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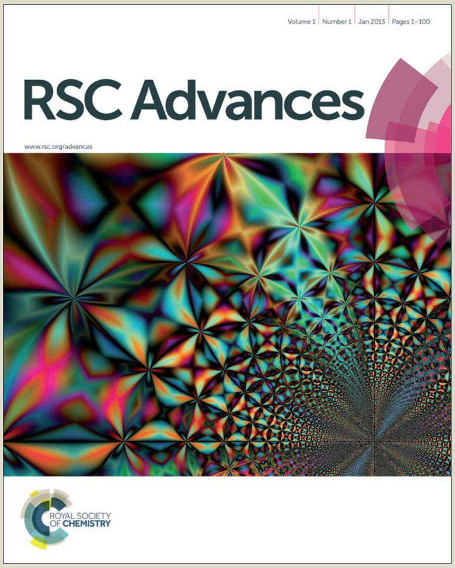

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Hydrothermal carbonization of bamboo in oxalic acid solution: effects of acid concentration and retention time on characteristics of products

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ABSTRACT: Bamboo was hydrothermally carbonized in a batch reactor using oxalic acid solution at 190 ℃ for the production of hydrochar and aqueous products. The influences of oxalic acid concentration and retention time were examined, and the products obtained were characterized in terms of energy yield, chemical component and structure properties. It was found that the energy densification values at a high acid concentration of 0.8 mol/L were comparable to most torrefied lignocelluloses. No hemicelluloses were detected in the hydrochar obtained at the highest severity (0.8 mol/L acid concentration and 20 min), indicating that lignocellulose hemicelluloses were completely removed. In addition, cellulose also showed some degradation, and the highest degradation rate of cellulose was 56.69% at the highest carbonization. The lignin content showed an increase trend in the hydrochar with increased carbonization severity. The thermal stability of the hydrochar increased with the carbonization severity. The aqueous solution obtained had a high antioxidant capacity with 2,2-diphenyl-1-picryl-hydrazyl inhabitation rate of 63.5%, higher than that of commercial antioxidant butylated hydroxytoluene (46.4%). The present study indicated that hydrothermal carbonization of bamboo produced solid hydrochar with high potential for application as a fuel and degraded chemicals as an antioxidant.

1. Introduction

Lignocelluloses are clean and renewable sources in nature, which can be transformed into various forms of energy by the thermochemical process. The production of energy from lignocellulose can reduce our dependence on foreign oil, improve the air quality as well as support the sustainable development of society. However, lignocelluloses show many drawbacks, such as high oxygen content, hygroscopic nature, low bulk density. Consequently, the utilization efficiency of lignocelluloses is low and they are not suitable for the further processing. Therefore, pretreatment technologies are needed to address these disadvantages for the preparation of solid fuel, which provides a more suitable feedstock for further conversion, such as combustion and gasification. Among the many protocols, carbonization attracts much attention since it improves not only the energy content of lignocellulose [1], but also the properties for handling, transportation, and storage [2].

Generally, there are two processes for carbonization of lignocellulose to intensify the energy: torrefaction and hydrothermal carbonization. Torrefaction is pyrolysis process at relatively low temperatures ranging from 200-300 ℃ under inert gas atmosphere. Many works have been conducted on analysis of the products for torrefaction of various feedstocks under different conditions [3-6]. During the process, 80-95% of the energy and 70-90% of the mass of lignocelluloses are preserved in solid chars [7]. On the other hand, much attention has been recently paid to preparation of hydrochar by hydrothermal carbonization of lignocelluloses for a range of uses. Hydrothermal carbonization refers to the preparation of solid residue (hydrochar) at temperatures ranging from 180 to 250 ℃ applying suspended lignocelluloses and water under saturated pressure. Three products: solid fuel, aqueous chemicals, and gases, are produced during the endothermic process. The study of loblolly pine carbonized by hot water at 200-260 ℃ indicated that hydrothermal carbonization achieved higher energy densification at the same mass yield as compared to dry torrefaction in N_2 at 250 -300 ℃ [8]. Hydrothermal carbonization can be conducted at temperatures 100 ℃ lower than that of torrefaction under gas when achieving the same calorific value. Generally, the energy density of lignocellulose is enhanced and the higher heating value (HHV) is increased by about 3-47% after hydrothermal carbonization [9]. In addition, the hydrochar obtained showed hydrophobic properties after carbonization, indicating better storage characteristics [10]. The hydrothermal process is associated with a series of hydrolysis, condensation, decarboxylation, and dehydration reactions [11]. During the hydrothermal carbonization process, acids are also produced and dissolved in the aqueous solution thus promote the reactions of lignocelluloses. For instance, it was reported that 0.025 g acetic acid was produced per gram of loblolly pine when hydrothermally carbonized at 230 ℃ for 5 min. Formic acid and lactic acid have also been reported during hydrothermal carbonization [8]. Since the major reactions during hydrothermal torrefaction are caused by the H^+ from water as well as the released acids, it is hoped that the addition of acid could promote the reaction thus reduce the reaction temperature.

