irradiation utilizes the ability of direct interaction between an object and an electromagnetic field to create heat, which shows many advantages including shortening the heating time, easiness of starting and stopping, and reduction in reactor size.[18] When a microwave is used to treat lignocellulose in water solution, it selectively heats the polar proportion and creates "hot spots" because the dielectric material is inhomogeneous. Because the major components of lignocellulose, water and inorganic acids are dielectrics, the mixture of them can be treated by microwave through a dielectric heating.[19] Thus, application of a microwave to heat lignocellulose for torrefaction deserves exploration.

Bamboo is viewed as a promising feedstock for the energy uses due to its short growth cycle (typically matures within 5−7 years) as well as good fuel characteristics such as low ash content and alkali index.[20] Annually, over 6 million tons of bamboo are produced in Asia. Bamboo is traditionally used for the production of paper, textile, furniture, etc., and exploring an efficient approach to convert this feedstock into useful products is an urgent issue. In the present work, bamboo was subjected to torrefaction in diluted acid solutions by microwave heating. The effect of acid concentration on the chemical component and structural properties of the torrefied bamboo was investigated by chemical and elemental component analyses, CP/MAS ^{13}C NMR, FTIR, XRD and TG/DTA. The study will provide a comparative evaluation of the performance of the conversion of bamboo, which is meaningful for its utilization.

■ EXPERIMENTAL SECTION

Raw Material. Bamboo was acquired from a plantation in Yunnan province, China. The bamboo culm was collected and air-dried. Then it was ground and sieved to obtain particles ranging from 20 to 80 mesh. The sample (S0) was stored in a desiccator at room temperature before use. Water with a conductivity of 18 MΩ cm^{-1} was used from a pall PALL Cascada I system. HCl (34%) was purchased from Beijing Chemical Regent Company. The monosaccharides (L-arabinose, D-xylose, D-glucose, D-mannose, and D-galactose) used for carbohydrate analysis were provided by Sigma-Aldrich.

Microwave Assisted Torrefaction. Wet torrefaction of bamboo was conducted by microwave heating in water and acid solutions under various times and acid concentrations (Table 1). In a typical run (E6), 10 g of bamboo was mixed with 100 mL of 0.2 M HCl solution, and then the mixture was transferred into a cylindrical reactor with a Teflon liner. The reactor was closely sealed after capped, shaken evenly and placed in a microwave oven and the vessel allowed microwave irradiation to heat the mixture. The maximum power was 500 W and the frequency was 2500 MHz. The temperature was monitored using a platinum resistor sensor system installed in the vessel. The temperature profile contained a fast heating step followed by a plateau one in which the power varied to maintain temperature at the target value. The samples were heated for 30 min at 180 °C before the microwave irradiation was stopped. The maximum pressure of the system was 1.05 MPa. Subsequently, the reactor was cooled to 50 °C and was removed from the oven. The temperature of the mixture was detected by a transducer and the time−temperature profile was recorded. The torrefied sample was separated by filter paper, and the filtrate was recovered and stored at 0 °C before analysis. The filtrated residue was washed thoroughly with hot water (200 mL and 90 °C) four times to remove the remained acid in the particles, reducing the effect of acid on the subsequent analysis of the sample. The residue obtained (S6) was dried at 105 °C for 12 h for further analysis.

Analysis of the Samples. The yield of the torrefied sample was determined by the ratio of the product over the original bamboo. The carbohydrate and lignin contents of the sample were determined according to the National Renewable Energy Laboratory (NREL) standard analytical procedures (LAP-002 and LAP-005). pH of the solution liquors (noted as B1, B2, B3, B4, B5, B6, B7 and B8) was examined by a digital pH meter (Sartorius PB-10). Elemental components (C, H and N) of the sample were determined on an elemental analyzer (Elemental Vario EL III). Oxygen content was estimated by difference. The higher heating value (HHV) was calculated by the Dulong formula: HHV (MJ/kg) = $0.3383Z_C + 1.422(Z_H - Z_O/8)$, where Z_C, Z_H and Z_O are the weight percentages of C, H and O, respectively.[21] The data were tested in triplicates and the errors were calculated.

