

Analysis of *Phyllostachys pubescens* Bamboo Residues for Liquefaction: Chemical Components, Infrared Spectroscopy, and Thermogravimetry

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Residues of *Phyllostachys pubescens* bamboo obtained from central Louisiana, USA, were comprehensively investigated for use in liquefaction. The results showed that bamboo branches had the highest Klason lignin and ash content, about 26% and 2.75%, respectively. The epidermis layer sample had relatively higher carbohydrate content, while the wax layer sample had the highest hot water and ethanol-toluene extractives and starch content. The results indicated that the bamboo processing residues showed potential for different chemical feedstocks. No significant differences were found in the infrared spectroscopy (FTIR) spectra of the different samples, indicating that the chemical functional groups were the same, despite variation in chemical components between samples. Klason lignin isolated from the residues showed a higher maximum degradation rate temperature (501 °C) and wider degradation temperature range (200 to 550 °C) than the carbohydrates.

Keywords: *Phyllostachys pubescens*; Chemical components; FTIR; Thermogravimetry

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INTRODUCTION

As one of the most important forest resources, bamboo is widely cultivated in Asia, Africa, and South and Central America and has been used as one of the main resources for flooring and furniture manufacturing (Gao *et al.* 2010). However, because of the limited processing technologies and the special characteristics of bamboo culms, process residues, such as bamboo branches, nodes, epidermis, wax, and pulping by-products, are cast aside as waste. Effective utilization of these bamboo residues is needed to address problems concerning both waste disposal and resource wastage.

Lignocellulosic biomass consists of cellulose, hemicellulose, and lignin, which can be converted into low-molecular weight compounds with high reactivity; the latter can be applied to the preparation of petroleum-based polyols (Pan *et al.* 2012). Liquefaction of biomass has become an effective process to convert lignocellulosic materials into value-added products that are alternatives to petroleum-based chemical feedstocks for the preparation of polyurethane foams, polyurethane films, and phenolic resins. Liquefaction of wood residue (Izumo and Fukushima 2010; Bai and Gao 2012), bagasse (Hassan and Shukry 2008), corncob (Zhang *et al.* 2012), and other forest or agricultural crop wastes have been studied through various liquefaction solvents, catalysts, and heating patterns.

However, the liquefaction processes in these studies cannot be directly used for the liquefaction of all lignocellulosic materials because of the differences in the

characteristics, chemical components, and end applications of the liquefaction products. An example of this was the experimental results of the influence of wood species on the properties of biopolyurethane prepared from liquefied wood with residue, in which the results showed that the liquefaction of softwood occurred in a shorter time than hardwood. Moreover results indicated that the biopolyurethane prepared from softwood was harder than that prepared from hardwood, which suggested that the properties of the liquefaction products and biopolyurethane were influenced by the chemical structure of lignin (Izumo and Fukushima 2010). It was also reported that the liquefaction residue content of cotton stalks was higher than that of bagasse under the same conditions, which indicated that bagasse was more susceptible to liquefaction than cotton stalks (Hassan and Shukry 2008). In the study of liquefaction of brown-rotted wood, wood samples with higher α -cellulose content were more difficult to liquefy and that lignin could be easily liquefied by phenol (Li *et al.* 2012).

The variations in chemical structure and chemical components among different lignocellulosic materials should be carefully considered for the optimization of liquefaction. Though selected properties of *Phyllostachys pubescens* bamboo are already available for evaluating bamboo as a construction material (Lee *et al.* 1994), information on the properties of bamboo processing residues has been ignored. Thus, to maximize the utilization of bamboo processing residues, a series of experiments were conducted to investigate the liquefaction behavior of bamboo residues in a glycerol-based solvent using a microwave-assisted heating system. The chemical properties of the bamboo residues such as epidermis, wax, nodes, and branches were evaluated for the optimization of an economical liquefaction process, and this will be discussed in a further work. Because Fourier transform infrared (FTIR) and thermogravimetric (TG) analyses have been used as effective methods to evaluate the chemical structural changes and degradation properties of liquefaction products (Pan *et al.* 2007; Kobayashi *et al.* 2004; Niu *et al.* 2011), the chemical functional groups and thermogravimetric degradation properties of the residues in this study were also investigated.

EXPERIMENTAL

Materials

Three-year-old bamboo (*Phyllostachys pubescens*) was harvested from the Kisatchie National Forest in Pineville, LA, USA. Bamboo branches and logs were transported to the laboratory and allowed to air-dry. The nodes were first cut off from the culms using an electric motor saw. Meanwhile, the epidermis and wax layers were split off with a fine blade, and the layers between the epidermis and wax were named as middle.

