CELLULOSE CHEMISTRY AND TECHNOLOGY

STEAM AND HOT WATER PREHYDROLYSIS OF BAMBOO AND ITS EFFECT ON RESIDUAL LIGNIN STRUCTUREAND PULPING

M. SARWAR JAHAN,[*] M. AZHARUL ISLAM,[*,**] M. MOSTAFIZUR RAHMAN,[*]JANNATUN NAYEEM,[*]SHAMIM AHMED[***]and M. A. QUAIYYUM[****]

[*]Pulp and Paper Research Division, BCSIR Laboratories, Dhaka, Dr. Qudrat-i-Khuda Road,
Dhaka 1205, Bangladesh
[**]Department of Chemistry, Dhaka College, Dhaka, Bangladesh
[***]INARS, BCSIR Laboratories, Dhaka, Dr. Qudrat-i-Khuda Road, Dhaka 1205, Bangladesh
[****]Applied Chemistry and Chemical Engineering, Dhaka University, Dhaka, Bangladesh
✉ *Corresponding author:M. SarwarJahan, sarwar2065@yahoo.co.uk*

Received November, 13, 2015

In this study, steam prehydrolysis (SP) and hot water prehydrolysis (HWP) of bamboo chips were carried out, followed by kraft cooking and bleaching under identical cooking and bleaching conditions. Then the obtained pulp composition and properties were evaluated, specifically, alkali solubility S_{10} and S_{18}, viscosity and brightness. The pentosan dissolution from bamboo chips was 51.2% for SP and 55.8% for HWP and it was found that, under the applied prehydrolysis conditions, direct delignification also took place, without affecting α-cellulose.The overall unbleached pulp yield after kraft cooking was almost similar, 32.7% for SP and 33.2% for HWP. The purity of the bleached pulp was 94% with degraded cellulose percentages (S_{10}-S_{18}) of 6.0-6.8% and brightness of 84.2%. To reveal prehydrolysis induced changes in the lignin structure by the SP and HWP processes, lignin was isolated by the acidic dioxane method and characterized. The formulae of lignin C_9 indicated a significant decrease in the number of methoxyl groups as the HWP was performed. ^{1}H-NMR spectra showed that bamboo lignin had 0.81 and 0.79 guaiacyl and syringyl protons per C_9 units, while the corresponding guaiacyl and syringyl protons for SP and HWP lignins were 0.67 and 0.87 and 0.57 and 0.63, respectively.

Keywords: bamboo, steam prehydrolysis, hot water prehydrolysis, dissolving pulp, lignin, methoxyl group

INTRODUCTION

In order to reduce greenhouse gas emission and problems associated with fossil resources exhaustion, the demand for biopolymers and bioenergy has increased. Lignocellulosic biomass, including agricultural residues, forestry wastes, energy crops, waste paper, *etc*. has received much attention, because it is the cheapest and most abundant natural resource on earth. Besides, it is renewable and relatively carbon-neutral, and has traditionally been considered as a potential sustainable source of biopolymers, biofuels and other value-added bio-based chemicals.[1,2]

Lignocellulosic biomass is mainly composed of three major components, which are cellulose, hemicelluloses and lignin. The percentages of the three components may vary depending on factors such as plant species and plant parts.[3-5]

The successful exploitation of biomass to produce value-added chemicals may lead to a stepwise move of the present global economy toward a sustainable bio-based economy with bio-based products, such as biochemicals, bioenergy and biomaterials. For lignocellulosic materials, pre-extraction of lignocellulosic materials prior to pulping has been considered as an important aspect for the implementation of integrated forest biorefinery.[1,6] In this context, the commercial pre-hydrolysis kraft-based dissolving pulp production process fits well into the biorefinery concept.[7] For such a process, the removal of hemicelluloses prior to pulping by steam explosion (or hot water) pre-hydrolysis technology is a critical step for producing high-quality dissolving pulp.[8]

A major challenge of hot-water (auto)hydrolysis is the partial dissolution of highly reactive lignin components. These components cause resinous precipitates during heating and storage at high temperatures. The precipitates were specified as a highly condensed form of the colloidal dissolved lignin fraction.[9] Further processing of the prehydrolysate, such as hydrolysis of oligosaccharides, concentration of sugars and separation of acetic acid, is impaired by lignin precipitation. In order to avoid the precipitation problems and to simultaneously benefit from autohydrolysis, steam prehydrolysis is conducted in industrial practice. To solve this problem, Gütsch and Sixta[10] developed a new high temperature adsorption process, where lignin was removed directly after the autohydrolysis, which enables further processing of the autohydrolysates.

