CELLULOSE CHEMISTRY AND TECHNOLOGY

HEMICELLULOSES EXTRACTION FROM GIANT BAMBOO PRIOR TO KRAFT AND SODA AQ PULPING TO PRODUCE PAPER PULPS, VALUE-ADDED BIOPOLYMERS AND BIOETHANOL

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Hemicelluloses were pre-extracted from giant bamboo with dilute H_2SO_4 prior to Kraft and soda AQ pulping. The reaction conditions were selected to convert most of the hemicelluloses into soluble monomeric sugars, leaving almost unaltered the cellulose and lignin from the residual solid phase. A Central Composite Design was used to study four pre-extraction variables: H_2SO_4 concentration (0.1-0.5% v/v), solid/acid solution ratio (1/3.5-1/5.5 g/mL), temperature (80-140 °C) and time (10-50 min). Temperature had a dominant influence on the hydrolysis process. A maximum xylose yield – of 83.4% – (based on oven dry raw material mass) was obtained at a 0.4% v/v H_2SO_4 concentration, a solid/solution ratio of 1/4 (g/mL), at 140 °C and an extraction time of 40 min. The bamboo, from which 2.4% hemicellulose had been extracted, was subsequently pulped by both Kraft and soda AQ pulping methods. Soda AQ pulping gave the best results in terms of pulp yield, viscosity and kappa number, compared to the non-extracted bamboo, pulped under similar conditions.

Keywords: biorefinery, hemicelluloses extraction, giant bamboo, dilute acid hydrolysis, Kraft pulping, soda AQ pulping, pulp yield, kappa number, pulp viscosity

INTRODUCTION

Hemicelluloses, solubilized during Kraft pulping of a suitable biomass, such as bamboo, are presently underutilized in pulp production, where they are incinerated in the recovery furnace together with the dissolved lignin.[1,2] However, within the biorefinery concept, the extraction of hemicelluloses from suitable biomass prior to pulping, followed by the fermentation of the monomeric sugars with genetically engineered yeast to produce bioethanol, could contribute to address the growing biofuel need. At the same time, pulp production is enhanced by improving the overall alkaline pulping, for both Kraft and soda AQ processes. Cooking time can be reduced and cooking liquor impregnation enhanced. Such integration of hemicelluloses extraction with alkaline pulping can lead to improved pulp properties and improved production capacity, as already demonstrated in recovery furnace limited Kraft pulp mills.[1,3]

As heteropolymers of neutral and modified pentoses and hexoses, hemicelluloses can constitute about 25-35% of the plant cell walls.[4] The extraction of hemicelluloses with dilute acid and the further production of ethanol from the extracted sugars have been extensively studied.[5,6] Hemicelluloses can be also extracted from the biomass, using water and/or alkaline solutions, if oligomers and polymers of hemicelluloses are desired.[1,7,8]

Bamboo, a naturally growing and a low-cost lignocellulosic material,[9] is most frequently used for the production of paper, textiles, food and reinforcing fiber, as well as

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in constructions.[10,11] Bamboo fiber morphology and its chemical constituents are comparable to those of wood.[12] The glucan content of giant bamboo (40-48%) is comparable to the reported[13] cellulose content of softwoods (40-52%) and hardwoods (38-56%). The main hemicellulose present in bamboo is a 4-O-methyl-D-glucuronoarabinoxylan linked by a β-(1→4) glycosidic bond, which accounts for approximately 25% of the cell wall components.[13,14] The acetyl group content represents 6-7% of the total xylan, compared to the 8-17% acetyl group content in hardwoods and 4-9% in softwoods. Bamboo lignins have a higher content of phenolic hydroxyl groups than wood lignins, resulting in a higher reactivity to pulping. However, during Kraft pulping, bamboo Kraft lignin shows a higher degree of condensation, thus it is more resistant to bleaching than wood pulps.[15]

Based on its high hemicelluloses content, bamboo can be considered as a very attractive raw material for combined ethanol and paper production. To obtain xylose-rich solutions from bamboo, the treatments of the raw material that hydrolyze the sugars from the hemicellulosic fraction, but do not affect significantly cellulose and lignin, should be selected. Several treatments that can perform such fractionation have been reported, the most frequently studied being hydrolysis with dilute acids.[5,6,16] It consists[17] of the hydrolysis of the hemicellulosic fraction with diluted acid concentrations, ranging between 0.1 and 1% v/v, performed at moderate temperatures, between 100-150 °C. Under such moderate extraction conditions, the acid medium hydrolyzes the hemicelluloses and affords a limited degradation of the cellulose fraction.[6,18] The liquid phase (hydrolysate) will be constituted of monomeric sugars, such as xylose, glucose, arabinose, as well as decomposition products of the hemicelluloses, such as oligomers and acetic acid, generated by the hydrolysis of the acetyl groups and/or decomposition products of monosaccharides, such as furfural, a product of pentose dehydration, and hydroxymethylfurfural, a product of hexose dehydration.[5,16] Hence, if ethanol is produced, the neutralization of the liquid fraction prior to fermentation will be required.

In this study, the reaction conditions under which hemicelluloses could be extracted with dilute sulphuric acid from hemicellulose-rich giant bamboo (*Bambusa balcooa*) grown in South Africa, prior to alkaline pulping, were investigated. The reaction conditions of this acid-catalyzed hydrolysis were selected to convert most of the hemicellulosic fractions into soluble monomeric sugars and leave the cellulose and lignin fractions mostly unaltered in the residual solid phase. The effects of acid concentration, temperature and reaction time were assessed using a central composite experimental design. The yield of the recovered sugars (*e.g.* glucose, xylose and arabinose) and of other by-products, such as hydroxymethylfurfural, furfural and acetic acid, present in the hydrolysate, were determined by HPLC. The solid residue was pulped by Kraft and soda anthraquinone (soda AQ) pulping methods. Pulp yields, kappa number and viscosities of the pulps produced from extracted and non-extracted bamboo were determined, to develop a combined process for the production of a hemicellulose hydrolysate and pulp from giant bamboo.