Methods

Chemical analysis

Air-dried strips were reduced to particles using a Wiley mill. The particles were placed in a shaker, and fractions with particle sizes of 40 to 60 mesh were collected. The ash, alpha-cellulose, holocellulose, and Klason lignin contents, hot-water extractive, and alcohol-toluene extractive of the bamboo samples were determined according to ASTM standards D1102-84, D1103-60, D1104-56, D1106-96, D1107-96, and D1110-96,

respectively. The starch content was determined according to a referenced method (Fan 2010). Three replicates were carried out for each portion sample.

FTIR spectroscopy

The FT-IR analysis of the bamboo residues was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of residue was applied directly on the diamond crystal. Data collection was performed with a 4 cm^{-1} spectral resolution and 32 scans were taken per sample.

TG/DTG analysis

TG/DTG analysis of the bamboo residues was conducted with a thermal analyzer, TGA (Q50), to simultaneously obtain thermogravimetric data. About 2 mg of sample was analyzed by the thermal analyzer. Pyrolysis was terminated at $800\text{ }^{\circ}\text{C}$ with a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ under a flow of 60 mL/min of nitrogen gas and 40 mL/min of air.

Statistical Analysis

Statistical analysis was carried out using SAS (version 9.1, SAS Institute, Cary, NC). Analysis of variance (ANOVA) was performed to determine significant difference ($\alpha=0.05$) among the different samples.

RESULTS AND DISCUSSION

Chemical Components

The main compounds that form an integral part of the cell walls of bamboo are carbohydrates (cellulose, hemicellulose) and lignin (acid-insoluble). The two compounds were found to collectively compose more than 80% (weight percent) of the dry weight of bamboo (Fig. 1a). The alcohol-toluene and hot water extractives ranged from 3.90 to 8.80% and 4.25 to 13.83%, respectively. The ash content, which was composed of inorganic minerals such as, primarily silica, calcium, and potassium (Lu *et al.* 2010), ranged from 1.32 to 2.75% (Fig. 1b).

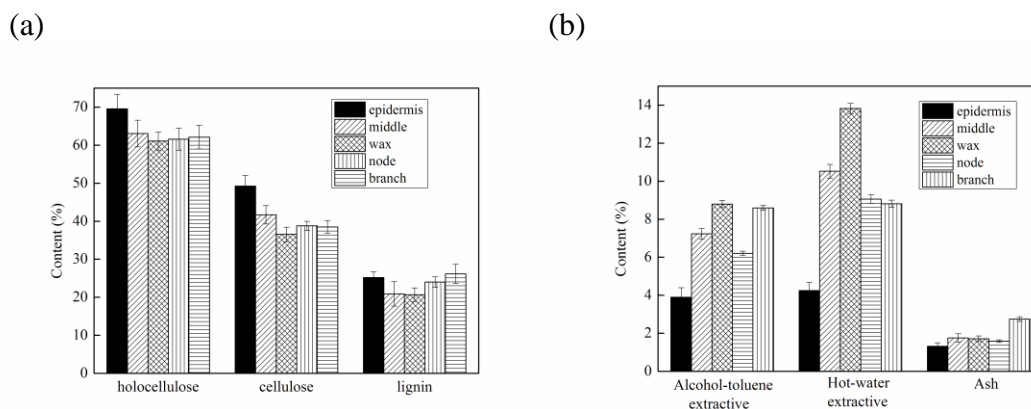


Fig. 1. Chemical components for different samples: (a) holocellulose, cellulose, and lignin; (b) alcohol-toluene extractive, hot-water extractive, and ash

In terms of the carbohydrates, the epidermis sample had the highest content, while the wax layer had the lowest. The carbohydrate content decreased from the epidermis to the middle and inner samples, and the node and branch samples had intermediate average values. Significant differences were found between the epidermis sample and the others. Although there was variation among the middle, wax, node, and branch samples, the difference was not significant, according to the Tukey pairwise comparison analysis. Hence, the bamboo nodes, branches, epidermis, and wax could be also used as raw materials for chemical feedstocks, despite the morphology variations that limited further utilization in machining operations (Xu *et al.* 2012).