It has been hypothesized that steam prehydrolysis (SP) and hot water prehydrolysis (HWP) processes change the physicochemical structure of raw materials very differently, and that these changes affect the hemicellulose mass transfer efficiency and the subsequent delignification rate.[11]

EXPERIMENTAL

To reveal prehydrolysis (HWE and ST) induced changes in the lignin structure by the SP and HWP prehydrolysis processes, lignin was isolated by the acidic dioxane method and characterized by UV, FTIR, ^{1}H NMR spectroscopy, molecular weight determination, and elemental and methoxyl analyses. In order to find differences, SP and HWP bamboo chips were also kraft cooked and bleached under identical cooking and bleaching conditions and pulp properties were evaluated in terms of cellulose and pentosan contents, S_{10}, S_{18}, viscosity and brightness.

Materials

Bamboo chips were collected from the Kharnaphuli Paper Mills (KPM). All chemicals used in this study were of GPR grades and received from E-Merck, Germany.

Prehydrolysis

Bamboo chips were prehydrolysed by water in a 20 L capacity digester. The prehydrolysis process was carried out at 170 °C for 60 min. For steam prehydrolysis, steam was injected into the digester until the temperature rose to170°C and prehydrolysis was continued for 60 min. The bamboo to liquor ratio was 1:4. The time required to rise to maximum temperature was 50 min. After completing prehydrolysis, pressure was released and the digester was cooled by circulating cold water. Samples were then collected from the drained off liquor for pH, solid content, lignin and sugars determination. The percentage of dissolved components was measured gravimetrically.

Analysis of prehydrolysed bamboo chips

Klason lignin and pentosan contents of bamboo, SP and HWP bamboo were determined according to TAPPI Test Methods number T211-om83 and T223-cm01, respectively. Holocellulose samples were prepared by treating extractives-free meal with $NaClO_2$ solution.[12] The pH of the solution was maintained at 4 by adding CH_3COOH-CH_3COONa buffer and the α-cellulose content was determined by treating holocellulose with 17.5% NaOH (T203 om 93). The ash content was determined using a Nuive muffle furnace at 525°C according to T 211 om-93.

Analysis of prehydrolysed liquor (PHL)

The total solid content in the PHL was determined gravimetrically by drying 50 ml sample at 105°C until constant weight. The dissolved lignin in the PHL was measured based on the UV/Vis spectrometric method at wavelength 205 nm (TAPPI UM 250). Sugars and organic acids were analyzed by high-performance liquid chromatography (HPLC),which was described elsewhere.[7]

The monomeric sugar contents in the prehydrolysis liquor and the acid hydrolysate were determined by using ion chromatography with a Pulse Amperometric Detector and CarboPacTM PA1 column (Dionex-300, Dionex Corporation, Canada). Deionized water was used as eluant with a flow rate of 1 mL/min. The regeneration agent used was 0.2 N NaOH with 1 mL/min flow rate and 0.5 N NaOH was used as the supporting electrolyte with 1 mL/min flow rate. The samples were filtered and diluted prior to analysis. The monomeric sugar contents in the post acid hydrolysate stood for the total saccharides in the prehydrolysis liquor. The sugar contents in oligomeric form in the prehydrolysis liquor were calculated from the difference of the monomeric sugar contents with and without the post acid hydrolysis.

Cooking

Hot-water (HWP) and steam prehydrolysed (SP) bamboo chips were cooked in the same digester. The following parameters were kept constant in the kraft process: active alkali charge of 16% on o.d. prehydrolysed bamboo, liquor to fiber ratio of 5:1, temperature of 170 °C, cooking time of 120 min.

After digestion, the pulp was washed until free from residual chemicals, and screened on a flat vibratory screener (Yasuda, Japan). The screened pulp yield, total pulp yield and screened reject were determined gravimetrically as percentage of o.d. raw material. The kappa number of the resulting screened pulp was determined in accordance to Tappi Test Methods (T 236 om-99).

Bleaching

Bamboo pulps were bleached by the $D_0E_pD_1E_pD_2$ bleaching sequence. The ClO_2 charge was 2% and the temperature was 70 °C for 45 min in the D_0 stage. The pH was adjusted to 2.5 by adding dilute H_2SO_4. Alkaline extraction was carried out with 2% NaOH and 0.5% H_2O_2charge, temperature was 70 °C for 120 min. In the D_1 and D_2 stages, ClO_2 charge was0.5, the pH was adjusted to 4.5 and 6.5, respectively, adding dilute alkali. The pulp consistency was 10% in all stages.