EXPERIMENTAL

Raw material

The bamboo used in the study, *Bambusa balcooa*, was collected in the Western Cape region of South Africa. Giant bamboo stems were chipped using a Wigger pilot chipper. The chips were screened and a 4-8 mm chip size fraction was selected for further investigation. The material was conditioned at 23 °C and 55% relative humidity before use.

The composition of the raw material was determined[19] by both standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI) (T264 om-88, T 211 om-85, T222 om-88; T 223 cm-84) and by the standard Laboratory Analytical Procedures for biomass analysis provided by the National Renewable Energy Laboratory (NREL; Colorado, USA, http://www.nrel.gov/biomass/analytical_procedures.html).

Determination of bamboo fiber length

Maceration was achieved by dissolving 10 g chromic acid in 190 mL of distilled water; 15 mL nitric acid was added, to form Jeffrey's solution.[20] The chips were placed in a test tube, covered with the solution and kept in an oven at 40 °C for 48-72 h. The solution was changed daily. The fibers were washed with distilled water, separated with a glass rod, stored in a safranin green solution for 5 min, after which the solution was drained. The fibers were then subjected to a 70% ethanol solution for 2 min, and finally immersed in xylene for 5 min. The fibers were mounted on microscope slides using Entellan and measured with a digitizer.

Experimental design and dilute acid extraction of giant bamboo

The experiments on dilute acid extraction were carried out[21] according to the Central Composite Design (CCD), created and evaluated by STATISTICA 7.1 (Statsoft Inc., Tulsa, USA). Acid concentration, solid/solution ratio, temperature and reaction time were systematically varied (Table 1) between 0.1-0.5% v/v, 1/3.5-1/5.5 g/mL, 80-140 °C and 10-50 min at the maximum temperature, respectively. The conditions were selected in agreement with previous works done on dilute acid pretreatments of non-wood materials.[5,6,18]

The bamboo chips and the acid solutions were mixed in the desired portions and introduced into microreactors (bombs) placed in a digester of 15 dm^3 capacity, enclosed by heating jackets. The reaction temperatures selected were monitored with thermocouples. At the end of the acid treatment, the bombs were cooled in water. The hemicellulose-rich hydrolysate was collected for further chemical analysis for sugars and by-products, and the solid residues were recovered by filtration, washed with water and air-dried. The percentage of solid recovery, based on the oven dry mass (DM) of the (original) raw material, was determined. A fraction of the extracted residue was sub-sampled and prepared for chemical analysis by applying the same standard methods as those used for the raw materials. The solid residue was then stored in the conditioning room prior to further pulping experiments.

Pulping processes

Run 22 from dilute acid treatment was selected for Kraft and soda AQ pulping experiments, as it afforded the maximum amount of glucose in the solid residue after dilute acid treatment, as illustrated in Figure 1B. The studied pulping conditions applied in this work were comparable to those used by other researchers,[11,12] yet with a slightly shorter reaction time at the maximum cooking temperature. The maximum cooking temperature was kept constant at 170 °C and the solid-to-liquid ratio was fixed at 1/5.5 (g/mL dry mass) for all pulping experiments. The cooking liquor used in Kraft pulping was prepared from commercial sodium hydroxide (Merck) and sodium sulphide (Merck). Sodium hydroxide and BUSPERSE 2262 Anthraquinone (Buckman Laboratories, Hammarsdale, South Africa) were used for soda AQ pulping. Pulping experiments were carried out (Table 2) in microbombs that could accommodate 80 g oven dry chips. Temperature and reaction time were monitored during the process. Cooking time was measured from the moment the system reached the maximum temperature. At the end of cooking, the fibers were separated from the black liquor and washed through a 10 mesh screen, to separate the rejects from the fibers; the accepted pulp was collected on a 100 mesh screen. The pulp was then screened in a Packer slotted laboratory screen. Total pulp yield and rejects were determined as a percentage of the original dry mass (DM) of the raw material. Pulp kappa number and viscosity were determined by standard TAPPI methods (T236 and T230, respectively). Pulp viscosities, determined in centipoises (cP), were converted to the degree of polymerization (DP) of the polysaccharides, according to the formula:[18,22]

$$DP^{0.905} = 0.75\,[954 \log (X) - 325]$$

where X is viscosity in centipoises.

Table 1
Sequence of experiments according to a central composite design for dilute acid pre-extraction of hemicelluloses from giant bamboo

Run	Acid concentration (v/v %)	Solid/acid concentration (g/ml)	Temperature (°C)	Residence time (min)
1	0.2	1/4	100	20
2	0.2	1/4	100	40
3	0.2	1/5	100	20
4	0.2	1/5	100	40
5	0.2	1/4	140	20
6	0.2	1/4	140	40

7	0.2	1/5	140	20
8	0.2	1/5	140	40
9	0.4	1/4	100	20
10	0.4	1/4	100	40
11	0.4	1/5	100	20
12	0.4	1/5	100	40
13	0.4	1/4	140	20
14	0.4	1/4	140	40
15	0.4	1/5	140	20
16	0.4	1/5	140	40
17	0.1	1/4.5	120	30
18	0.5	1/4.5	120	30
19	0.3	1/4.5	80	30
20	0.3	1/4.5	160	30
21	0.3	1/3.5	120	30
22	0.3	1/5.5	120	30
23	0.3	1/4.5	120	10
24	0.3	1.4.5	120	50
25	0.3	1/4.5	120	30