FTIR spectra were collected in the range of 4000−650 cm^{-1} at a resolution of 4 cm^{-1} on a Nicolet iN10 spectrophotometer with an MCT detector. X-ray diffractograms were obtained by using a XRD-6000 instrument (Shimidzu, Japan). The preparations were laid on a glass sample holder and analyzed under plateau conditions. The X-ray diffractograms were recorded from 5° to 43° (2θ) at a scanning speed of 5° min^{-1}. CP/MAS ^{13}C NMR spectra were acquired on a spectrometer (100 MHz) at 25 °C with a 4 mm MAS BBO probe. About 250 mg of the sample was packed into zirconia rotors for MAS. The measurement was performed using a CP pulse program with acquisition time 0.034 s, delay time 2 s and accumulation 5000 scans. Thermal degradation behavior of the samples was investigated by a thermogravimetric analyzer (SDT Q600, TA Instrument). Samples (5−10 mg) were heated from 30 to 750 °C under nitrogen atmosphere at a flow rate of 50 mL min^{-1} and a heating rate of 10 °C min^{-1}. The combustion characteristics were determined by the same thermogravimetric analyzer under air atmosphere with a flow rate of 50 mL min^{-1} and a heating rate of 10 °C min^{-1}.

■ RESULTS AND DISCUSSION

Component Analysis of the Sample. Bamboo was torrefied by microwave-assisted heating in aqueous solution at different acid concentrations as compared to water. When compared to alkaline media, carbonization in acid solution shows more effect on the increment of elemental carbon which contributes to the increment in energy yield during the process.[22] In this study, HCl was selected as the acidic medium because it was a strong acid and was easy to recovery. Among the acids, although H_2SO_4 also showed a strong acidic property, it is not easy to recover for its poor volatility. The temperature−time profiles during the heating and cooling process are illustrated in Figure 1. The severity parameter (S_o) of the sample was calculated by the equation below:

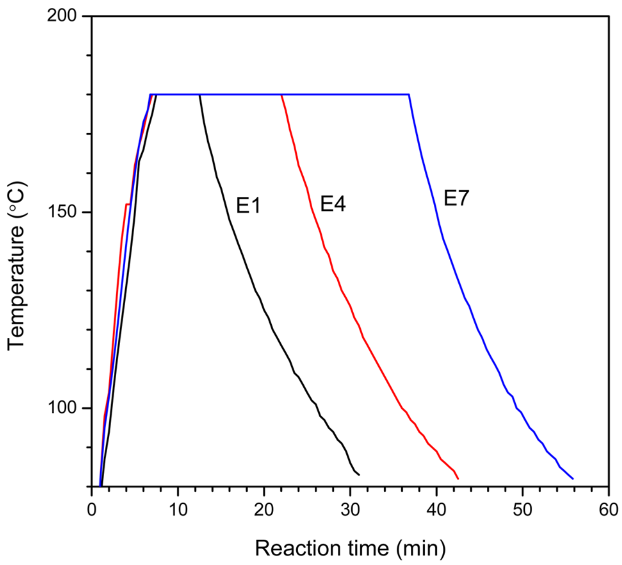


Figure 1. Temperature profile of bamboo torrefaction in acid solutions.

$$S_O = \log R_O = \log(R_{O\text{heating}} + R_{O\text{cooling}})$$
$$= \log\left[\int_0^{t_{\text{Max}}} \exp\frac{T(t) - T_{\text{Ref}}}{\omega}\text{d}t + \int_{t_{\text{Max}}}^{t_F} \exp\frac{T'(t) - T_{\text{Ref}}}{\omega}\text{d}t\right]$$

where t_{Max} and t_F are the time at maximum heating temperature and the time at the whole heating−cooling process, $T(t)$ and $T'(t)$ are the temperatures during the heating and cooling process, and ω and T_{ref} are 14.75 and 100 °C, respectively, according to the literature.[23] The severities were 3.27, 3.61 and 3.89 during the torrefaction for 5, 15 and 30 min at 180 °C in the present study (Table 1). The changes of the pH value of the aqueous solutions are depicted in Table 2. The pH of the aqueous solution without the addition of acid was 6.10 due to the existence of a minor amount of CO_2 in water, and it decreased with the increase of the acid concentration. After the torrefaction, the pH value decreased with the prolongation of the reaction time. The drop of the pH value was mainly due to the formation of acetic acid, formic acid, etc., during the torrefaction process.