Bamboo has recently received special attention due to its easy propagation, fast growth and regeneration, high productivity as well as rapid maturity. The plantation of bamboo achieves efficient utilization of land and yields more biomass per unit area than other plants [12]. Bamboo represents an important natural resources traditionally used to produce furniture, veneers and flooring. A significant amount of bamboo is unsuitable for manufacturing products and is available in processing sites. Thus, the utilization of bamboo for bioenergy production is deserved to explore. Since the potential of products from bamboo hydrothermally carbonized under acid solution has not been investigated, a comprehensive study is required to achieve the value-added utilization of bamboo. In this work, oxalic acid solution was used as the reaction medium. Oxalic acid was selected since it is more environmentally friendly than mineral acids such H_2SO_4 and it is natural as a secondary metabolite products in some plants. The influences of oxalic acid concentration and retention time during bamboo carbonization were examined. The results about hydrochar in terms of energy yield, chemical component and structural properties were presented. In addition, the liquid product obtained after the hydrothermal carbonization was also investigated with respect to the antioxidant capacity.

2. Materials and Methods

2.1. Materials

Bamboo (*Phyllostachys acuta*) was obtained from a firm in Yunnan province (China). The culm of bamboo was chopped and smashed to obtain the particles with sizes of 20-80 mesh. The powder was de-waxed with methylbenzene/ethanol (2/1, v/v) in a Soxhlet extractor for 8 h and then treated with water at 80 ℃ for 6 h to remove starch before air-drying. The chemical components of the bamboo sample were glucan 46.03%, xylan 25.27%, arabinan 0.90%, galactan 0.32%, Klason lignin 24.19% and acid soluble lignin 1.67%, which were determined according to the method reported previously [13].

2.2. Carbonization of Bamboo

The bamboo powder was hydrothermally carbonized in a cylindrical reactor with Teflon liner under varied acid concentrations and retention times as shown in Table 1. The selection of acid concentrations and retention times was conducted according to the preliminary investigations. The initial studies indicated that the torrefaction with acid concentrations of 0.4-0.8 mol/L and retention times of 0-20 min resulted in marked changes of mass yield and product characteristics. In a typical run (R4), 3 g of bamboo sample (S0) was mixed with 30 mL of 0.6 mol/ L oxalic acid solution. The mixture was added in a 100-mL cylindrical reactor manufactured by chemically modified Teflon, which was lined with ultra-strong aerospace composite fiber material. The pressure of the reactor was monitored by a piezoelectric crystal pressure sensor (0-10 ±0.01 MPa) and the temperature was controlled by a platinum resistance control system (0-300 ±1 ℃). After sealed by screwing, the reactor was heated in a microwave oven (MDS-6G, Sineo Microwave Chemistry Technology Co., LTD). The main parameters were frequency 2500 MHz and maximum output power 500 W. The sample was heated by microwave irradiation at 190 ℃ for 0 min, and then the heating was stopped before cooling to temperature below 50 ℃. The temperature profile was recorded (Fig. 1) and the severity was determined according to the previous report [14, 15]. Briefly, severity (So) was calculated by the equation: $S_O = \log\left[\int_0^t \frac{T(t)-100}{14.75}\, dt\right]$, where t is time and T(t) is temperature during the process. The mixture was separated by a filter paper. The filtrate was recovered and stored at 4 ℃ for further analysis. The filtered residue was further washed with water to neutral, and dried at 105 ℃ for 12 h before analysis.

2.3. Characterization of the Products

The chemical component was analyzed according to the National Renewable Energy Laboratory (NREL) standard protocol [13]. Sugar and lignin components were assayed with a two-step hydrolysis process by H_2SO_4. The solid residue after the hydrolysis represents

Klason lignin and the hydrolysate was used for the analysis of acid soluble lignin and sugars. Acid soluble lignin was determined using an UV spectrometer (UV 2300, Shanghai Tianmei Science and Technology Corporation, China) and sugars were quantified on a high performance anion exchange chromatography system (Dionex ISC 3000, USA) according to a previous report [16]. The sugars including L-arabinose, D-xylose, D-glucose, and D-galactose were separated with isocratic 5 mM NaOH for 20 min followed by a 0-75 mM NaAc gradient in 5 mM NaOH for 15 min under nitrogen atmosphere. The contents of glucan, xylan, galactan, and arabian in the samples were calculated according to stoichiometry during the hydrolysis of polysaccharides into monosaccharides. Cellulose was measured as glucan, hemicelluloses were quantified by the sum of xylan, arabinan and galactan, and lignin was calculated as the sum of Klason lignin and acid soluble lignin.

Elemental (C, H, O, N, and S) contents were estimated using an elemental analyzer Vario EL III (Elementar, Germany). Higher heating value (HHV) was estimated according to the 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 (since no N and S were detected), after the correction of ash and moisture [17]. The mass yield of hydrochar (M_Y), energy densification (E_D) and energy yield (E_Y) were calculated as follows: $M_Y(\%)=Mass_{char}/Mass_{bamboo} \times 100$; $E_D=HHV_{char}/HHV_{bamboo}$; $E_Y=E_D \times M_Y$.

FTIR spectra were recorded using an FTIR Spectroscope (Thermo Nicolet Corporation, Madison, US) with a MCT detector cooled by liquid nitrogen according to a previous report [18]. The data were recorded in the wavenumber ranging from 4000-850 cm^{-1}. XRD analysis of the sample was conducted by scanning the sample on an XRD-6000 instrument (Shimidzu, Japan). The samples were placed on a glass holder, and the X-ray diffractograms were recorded from 2θ=5° to 40° at a scanning speed of 5 °/min. Thermogravimetric analysis (TGA) was performed using a simultaneous thermal analyzer (SDT Q600, TA Instrument). Samples of 5-10 mg placed in alumina crucibles were heated from 30 ℃ to 750 ℃ at a heating rate of 10 ℃/min in the presence of nitrogen (50 mL/min).