Chemical analysis

The hydrolysate fraction obtained after dilute acid extraction was filtered through 0.45 µm membranes and analyzed for its content of monomeric sugars, soluble oligomers and by-products. Oligosaccharide concentration was determined as the difference in monomeric sugar concentration, before and after acid hydrolysis of oligosaccharides to monomeric sugars. The sugars (glucose, xylose and arabinose) and by-products (acetic acid, hydroxymethylfurfural and furfural) present in the liquid fraction were analyzed with an Aminex HPX-87H Ion Exclusion Column equipped with a Cation-H cartridge (Biorad, Johannesburg, RSA). Sugars were measured with an RI detector (Waters 2141, Microsep, Johannesburg, RSA), whereas the by-products were analyzed with a UV detector at 220-280 nm (Waters 2487, Microsep, Johannesburg, RSA). The column was operated at 65 °C with a mobile phase of 5 mM sulphuric acid and a flow rate of 0.6 mL/min. Likewise, after completion of mild acid hydrolysis (4% [v/v] H_2SO_4, 121 °C, 60 min) of the solid fraction obtained after each extraction, the glucose, xylose and arabinose concentrations were measured by HPLC, as described above.

RESULTS AND DISCUSSION

Raw material composition and fiber length

The chemical composition and fiber lengths of South African giant bamboo are shown in Table 3. A cellulose content of 44.4% and a pentosan component of 24.7%, consisting of about 90% of the xylose present in the dry mass of the original material and of arabinose traces, were observed. The lignin content (22%) and average fiber length (2.9 mm) values agreed with those reported in literature.[11,12,23]

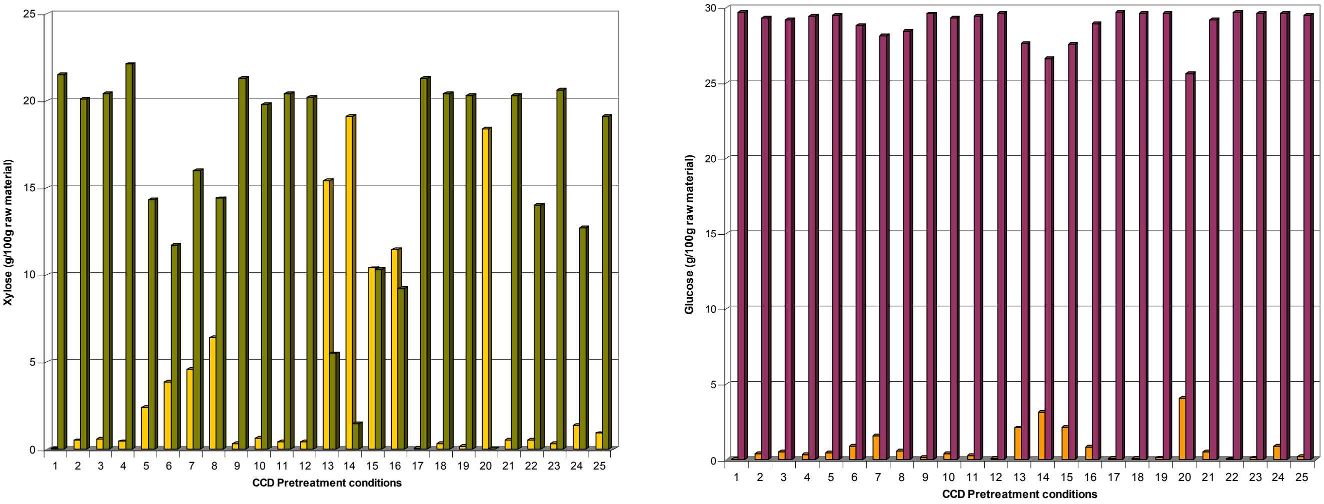
Table 2
Sequence of experiments for Kraft and soda AQ pulping of hemicellulose extracted from giant bamboo (DM= based on oven dry mass of original raw material)

Run	1	2	3	4	5	6
Active alkali (% DM)	14	14	16	16	15	15
Sulfidity (% DM)	15	35	15	35	25	25
Anthraquinone (% DM)	0.05	0.05	0.05	0.05	0.117	0.075
Time at 170 °C (min)	30	30	30	30	70	45

Table 3
Chemical composition expressed as percentage of the original oven dry mass material and fiber length of giant bamboo before extraction

Component			Content, %* (based on oven dry mass)
Ethanol/cyclohexane soluble extractives			4.1 ± 0.1
Water soluble extractives			3.0 ± 0.2
Ash			2.4 ± 0.01
Cellulose			44.4 ± 0.4
Pentosan			24.7 ± 1.7
Monosaccharides	Glucose		30.5 ± 2.0
	Xylose		22.9 ± 0.4
	Arabinose		0.20 ± 0.01
Klason lignin (acid insoluble)			22.0 ± 0.9
Fiber characteristics	Min	Max	Average, mm
Fiber length	2.1	4.0	2.9 ± 1.3

*Mean values and standard deviation of four measurements



A B

Figure 1: Total xylose yield (A) expressed as g/100 g of the original raw material, and total glucose yield; (B) expressed as g/100 g of raw material
(A) liquid (🟨) and solid (🟩) fractions under different extraction conditions
(B) liquid (🟧) and solid (🟥) fractions under different extraction conditions