Table 2. pH of the Aqueous Solution before and after the Wet Torrefaction

aqueous solution sample	heating time (min)	concentration of HCl (M)	pH of the solution before torrefaction	pH of the solution after torrefaction
B1	5	0	6.10 ± 0.05	4.33 ± 0.10
B2	15	0	6.10 ± 0.05	3.84 ± 0.09
B3	30	0	6.10 ± 0.05	3.69 ± 0.12
B4	5	0.2	0.88 ± 0.09	1.02 ± 0.06
B5	15	0.2	0.88 ± 0.09	0.98 ± 0.04
B6	30	0.2	0.88 ± 0.09	0.93 ± 0.02
B7	5	0.4	0.69 ± 0.07	0.76 ± 0.03
B8	15	0.4	0.69 ± 0.07	0.71 ± 0.04
B9	30	0.4	0.69 ± 0.07	0.65 ± 0.03

In this work, the compositional changes were studied by quantification of each component as listed in Table 1. For bamboo torrefied in water, the yield of the torrefied bamboo decreased slightly from 96.15% to 85.83% and the hemicellulose content (sum of the contents of xylan, arabian, and galactan) decreased from 31.78% to 25.71% with increased torrefaction severity from 3.27 to 3.89. Whereas for bamboo torrefaction in acid solutions, the yield of the torrefied bamboo was below 51% and hemicellulose was completely removed as evidenced by the fact that the solid residue contained no hemicellulose. Especially, the torrefaction with 0.2 M HCl solution for as short as 5 min resulted in the complete elimination of hemicellulose, and the cellulose content decreased while the lignin content increased when further propagation of the heating time to 30 min. The reduction of carbohydrates, especially hemicellulose, was also reported by many other studies of hydrothermal treatment. Xiao et al. have reported that a significant amount of hemicellulose was lost in the hydrothermal liquefaction of corn stalk and *Tamarix ramosissima*.[24] Solublization of arabinoxylan has also been observed in hydrothermal treatment of wheat straw by Holopainen-Mantila.[25] At a high temperature, water auto-ionized to produce hydronium ions resulting in hydrolysis and deacetylation of hemicellulose. The released acetic acid further generated hydronium ions, which enhanced the degradation of hemicellulose. When the concentration of acid increased from 0.2 to 0.4 M, both the yield of the solid and the cellulose content decreased. This indicated that the acid solution played an important role to intensify the decomposition of both hemicellulose and cellulose. Similar results have been reported in dilute acid hydrolysis of loblolly pine, in which the addition of dilute acids (trifluoroacetic acid, H_2SO_4, H_3PO_4 and HCl) resulted in more intense degradation of carbohydrates.[26]

Table 3. Elemental Components, HHV and Energy Yield of the Torrefied Bamboo as Compared to the Raw Material

solid sample	elemental analysis (%)				
solid sample	C	H	O	HHV (MJ kg $^{-1}$)	energy yield (%)
S1	49.44 ± 0.06	6.02 ± 0.08	44.54 ± 0.14	17.38	97.61
S2	49.58 ± 0.13	5.84 ± 0.04	44.58 ± 0.17	17.16	90.80
S3	49.99 ± 0.05	6.10 ± 0.18	43.91 ± 0.23	17.79	89.19
S4	54.03 ± 0.12	5.72 ± 0.13	40.26 ± 0.25	21.12	62.26
S5	59.01 ± 0.11	5.51 ± 0.19	35.49 ± 0.30	24.19	58.44
S6	64.65 ± 0.01	5.14 ± 0.02	30.21 ± 0.03	24.86	53.32
S7	58.40 ± 0.16	5.46 ± 0.07	36.14 ± 0.23	19.27	45.54
S8	65.77 ± 0.06	5.00 ± 0.11	29.23 ± 0.17	21.51	47.07
S9	67.03 ± 0.29	5.01 ± 0.07	27.96 ± 0.36	23.84	50.14
S0	48.82 ± 0.25	6.06 ± 0.08	45.12 ± 0.33	17.12	