Aqueous phases were subjected to the antioxidant ability analysis against 2,2-diphenyl-1-Picrylhydrazyl (DPPH) radical referring to the method developed by Brand-Williams et al [19].The aqueous phases were diluted in water at a concentration of 3 g/L, the 0.1 mL solution were mixed with 3.9 mL of 25 mg/L DPPH in methanol solution, and the absorbance at 518 nm of the mixture was recorded at 30 min. Solution of commercial antioxidant butylated hydroxytoluene (BHT) was also determined for comparison. The DPPH radical-scavenging activity was calculated using the following formula: DPPH radical scavenging activity (%) = $(A_0 - A_1) / A_0$, where A_0 is the absorbance of control, and A_1 is the absorbance of lignin sample. In the experiments above, the analyses were performed in triplicates and the errors were reported. The significant difference was estimated with a two-sided t test, in which p value <0.05 represents statistical significance [20].

3. Results and Discussion

3.1. Mass Yield and Fuel Characteristics of Char

Mass yield of hydrochar was significantly influenced by reaction conditions, which decreased with increased acid concentration and retention time (Fig. 2). The highest yield was obtained at retention time of 0 min and acid concentration of 0.4 mol/L. The mass yield in the present study was comparable to the char obtained by torrefaction in inert gas previously as well as hydrochar from grape pomace obtained at hydrothermal carbonization at 200-300 ℃ [21, 22]. It was apparent that hemicelluloses were significantly degraded due to carbonization, starting from the sample carbonization at the lowest severity, where the hemicellulose content was reduced from 35.18% in S0 to 1.09% in S1 ($p < 0.05$). Galactan was the most unstable hemicellulose which was degraded even at the lowest severity. No hemicelluloses were detected for the hydrochar obtained at the highest severity (S9), indicating that hemicelluloses were completely removed. In addition, cellulose also showed some degradation, and the highest degradation rate of cellulose was 56.69% at the highest carbonization severity. The Klason and acid soluble lignin contents, representing the acid insoluble components (including modified lignin as well as condensed products from cellulose and hemicellulose degradation), showed an increase trend in the hydrochar with increased carbonization severity. The sample carbonized showed an increase in lignin content. This was due to the structural changes of lignin (mainly cleavage of the ether bonds), together with the poly-condensation reaction between carbohydrate degradation products that formed pseudo-lignin during the acid carbonation process, which resulted in an overestimation of lignin content [6].

3.2. Energy Characteristics

The energy characteristics of the hydrochars obtained from different retention times and oxalic acid concentrations are illustrated in Fig. 3. The contour graph was drawn with Originpro 2015 (OriginLab Corporation, USA), in which the color represents the HHV, energy yield, and energy densification resulted from the variations of concentration of acid and retention time. The value corresponding to the color is indicated in the legends on the right part of the graph. As expected, the higher heating value of bamboo was improved after carbonization, with the HHV of the hydrochars enhanced as the retention time and oxalic acid concentration increased. The lowest HHV value was achieved from the carbonization with 0.4 mol/L oxalic acid for retention time of 0 min (18.37 MJ/kg), those obtained at oxalic acid concentration of 0.6 mol/L for retention time of 0-20 min were in the range of 19.51-20.00 MJ/kg, and those obtained at oxalic acid concentration of 0.8 mol/L for retention time of 0-20 min were in the range of 19.59-20.47 MJ/kg, respectively. These values were comparable to the hydrochars obtained from bedding material [23].

Energy yield, a means to evaluate the energy retained in hydrochars as compared to that of the original bamboo, is energy densification ratio times mass yield of hydrochars. As seen, the energy yield was significantly affected by acid concentration and retention time. The energy yield was in the ranges of 59.81-60.81%, 58.89-62.67%, and 55.26-59.74% for carbonization at acid concentrations of 0.4, 0.6 and 0.8 mol/L. Energy was intensified when the solid mass decreased as the increase of the acid concentration and retention time. This was due to the dehydration and decarboxylation reactions, as evidenced by the increase in the carbon content as well as the decrease in oxygen and hydrogen contents. Energy densification after carbonization was associated with both retention time and acid concentration, which was in the ranges of 1.07-1,12, 1.14-1.17 and 1.14-1.19, respectively, as carbonized at acid concentrations of 0.4, 0.6 and 0.8 mol/L. The energy densification values at high acid concentration were comparable to most torrefied lignocelluloses (such as rich husk, empty fruit bunches, eucalyptus) obtained at high temperature (200- 300 ℃) in inert gas [2]. Under the same acid concentration, the torrefaction under oxalic acid solution at 190 ℃ for 20 min (severity 4.02) produced hydrochars having HHV, mass yield, and energy yield of 19.21 MJ/kg, 55.06%, and 59.81%, as compared to 21.56 MJ/kg, 37.46%, and 47.07% of the hydrochars obtained from the torrefaction under HCl solution at 180 ℃ for 15 min (severity 3.61), respectively [24]. It was concluded that the torrefaction with oxalic acid solution resulted in relatively higher mass and energy yields but lower HHV as compared to the torrefaction in HCl solution.