Dilute acid extraction

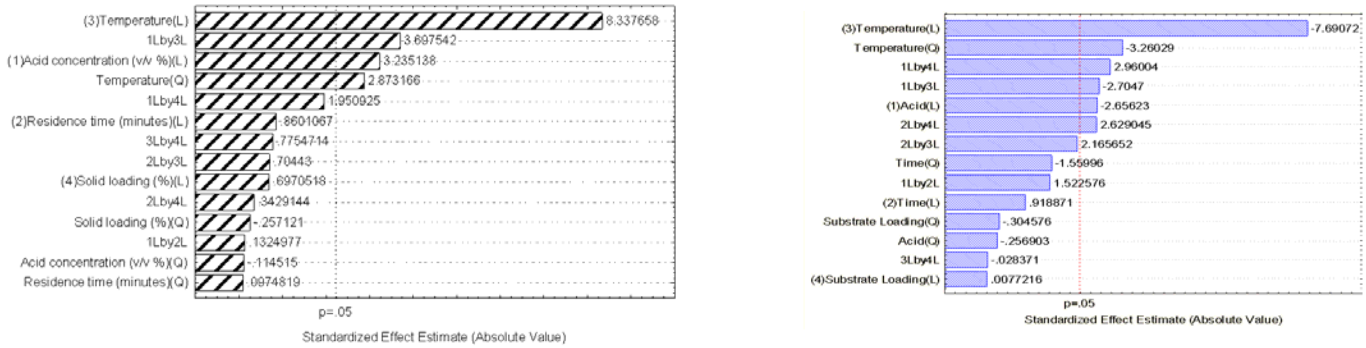
Yield of sugars in the liquid fraction

The composition of the hydrolysate fraction after the dilute acid extraction of giant bamboo is illustrated in Figure 1A. To evaluate the efficiency of dilute acid as a fractionation method for hemicelluloses solubilization, without cellulose and lignin degradation, the effect of acid concentration, temperature, reaction time and solid loading on the hydrolysis of the xylan and glucan from bamboo was determined by a statistically experimental design. The effects and their significance are given in the standardized Pareto chart (Fig. 2A). Both temperature and acid concentration influenced the xylose yield in the liquid fraction, but temperature showed the strongest effect. Loading of solids and the reaction time had no significant effect on xylan hydrolysis under the selected extraction conditions.

Spearman's rho statistical tests were also used to assess the effect of different extraction conditions.[24] A significant correlation between xylan hydrolysis and temperature was noticed, as a p value below 0.01 was shown. In the present study, the highest xylose amount recovered in the liquid fraction ranged between 18.4 and 19.1

g/100 g of the xylose present in the raw material, achieved in Runs 20 (temperature – 160 °C, acid concentration – 0.3%) and 14 (temperature – 140 °C, acid concentration – 0.4%), respectively (Fig. 1A). This represents approximately 80-83.4% of the xylose present in the original dry raw material. This effect has been reported[25] on the other lignocellulosic material, where 79.6% of the total xylose of *Eucalyptus grandis* residues were obtained utilizing 0.65% of sulphuric acid concentration at 157 °C. The treatment of hardwoods with 0.8% sulphuric acid at 190 °C produced[26] 87% xylose.

Glucose concentration in the liquid hydrolysate fraction ranged between 0.8-4.1 g/100 g original material, when the bamboo was treated at temperatures between 140-160 °C, and the soluble lignin content was equivalent to 0.18% of the lignin present in the raw material, solubilized under the above-described conditions (Fig. 3). These results indicated a minor degradation of cellulose and lignin. The highest concentration of HMF (1.36 g/100 g DM), furfural (0.41 g/100 g DM) and acetic acid (1.34 g/100 g DM) was obtained at the temperature of 160 °C and acid concentration of 0.3%. A similar behavior during the degradation of the cell wall components at high temperatures was previously reported.[6,27] Literature data on the inhibiting effect of these compounds show that the acetic acid[18] can be an inhibitor of microbial growth from 4 to 10 g/L, about (0.5-2 g/L) being reported[28] for both HMF and furfural. The concentrations of inhibitors in the hydrolysate are therefore acceptable for the fermentation of the xylose, glucose and arabinose components.



A B

Figure 2: Standardized Pareto charts for (A) xylose solubilised in the liquid fraction and for (B) glucose retained in the solid residue

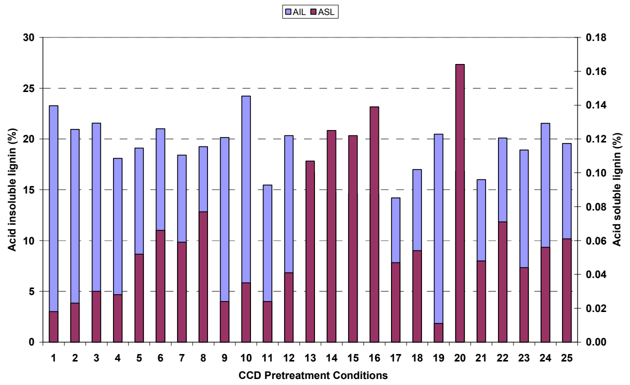


Figure 3: Acid insoluble lignin (%) in the solid fraction and acid soluble lignin (%) in the liquid fraction from each extraction condition of CCD