Elemental Analysis. The results of elemental analysis of the torrefied bamboo samples are listed in Table 3. The carbon content of bamboo was 48.82% and it increased slightly after torrefaction in water. It raised largely up to 67.03% under the torrefaction with 0.4 M HCl solution at 180 °C for 30 min. The atomic H/C and O/C ratios of bamboo were 1.479 and 0.694, and as bamboo was wet torrefied, they were in the range of 0.891−1.454 and 0.313−0.676, respectively. Clearly, the atomic H and O were lost notably during the torrefaction. Similar findings have also been reported in the hydrothermal carbonization of eucalyptus sawdust and barley straw at 250 °C.[11] Generally, lignocelluloses have high oxygen contents as compared to other fuels. The significant decrease in H and O contents was mainly due to the dehydrogenation, deoxygenation and dehydration reactions during the process. To have a comprehensive overview of the effect of torrefaction on the atomic H/C and O/C ratios, the data from Table 3 were further processed and are plotted in a van Krevelen diagram in Figure 2. The plot of atomic H/C versus atomic O/C in the van Krevelen diagram showed a strong linear correlation (R^2 = 0.991), i.e., an increase of the severity of torrefaction resulted in a reduction of both H/C and O/C ratios. The figure showed that the torrefaction followed a dehydration process, similar to the case in the hydrothermal process of simple saccharides such as glucose, sucrose and starch.[27] In addition, there is a slight deviation from the line with respect to the variation from the raw material to the torrefied samples, indicating the occurrence of decarboxylation.[11] For comparison, the values for peat[28] and lignite[29] are also depicted in the figure. It was found that the atomic H/C and O/C values in wet torrefaction approached to those of peat and lignite. The HHV of the torrefied sample showed a higher value than that of the original sample and it increased by 45.20% after torrefaction at 0.2 M HCl for 30 min, which (24.86 MJ kg^{-1}) was higher than that of Converse School-Sub C coal (21.67 MJ kg^{-1}) and comparable with that of German Braunkohole lignite (25.10 MJ kg^{-1}).[30]

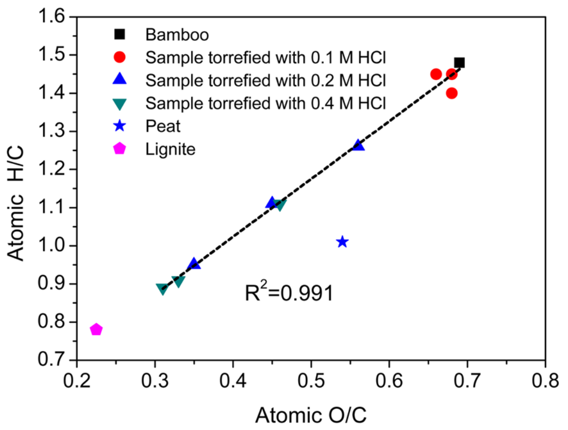


Figure 2. van Krevelen diagram for bamboo torrefaction.

Energy yield was calculated according to the following equation: energy yield = solid yield × the HHV ratio of pretreated biomass to that of the original bamboo. The calculated value is illustrated in Table 3. During the torrefaction with water only and low concentration acid, the energy yield decreased with the prolongation of reaction time, whereas when bamboo was torrefied with a high concentration acid, the energy yield was lower, but it showed a slight increase trend with the prolongation of the reaction time, probably due to the relative predominance of condensed reactions to form solid products with a higher HHV.

Structural Analysis. In addition to the indirect methods to characterize the chemical structural modification of the bamboo during the torrefaction, CP/MAS ^{13}C NMR was used to analyze the original and the torrefied bamboo samples as shown in Figure 3. The intensity at 153 and 148 ppm corresponding to aromatic C−O bonds (ether linkage at 153 and free phenoic hydrogen groups at 148 ppm) increased from S0 to S6, indicating that more free phenolic hydroxyl groups were generated after the torrefaction. The increase of the intensity at 148 ppm indicated that aryl ether bonds cleaved during the torrefaction. The signal at around 130 ppm also increased after the torrefaction, suggesting that aromatic C−C bonds in lignin increased, mainly attributed to the cleavage of lignin ether bonds which recondensed to form aromatic C−C bonds.[31,32]

In addition, some carbohydrates also converted into aromatic substances.[33,34] The signals at 89 and 84 ppm are indicative of crystalline and amorphous cellulose, respectively. For the raw material, the signal assigned to crystalline cellulose was less than that of amorphous cellulose. These signals were observed in the sample torrefied under mild conditions in water (S3), but the intensity at 84 ppm decreased due to the removal of amorphous cellulose (S6), and both the signals at 84 and 89 ppm disappeared in the sample (S9) subjected to intense treatment.