Evaluation of pulps

Pulp tests were performed according to the Standard Methods of the Technical Association of the Pulp and Paper Industry (TAPPI, Atlanta, GA): brightness (T 452 om-92); viscosity (T 230 om-89); carbohydrate (T249 cm00); α-cellulose (T 203 om-88); and alkali solubility $S_{10}$and S_{18} (T 235 cm-85). Alpha-cellulose is the pulp fraction resistant to treatment in an aqueous solution containing 17.5% sodium hydroxide and indicates undegraded, high molecular weight cellulose content in pulp. Alkali solubilities $S_{10}$and S_{18} provide information on the low molecular weight carbohydrates (degraded cellulose and hemicellulose) in pulp. A 10% sodium hydroxide solution dissolves both degraded cellulose and hemicellulose (S_{10}), whereas hemicellulose is soluble in an 18% sodium hydroxide solution (S_{18}). All pulp properties were analyzed in duplicate.

Lignin extraction

Bamboo, SP and HWP bamboo chips were ground (40/60 mesh) in a Wiley mill, extracted with acetone and dried in vacuum over P_2O_5.

The acetone extract free meals were refluxed with acidic dioxane (9:1) solution. The concentration of HCl in dioxane solution was made 0.2N. The dioxane to meal ratio was 8. The wood meal was refluxed with dioxane solution for about 1 hour in N_2 atm. The N_2 flow was maintained at 50mm/min. After completing the reflux time, the wood meal dioxane mixture was filtered in a Buckner funnel using filter no.2. The residue was washed with a dioxane solution (9:1). The dioxane solution was then neutralized by adding solid Na_2CO_3 and filtered. The filtrate was concentrated in a vacuum evaporator at 40 °C. Then the concentrated dioxane solution was added dropwise to water to precipitate lignin. The lignin precipitate was washed and dried in vacuum over P_2O_5.

Dried crude lignin was dissolved in dioxane (9:1), and again precipitated in ether with constant stirring by a magnetic bar. The precipitated pure lignin was dried in vacuum over P_2O_5 and weighed. The yield of dioxane lignin was calculated based on Klason lignin. The purity of dioxane lignin was determined by measuring Klason lignin.

Acetylation

Dioxane lignin (100 mg) was added to 1.5 ml of dry pyridine-acetic anhydride (1:1) and kept for 72 h. The solution was added to a 10-fold volume of ice-cold water, whereupon the acetylated sample was recovered as a precipitate, which was purified by successive washing with water and dried under vacuum over P_2O_5.

Elemental analysis

C, H, O and N analyses were carried out in the Analytical Research Division, BCSIR. The methoxyl content in dioxane lignin was determined in accordance with the Zeisel–Viebock–Schwappach method.

According to this method, a lignin sample of 0.03 g, 0.6 ml (0.5 gm) phenol, 6 drops of acetic anhydride and 3.5 ml of hydroiodic acid were introduced into a reaction flask, which was fitted with a condenser. The upper head of the condenser was fitted with two absorption tubes, which were filled with 15 ml of bromine solution. The reaction flask was heated at 140 °C by an oil bath for 30 min. Water at 50 °C was circulated through the condenser by a force circulation water bath. Carbon dioxide gas was passed through the reaction vessel to the absorber to carry the reaction product. The absorption solution was transferred quantitatively to a 250 ml conical flask, shaking vigorously with 25 ml of 20% sodium acetate solution and 4% formic acid was added drop by drop until the solution was decolorized. Two more drops of methyl red were then added and pink color was observed. Then 20 ml of 10% sulfuric acid (H_2SO_4) and 5 ml of 10% potassium iodide (KI) were added. The flask was closed with a glass ground stopper and allowed to stand for 5 min. The iodine formed was titrated with 0.1 N sodium thiosulfate solution ($Na_2S_2O_3$) using a starch indicator.

Methoxy group $[OCH_3]$, (%) = $[(a*f*0.5172)/A]*100$

where a is the volume of 1 N $Na_2S_2O_3$;f– the titer factor for 0.1 N $Na_2S_2O_3$;0.5172– the quantity of OCH_3 groups, corresponding to 1 ml of 0.1 N $Na_2S_2O_3$;A – mg of lignin sample.

Spectroscopy

FTIR spectra were recorded by using a Shimadzu FTIR spectrometer model 8201PC. The dried samples were embedded in KBr pellets in the concentration of about 1 mg/100 mg KBr. The spectra were recorded in the absorption band mode in the range 4000-400 cm^{-1}.

^1H NMR spectra of a lignin solution (100 mg of acetylated lignin in 0.5 ml $CDCl_3$) were recorded on a Bruker 400 spectrometer. Solvent was used as internal standard (ppm 7.25). For quantification of protons, the signals in specified regions of the spectrum were integrated with respect to a spectrum-wide baseline drawn at the level of the background noise, and the results were referred to the signal for methoxyl protons, whose average number per C_9 unit was established as described above.