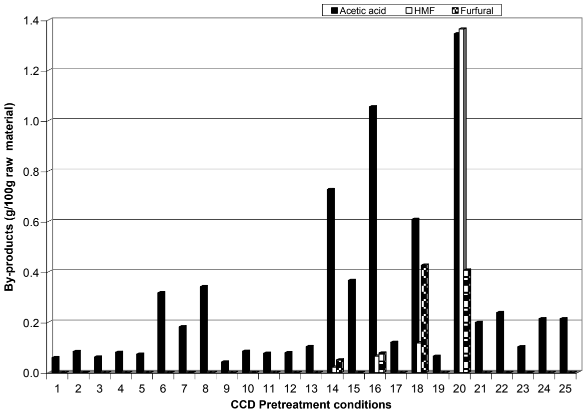


Figure 4: Degradation products present in the liquid fraction

Composition of solid residue after dilute acid extraction

The total glucose remaining in the solid fraction after dilute acid hydrolysis was of 83.0-99.2% of the glucose present in the raw material (Fig. 1B). These results demonstrate that the degradation of the cellulose fraction in the raw material was limited during dilute acid hydrolysis. However, temperatures between 140 and 160 °C and an acid concentration above 0.3% resulted in the formation of HMF (Fig. 4), indicating the degradation of the glucose portion. As shown in Figure 2B, temperature had a dominant influence on the glucose retained in the solid residue. The xylose retained in the solid fraction constituted between (0 and 94%) of the original dry material (Fig. 1B). At a high temperature (160 °C), no xylose was detected in the solid fraction and the formation of furfural was observed in the liquid fraction (Fig. 4). As indicated by the statistical analysis, temperature was the main limiting factor of acid hydrolysis for the maximum xylose removal.

After dilute acid fractionation, the acid insoluble lignin in the solid fraction varied from 64.54 to 110.1% of the lignin present in the raw material (Fig. 3). The high lignin content in the solid fraction might have resulted from the tendency of lignin to be depolymerized and then condensed in a different morphology during hemicelluloses hydrolysis.[29] When dilute acid extraction is performed in batch systems, both lignin dissolution and precipitation is promoted.[30] Large fractions of lignin react with the soluble products, which further react[30] to form insoluble compounds, if left in the reactor. Moreover, the coating of cellulosic fibers with this lignin-like material would restrict the substrate area availability for subsequent treatments.[31] Dilute acid extraction of bamboo supports the idea of a possible optimization for removing sufficient hemicelluloses by dilute acid treatment, while not affecting adversely the cellulose and lignin fractions, which will therefore be favorable at a temperature of 120 °C, acid concentration of ≤0.3% and a shorter reaction time.

Pulping of hemicelluloses extracted from bamboo

After the extraction of hemicelluloses from bamboo with dilute acid, a solid residue from Run 22 was selected for pulping. These conditions were preferred since a maximum glucose content was observed in the solid residue after dilute acid extraction. The extracted solid residue was subjected to Kraft pulping under different cooking conditions (effective alkali – 14-16%, sulfidity – 15-35% and time at the maximum temperature – 30-70 min). Soda AQ pulping conditions: active alkali – 14-16%, anthraquinone – 0.05-0.1% and time at the maximum temperature – 30-70 min. Temperature and solid loading were kept constant at 170 °C and 5.5 mL/g, respectively, in all pulping experiments. The pulp properties of bamboo produced after Kraft and soda AQ pulping were determined. The non-extracted bamboo was also pulped under similar conditions and used for comparison purposes.

Kraft pulping

Tables 4A and 4B list the comparative values of pulp yield, viscosity, kappa number and degree of polymerization of the pulps obtained from both extracted and non-extracted bamboo chips. The pulping yields recorded for non-extracted bamboo were of 45.5-55.1%, compared to 40.7-50.3%, recorded for extracted bamboo. Under similar pulping conditions, the Kraft pulp yields obtained from bamboo were comparable to those given in literature,[11,12] of 48.1-54.3% and 42.7-48.9%, respectively. Comparing the best pulping yields (Run 5 in Tables 4A and 4B), non-extracted bamboo produced by 9% higher pulp yields than those of extracted pulps. The yield loss during pulping, due to extractions of hemicelluloses with dilute acid and hot water, was previously reported.[32] Kraft pulp yields of 51.1% and kappa number of 17.1 for acid extracted mixed hardwoods, compared to the pulp yield of 53.2% and kappa number of 16.7 for non-extracted yields were reported.[33]

Table 4A
Kraft pulping results for 2.4% hemicelluloses extracted from giant bamboo
(0.3% v/v, 1/5.5 solid/acid solution ratio, 120 °C for 30 min)

Kraft pulping conditions				Pulp characteristics of extracted material				
Run	Effective alkali (% DM)	Sulfidity (% DM)	Time at 170 °C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cp)	Pulp DP
1	14	15	30	43.3	10.5	7.3	8.5 ± 0.9	794
2	14	35	30	40.7	7.3	8.8	7.3 ± 1.1	696
3	16	15	30	41.7	9.4	5.6	7.7 ± 0.3	731
4	16	35	30	41.9	7.4	4.4	8.5 ± 0.9	794
5	15	25	70	50.3	14.7	12.8	4.8 ± 0.3	434
6	15	25	45	46.7	13.1	11.0	4.3 ± 2.5	367

Table 4B
Kraft pulping results for non-extracted giant bamboo

Kraft pulping conditions				Pulp characteristics of non-extracted raw material				
Run	Effective alkali (% DM)	Sulfidity (% DM)	Time at 170 °C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cp)	Pulp DP
1	14	15	30	47.0	9.4	12.9	14.5 ± 1	1147
2	14	35	30	47.5	7.0	10.9	8.2 ± 0.3	771
3	16	15	30	48.2	5.5	10.1	6.3 ± 0.4	603
4	16	35	30	45.5	4.4	6.5	8.8 ± 0.4	817
5	15	25	70	55.1	15.3	13.8	16.0 ± 5.6	1213
6	15	25	45	49.9	14.5	12.2	4.4 ± 2.7	381

