

COMPARISON OF BAMBOO FIBERS IN SULFURIC
ACID, SODIUM HYDROXIDE AND GLYCERIN
PRETREATMENTS

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ABSTRACT

The chemical compositions and structural characterizations of bamboo samples with three pretreatments using sand bath to heat were comparatively studied with Fourier infrared spectrum (FTIR). The results showed that the holocellulose and cellulose yields increased significantly and the dilute alkali (NaOH) pretreatment performed better lignin removal rate than that of dilute acid (H₂SO₄) and glycerin pretreatments. Furthermore, when the same solutions were used, the compositional changes were more remarkable at 135 than at 117°C, and the similar degradation of hemicelluloses was observed for the different pretreatments. With sodium hydroxide at 135°C, compared to un-treated bamboo, cellulose increased by 14.21 % and hemicellulose decreased to 13.98 %, counting the removal of lignin to 20.29 %. In which, the bamboo expressed the better delignification with sand bath and higher temperature and combinations with other methods of glycerin pretreatment should be evaluated in the future work.

KEYWORDS: Delignification; bamboo; chemical compositions; pretreatment.

INTRODUCTION

With the development of the low carbon economy in the world, efficient utilization of biomass energy has been the current research topic. It is very essential to maximum efficiency in the use of the existing biomass resources, and developed more available to improve the high value utilization of wood biomass resource (Scurlock et al. 2000). Recently, agricultural and forestry waste residues, grass, and other wood biomass were considered as a viable and sustainable energy sources for the production of biofuels after pretreatment (Mosier et al. 2005) because they are renewable, widely distributed and grow fast (Himmel et al. 2007). Bamboo, as a new natural material with unique fiber structure makes it superior over other natural lignocellulosic fibers and has been a potential natural resource in field (Garcí-Aparicio et al. 2011; Leenakul and Tippayawong 2010).

There are quite a few bamboo resources in the world, such as in East Asia. According to the Food and Agriculture Organization (FAO) of the United Nations, approximately 1,0 ha commercial applications of bamboo have been identified (Scurlock et al. 2000, and more than 200,000 ha has been widely used as a raw material for paper, textiles, food, construction and reinforcing fibers. Especially more than 10,000 ha of bamboo fiber has been utilized efficiently in architecture, national defense, industry transportation, bio-based energy field (Shimokawa et al. 2009) and other industries in China. With the development of technology, its application continues to expand in nearly ten years because of its short renewal and easy propagation (Xin et al. 2015).

To realize the efficient utilization of renewable wood biomass, the chemical pretreatment is pivotal step (Chundawat et al. 2011), and increase production of cellulose (Karp et al. 2015).

Among the representative technologies of woody biomass pretreatment, Li et al. 2012a, b researched the digestion rate of bamboo structure after different pretreatment by acid, alkali and sulfate. Li and Zhang 2012c studied chemical composition change of pretreated bamboo and suggested that the application of dilute organic acids in the pretreatment of bamboo can be effective and observably influences the cell-wall structure and enzymatic digestibility of bamboo (Sluiter et al. 2008). Also Jiang provided bamboo after pretreatment with the same sodium hydroxide loading, more hemicellulose and lignin were removed and the efficiency of removal increased as the pretreatment temperature increased. The above reported investigations of acid and alkali pretreatment of bamboo is considered to be a more effective way to improve wood fiber content whatever it is used in the production of bioethanol and other fields. However, to our knowledge, less attention has been focused on chemistry and molecular structure change, and on the change of processes of chemical composition

Therefore, in this work, the content of cellulose, hemicelluloses and lignin, extract and ash content based on different processing conditions (dilute acid, strong alkali and glycerin) according to the international standard and using FTIR to further study the influence of different heat treatment methods on the bamboo chemical composition.

MATERIAL AND METHODS

Materials

Bamboo powder sample was acquired from USDA Forest Service, Southern Research Station in Pineville in the summer of 2015. Air-dried bamboo was milled using a hammer mill 1.0 mm before chemical pretreatment. The average moisture content of the ground air-

dried bamboo was 6.18 % (wt. %). The bamboo was sealed in a zip lock bag, and kept in a 4°C refrigerator until use of it.