RESULTS AND DISCUSSION

Steam and hot water prehydrolysis

The bamboo chips were prehydrolysed at 170°C for 1 h by hot water (HWP) and steam prehydrolysis (SP) processes and the results for the solid residue yield and composition are shown in Table 1. These prehydrolysis conditions were used by Kharnaphuli Rayon Mills for producing dissolving pulp from bamboo. HWP produced slightly lower solid residue compared to SP. However, Luo *et al.*[11] observed that the solid residue yield from bamboo was 77.1% for steam and 90.4% for water prehydrolysis at P-factor 992. The cellulose loss in both prehydrolysis processes was not observed under our applied conditions (Table 1).

The pentosan dissolution from bamboo chips was 51.2% for SP and 55.8% for HWP. Klason lignin was determined before and after prehydrolysis. It was found that under the applied prehydrolysis conditions direct delignification (based on Klason lignin content) took place, since the starting material contained 25.5%, while the SP fibers contained 23.9% and HWP contained 22.8%. Lignin removal from bamboo chips by HWP was also higher than that of SP (19.6% *vs.* 25.5%). The dissolution behavior of pentosan and lignin can explain the slightly lower solid yield of HWP. Another study showed that pentosan and lignin dissolution in both SP and HWP were similar up to a certain point, followed by lower lignin dissolution in HWP.[11] In our case, prehydrolysis was not reached to such a severe condition. Therefore, the differences of these prehydrolysis processes were not evident.

Prehydrolysis liquor

Biomass dissolution during prehydrolysis is dependent on the pH of the reaction medium. The pH of the prehydrolysis liquor (PHL) of both processes was similar (Table 2). The solid content, lignin, acetic acid and sugars in the PHL obtained by HWP were slightly higher than those of SP. These results are consistent with the solid residue yield (Table 1).Commercial exploitation of these by-products could convert a dissolving pulp mill into an integrated biorefinery and will reduce the dependence on fossil fuel-based products with a turn to bio-based products. Furfural, ethanol, lactic acid, propionic acid, succinic acid can be produced from the dissolved hemicelluloses in the PHL,[13-16] the acetic acid generated from the acetyl group of hemicelluloses was 0.79% in the SP process, while in the HWP process it was 1.0%.

Table 1
Effect of SP and HWP on bamboo composition

	Yield (%)	α-cellulose (%)	Pentosan (%)	Lignin (%)	Ash (%)
Bamboo	100	50.2	24.2	25.5	0.922
SP bamboo	85.9	58.4 (50.1)	13.7 (11.8)	23.9 (20.5)	0.327 (0.281)
HWP bamboo	84.6	59.4 (50.2)	12.6 (10.7)	22.8 (19.0)	0.612 (0.518)

Data inside parenthesis indicates yield based on staring raw material

Table 2
Effect of SP and HWP on prehydrolysedPHL composition

	pH	Solid content (%)	Lignin (%)	Total sugars (%)	Acetic acid (%)
SP	4.53	7.71	0.7	5.53	0.79
HWP	4.57	9.22	1.2	6.78	1.00

Table 3
Effect of SP and HWP on bleached pulp properties

Properties	Steam prehydrolysis	Hot water prehydrolysis
α-cellulose (%)	94.3	94.2
Pentosan (%)	5.4	5.7
S_{10}(%)	12.5	11.7
S_{18} (%)	5.7	5.7
Brightness (%)	84.2	86.7
Viscosity (mPa.s)	3.26	3.21
Ash (%)	0.46	0.51

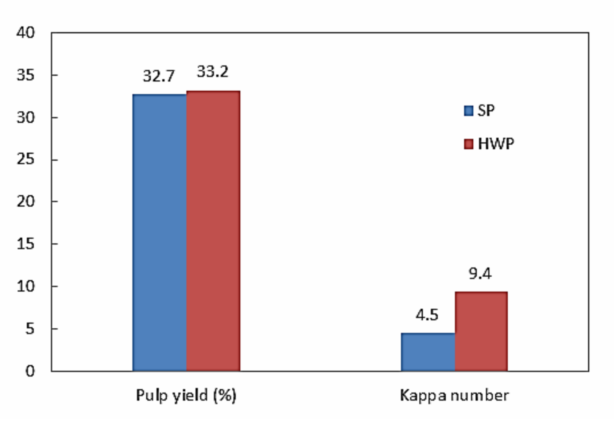

Figure 1: Effect SP and HWP on the yield and kappa number of bamboo pulp

The percentage of generated acetic acid from hemicelluloses is dependent on the temperature and time. The acetic acid can be separated and concentrated by nanofiltration and reverse osmosis.[17] A considerable amount of lignin (0.7-1.2%) was dissolved in the prehydrolysis process. PHL lignin has a higher content of phenolic hydroxyl groups,[18] therefore, it can be a good source for phenolic resin.