The kappa number was lower for extracted pulps (4.4-12.8) than for the non-extracted ones (6.5-13.8). The results showed that an increase in active alkali from 14 to 16%, combined with an increase in sulfidity from 15 to 35% resulted in a decrease in kappa number for both extracted and non-extracted pulps (Run 4 in Tables 4A and 4B). The reduction in kappa number is explained by the higher delignification rate induced by the presence of sodium hydrogen sulfide in the pulping liquor, resulting[29] in lignin dissolution. A high sulfidity (35-45%) and lower effective alkali (14-16%) resulted[11] in pulps with lower kappa numbers (11-15).

In this work, cellulose degradation during pulping was measured in terms of viscosity, values of 4.3-8.5 cP and 4.4-16 cP being obtained from extracted and non-extracted pulps, respectively. The viscosity values here measured were comparable to the results obtained[34] when *Panus tigrinus* delignification strains were used prior to Kraft pulping of sugarcane bagasse (2.3-6.8 cP). According to literature data,[35] in modern Kraft pulp mills, viscosity ranges from 30 cP after Kraft pulping of wood. The variation in pulp viscosity is associated with the hemicelluloses content of pulps.[36] The pulp with high hemicelluloses content is reported[22] to undergo low cellulose degradation, resulting in high viscosity pulps. A decrease in the DP of cellulose beyond ~1600 post pulping and beyond ~700 after bleaching, respectively, could reduce[3] the paper sheet strength properties. According to the present study, the extractions of hemicelluloses with dilute acid might have reduced viscosity. Vapour-phase treatment with hydrochloric acid was reported to cause cellulose degradation.[37]

Soda anthraquinone (AQ) pulping

A comparison of extracted and non-extracted bamboo chips by soda AQ pulping is presented in Tables 5A and 5B. Dilute acid extraction resulted in higher pulp yields (41.36-55.02%), compared to the values registered in non-extracted material (40.36-48.85%), which could be explained by the decrease in the branching degree on xylan during dilute acid extraction. A higher frequency of hydrogen bonds between xylan chains, and between xylan and the accessible fraction of cellulose could have been promoted, leading to a lower degradation of carbohydrates.[2] The composition of the raw material and process modifications prior to pulping may affect the pulp yield.[38] A study was conducted on dilute acid and alkaline extraction of hemicelluloses from Aspen, alfalfa stems, switch grass and hybrid poplar, the solid residue being subsequently subjected to Kraft and Soda AQ pulping.[32] The best preliminary results obtained gave a pulp yield of around 43%, obtained for poplar and switch grass. It was explained that the overall composition of the raw material could also affect the pulp yield. Acid extraction prior to soda AQ pulping of hardwood showed pulp yields of 52.7%, and a kappa number of 15.9, compared to the pulp yield of 53% and kappa number of 16.6 for non-extracted pulps.[39]

The kappa numbers observed for pre-extracted pulps were lower (31.0-33.4), compared to those of non-extracted pulps (35.6-38.8). Although anthraquinone has been reported to have a maximum effect on lignin degradation, in the present study, bamboo delignification was difficult to attain, as can be inferred by the kappa number values obtained (over 30). Nonetheless, the addition of soda AQ to adjust pulping conditions could also result in a lower kappa number reduction and a higher pulping yield.[12] Literature reports that the condensation reactions of lignin occur at a higher rate during soda AQ pulping,[40] which could be a disadvantage of soda AQ pulps, because most of the condensed lignin structures are less reactive to conventional bleaching chemicals, compared to the uncondensed ones.[40]

Out of the six sets of pulping conditions shown in Table 5, the optimum one, based on viscosity, was used in Run 5. The extracted pulp showed a pulp yield = 41.36, kappa number = 33.35 and pulp viscosity = 13.8 cP, compared to the pulp yield = 41.44, kappa number = 35.6 and pulp viscosity = 17.33 cP for non-extracted bamboo. The advantage of the pulps with high viscosity and low kappa number is that, if a lower kappa number is required, subsequent delignification through bleaching could be carried out with less bleaching chemicals, while retaining appropriate pulp strength values.[41]

Comparative Kraft and soda AQ pulping behavior of extracted giant bamboo

Generally, soda AQ pulping of extracted bamboo had a positive effect on pulp yield (41.36-55.02%) compared to Kraft pulping with 40.7-50.3% pulp yields. Kraft pulps are well-known for their low pulp yields, compared to soda AQ pulps.[2,12]