Chemical reagents are H_2SO_4 , NaOH, $NaClO_2$, toluene, methanol, ethanol, glacial acetic acid and they were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Pretreatment equipment includes electronic sand bath pot and thermometer. Bamboo sample of 100 g oven-dry (OD) basis was used for each pretreatment experiment.

Pretreatment procedure

Treatment of samples by sulfuric acid at 135°C

About 10 g of bamboo power (dry weight) were pretreated with prepared pretreatment reagents (1.5 % H_2SO_4 , 10 % NaOH, and 10 % glycerol) in sand bath at 117 and 135°C for 1 h at a solid and liquid ratio of 1:10 respectively. After pretreatment, the solids were washed and centrifuged (5000×g for 10 min) repeatedly using distilled water until the pH of supernatant was neutral. Then, the obtained solids were air-dried and stored for structure analysis.

Samples of different processing conditions are shown in Tab. 1. The dry samples and the filtrate from different processing conditions are shown in Figs.1 and 2.

Preparation of holocellulose and cellulose and determination of lignin

Approximately 8 g of dry bamboo powder was placed into a 250 mL flask, 80 mL of ethanol was added: 40 mL methyl benzene, extracted 12 h with Soxhlet extractor (bad grammar). 2 g of (extracted) sample was then taken in into a 250 mL round-bottom flask, 150 mL water, 0.2 mg of glacial acetic acid, and 1 g $NaClO_2$ were added. The mixture was heated for 5 h. During this time, 0.2 mg glacial acetic acid and 1 g $NaClO_2$ were added every one hour and finally cooled it to room temperature. The reaction mixture was then filtered using sand core filter funnel, dried, and weighed, to afford samples with different processing.

Tab. 1: Experiment values with different pretreatment conditions.

Test number	Pretreatment temperature (°C)	Pretreatment solution	Pretreatment time (h)
Native (NA) (Untreated Bamboo)a	--	--	--
SA117b	117	Sulfuric acid	1
SA135c	135	Sulfuric acid	1
SH117d	117	NaOH	1
SH135e	135	NaOH	1
GL117f	117	Glycerol	1

Note: a: Native bamboo is untreated sample; b: SH117 is samples of 117°C, treatment with sulfuric acid; c: SH135 is samples of 135°C, treatment with sulfuric acid; d: SA117 is samples of 117°C temperature with Alkali; e: SA135 is samples of 135°C temperature with Alkali; f: GL117 is samples of 117°C temperature with glycerin.

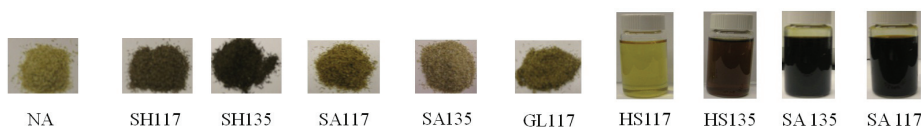


Fig. 1: Dry samples under different processing conditions.

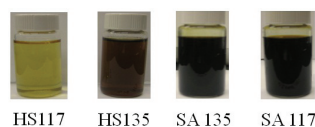


Fig. 2: The filtrate of different processing conditions.

Analytical methods

Chemical Analysis

The bamboo samples were evaluated in accordance with ASTM D1105-96 - 1996 and ASTM D-1102-84-1990. Each evaluation was performed twice.

Fourier Transform-Infrared Spectroscopy (FTIR)

Image acquisition of Fourier Infrared spectrum (FTIR). We used a Nicolet iS10 Fourier transform infrared spectrometer produced by the Thermo Nicolet company (USA) with the following test conditions: The spectral range was 4000-400 cm^{-1} , the spectral resolution was 4 cm^{-1} , and the scans were performed 64 times.

Analysis of Crystallinity by X-ray diffraction (XRD)

The crystallinity of the samples was determined by X-ray diffraction (XRD) using Rigaku Ultima3 x (Louisiana State University, USA) with the scanning parameters of Ni-filtered Cu K α radiation $\lambda = 1.54060$.