Pulping

To compare the effect of SP and HWP on the properties of unbleached dissolving pulp, prehydrolysed bamboo chips were subjected to kraft pulping under identical conditions. As shown in Figure 1, the overall unbleached pulp yield was almost similar, 32.7% for SP and 33.2% for HWP. Prehydrolysed bamboo chips were delignified very easily. Only at 16% active alkali charge, the kappa numbers of the pulps were 4.5 and 9.4 for SP and HWP, respectively. It was observed in another study that severe prehydrolysis conditions enhanced delignification significantly in subsequent kraft cooking.[5,19] Prehydrolysis creates pores in the chips, which help the penetration of cooking chemicals in subsequent pulping. Similar results were found in our earlier study.[2] Luo *et al.*[11] also observed that at almost similar residual pentosan and cellulose purity, the overall pulp yield from bamboo was 32.8% with kappa number 9.5 by HWP at P-factor 1379, followed by kraft cooking with 23% active alkali and pulp yield of 36.0% with kappa number 12.2 in SP at P-factor 756, followed by kraft cooking with 17% active alkali. For paper grade pulp, bamboo chips produced a pulp yield of 44.3% with kappa number 28.1.[20]

Bleaching

The purity of bleached pulp at a given residual pentosan and lignin content is another key parameter for the manufacture of dissolving pulp at an industrial scale. A comparison of the results from HWP- and SP-kraft pulping processes is provided in Table 3. The purity of bleached pulp was dependent on the severity of the prehydrolysis and active alkali in cooking. At identical prehydrolysis and cooking conditions, the α-cellulose contents in the SP and HWP were very similar (94%). This was also cross-checked by S_{18} values and pentosan content, which are almost identical in both processes. Degraded cellulose percentages (S_{10}-S_{18}) in SP and HWP were 6.8 and 6.0, respectively. The viscosity of these pulps was also identical, of 3 mPa.s. Pulp brightness was 84.2% for SP and 86.7% for HWP. From the final pulp properties data, it can be concluded that the produced pulp can be used in rayon production.

Lignin characterization

Elemental analysis and methoxyl content

Elemental analysis and determination of functional groups are important to understand the chemical structure of isolated lignin. Nitrogen was found in bamboo lignin, which was derived from the protein–lignin complexes. Lignin C_9 formulae are listed in Table 4, revealing that the methoxyl content in original bamboo was 22.14%, which was decreased to 20.11% in SP and 16.85% in HWP. The more significant decrease in the number of methoxy groups was observed in HWP bamboo. This can be attributed to the fact that HWP breaks down lignin α-O-4 linkages. A similar result was reported by Li and

Gellerstedt,[21] in their investigation, autohydrolysis broke down lignin α-O-4 linkages *via* both acidolysis and homolytical cleavage. Actually, the hydrolysis is an oxidative process that can cause demethylation. Nevertheless, experimental results indicated that under the used experimental conditions, no significant demethylation occurred in SP. However, Montané *et al.*[22] found that rapid demethylation occurred during steam explosion of wheat straw. It can be concluded that prehydrolysis modified the residual lignin structure, which was characterized by low methoxyl content.

^{1}*H-NMR*

Considering both aliphatic and aromatic hydroxyls per C_9 unit (Table 5), the mole ratio OAc/OCH_3 = (0.81 + 5.24)/4.26 = 1.42. Thus, the total OAc/C_9 ratio = (1.42 OCH_3) x (1.42 OAc/1 OCH_3) = 2.02; the number of aliphatic OAc/C_9, = (1.42 OCH_3/C_9) x (5.24 OAc/4.26 OCH_3) = 1.75 and the number of aromatic OAc/C_9, = (1.42) x (0.81/4.26) = 0.27. Therefore, the numbers of aliphatic and the free phenolichydroxyls for bamboo were estimated to be 175 and 27 resp. per 100 C9 units. Aliphatic hydroxyl groups were decreased to 171 and 118 and aromatic hydroxyl groups increased to 36 and 30 in SP and HWP, respectively. The integrals of signals centered around 6.6 and 6.9 ppm in the^{1}H-NMR spectra of dioxane lignins isolated from bamboo, SP bamboo and HWP bamboo, assigned to aromatic protons in syringylpropane and guaiacylpropane structures, respectively,[23] suggest the presence of similar relative contents of S and G in all lignins. Bamboo lignin had 0.79 + 0.81 = 1.60 aromatic protons per C_9 units. The corresponding aromatic protons SP and HWP lignins were 1.63 and 1.20, respectively. The broad signal at 7.5 ppm can be assigned to the aromatic protons in positions 2 and 6, in structures containing a Cα=O group,[24] to aromatic protons in positions 2 and 6 of H units conjugated with a double bond, and to the proton in H Cα=Cβ structures, confirming the presence of *p*-coumarate-type structures and Cα=O groups in all lignins. Similar *p*-coumarate-type structures were observed in *Arundodonax* reed lignin.[23] A clear signal between 7.3 and 7.6 ppm is assigned to aromatic protons of *p*-coumaric acid and ferulic acid, usually found in non-wood, such as grass lignins. The presence of formate ester at 8.2 ppm (weak signal) is seen in all lignins, but is predominant in HWP lignin. The ^{1}H NMR spectrum (Fig. 2) allows the abundance of different kinds of aldehyde groups to be determined by integration of resonances from specific formyl protons in the lignin.