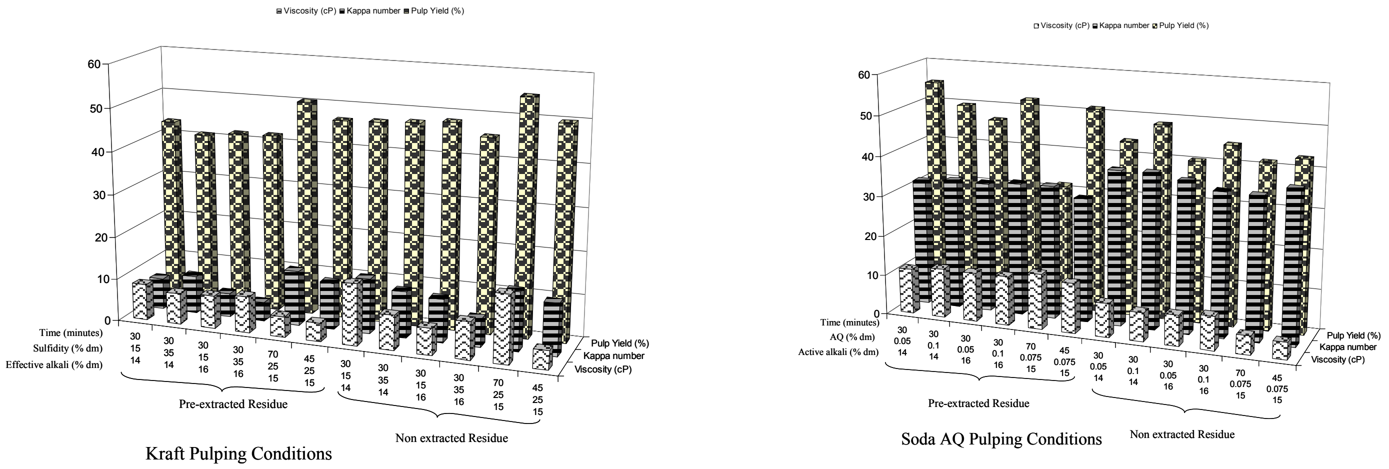
A high delignification efficiency was shown for extracted Kraft pulps compared to extracted soda AQ pulps. Kappa number values of 4.4-12.8 were observed for extracted Kraft pulps compared to 31.0-33.4 – for extracted soda AQ pulps.

Table 5A
Soda AQ pulping results for 2.4% hemicelluloses extracted (5A) from giant bamboo
(0.3% v/v, 1/5.5 solid/acid solution ratio, 120 °C for 30 min)

Soda AQ pulping conditions				Pulp characteristics of pre-extracted material				
Run	Active alkali (% DM)	Anthraquinone (% DM)	Time at 170 °C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cp)	Pulp DP
1	14	0.05	30	55.02	5.16	31.64	11.33 ± 1.0	982
2	14	0.1	30	49.73	11.81	32.49	12.33 ± 0.3	1038
3	16	0.05	30	46.61	12.71	32.49	12.17 ± 0.3	1030
4	16	0.1	30	52.23	13.22	33.23	14.33 ± 0.6	1139
5	15	0.075	70	41.36	12.48	33.35	13.83 ± 0.3	1115
6	15	0.075	45	51.2	7.54	31.0	12.5 ± 0.9	1048

Table 5B
Soda AQ pulping results from non-extracted (5B) giant bamboo

Soda AQ pulping conditions				Pulp characteristics of non-extracted raw material				
Run	Active alkali (% DM)	Anthraquinone (% DM)	Time at 170 °C (min)	Screened pulp yield (%)	Rejects (%)	Kappa number	Viscosity (cp)	Pulp DP
1	14	0.05	30	43.82	17.22	38.7	20.5 ± 0.9	1381
2	14	0.1	30	48.56	17.82	38.8	15.3 ± 1.1	1184
3	16	0.05	30	40.36	10.81	37.6	12.7 ± 0.3	1030
4	16	0.1	30	44.84	17.28	35.8	12.33 ± 0.9	1038
5	15	0.075	70	41.44	13.47	35.6	17.33 ± 0.3	1267
6	15	0.075	45	42.95	15.5	38.0	14.17 ± 2.5	1131



A B

Figure 5: Pulp properties of extracted and non-extracted giant bamboo after Kraft pulping (A) and soda AQ pulping (B) processes

However, although the kappa number is an important pulp quality index and also a key parameter for pulping, a higher kappa number reduction in Kraft pulps also caused a higher reduction in pulp viscosity (4.3-8.5 cP), compared to soda AQ pulps with the highest viscosity (11.3-14.33 cP). This called for an economic balance between the environmental benefits and pulp degradation. Compared to the raw material, dilute acid extracted residues with a constant kappa number, pulped by soda AQ, will maximize product yield and pulp quality, while minimizing consumption of energy and chemicals (Fig. 5B).

CONCLUSIONS

- About 80-83% of the xylose present in giant bamboo can be hydrolyzed with 0.3% (v/v) acid concentration at 160 °C, and 0.4% (v/v) acid concentration at 140 °C, respectively. However, these conditions showed a slight degradation of cellulose and hemicelluloses, as indicated by the presence of 0.41 g/100 g (DM) furfural and 1.36 g/100 g (DM) HMF at 160 °C. The amount of acetic acid in the hydrolysate was of 1.34 g/100 g (DM).
- Kraft pulping of the extracted solid residue resulted in a 9% yield reduction, compared to non-extracted bamboo, under optimum cooking conditions (Run 5, Table 4). Lower kappa number and very low viscosity were observed for the extracted pulps.
- An increase in pulp yield by 7.4% was obtained from pre-extracted soda AQ pulps compared to the non-extracted soda AQ pulps generated under similar pulping conditions (Run 4, Table 5). Lower kappa numbers and high viscosity were observed.
- When selecting the best pulping process for the integration of dilute hemicelluloses extraction and for a pulping process, soda AQ pulping is recommended. Although we

are still considering the experiments for the optimum conditions, the present trial appears as very promising in integrating the extraction of hemicelluloses with dilute acid and utilizing the solid residue for pulp production.

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REFERENCES

[1] A. Van Heiningen, in *Procs. Annual Meeting of PAPTAC*, Canada, 2006, pp. 167-176.

[2] P. C. Pinto, D. V. Evtuguin and C. P. Nett, *Carbohydr. Polym.*, **60**, 489 (2005).