RESULTS AND DISCUSSION

Changes in chemical composition of pretreated bamboo

The main chemical composition changes of bamboo after different chemical treatment solutions and temperatures of pretreatment are shown in Tab. 2.

Tab. 2: Main chemical component measurements in different pretreatment.

Test number	Holocellulose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extract (%)	Ash (%)
1(SA117)	70.07	53.24	16.83	22.71	6.11	2.11
2(SA135)	68.01	51.12	16.89	21.68	6.99	1.87
3(SH117)	77.38	56.94	20.44	19.93	3.12	1.03
4(SH135)	75.13	61.15	13.98	20.29	1.48	1.66
5(GL117)	65.45	49.76	15.69	22.96	8.39	4.12
6Native(NA)	62.53	46.94	15.59	23.39	11.54	3.19

It can be seen from Tab. 2, chemical components were obviously changed with different pretreatment. Trend is that the content of cellulose, hemicelluloses increased, by contrast, the lignin greatly reduced. The degradation of hemicelluloses increased with different pretreatment. The extracts and ash were also found to be different.

Comparison sodium hydroxide and sulfuric acid (bad grammar), the pretreatment effect of sodium hydroxide was much better than that of sulfuric acid at the temperatures of 135, 117°C, and the yield of cellulose increased obviously with sodium hydroxide at 135°C. Remarkable effect is due to the lignin removed with sodium hydroxide and the average removal rate reached to 14.69%. However, the pretreatment with glycerin was not obvious.

Fig. 3 shows main chemical component measurements by different pretreatment conditions. Among them, the change order of holocellulose of SH117 > SH135 > SA117 > SA135 > GL117 > NA; the cellulose change order of SH135 > SH117 > SA117 > SA135 > GL117 > NA; amount of lignin removal is SH117 > SH135 > SA135 > > SH117 > GL117 > NA; and degradation changes of hemicelluloses are SH135 > GL117 > SA117 > SA135 > SH117.

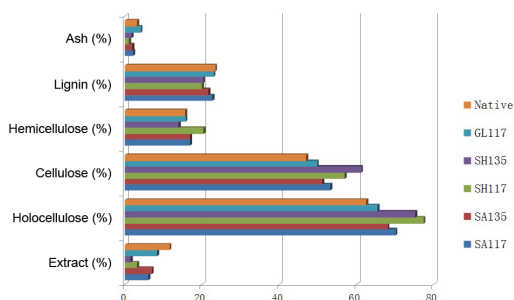


Fig. 3: Main chemical component measurements by different pretreatment conditions.

Analysis of the bamboo samples by infrared spectrum characteristics

Bamboo is natural cellular material and its main chemical composition includes cellulose, hemicelluloses and lignin. They may show different infrared absorption spectra in different wave band due to component content changes after pretreatment (Li 2003a, b, c).

Cellulose is composed of d-glucose (Zhu et al. 2005), and its infrared sensitive group is hydroxyl (OH). The cellulose has special X-ray spectrum in free hydroxyl on C4. Hemicellulose is heterogeneous polymer that composes of two or more kinds of monosaccharide. It contains infrared sensitive groups such as acetyl and hydroxyl. Lignin is aromatic macromolecule connected through ether bond and the carbon-carbon bond. Lignin contains many kinds of infrared sensitive groups, such as methoxy group, hydroxyl, carbonyl, double bonds and benzene ring.

The purpose of pretreatment is to remove lignin in plant cell wall through chemical decomposition or thermal chemical conversion, which makes hemicellulose change too and breaks the glycosidic bonds in cellulose (Li 2003a, b, c). Hence, FTIR analysis understands the position and intensity changes of functional groups of cellulose, hemicelluloses, and lignin after the pretreatment. Extrapolating changes of corresponding functional groups in the infrared absorption peaks between native and pretreated samples, will further provide clear evidence of the change of chemical composition and structure.