The signal at 25 ppm corresponding to methyl carbons in hemicellulose acetyl groups was still present in the spectrum of S3 but disappeared in the spectra of S6 and S9, suggesting that serious torrefaction resulted in the complete deacetylation. During torrefaction, the intensity corresponding to the methoxyl group in lignin (55 ppm) steadily increased with the increase of the concentration of HCl. The release of

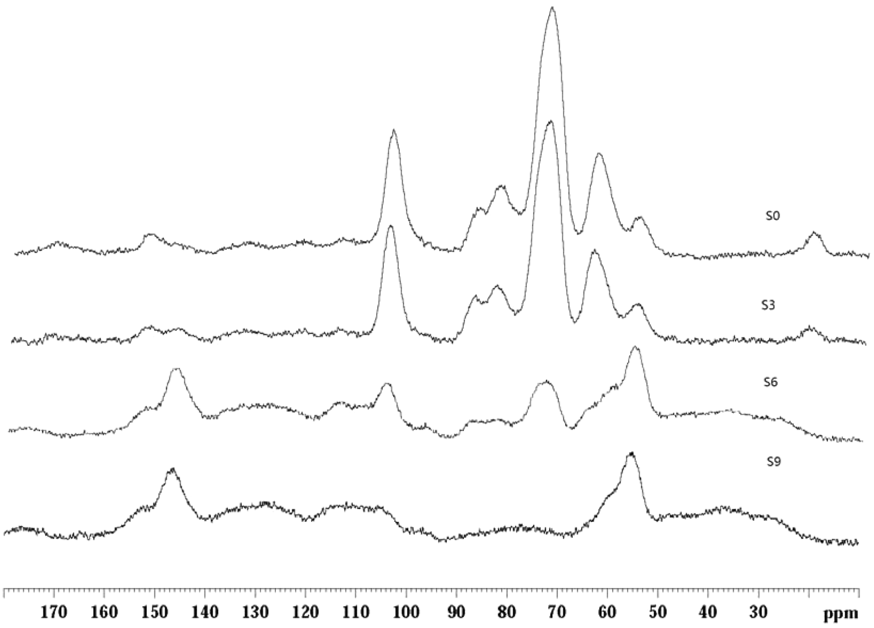


Figure 3. CP/MAS ^{13}C NMR spectra of the torrefied bamboo samples (S3, S6 and S9) as compared to the raw material (S0).

carbohydrates and the concentration of lignin, resulting a higher signal for methoxyl group for torrefied bamboo.

All the data above indicated that the decomposition reaction was accelerated under higher acid concentration. For the sample under serious acid torrefaction (S6), the signals for cellulose and hemicellulose nearly completely disappeared and the residue enriched in complex condensed aromatic substance including carbonyl groups, aromatic and methoxyl groups, as indicated by the signals at 100−60 ppm (C−O bonds) and 55 ppm. However, these signals also disappeared for sample S9. This suggested that the structure of cellulose was substantially modified under intense torrefaction. The decrease of signal of cellulose was also observed in the torrefaction of loblolly pine under inert gas atmosphere, in which the structure of cellulose was modified with increase of the severity of torrefaction.[2] It has also been reported that the structure of ordered cellulose was modified under serious torreification.[35] In an early report on the hydrothermal carbonization of corn cob and *Miscanthus* at 230 °C for 6 h, it has also been observed that the signal corresponding to aromatic substance was enhanced but that for cellulose was decreased noticeably as compared to the raw material.[36]

Fourier transform infrared spectroscopy was used to characterize the structural modification of bamboo, and the spectra obtained are shown in Figure 4. The main absorption signals for the original bamboo sample (S0) were assigned as (a) the peaks at 2900 and 2850 cm^{-1}, C—H stretching and deforming vibrations, (b) the peak at 1740 cm^{-1}, C═O stretching vibration, carbonyl and ester groups from hemicellulose, (c) the signals at around 1610−1450 cm^{-1}, C═C stretching of aromatic groups and (d) the peak at 1160 cm^{-1}, C—O—C vibrations of cellulose and hemicellulose.