The elemental content of the hydrochars after carbonization is shown in Fig. 4. The ternary diagram (plotted by Originpro 2015) presents the variation of carbon-hydrogen-oxygen (C-H-O) for the samples (from S0 to S9), in which the total contents of carbon, hydrogen and oxygen for a given sample equal to 100% and the amount of each component can be read in the corresponding scale. It showed an increase in carbon content but decrease in oxygen content with an increase in both acid concentration and retention time. The figure showed that with the increase of the carbonization severity, dehydration and decarboxylation reactions occurred. The highest carbon content of 55.44% and the lowest oxygen content of 38.55% were achieved in S9, as compared to those of the raw material (bamboo showed carbon content of 49.67% and oxygen content of 44.53%) and other hydrochars.

3.3. Morphological and Structural Characterization of Char

To get a better insight into the impact of carbonization conditions on the structure of bamboo, the SEM images of bamboo after and before torrefaction are illustrated in Fig. S1 in Supplementary content. The images observed by SEM are amplified by factors of 10 K to demonstrate the microstructures (left column) and the images from a camera are presented (right column). It was expected that with the presence of the main components of lignocellulose, the SEM images of the hydrochar looked more like the raw material; however, the SEM images of hydrochar showed a very clear difference, suggesting the rupturing of the lignocellulose structure after the carbonization process. The raw material was light yellow, whereas the hydrochar S3 and S6 had a brown color, consistent with the partial carbonization, and hydrochar S9 was deep brown in color. The image of bamboo shows a cellular structure of lignocellulosic materials. The SEM image of hydrochar S3 indicates some breakdown of the lignocellulose material. Numerous sphere-like micro-particles were observed on the surface of the hydrochars in which S9 showed the biggest particle. These micro-particles were generated by degradation of the carbohydrates during carbonization, followed by precipitation and growth to form spheres [25]. The hydrochar samples became crustier than the raw material. This was mainly due to the lignin component underwent partial degradation due to its greater thermal stability. In an earlier study by Lynam et al., he explained that among all lignocellulose components, lignin was found most on the cell wall and thus the presence of more lignin or absence of carbohydrates made hydrochar crusty [26].

The effects of acid concentration and retention time on the degradation of cellulose and hemicelluloses were also supported by the FTIR spectra obtained from the hydrochar and raw material (Fig. S2 in Supplementary content). The absorption bands in the spectra were assigned below: (a) the peaks around 2900 cm^{-1}, C-H stretching and deforming vibration in CH_2 and CH_3; (b) the peak at 1730 cm^{-1}, C=O stretching vibration mainly from carbonyl and ester groups of hemicelluloses; (c) the peaks around 1610-1460 cm^{-1}, C=C stretching from aromatic rings from lignin; and (d) the peak at 1160 cm^{-1}, C-O-C vibrations from cellulose and hemicelluloses. As seen, the presence of the peaks around 2900 cm^{-1} in both the raw material and hydrochar suggested the existence of CH_2 and CH_3 groups. The peak at 1730 cm^{-1} appeared in the spectrum of the raw material but was not observed in the spectra of the hydrochar samples, indicating the degradation of hemicelluloses under the carbonization process. The signals of the peaks at 1460, 1510 and 1600 cm^{-1} attributed to lignin became stronger with increased carbonization severity, consistent with the enrichment of lignin content after carbonization. This implied that some fragments and intermediate structures from lignin remained in hydrochars, i.e., lignin was not completely decomposed and dissolved into aqueous solution under the carbonization conditions.

The XRD patterns for the raw material and hydrochars were also compared (Fig. S3 in Supplementary content)). The distinct and sharp peak of cellulose (2θ=22.7 °) were presented in all curves of the samples. The patterns of all the hydrochars were similar to that of the raw material, suggesting that the microcrystalline structure of cellulose was preserved after carbonization under the experimental conditions. The calculated CrI values of the hydrochars were 35.2%,33.9%, and 35.5% for the samples carbonized with retention time of 0, 10, and 20 min in 0.4 mol /L acid, were 36.4%,32.2%, and 31.0% for the samples carbonized with retention time of 0, 10, and 20 min in 0.6 mol /L acid, and were 37.9%, 32.4%, and 29.9% for the samples carbonized with retention time of 0, 10, and 20 min in 0.8 mol /L acid. Overall, higher concentration of acid and longer retention time resulted in lower CrI. The decrease in CrI of the sample can be explained by the fact that partial crystalline cellulose was decomposed in the carbonization process.

3.4. Thermal Behavior of Hydrochar

The thermal degradation behavior of the hydrochar and the raw material was examined by thermogravimetry. Fig. S4 in Supplementary content shows the TG/DTG curves of the samples. There was a slight mass lose in the initial stage below 120 ℃ attributed to the removal of moisture. Hemicellulose degradation occurred at 200 ℃ and achieved a maximum at 270 ℃. The degradation of hemicelluloses also overlapped with that of cellulose and the peak at 320 ℃ is assigned to cellulose degradation. The peak at

500 ℃ corresponds to the lignin degradation. From the curves, it can be seen that the thermal degradation behavior of the sample was notably modified after the carbonization. For the samples S3 and S9, degradation occurred in a narrow range, and the one peak at 349-354 ℃ was indicative of the most degradation of cellulose and lignin. No notable degradation peak was observed at 500 ℃ for the curves of S3 and S9, indicating that the structure of the lignin in the hydrochar was modified, which was mainly due to the re-polymerization of the primary degradation products. It was also noted that the the residual mass of the residue after the thermal degradation at 750 ℃ was 7.55 ±1.1% and 13.8 ±1.5% for S3 and S9, as compared to 0% for S0. Overall, the thermal stability of the hydrochar increased significantly after torrefaction ($p< 0.05$).