FTIR spectra within the range of 4000-400 cm^{-1} are illustrated in Fig. 4. Absorption peak changes with different chemical composition structure are in Fig. 5.

The changes of characteristic spectrum of cellulose, hemicelluloses and lignin

The absorbance band at 897 cm^{-1} is a characteristic peak for β -glucose anhydride and bond C-H bending vibration of cellulose. In native spectrum, the 897 cm^{-1} absorbance band is a single peak. By contrast, it was divided into two peaks at 880 and 895 cm^{-1} in the corresponding samples SH117, SH135, SA135, and SA117. In 828 cm^{-1} (Fig. 5), the absorption peak intensity increased which indicated the change of content of cellulose after pretreatment. Crystallization of water O-H damaged in cellulose at 828 cm^{-1} with acid treatment. Another characteristic absorption peak of cellulose is at 2900 and 3308 cm^{-1} , the change is little at this region, and any other obvious absorption peak near the band was not observed. Scope of the change range of cellulose content can be obtained in the order SH135 > SH117 > SA117 > SA135 > GL117, namely in the order of the 1, 2, 3, 4, 5 (Fig. 4). It is consistent with the standard method for determination of cellulose content increase as discussed above in Fig. 5.

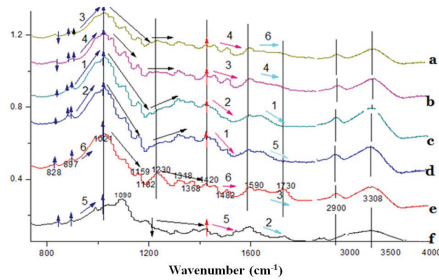


Fig. 4: Composition change of infrared spectra of pretreatment and native bamboo a) SA117; b) SA135; c) SH117; d) SH135; e) Native; f) GL117.

Note: → cellulose changing → lignin changing; → hemicellulose changes; 1,2,3,4,5,6 is chemical composition change of different processing conditions respectively

Acetyl and hydroxyl groups at 1730 cm^{-1} absorbance band are characteristic peaks and different from other components for hemicelluloses (Rout et al. 2003). It can be seen from the Fig. 4, the strong absorbance peak of 1730 cm^{-1} in spectrum of native bamboo become gentle after different pretreatment, and it disappeared completely at the SH135 and SH117, which confirmed that the degradation of hemicellulose occurred. In addition, the newly formed C-O-C stretching vibration in 1021 cm^{-1} , and steep fall in the intensity of 1159 cm^{-1} , indicate that the degradation degree of hemicelluloses is higher. From the slopes of peaks from 1021 to 1182 cm^{-1} , the changes of content of hemicelluloses was found to be in the order SH135 > GL117 > SA117 > SA135 > SH117. Also in the spectrum there was C=O stretching and OH deformation and vibration at 1090 cm^{-1} . For glycerol (GL117), the absorption peak decline at 1230 cm^{-1} showed the degree of hemicelluloses degradation, but the reasons for such changes could not be determined.

It was found more complex changes for the functional groups of lignin. The common functional groups of lignin, the stretching vibration of C-C bond of benzene was observed around 1420 cm^{-1} (Zhu et al. 2009). There are quite strong absorbance bands found at 1230 cm^{-1} of diaryl ether bond for native lignin and the absorption got weakened for this bond after pretreatment. In addition, absorption peaks in the regions of 1420 to 1506 cm^{-1} (Fig. 5). So, this proved that lignin removal effect is remarkable after pretreatment.

According to the changes in the characteristic bands of lignin, it can be speculated that the lignin removal was in the order of SH117 > SH135 > SA135 > > SH117 > GL117 > NA, which also agree well with the former test results (Zhang et al. 2013).

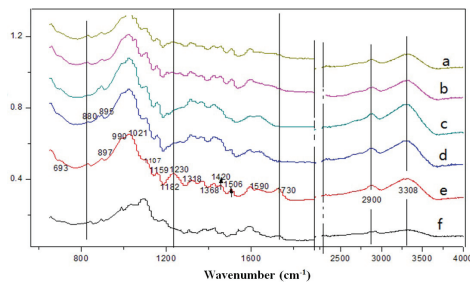


Fig. 5: Infrared spectra of pretreated and native bamboo. a) SA117; b) SA135; c) SH117; d) SH135; e) Native; f) GL117.

