Function and Potential of Bamboo Lignins

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ABSTRACT: Bamboo has been widely used for the production of papers and paperboards in Asia. Due to its low cost and wide distribution, its applications have attracted increasing attention in the world. However, the research up to now has been limited to carbohydrates, and completely effective use for the bamboo resource has not been achieved yet. In the present work, bamboo lignocellulosics were conversed and separated into carbohydrates and ligno-*p*-cresols quantitatively through the phase-separation process. The conversion patterns were discussed and the resulting ligno-*p*-cresols and carbohydrates were characterized in comparison with those from woody materials. The analytical data indicated that the bamboo ligno-*p*-cresols had a high frequency (0.8 mol/C_9) of 1,1-bis(aryl) propane-type structures in their molecules.

Key words: bamboo, lignin, carbohydrates, the phase-separation system, ligno-*p*-cresols

1. INTRODUCTION

Bamboo species are distributed throughout the tropics, subtropics and temperate zones of world. Many bamboo species, *ca* 1250 species and 100 genera [1] are known. The genus Phyllostachys is one of the largest genera of bamboo and about 30 species are known in the East Asia. In Japan, three Phyllostachys species, *P. bambusoides*, *P.heterocycla*, *P.nigra*, are widely distributed, most of which are fast-growing, attaining stand maturity within five years, but flowering infrequently[2]. Therefore, the relatively high level of bamboo production has been formed and may be continued for a long time. However, the utilization of bamboo is limited in using for structural materials [3], paper and paperboard [4], and bamboo charcoal [5] etc.[6,7,8], a large amount of bamboo still remains unused and is dumped as landfill. A completely effective use becomes very necessary.

In recent years, a rapid technique for separating wood into lignin and carbohydrates with a concentrated acid-phenol system was developed successfully in our laboratory[9]. The key point of the process is that lignin and carbohydrates, which form an interpenetrating polymer network within the cell wall, are separated into different phases and their modifications are controlled individually[10]. As for bamboo, although they are known to belong to graminaceous plants , have similar compositions to hardwood [11], the lignin is GSH type lignin[12,13]and the content is lower than its in woody materials and higher than other non-woody materials[14], the utilization of both lignin and carbohydrates at industrial level has never been heard.

In the present work, three species bamboo (*Phyllostachys bambusoide*, *Phyllostachys heterocycl*, *Phyllostachys nigra*) are adapted to the phase-separation system, as comparison Western hemlock (*Tsuga heterophylla*) and Poplar (*Populus salicaceae*) were treated with the same method. The function and potential of bamboo as industrial raw materials were discussed.

2. EXPERIMENTAL

2.1 Materials

Internodal pieces of bamboo were mechanically liberated from the epidermis, cut into short rings (about 1 cm in length) and reduced to small pieces. Air dried bamboo chips were ground successively in a Wiley mill and a vibrational mill to pass an 80 mesh screen, and extracted with ethanol-benzene (1:2, v/v) for 48hr.

2.2 Composition analyses of bamboo

Dry matter content

The dry matter content of bamboo meals were gravimetrically determined by drying samples at 105 ℃ to constant weight.

Ash Content

The ash contents of all the bamboo meals were obtained gravimetrically after in muffle calcinations for 4h at 600 ℃.

Extractives

Bamboo meals (40~60 mesh , 1 g) were extracted with cold water for 48h, hot water for 3h with refluxing, and 1% NaOH solutions for 1h with refluxing respectively. The extractives contents were gravimetrically determined by drying treated samples at 105 ℃ to constant weight.

Lignin

Lignin contents were determined on Klason method (TAPPI T 13 m-54) with acid-pepsin pretreated bamboo meals [15].

Holocellulose and α-cellulose

Holocellulose and α-cellulose were extracted with sodium chlorite, acetic acid and KOH solution respectively according to Tappi Standard T203 cm-99.

2.3 Synthesis and isolation of ligno-p-cresols

Synthesis and isolation of ligno-p-cresols were carried out with the method in literature [18].

2.4 Physicochemical characterization analysis of ligno-p-cresols

Molecular weight distribution of ligno-p-cresols

Gel permeation chromatography (GPC) of ligno-p-cresols were determined on SHIMADZU CLASS LC-10 system (LC-10AD, SPD-10AD, SPD-10A) equipped with JASCO MD-1515 multi wavelength detector. Shodex GPC KF-801,802,803 and 804 (8 mm ID × 300 mm) were connected in series and tetrahydrofuran (THF) used as an eluent [flow rate: 1.0 mL/min]. Calibration for weight-average molecular weight $(\overline{Mw})$, number-average molecular weight $(\overline{Mn})$ and polydispersity $(\overline{Mw}/\overline{Mn})$ was performed using standard polystyrene.