The integration of signals of the formyl protons at 9.55-9.75 ppm gives the contents of aldehyde groups linked at C$\gamma$and conjugated with vinylic moieties (in cinnamaldehyde type units).

Table 4
Elemental analysis, methoxyl contents and per-C_9-unit formula of bamboo, SP and HWP bamboo

Lignin sample	Elemental analysis, %					C_9 formula*
	C	H	N	O	OCH_3	
Bamboo	62.57	5.67	0.15	31.67	22.14	$C_9H_{7.06}O_{2.53}(OCH_3)_{1.42}$
SP bamboo	57.73	5.94	0.00	36.18	20.11	$C_9H_{8.64}O_{3.48}(OCH_3)_{1.40}$
HWP bamboo	60.88	5.67	0.00	33.45	16.85	$C_9H_{8.03}O_{3.07}(OCH_3)_{1.08}$

*Empirical analyses formula $C_xH_yO_z(OCH_3)_n$ were calculated as follows: n = (%OCH_3)/31.04; x = (%C)/12 – n; y = (%H) - 3n; z = (%O)/16 – n

Table 5
Assignment of signals and protons per C_9 structural unit in ^{1}H NMR spectra of acetylated lignin

Range ppm	Main assignments	Proton per C_9 unit		
		Bamboo	SP bamboo	HWP bamboo
7.25-6.80	Aromatic proton in guaiacyl units	0.79	0.67	0.57
6.80-6.25	Aromatic proton in syringyl units	0.81	0.87	0.63
6.25-5.75	Hα of β-*O*-4 and β-1 structures	0.31	0.28	0.27
4.00-3.48	H of methoxyl groups	4.26	4.20	3.24
2.50-2.22	H of aromatic acetates	0.27*	0.36*	0.31*
2.22-1.60	H of aliphatic acetates	1.75*	1.71*	1.18*

*by dividing 3

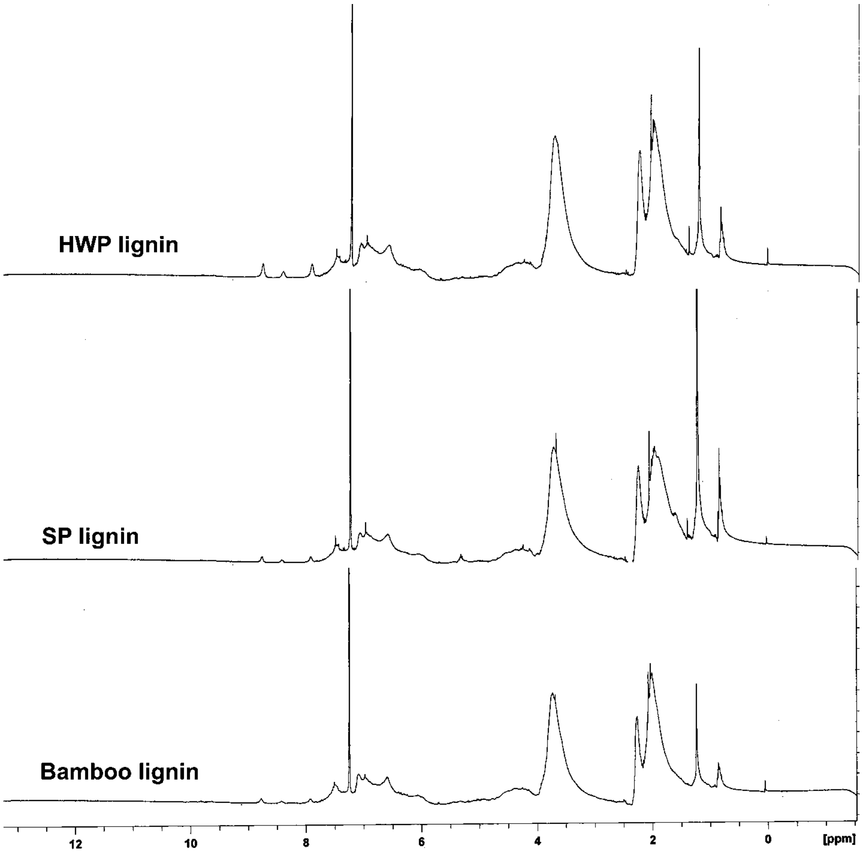

Figure 2: ^{1}H-NMR spectra of dioxane lignins from bamboo, SP bamboo and HWP bamboo