Moreover, there was an obvious change for hemicelluloses with glycerol pretreatment, and the removal of lignin and incremental change of cellulose was not noteworthy, the reasons for this change need further study.

In order to compare clearly the chemistry changes between native and pretreated samples, this study summarized the changes in the main bands in the infrared spectrum corresponding to the functional group as shown in Tab. 3 to Tab. 5.

Tab. 3: Functional groups absorption infrared spectra of cellulose.

V/ cm ⁻¹	Functional groups
693	The hydroxyl O-H plane vibration
880,895	C-O-C asymmetric surface
897	C-H deformation and vibration
1059	C-O-C stretching vibration
1368	C-H bending vibration (cellulose and hemicellulose)
2900	C-H stretching vibration
3308	O-H stretching vibration

Tab. 4: Absorption band of infrared spectra of hemicelluloses.

V/ cm ⁻¹	Functional groups
1730	C=O stretching vibration (Xylan acetyl groups CHC=O)
1318	O-H stretching vibration
1159	C-O-C stretching vibration (Xylose and pyran ring structure)

Tab. 5: Functional groups of absorption band of infrared spectra of lignin.

V/ cm ⁻¹	Functional groups
990	C-H Olefin bending vibration
1021	C-O-C(asymmetric aromatic ether, stretching vibration)
1107	C-O stretching vibration from secondary alcohol and ether
1182	C-O-H(ether ethanol and tertiary asymmetric)
1230	C=O (phenol)
1318	base C-O, CH bending vibration
1420	benzene ring skeleton C-H plane deformation stretching vibration
1506	C=C-OH carbon skeleton vibration (benzene)
1590	C=C stretching vibration

To sum up, cellulose, hemicelluloses, and lignin of bamboo changed significantly after different pretreatment. aliphatic C-H stretching vibration, structure of molecular chain changed, the ratio of composition of cellulose increased; hemicelluloses has acetylated, part of structure degraded; C-C double bond and ether bonds were cleaved during pretreatment which led to lignin removal and eventually cellulose yield improved.

Different pretreatment had different degree of change among components. Higher cellulose yield was obtained at 135°C using sodium hydroxide, by contrast, at 117°C dilute acid treatment was found to be better. However, the glycerol pretreatment was inferior to the results of acid and alkaline pretreatment.

The research analyzed the chemical composition change of pretreated and native bamboo using the Fourier transform infrared spectroscopy. The results showed that the lignin can be removed and, a lot of hemicelluloses be degraded, which greatly improved the cellulose production that benefits the efficient utilization of lignocellulosic biomass resources.

CONCLUSIONS

1. Pretreated bamboo with three different processing mediums media (sulphuric acid, NaOH and glycerin), at different processing temperatures (117 and 135°C) were studied. Changes of chemical composition, hemicellulose degradation degree, and the rate of lignin were compared. The results showed that the yield of cellulose increase increased, lignin removal efficiency and hemicelluloses saccharification after different pretreatments. Among them, the effect of pretreat pretreatment with sodium hydroxide was relatively better than that with sulfuric acid, under the same condition. Pretreatment with glycerol was not ideal.
2. Different pretreatment methods. The results showed that yield of holocellulose and cellulose increased after pretreatment. The changes indicated that the effect was better with dilute alkali (NaOH) than that of with dilute acid (H₂SO₄) and glycerin (glycerin). In addition, in the same solutions 135°C was found to be better than that at 117°C, and the degree of the degradation of hemicellulose hemicelluloses was the same.
3. The analysis with Fourier infrared spectrum proved that pretreatment of cellulose, hemicelluloses degradation, and lignin removal.
4. This study further confirmed the changes of chemical composition after pretreatment and with three different processing solutions (sulfuric acid, NaOH and glycerin) and easily, simple, and effective way for identification of samples after pretreatment.

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