The alpha-cellulose content of the wax sample was 36.65%, which was more than 12% lower than that of the epidermis sample. This may be explained by the significant difference between the anatomical structure of the epidermis and wax layers. Higher proportions of fiber tissues and denser vascular bundles in the epidermis layer contributed to the higher cellulose content, while more parenchyma and conducting cells in the wax layer were associated with lower cellulose content (Wahab *et al.* 2009; Wang *et al.* 2011). The bamboo node and branch samples had lower cellulose contents than the middle sample, and significant differences in cellulose contents among the samples were observed.

From the horizontal outer epidermis to the inner wax layer of the internodes, the Klason lignin content showed a similar trend to that of carbohydrates, and the variation among the three different samples was significant. However, the significance was mainly due to the variation between the epidermis and middle samples; the difference between the middle and wax samples was insignificant. It was surprising to find that the bamboo branch and node samples had visibly higher Klason lignin contents than the middle sample. This indicated that, for chemical feedstock purposes, the bamboo processing residues discarded as waste are appropriate for phenolic products.

The alcohol-toluene and hot water extractives differed significantly among the five samples; an obvious increasing trend was observed from the horizontal epidermis layer to the wax layer. The wax layer sample had the highest alcohol-toluene and hot water extractives, and the epidermis layer sample had the lowest extractives. The starch contents for the epidermis, middle, wax, node, and branch samples were 0.37, 1.65, 3.28, 1.73, and 0.97, respectively (data not shown in figure). These results were consistent with the fact that the wax layer of bamboo culms can be easily decayed or attacked by molds, fungi, and borers due to the abundant available sugars and starches.

The branch sample had particularly high ash content, and the ash content differed significantly between the five samples. The ash content of several agricultural residues, such as corn stover, is around 10% (Li *et al.* 2012). The ash content of the bamboo samples was distinctly lower than that of agricultural residues. However, it was significantly higher when compared to common wood species, which have ash contents lower than 1% (Tsuchiya *et al.* 2010). With the development of woody biomass resources as fuel, woody ash will become as significant a problem as coal ash. However, silica may be considered an enhanced chemical because it benefits plant development and increases pest resistance (Ma and Yamaji 2006). On this basis, fraction of chemicals is required in order to achieve economically and environmentally beneficial results.

In the liquefaction of the epidermis samples, a higher reaction temperature may be necessary because cellulose is resistant to thermochemical treatment. Meanwhile, this critical temperature needed for the degradation of cellulose will also provide a proper environment for the re-condensation of the lignin or hemicellulose decomposed

compounds. Therefore, the liquefaction temperature, time, and catalyst concentration should be comprehensively considered for the liquefaction of different bamboo residues (Li *et al.* 2012).

FTIR Spectra

FTIR spectra of the bamboo samples are shown in Fig. 2. The spectra were recorded in the range of 800 to 3800 cm^{-1} . The FT-IR spectra were separated into two information-rich regions: strong and prominent stretching vibration modes in the 3800 to 2800 cm^{-1} region, and the fingerprint region at 1800 to 800 cm^{-1} . The -OH stretching vibration at 3300 to 3310 cm^{-1} and the C-H stretching vibration at 2870 to 2920 cm^{-1} in the 2800 to 3800 cm^{-1} region are common to all the chemical components (Popescu *et al.* 2009).

In the fingerprint region, the peak at 1720 to 1730 cm^{-1} was assigned to C=O stretching vibration of the carboxyl and acetyl groups in hemicellulose. The peak at 1590 cm^{-1} for C=C stretching vibration and 1456 cm^{-1} for C-H deformation are common to lignin, and the peak at 1230 cm^{-1} was assigned to syringyl ring breathing and C-O stretching in lignin and xylan (Poletto *et al.* 2012). The peak at 1316 cm^{-1} assigned to the OH in plane bending and CH₂ wagging, 1106 cm^{-1} assigned to glucose ring asymmetric valence vibration, and 895 cm^{-1} assigned to anomere C-groups are attributed to cellulose. The predominant absorbance at 1020 cm^{-1} was attributed to C-OH bending modes (Luo *et al.* 2012).

As can be seen in Fig. 2, there was no significant difference between the transmittance spectra of the samples. The results indicated that the chemical structures of the samples from the five portions were the same. However, this does not mean that the effect of differences in chemical structure should be overlooked when comparing the liquefaction of *Phyllostachys pubescens* bamboo residues to that of lignocellulosic biomasses such as softwood, hardwood, and agricultural crops.