As it can be seen, there were some structural modifications in the bamboo sample after the torrefaction treatment based on the changed chemical components. The signal corresponding to the O−H group (3400 cm^{-1}) was still presented in the torrefied sample. The peak at 2920 cm^{-1} was observed in all the spectra, indicating that aliphatic and hydroaromatic groups were present in both bamboo and the torrefied samples. The signal at 1740 cm^{-1} sharply decreased in the spectrum of S3 but disappeared in the spectra of S6 and S9, suggesting the removal of acetyl groups of hemicellulose. On the other hand, the signal at 1700 cm^{-1} corresponding to C═O vibrations of carbonyl, quinone, ester, or carboxyl groups was observed in the spectra of S6 and S9. In addition, the signals attributed to aromatic skeletal vibration at 1608, 1510 and 1270 cm^{-1} became relatively intense as compared to those for carbohydrates, indicating the aromatization of bamboo. The appearance of more intense peaks at 1700, 1610 and 1510 cm^{-1} can also be attributed to the furnic substance generated from carbohydrates during the torrefaction.[37] The intensity at 897 cm^{-1} was attributed to the C−H deformation of cellulose. This peak was observed in the spectra of S0 and S3 but shifted to 910 cm^{-1} in the spectra of S6 and S9. The changes of signals of bamboo were analogous to those in hydrothermal torrefaction of

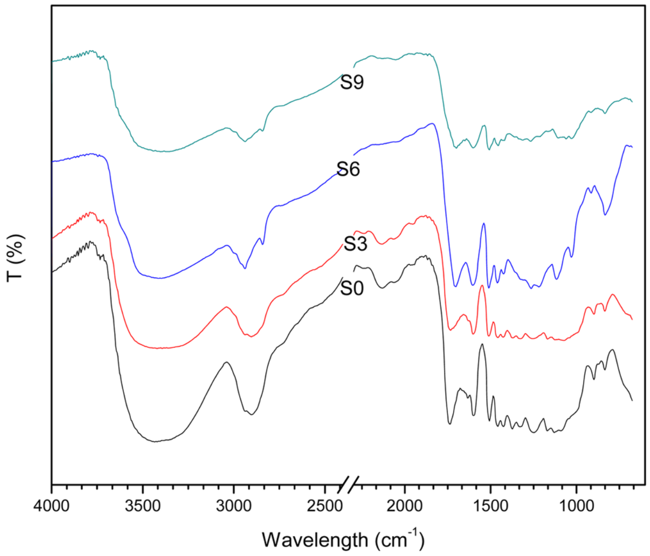


Figure 4. FTIR spectra of the torrefied bamboo samples (S3, S6 and S9) as compared to the raw material (S0).

sprucewood and bagasse where signals for carbohydrates decreased while that for lignin increased.[38]

For the major components in lignocellulose, only cellulose is crystalline whereas hemicellulose and lignin are amorphous. Because the chemical component of bamboo was modified after the torrefaction, the crystalline structure of lignocellulose will be modified. As a useful approach to analyze the crystalline structure of lignocellulose, X-ray diffraction was utilized to investigate the effect of torrefaction on the crystallinity of the samples (Figure 5). For the original bamboo, the signals at 2θ = 16° and 22° are indicative of celluloses I and corresponds to the (110) and (200) planes of cellulose. There was a slight increase of the signals after the torrefaction under mild conditions (S3) but they sharply decreased after the torrefaction under acid conditions (S6 and S9). The calculated crystallinity of the original sample was 29.6%, and it increased to 33.3% after torrefaction in water for 30 min (S3) mainly due to the removal of amorphous components, but it decreased to 15.2% in S6 after torrefaction in acid solution. However, the sample became amorphous (S9) when torrefied in more concentrated acid. Similar findings have also been reported in the torrefaction of sprucewood and bagasse in an auger reactor, in which the crystallinity of cellulose was observed to decrease after hydrothermal torrefaction at 300 °C.[38]

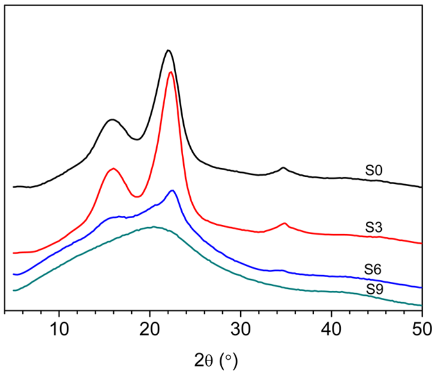


Figure 5. X-ray diffraction pattern of the torrefied bamboo samples (S3, S6 and S9) as compared to the raw material (S0).