[3] A. J. Ragauskas, M. Nagy, D. Ho Kim, C. A. Eckert, J. P. Hallett and C. L. Liotta, *Ind. Biotechnol.*, **2**, 55 (2006).

[4] E. Sjöholm, K. Gustafson, F. Berthold and A. Colmsjo, *Carbohydr. Polym.*, **41**, 1 (2000).

[5] M. Neureiter, H. Danner, C. Thomas, B. Saidi and R. Braun, *Appl. Biochem. Biotechnol.*, **98-100**, 49 (2002).

[6] I. C. Roberto, S. I. Mussatto and R. C. L. B. Rodrigues, *Ind. Crop. Prod.*, **17**, 171 (2003).

[7] J. M. Lawther, R. Sun and W. B. Banks, *J. Agric. Food Chem.*, **43**, 667 (1995).

[8] S. De Lopez, M. Tissot and M. Delmas, *Biomass Bioenerg.*, **10**, 201 (1996).

[9] M. Tsuda, M. Aoyam and N.-S. Cho, *Biores. Technol.*, **64**, 241 (1998).

[10] X. Zhang, H. Yu, H. Huang and Y. Liu, *Int. Biodeter. Biodegr.*, **60**, 159 (2007).

[11] T. H. M. Vu, H. Pakkanen and R. Alén, *Ind. Crop. Prod.*, **19**, 49 (2004).

[12] S. Kamthai and Chaing Mai, *J. Sci.*, **34**, 97 (2007).

[13] J. M. O. Scurlock, D. C. Dayton and B. Hames, *Biomass Bioenerg.*, **19**, 229 (2000).

[14] J. Scurlock, *Bioenergy Feedstock Characteristics*, Oak Ridge National Laboratory, Bioenergy Feedstock Development Programs.

[15] M. Samoa, R. Alén, and M. T. H. Vu, *Ind. Crop. Prod.*, **28**, 47 (2008).

[16] E. V. Canattieri, G. J. De Moraes Rocha, J. A. J. De Carvalho and J. B. De Almeida de Silva, *Biores. Technol.*, **98**, 422 (2007).

[17] C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch and Y. Y. Lee, *Biores. Technol.*, **96**, 1959 (2005).

[18] S. Gamez, J. J. Gonzalez-Cabriales, J. A. Ramirez, G. Garrote and M. Vazquez, *J. Food Eng.*, **74**, 78 (2006).

[19] *TAPPI TEST METHODS*, 1992-1993.

[20] R. W. Kigkr, *Biotech. Histochem.*, **6**, 71 (1971).

[21] D. C. Montgomery, in "Design Analysis of Experiment", John Wiley and Sons Inc., 2005, pp. 219-286.

[22] B. B. Mazumder, Y. Ohtani and Z. Cheng, *Jpn. Wood Res. Soc.*, **46**, 364 (2000).

[23] B. O. Ogunsile and C. F. Uwajeh, *World Appl. Sci. J.*, **6**, 536 (2009).

[24] J. S. Maritz, in "Distribution-Free Statistical Methods", 2nd ed., London, Chapman and Hall, 1995, pp. 206-208.

[25] E. V. Canettieri, G. J. d M. Rocha, J. J. A. de Carvalho and J. B. de Almeida e Silva, *Biores. Technol.*, **98**, 422 (2007).

[26] E. L. Springer, *Ind. Eng. Chem.*, **24**, 614 (1985).

[27] S. M. Tunc and R. P. A. Van Heiningen, *Ind. Eng. Chem. Res.*, **47**, 7031 (2008).

[28] S. I. Mussatto and I. C. Roberto, *Biores. Technol.*, **93**, 1 (2004).

[29] T. H. M. Vu, R. Alén and H. Pakkanen, *Holzforschung*, **57**, 619 (2003).

[30] B. Yang and C. E. Wyman, *Biotechnol. Bioeng.*, **86**, 88 (2004).

[31] A. Emmel, A. L. Matias, F. Wypych and L. Ramos, *Biores. Technol.*, **86**, 105 (2003).

[32] J. Ai and U. Tschirner, *Biores. Technol.*, **101**, 215 (2010).

[33] R. C. Francis, T. E. Amidon, N.-H. Shin, T. S. Bolton and D. Kanungo, *3rd International Colloqium on Eucalyptus Pulp*, Brazil, 2007, p. 108.

[34] A. R. Gonçalves, S. M. Costa and E. Esposito, *Appl. Biochem. Biotechnol.*, **98**, 373 (2002).

[35] J. M. MacLoed, F. J. McPhee, K. A. Kingsland, R. W. Tristram, T. J. O'Hogan, R. E. Kowalska and B. C. Thomas, *Tappi J.*, **78**, 153 (1995).

[36] Z. Feng and R. Alén, *Ind. Crop. Prod.*, **14**, 31 (2001).

[37] N. Gurnagul, D. H. Page and G. M. Paice, *Nordic Pulp Pap. Res. J.*, **3**, 152 (1992).

[38] M. Akgül, Y. Çopür and S. Temiz, *Build. Environ.*, **42**, 2586 (2007).

[39] R. C. Francis, N.-H. Shin, S. Omari and T. E. Amidon, *J. Wood Chem. Technol.*, **26**, 141 (2006).

[40] S. K. Bose, S. Omori, D. Kanungo, R. Francis and N.-H. Shin, *J. Wood Chem. Technol.*, **29**, 214 (2009).

[41] C. L. Elmore and Glen Falls, U.S. Patent 4,436,586, New York, March 13, 1984, pp. 1-4.