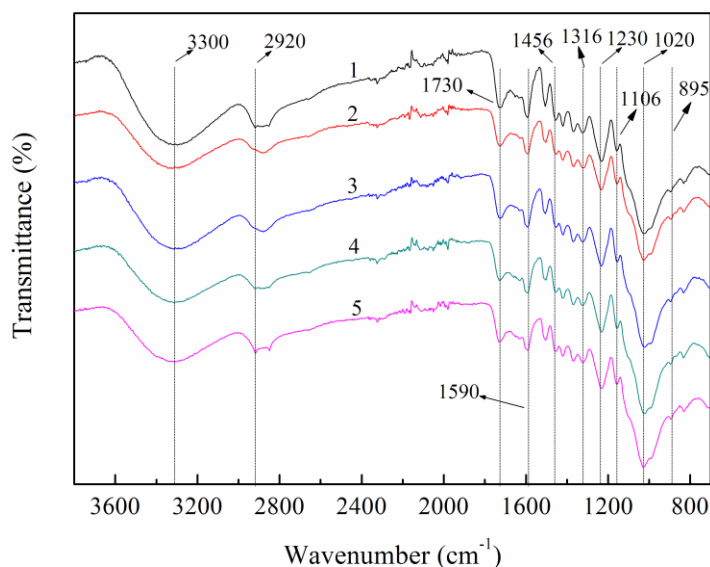


Fig. 2. FT-IR spectra of (1) epidermis, (2) middle, (3) wax, (4) node, and (5) branch samples

Thermogravimetric Analysis

Analysis of carbohydrates and lignin

The thermal properties of the carbohydrates and Klason lignin isolated from the original samples were first investigated to gain a better understanding of the degradation characteristics of bamboo residues. The degradation of carbohydrates and Klason lignin occurred over a wide temperature range, from 190 to 550 °C.

As shown in Fig. 3, three peaks were observed in the DTG curve of carbohydrate. The degradation of carbohydrates occurred as a two-step process. Due to the lower depolymerized temperature of hemicellulose, the first peak at 282 °C was related to the maximum degradation rate of hemicellulose. The second peak at 405 °C primarily corresponded to the maximum decomposition rate of cellulose. During the degradation of hemicellulose and cellulose, a charred residue formed from the depolymerization, dehydration, and decomposition of glycosyl units in the cellulose and hemicellulose (Roman and Winter 2004). The DTG peak at 451 °C was attributed to the oxidation and breakdown of the charred residue to lower molecular weight gaseous products.

In the DTG curve of Klason lignin, two obvious peaks at 300 °C and 501 °C were observed. Lignin is constructed of three basic phenylpropane units through ether bonds, containing a number of hydroxyl groups and methoxy groups. Therefore, the peak appearing at 300 °C was considered to be the weight loss of H₂O and volatile substances that were formed by the breakdown of aliphatic hydroxyl groups (R-COOH) on the side chain of the lignin (Amen-Chen *et al.* 2001). In addition, the maximum weight loss rate at 501 °C was caused by the cleavage of ether bonds, yielding phenols (Zhang *et al.* 2012).

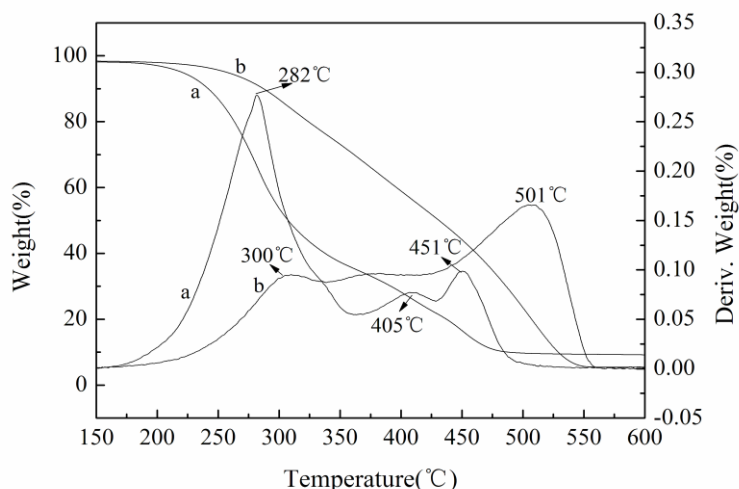
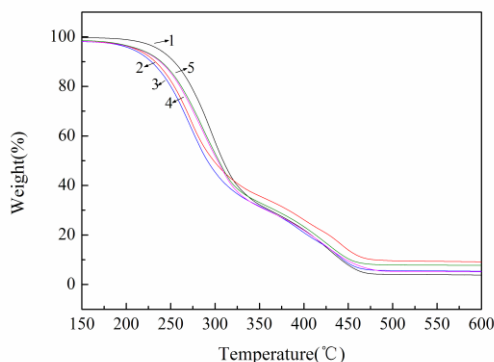


Fig. 3. TG/DTG curves of (a) carbohydrate sample, (b) Klason lignin sample isolated from the residues

Analysis of different bamboo residues

The TG and DTG curves of the five different samples are shown in Fig. 4. Three weight loss processes were observed in the TG curves (Fig. 4a): evaporation of moisture and extractives (<190 °C), degradation of carbohydrates (190 to 340 °C), and decomposition of lignin and charred residue (340 to 465 °C) formed in the degradation of carbohydrates.