The integration of formyl proton signals at 9.75-10.0 ppm gives the quantity of aldehyde groups in benzaldehyde type units.[26]

The resonances detected at 9.30-9.55 ppm can be assigned to formyl protons in non-conjugated aldehyde groups. Such groups appear at Cγduring lignin acidolysis as a result of partial degradation of *β*-*O*-4 linkages.[27] The aryl glycerol β-*O*-4 aryl ether linkage constitutes the main intermonomeric connection in lignin.[28] NMR spectra of bamboo, SP and HWP bamboo lignins show that the structural element may contain both *erythro* and *threo* configurations due to the presence of proton at the C-α position of the side chain. The *erythro* protons (Hα) peak at 6.01 ppm give an almost similar intensity peak for the *thero* form at δ 6.09 in all lignins.

FTIR

Typical infrared spectra of bamboo, SP bamboo and HWP bamboo are shown in Figure3. The spectra exhibit characteristic "lignin bands", *e.g.* at 1600cm^{-1} and 1510cm^{-1}, which are due to aromatic groups.[29]

Autohydrolysis of lignin leads to a large reduction in the number of aliphatic hydroxyl groups and a large increase in phenolic hydroxyl groups. The ester carbonyl signal at 1714 cm^{-1} together with the shoulder at 1166 cm^{-1} and the band at 835 cm^{-1}suggests the presence of esterified *p*-coumaric units in all lignin,[30] which are consistent with H-NMR results.

The band at around 1680 cm^{-1} was found in all lignins, but intensity increased upon prehydrolysis, which was associated with the conjugated carbonyl–carboxyl stretching. In the carbonyl/carboxyl region, weak to medium bands were found at 1705-1720 cm^{-1}, originating from unconjugated carbonyl/carboxyl stretching. The band at 1705 cm^{-1} increases in prehydrolysed lignins. Spectra of lignins show a band at 1327 cm^{-1}, which is characteristic for the syringyl (S) ring plus guaiacyl (G) condensed ring.

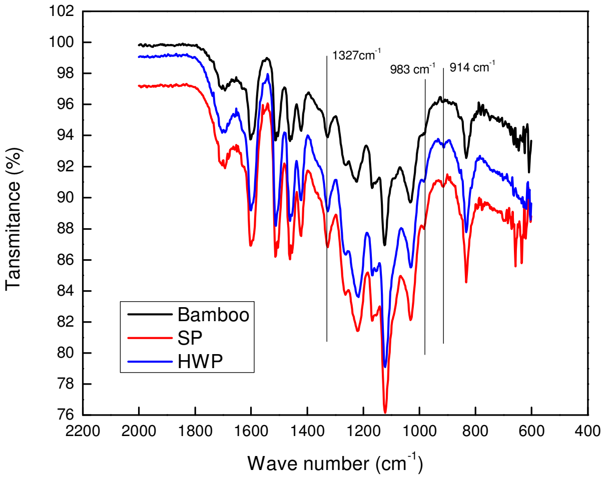

Figure 3: FTIR spectra of dioxane lignins from bamboo, SP bamboo and HWP bamboo

CONCLUSION

Hot-water and steam prehydrolysis processes of bamboo chips were compared at 170°C for 1h, in terms of prehydrolysis liquor properties, residual bamboo lignin structure and subsequent pulp properties. HWP dissolved biomass slightly higher than SP under the applied conditions, consequently dissolved slightly higher lignin and pentosan amounts. The α-cellulose in both processes was highly protected. HWP significantly decreased the number of methoxy groups of residual lignin, which was consistent with the breakdown of β-O-4 linkages of lignin in HWP bamboo. The numbers of aliphatic and free phenolic hydroxyls for bamboo were estimated to be 175 and 27, respectively, per 100 C_9 units. Aliphatic hydroxyl groups were decreased to 171 and 118, and aromatic hydroxyl groups increased to 36 and 30 upon SP and HWP, respectively.The overall unbleached pulp yield was almost similar, 32.7% for SP and 33.2% for HWP. Prehydrolysed bamboo chips were delignified very easily. Only at 16% active alkali charge, the kappa numbers of the pulps were 4.5 and 9.4 for SP and HWP, respectively. At identical prehydrolysis, cooking and bleaching conditions, the α-cellulose contents in the SP and HWP were very similar (94%). This was also cross-checked by S_{18} values and pentosan content, which are almost identical in both processes. The viscosity of these pulps was also identical, of 3 mPa.s. Pulp brightness was 84.2% for SP and 86.7% for HWP.