Amounts of combined p-cresols

^{1}H-NMR analyses of ligno-p-cresols were acquired with a JOEL JNM-A500 FT-NMR System. The amounts of combined cresols were calculated on the signal intensity of cresolic methyl protons (1.6-2.4 ppm) against aromatic protons (7.8-8.4 ppm) of internal standard (p-nitrobenzaldehyde) on ^{1}H-NMR spectra.

FT-IR spectra of ligno-p-cresols

FT-IR spectra were obtained on Perkin Elmer Spectrum GX FT-IR Spectroscopy using KBr discs. The spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans.

UV-Vis spectra of ligno-p-cresols

Ultraviolet and Visible spectra of ligno-p-cresols were determined on a JASCO V-560 spectrophotometer. They are measured continuously in the wavelength region of 200-600 nm.

Thermo mechanical analysis (TMA) of ligno-p-cresols

Thermo mechanical analyses of ligno-p-cresols were performed on a SEIKO EXSTAR 6000 TMA/SS. About 3 mg sample powder was set in an aluminum pan (5 mmφ×2 mm) and a smaller aluminum operculum (2 mmφ) was put on the center over the sample. Under 49 mN loading by quartz needle, the solid-liquid transitions of ligno-p-cresols were measured by programmed heating from 50 ℃ to 250 ℃ (2 ℃/min) under 200 mL/min of N₂.

3. RESULTS AND DISCUSSION

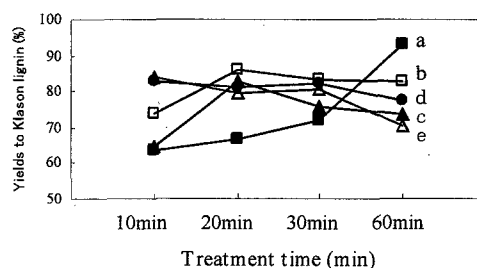*3.1 Chemical compositions of bamboo and yields of ligno-p-cresols*

Fig.1 Yields of ligno-p-cresols. (a) Western hemlock, (b) Poplar, (c) *P.bambusoides*, (d) *P.nigra*, (e) *P.heterophylla*.

As summarized in Table I , the three species bamboo contain 20~24% lignin and 77~79% holocelluloses respectively. The yields of softwood ligno-p-cresols (ether-insoluble) are increased gradually up to 60 min (about 93% to Klason lignin), while yields of hardwood, bamboo ligno-p-cresols (ether-insoluble) reach to the maximum (about 70~77% to Klason lignin) at 10-20 min respectively and decreased gradually after that

(Fig.1). The differences of conversion rates are resulted from the differences in frequency of condensed structures between with and without syringyl units (S nucleus).

Table I   Chemical compositions of bamboo

Chemical compositions	P.B.(%)	P.H.(%)	P.N.(%)
Ash	0.94	0.97	0.65
Cold water extractives	4.34	9.09	7.61
Hot water extractives	5.83	9.50	8.52
NaOH extractives	26.44	22.91	22.72
Solvent extractives	4.08	8.32	10.03
Holocellulose	77.54	78.70	78.93
α-cellulose	44.37	49.75	49.90
Lignin	20.40	24.03	23.44
Acid soluble lignin	0.59	0.85	0.69
Acid insoluble lignin	19.81	23.18	22.75

3.2 Molecular weights and amounts of combined cresols in bamboo ligno-p-cresols

Weight average molecular weight ($\overline{Mw}$) of P.B. ligno-p-cresols are 5975~7476 ($\overline{Mw}/\overline{Mn}$=1.48~1.72). Weight average molecular weight ($\overline{Mw}$) of P.N. ligno-p-cresols are 5045~7394 ($\overline{Mw}/\overline{Mn}$=1.68~2.15). Weight average molecular weight ($\overline{Mw}$) of P.H. ligno-p-cresols are 4955~5949 ($\overline{Mw}/\overline{Mn}$=1.52~1.67).

Increasing with the phase separation treatment time from 10 min to 60 min, not many changes of weight average molecular weight have been found distinguishedly. That is to say the conversion of bamboo lignin has been finished nearly at the first reaction stage, and the molecular sizes of ligno-p-cresols are in order.

The amounts of combined cresols (0.8 mol/C9) in bamboo ligno-p-cresols are higher than softwood, which are similar to hardwood [10].