3.5. Antioxidant Activity of Aqueous Solution for Carbonization

The waste aqueous phase from hydrothermal carbonization is a drawback. To overcome the problem, the waste liquid should be treaded to reduce the amount of organics prior to discharge. The recovery and utilization of the chemicals dissolved in the solution can improve the economics of the whole carbonization process. Bamboo contained lignin and degradaded products were rich in phenolics, which was water soluble. Under the carbonization at 0.8 mol/L acid for retention time 0 min, the maximum organic material amount of 44.98 mg/mL was recovered. Based on the previous study, the antioxidant activity of the aqueous solution obtained from carbonization was investigated. As seen from Fig. 5, the increase in acid concentration and retention time notably enhanced the antioxidant. Under the experimental conditions (concentration of 3 mg/mL, test time 30 min), the carbonization with retention of 10 min produced aqueous solutions of inhabitation rate of 39.1-47.1%, comparable to that of commercial antioxidant BHT (46.4%). The highest antioxidant capacity of inhabitation rate of 63.5% was obtained for the aqueous solution from carbonization at the highest severity. The behavior was mainly due to the enhancement of the degradation of lignin into small fragments which was soluble in water when carbonization was conducted under concentrated acid and long retention time. This was in well agreement with the previous results from subcritical water treatment of plants [27]. It was concluded that bamboo can be converted into degraded chemicals after the hydrothermal carbonization process.

4. Conclusion

Bamboo was carbonized in oxalic acid solution for the production of hydrochar and aqueous products. The energy densification values at a high acid concentration of 0.8 mol/L were comparable to most torrefied lignocelluloses. The increase of the HHV was due to the dehydration and decarboxylation reactions, as evidenced by the increase in the carbon content as well as the decrease in oxygen and hydrogen contents. Hemicelluloses were significantly degraded due to carbonization, whereas the lignin content showed an increase trend in the hydrochar with increased carbonization severity. The thermal stability of the hydrochar increased with the carbonization severity. The aqueous solution obtained under the optimized conditions had a high antioxidant capacity than that of commercial antioxidant BHT.

Acknowledgements

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References

1 S. M. Kang, X. H. Li, J. Fan and J. Chang, *Ind. Eng. Chem. Res.*, 2012, **51**, 9023-9031.

2 W.-H. Chen, J. Peng and X. T. Bi, *Renewable Sustainable Energy Rev.*, 2015, **44**, 847-866.

3 G. Almeida, J. O. Brito and P. Perre, *Bioresour. Technol.*, 2010, **101**, 9778-9784.

4 D. Medic, M. Darr, A. Shah, B. Potter and J. Zimmerman, *Fuel*, 2012, **91**, 147-154.

5 J.-W. Lee, Y.-H. Kim, S.-M. Lee and H.-W. Lee, *Bioresour. Technol.*, 2012, **116**, 471-476.

6 S. Neupane, S. Adhikari, Z. Wang, A. J. Ragauskas and Y. Pu, *Green Chem.*, 2015.

7 R. B. Bates and A. F. Ghoniem, *Bioresour. Technol.*, 2012, **124**, 460-469.

8 W. Yan, T. C. Acharjee, C. J. Coronella and V. R. Vasquez, *Environ. Prog. Sustain.*, 2009, **28**, 435-440.

9 J. G. Lynam, C. J. Coronella, W. Yan, M. T. Reza and V. R. Vasquez, *Bioresour. Technol.*, 2011, **102**, 6192-6199.

10 T. C. Acharjee, C. J. Coronella and V. R. Vasquez, *Bioresour. Technol.*, 2011, **102**, 4849-4854.

11 X. Lu, B. Jordan and N. D. Berge, *Waste Manage.*, 2012, **32**, 1353-1365.

12 L. Fryda, C. Daza, J. Pels, A. Janssen and R. Zwart, *Biomass Bioenerg.*, 2014, **65**, 28-41.

13 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, in *Laboratory Analytical Procedure*, 2008.