Thermal degradation and combustion behaviors of bamboo and the torrefied samples were examined by thermogravimetry, and the TG/DTA curves are illustrated in Figure 6. For the degradation under inert atmosphere (Figure 6a,b), the slight weight loss that occurred at temperatures below 130 °C was due to the valorization of small molecule. The main degradation occurred between 200 and 460 °C. Hemicellulose began to decompose at 200 °C and the maximum degradation was reached at 260 °C. At temperatures higher than 320 °C, cellulose began to decompose and the peak centered at 432 °C corresponding to the degradation of lignin. From the curves, it can be seen that there was a slight change of the profile of the sample after torrefaction in water. For S3, the peak below 130 °C became smaller, indicating that it contained less volatile molecules. The change of the peak at around 432 °C indicated the degradation of cellulose and lignin. For comparison, the appearance of the peak at around 400 °C in the curves of S0

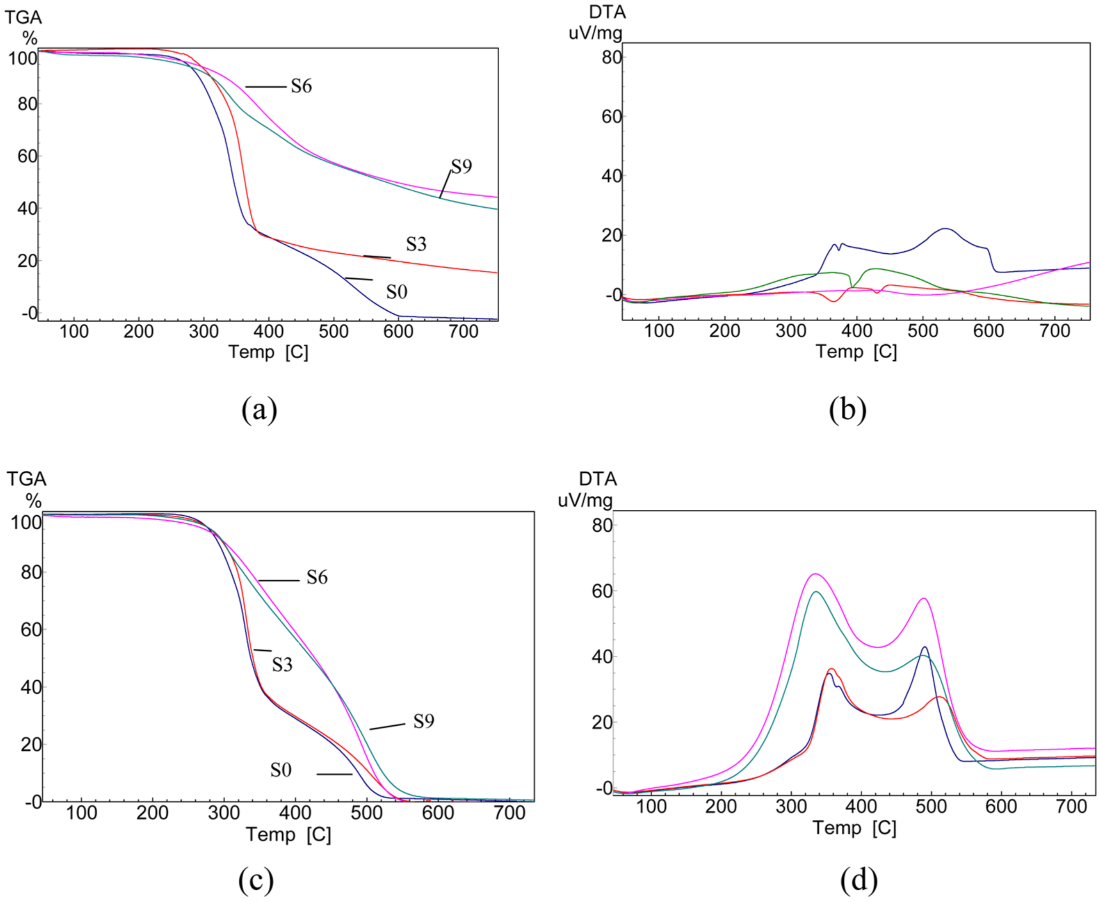


Figure 6. TG/DTA curves of the torrefied bamboo samples (S3, S6 and S9) as compared to the raw material (S0).