3.3 FT-IR and UV-Vis spectra of ligno-p-cresols

The FT-IR spectra of three species bamboo ligno-p-cresols show bands at 1325,1220,1130 cm⁻¹ which belong to vibrations of syringyl group and 1270, 1040 cm⁻¹ which belong to vibrations of guaiacyl group, 815 cm⁻¹ resulted from combined cresols, which are similar to hardwood ligno-p-cresols (Fig.2). A distinct

C=O vibration belonging to carboxyl or ester group at 1730 cm⁻¹ is found. In the case of MWL, the distinct absorption band is attributed to the coumaryl ester structure by Higuchi et al. (1967) [16]. That is to say, a part of esterified p-coumaric acid in bamboo native lignin is remained through the phase-separation system. They also may be resulted from the non-conjugation carbonyl groups coming from polysaccharides [17].
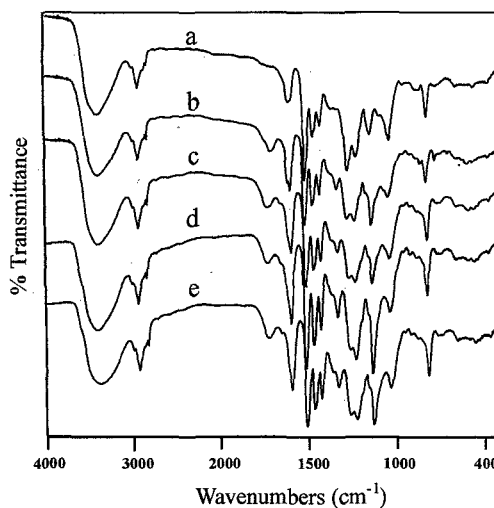

Fig.2 FT-IR spectra of ligno-p-cresols. (a)Western hemlock (b) Poplar (c) *P.bambusoides* (d) *P.nigra* (e) *P.heterophylla*.

UV-Vis spectra of bamboo ligno-p-cresols are characterized by a sharp band at 280 nm, a shoulder at 305 to 370 nm (Fig.3). During the phase-separation treatment, selective and effective grafting of cresol at reactive sites in the side chains, leading to the disappearance of conjugated systems had been known by the previous research [18]. The shoulder peaks of bamboo ligno-p-cresols come from the conjugation structures of the esterified p-coumaric acid [19].

3.4 TMA analysis of ligno-p-cresols

The TMA curves of ligno-p-cresols from bamboo and woody materials revealed volume decreasing at 150-160 °C due to the solid/liquid phase transition[20]. The transition points of bamboo ligno-p-cresols indicate higher values than wood ligno-p-cresols (Fig.4).The polydispersity of bamboo ligno-p-cresols (by GPC) is lower than wood materials. Therefore this is based on the scarcity in low molecular compositions that function as internal plasticizer.
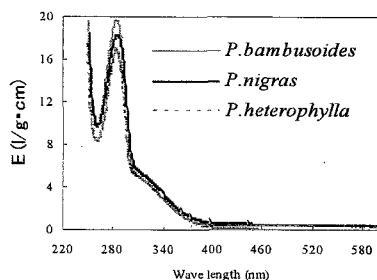
Fig.3 UV spectra of bamboo ligno-*p*-cresols.

Fig.4 TMA profiles of ligno-*p*-cresols. (a) Western hemlock, (b) Poplar, (c) *P.bambusoides*, (d) *P.nigra*, (e) *P.heterophylla*.

In summary, as herbaceous resources, bamboo are converted into carbohydrates and ligno-*p*-cresols rapidly than woody materials through the phase-separation system. The analytical data indicate that the bamboo ligno-*p*-cresols have a high frequency of 1,1-bis (aryl) propane-type structures in their molecules. The characteristics of bamboo ligno-*p*-cresols are similar to hardwood ligno-*p*-cresols. However, a part of esterified *p*-coumaric acid in native lignins remained. All prenominate data indicate that bamboo has an excellent potential as industrial raw materials.

4. REFERENCES

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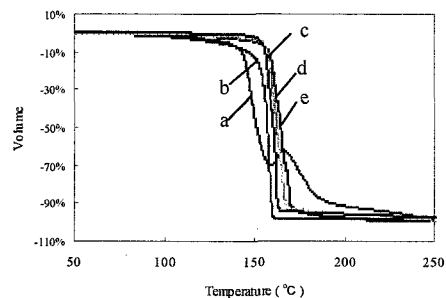[8] S. Chang, T. Yeh and J. Wu, *Polymer Degradation and Stability*, **74** , 551-557 (2001).

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