14 S. M. Lee and J.-W. Lee, *Bioresour. Technol.*, 2014, **172**, 438-443.

15 T. A. Lloyd and C. E. Wyman, *Bioresour. Technol.*, 2005, **96**, 1967-1977.

16 M. F. Li, Y. M. Fan, F. Xu, R. C. Sun and X. L. Zhang, *Ind. Crop. Prod.*, 2010, **32**, 551–559.

17 X. Z. Yuan, J. Y. Tong, G. M. Zeng, H. Li and W. Xie, *Energ. Fuel.*, 2009, **23**, 3262-3267.

18 C.-Z. Chen, M.-F. Li, Y.-Y. Wu and R.-C. Sun, *Ind. Eng. Chem. Res.*, 2014, **53**, 12935-12942.

19 W. Brand-Williams, M. E. Cuvelier and C. Berset, *LWT - Food Sci. Technol.*, 1995, **28**, 25-30.

20 S.-P. Nie and M.-Y. Xie, *Food Hydrocolloid.*, 2011, **25**, 144-149.

21 J. J. Chew and V. Doshi, *Renewable Sustainable Energy Rev.*, 2011, **15**, 4212-4222.

22 M. Pala, I. C. Kantarli, H. B. Buyukisik and J. Yanik, *Bioresour. Technol.*, 2014, **161**, 255-262.

23 I. Oliveira, D. Blohse and H. G. Ramke, *Bioresour. Technol.*, 2013, **142**, 138-146.

24 M.-F. Li, Y. Shen, J.-K. Sun, J. Bian, C.-Z. Chen and R. Sun, *ACS Sustainable Chem. Eng.*, 2015.

25 A. B. Fuertes, M. C. Arbestain, M. Sevilla, J. A. Macia-Agullo, S. Fiol, R. Lopez, R. J. Smernik, W. P. Aitkenhead, F. Arce and F. Macias, *Aust. J. Soil Res.*, 2010, **48**, 618-626.

26 J. Lynam, M. T. Reza, W. Yan, V. Vásquez and C. Coronella, *Biomass Convers. Biorefin.*, 2014, 1-9.

27 B. Aliakbarian, A. Fathi, P. Perego and F. Dehghani, *J. Supercrit. Fluids*, 2012, **65**, 18-24.

Figure captions

Fig. 1. Temperature profile during bamboo carbonization process

Fig. 2. Mass yield, carbohydrates, and lignin content of hydrochar from bamboo carbonization.

Fig. 3. Energy yield, HHV, and energy densification of hydrochar from bamboo carbonization at different acid concentrations and retention times.

Fig. 4. C-H-O ternary diagram of hydrochar from bamboo carbonization.

Fig. 5. Antioxidant capacity of liquid phase form bamboo carbonization as compared to BHT.

Table 1

Reaction conditions for bamboo carbonization under various acid concentrations and retention times

Run	Temperature (℃)	Oxalic acid concentration (mol/l)	Retention time (min)	Severity	Hydrochar	Liquid phase
R1	190	0.4	0	3.33	S1	L1
R2	190	0.4	10	3.71	S2	L2
R3	190	0.4	20	4.02	S3	L3
R4	190	0.6	0	3.33	S4	L4
R5	190	0.6	10	3.71	S5	L5
R6	190	0.6	20	4.02	S6	L6
R7	190	0.8	0	3.33	S7	L7
R8	190	0.8	10	3.71	S8	L8
R9	190	0.8	20	4.02	S9	L9

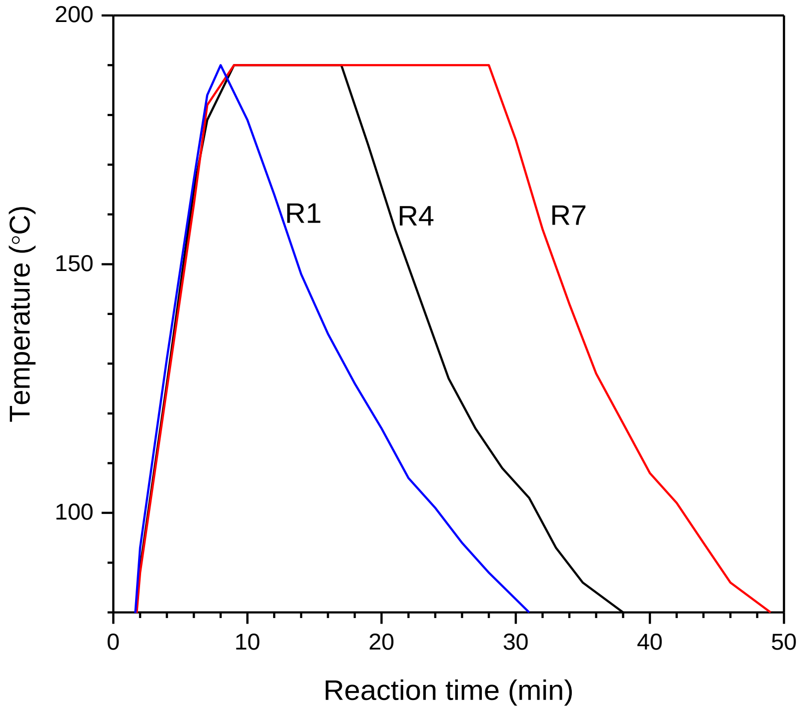
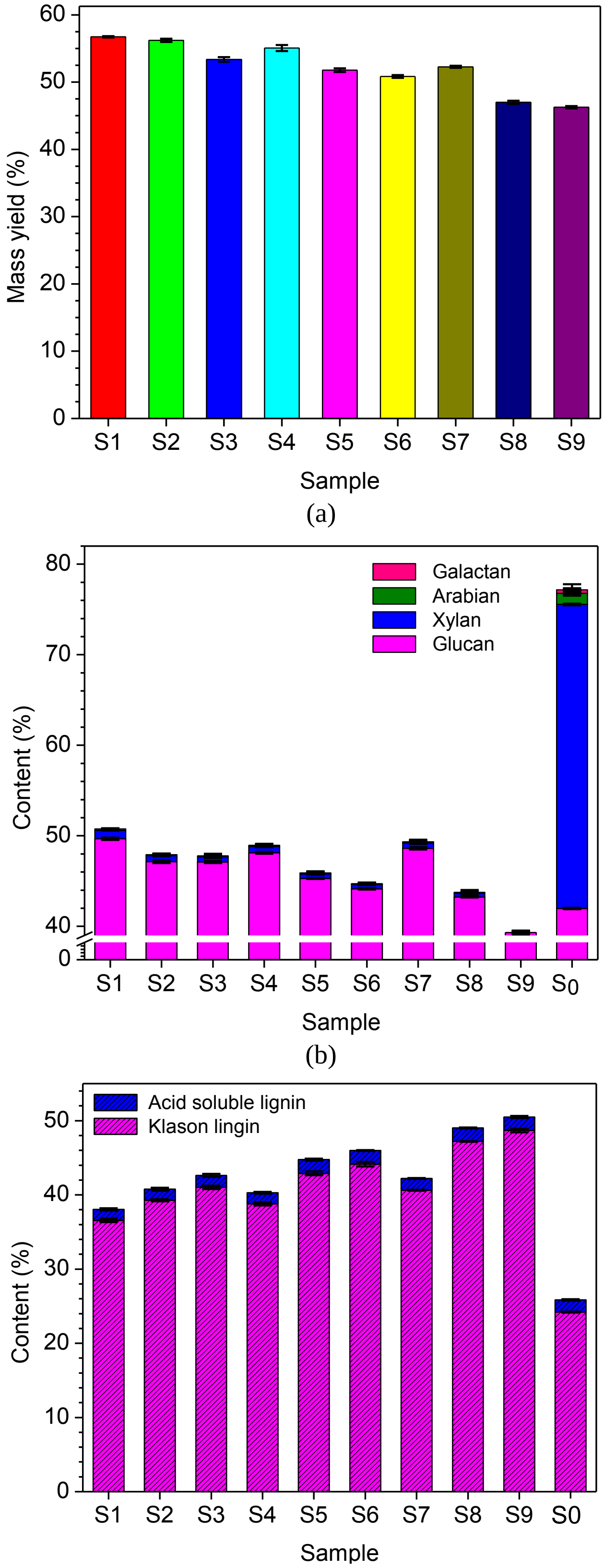