ACKNOWLEDGEMENTS: Authors wish to thank BCSIR authority for providing funds to carry out the research.

REFERENCES

[1] T. E. Amidon and S. Liu, *Biotechnol. Adv.*, **27**, 542 (2009).

[2] M. Matin, M. M. Rahaman, J. Nayeem, M. Sarkar and M. S. Jahan, *Carbohyd. Polym.*, **115**, 44 (2015).

[3] M. S. Jahan, R. Sabina, B. Tasmin, D. N. Chowdhury, A. Noori *et al.*, *BioResources*, **4**, 471 (2009).

[4] M. S. Jahan, N. Chowdhury and Y. Ni, *Bioresour. Technol.*, **101**, 1892 (2010).

[5] M. S. Jahan, N. Sultana, M. Rahman and A. Quaiyyum, *Biomass Convers. Biorefin.*, **3**, 179 (2013).

[6] A. R. P. vanHeiningen, *Pulp Pap. Can.*, **107**, 38 (2006).

[7] A. Saeed, M. S. Jahan, H. Li, Z. Liu,Y. Ni *et al.*, *Biomass Bioenerg.*, **39**, 14 (2012).

[8] H. Sixta, "Handbook of Pulp", first ed., Wiley-VCH, Weinheim, 2006.

[9] M. Leschinsky, PhD thesis, University of Hamburg, Faculty of Mathematics, Informatics and Natural Sciences, 2009.

[10] J. S. Gütsch and H. Sixta, *Lenzinger Ber*, **89**, 142 (2011).

[11] X. Luo, J. Liu, H. Wang, L. Huang and L. Chen, *Cellulose*, **21**, 1445 (2014).

[12] L. Browning, "Methods in Wood Chemistry", Wiley and Sons Interscience, New York, 1967.

[13] G. Bustos, N. de la Torre, A. B. Moldes, J. M. Cruz and J. M. Domínguez, *J. Food Eng.*,**78**, 405 (2007).

[14] K. Tanifuji, S. Takahashi, K.S hiell, M. S. Jahan, Y. Ni *et al.*, *BioResources*, **8**, 3912 (2013).

[15] H. Liu, H. Hu, M. S. Jahan and Y. Ni, *Bioresour. Technol.*, **131**, 315 (2013).

[16] J. Hughes, U.S. Patent No. 7,455,997, Washington, DC, U.S. Patent and Trademark Office,2008.

[17] L. Ahsan, M. S. Jahan and Y. Ni, *Bioresour. Technol.*, **155**, 111 (2014).

[18] M. S. Jahan, Z. Liu, H. Wang, A. Saeed and Y. Ni, *Cellulose Chem. Technol.*, **46**, 261 (2012).

[19] M. S. Jahan, L. Ahsan, A. Noori and M. A. Quaiyyum, *BioResources*, **3**, 816 (2008).

[20] M. S. Jahan, M. Sarkar and M. M. Rahman, *Cellulose Chem. Technol.*, **51**, 307 (2017).

[21] J. Li and G. Gellerstedt, *Ind. Crop. Prod.*, **27**, 175 (2008).

[22] D. Montané, X. Farriol, J.Salvadó, P. Jollez and E. Chornet, *J. Wood Chem. Technol.*,**18**, 171(1998).

[23] O. Faix, D. Meier and O. Beinhoff, *Biomass*, **18**, 109 (1989).

[24] K. Lundquist, in "Methods in Lignin Chemistry", edited by S. Y. Lin, C. W.Dence, Springer-Verlag, Berlin, 1992, pp. 242-249.

[25] M. Seca, J. A. Cavaleiro, F. M. Domingues, A. J. Silvestre, D. Evtuguin *et al.*, *J. Agric. Food Chem.*, **48**, 817 (2000).

[26] C.-L. Chen and D. Robert, in "Methods in Enzymology", vol. 161,edited by W. A. Wood, S. T. Kellogg, Academic Press, New York, 1988, pp. 137-158.

[27] E. Adler, *Wood Sci. Technol.*, **21**, 169 (1977).

[28] K. Lundquist, *Acta Chem. Scand. B*, **33**, 27 (1979).

[29] K. V. Sarkanen and C. H. Ludwig, "Lignins: Occurrence, Formation, Structure and Reactions", Wiley, New York, 1971.

[30] O.Faix, in "Methods in Lignin Chemistry", edited by S. Y. Lin, C. W. Dence, Springer-Verlag, Berlin, 1992, pp. 83-109.