and S3 suggested that the structure of cellulose did not change much. Whereas for the samples S6 and S9, the peak below 130 °C became smaller due to the removal of volatile molecules. The main degradation stage of the sample occurred at temperatures over 300 °C, ascribed to cellulose. Lignin began to degrade at 420 °C, and the peak at around 550 °C was ascribed to the rapid degradation of lignin. At 750 °C, the solid residue yields were 0, 16.1%, 44.2% and 40.5% for S0, S3, S6 and S9, respectively. In a previous study conducted by Chang et al., it was also found that the intense severity of torrefaction resulted in higher solid residue during TG analysis.[38] The results were in accordance with the fact that the torrefaction with water mainly led to the partial removal of hemicellulose whereas the torrefaction under acid solutions caused the serious degradation of cellulose besides hemicellulose. In the DTA figure, the significant change of the peaks of S6 and S9 as compared to S0 was ascribed to the degradation of the repolymerization products, which were formed during the torrefaction under acid conditions. A similar phenomenon was also observed when torrefaction of grape pomace under serious conditions.[14]

Thermogravimetric analysis of the samples under air atmosphere was conducted to reveal the information on the combustion behavior of hydrochars. As shown in Figure 6c,d, the combustion process was divided into two stages where the loss of volatile compounds occurred in the first stage and the compounds with high molecular weight and char were oxidized in the second stage. The second combustion stage was related to the lignin content. Ignition temperature was determined according to the temperature at which the differential curve showing its peak and the corresponding slop to the intersection to TG profile. Burnout temperature represented the temperature at which the mass loss rate was less than 1%/min. For the samples S0, S3, S6 and S9, the ignition temperatures were 293, 306, 280 and 270 °C, whereas the burnout temperatures were 518, 542, 546 and 552 °C, respectively. Burnout temperature manifests the residence time of the fuel. The increase of the burnout temperature of the sample after carbonization indicated that these torrefied bamboo samples showed longer residence time in the combustion process than the original bamboo. In addition, the combustion processes of the torrefied bamboo samples exhibited higher exothermal changes than the thermal degradation processes under nitrogen medium as evidenced by the DTA data in Figure 6b,d.

CONCLUSIONS

Bamboo was wet torrefied with microwave heating at a mild temperature of 180 °C. For bamboo torrefied in water, the yield of the torrefied bamboo decreased from 96.15% to 85.83% and the hemicellulose content decreased from 31.78% to 25.71% with increased torrefaction severity from 3.27 to 3.89. Whereas for bamboo torrefaction in acid solutions, the yield of the torrefied bamboo was below 51% and hemicellulose was completely removed. The carbon content of bamboo raised largely up to 67.03% under torrefaction with 0.4 M HCl solution for 30 min. The atomic H/C and O/C ratios of the torrefied bamboo samples were in the range of 0.891−1.454 and 0.313−0.676, respectively. The HHV of the torrefied bamboo (24.86 MJ kg^{-1}) was higher than that of Converse School-Sub C coal (21.67 MJ kg^{-1}) and comparable with that of German Braunkohole lignite (25.10 MJ kg^{-1}). Structural analysis indicated that the signal corresponding to aromatic substance was enhanced but that for cellulose decreased after torrefaction under acid solution. Bamboo became amorphous when torrefied in concentrated acid as evidenced by XRD analysis. The torrefied bamboo samples exhibited longer residence times in the combustion process than the original bamboo.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Fundamental Research Funds for the Central Universities (No. YX2015-01), Beijing Natural Science Foundation (6154031) and the National Natural Science Foundation of China (31400508, 31110103902).

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DOI: 10.1021/acssuschemeng.5b00296
ACS Sustainable Chem. Eng. 2015, 3, 2022−2029