200
150
100
Temperature (°C)
0
10
20
30
40
50
Reaction time (min)
R1
R4
R7

Fig. 1

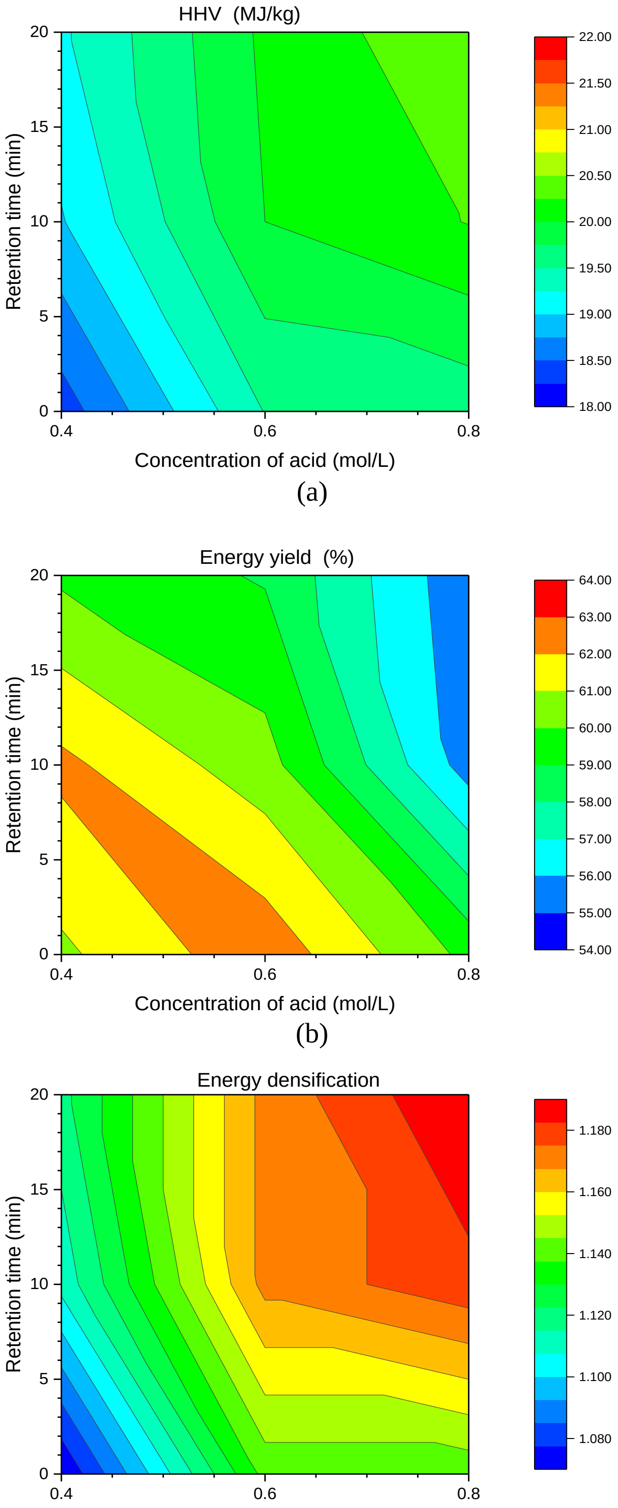

60
50
40
30
20
10
0
Mass yield (%)
S1
S2
S3
S4
S5
S6
S7
S8
S9
Sample
Galactan
Arabian
Xylan
Glucan
80
70
60
50
40
0
Content (%)
S1
S2
S3
S4
S5
S6
S7
S8
S9
S_0
Sample
Acid soluble lignin
Klason lingin
50
40
30
20
10
0
Content (%)
S1
S2
S3
S4
S5
S6
S7
S8
S9
S0
Sample