(a)



(b)

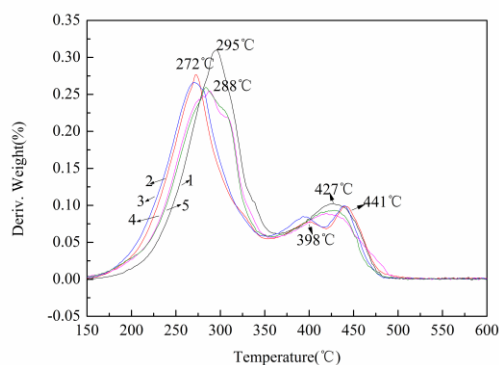


Fig. 4. TG (a) and DTG (b) curves of (1) epidermis, (2) middle, (3) wax, (4) node, and (5) branch samples

In the first degradation process, the epidermis sample (Fig. 4a, curve 1) showed a minute weight loss (0.70%). The weight loss of the inner sample was 2.37%, which was more than twice that of the outer sample. According to Poletto *et al.* (2012), this behavior is associated with the highest content of extractives being found in the wax samples. In this investigation, an interesting finding was that the hot water extractives found in the inner sample were about three times that in the outer samples. These results indicated that the extractives existing in bamboo samples contributed significantly to the initial weight loss prior to the degradation of carbohydrates and lignin.

During the degradation of carbohydrates, the wax sample presented a minimum degradation temperature that was around 25 °C lower than that of the epidermis sample (Fig. 4b and Table 1). This finding was in agreement with the fact that low-molecular weight components (such as extractives) that can be volatilized at lower temperatures may accelerate the degradation of other compounds (such as cellulose and lignin) that will be decomposed at higher temperatures (Poletto *et al.* 2012). An interesting finding was that there was a significant inverse correlation between the maximum degradation rate temperature and the hot water extractives ($R=-0.92$, $p<0.05$). The higher carbohydrate content in the epidermis sample, which was more than 8% higher than the wax sample, may have also contributed to the higher maximum degradation rate temperature. It can be concluded that the epidermis sample had better thermal stability.

Table 1. Degradation Temperature Range (T_r), Degradation Temperature at Maximum Degradation Rate (T_{max}), Weight Loss (WL), and Residue Yield Obtained from TG-DTG Curves

Samples	Evaporation of Moisture and Extractives			Carbohydrate Degradation			Lignin/char Decomposition			Residue (%)
	T_r (°C)	T_{max} (°C)	WL (%)	T_r (°C)	T_{max} (°C)	WL (%)	T_r (°C)	T_{max} (°C)	WL (%)	
Epidermis	<187	187	0.70	187-340	295	64.59	340-465	427	29.61	3.90
Middle	<176	176	2.29	176-328	272	57.62	328-455	441	27.35	8.95
Wax	<170	170	2.37	170-315	270	58.19	315-440	440	28.19	5.07
Node	<172	172	2.25	172-326	288	60.57	288-460	419	29.32	5.22
Branch	<175	175	1.99	175-320	283	57.46	283-455	428	31.00	7.90

CONCLUSIONS

1. The carbohydrate (cellulose, hemicellulose), Klason lignin, extractives, and ash contents showed significant differences between residue samples from *Phyllostachys pubescens* bamboo. The epidermis sample had higher carbohydrate and lignin contents, and the wax sample had the highest extractive content.
2. The chemical functional structures were the same, despite the variation in chemical components between different samples.
3. The maximum degradation temperature for lignin was higher than for carbohydrates. The epidermis sample showed superior thermal stability compared to the other residue samples.
4. With higher carbohydrate content, the epidermis residues should be liquefied under higher temperature for the preparation of methyl sugar derivatives; while the wax layer residues could be easily liquefied under mild conditions. Due to the higher lignin content in the branch, it should be a good raw material for the production of phenolics via liquefaction.
5. The results obtained in this study can provide important information for optimizing the liquefaction process for the preparation of bio-based products.

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