(a)

(b)

(c)

Fig. 2


HHV (MJ/kg)
Retention time (min)
Concentration of acid (mol/L)
0
5
10
15
20
0.4
0.6
0.8
22.00
21.50
21.00
20.50
20.00
19.50
19.00
18.50
18.00
Energy yield (%)
64.00
63.00
62.00
61.00
60.00
59.00
58.00
57.00
56.00
55.00
54.00
Energy densification
1.180
1.160
1.140
1.120
1.100
1.080

(a)

(b)

(c)

Fig. 3

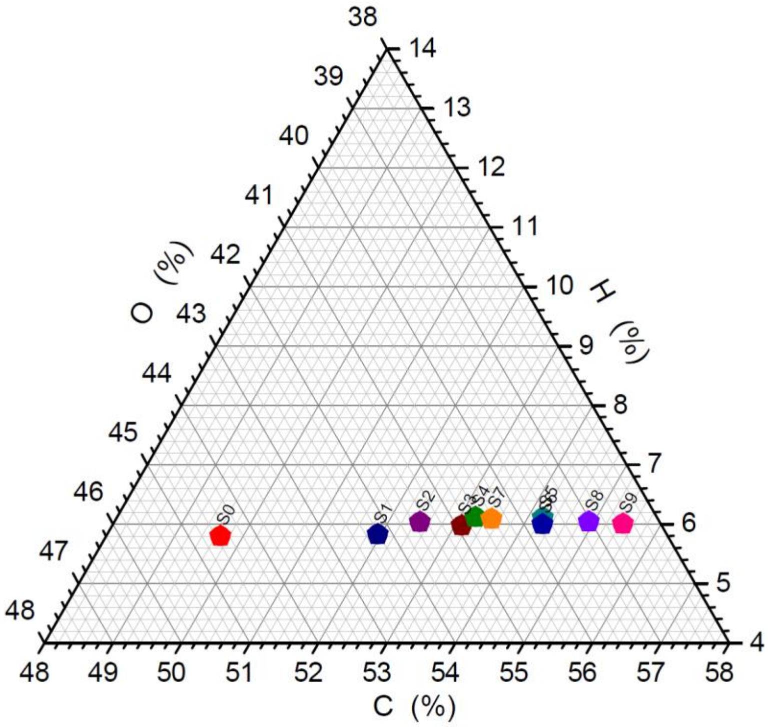

O (%)
H (%)
C (%)
38
39
40
41
42
43
44
45
46
47
48
14
13
12
11
10
9
8
7
6
5
4
48
49
50
51
52
53
54
55
56
57
58
S0
S1
S2
S3
S4
S7
S5
S6
S8
S9

Fig. 4

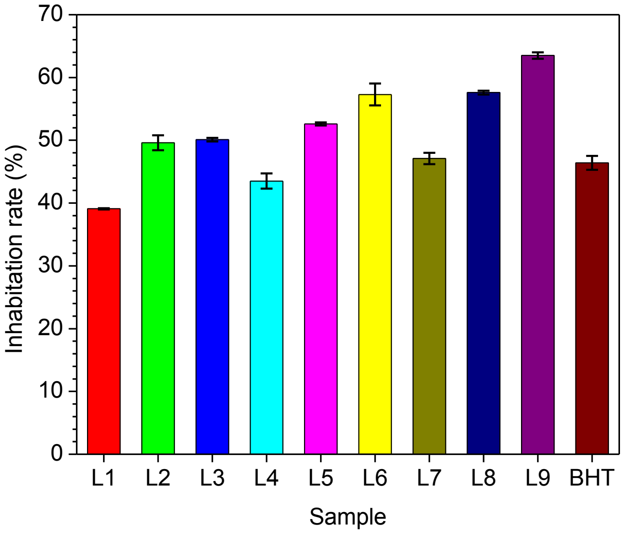

Inhabitation rate (%)
70
60
50
40
30
20
10
0
L1
L2
L3
L4
L5
L6
L7
L8
L9
BHT
Sample

Fig. 5

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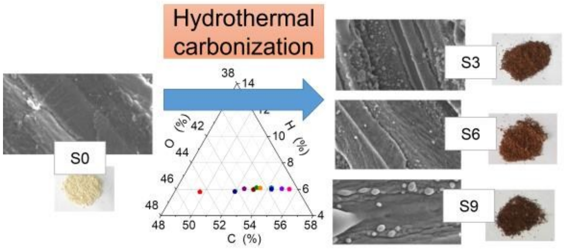

Title: Hydrothermal carbonization of bamboo in oxalic acid solution: effects of acid concentration and retention time on characteristics of products

Author(s): Xun Li, Ming-Fei Li *, Jing Bian, Bo Wang, Ji-Kun Xu, Run-Cang Sun*

Synopsis: Bamboo was hydrothermally carbonized in oxalic acid solution by microwave heating for the production of hydrochar and antioxidant.