

DISSOLVING PULP PRODUCTION FROM BAMBOO

Larisse A. Ribas Batalha,^{*,a} Jorge L. Colodette,^b José L. Gomide,^b Luiz C. A. Barbosa,^a Célia R. A. Maltha,^a and Fernando J. Borges Gomes^b

Commercial bamboo chips were evaluated as raw material for dissolving pulp production. The chips were auto-hydrolyzed (AH) and subsequently cooked by the NaOH/AQ process and bleached to full brightness with the O-CCE-D-(EP)-D-P sequence. The term CCE designates a cold caustic extraction stage. The bamboo chip chemistry (22.4% lignin, 19.5% xylans, 49.3% cellulose, 16.8% total extractives, and 1.5% ash) was apparently unfavorable; however high quality dissolving pulp was produced using the aforementioned technologies, even when compared to results obtained with traditional eucalypt commercial wood chips. The pulp showed high brightness (92.4 % ISO) and α -cellulose content (94.9%). Its contents of hemicelluloses, extractives and ash were within acceptable levels for a dissolving pulp aimed at viscose rayon production. Thus, the bamboo chip furnish investigated can be regarded as a viable raw material for dissolving pulp production.

Keywords: Bamboo; Dissolving pulp; Auto-hydrolysis; Cold caustic extraction

*Contact information: a: Department of Chemistry at Federal University of Viçosa, Viçosa, MG 36570-000, Brazil; b: Department of Forestry Engineering at Federal University of Viçosa, Viçosa, MG 36570-000, Brazil; * Corresponding author: larisse.batalha@ufv.br*

INTRODUCTION

Dissolving pulps require a high degree of purity. They are used for production of cellulose derivatives such as cellulose acetate, cellulose nitrate, viscose, rayon, methyl cellulose, and carboxymethylcellulose, among many others. The overall fiber line yield for dissolving pulp production rarely exceeds 30 to 35%, and compared to regular paper pulp their production costs are quite high. These pulps contain a high alpha-cellulose content (95 to 98%) and relatively low hemicelluloses (1 to 10%) and lignin (<0.05%) contents (Christov et al. 1998).

Dissolving pulps typically are produced from cotton linters (soda pulping) and from wood via the pre-hydrolysis kraft and acid sulfite pulping processes (Barba et al. 2002). Wood pulps, especially those derived from the sulfite process, require a subsequent hemicellulose removal step; this is usually done through the so-called cold caustic extraction (CCE), which is performed during the bleaching operation. The current high costs of wood and cotton linters, combined with environmental constraints against standard bleaching (chlorine and hypochlorite), have caused a significant increase in the cost of dissolving pulp derived from these raw materials. Therefore, it is appropriate to evaluate new sources of fiber for the manufacture of dissolving pulp.

In this context, bamboo appears as an alternative source for pulp and paper industries, particularly in the tropical areas of the world. Bamboo is the vernacular or common term for members of a particular taxonomic group of large woody grasses

(subfamily Bambusoideae, family Andropogoneae=Poaceae). Bamboos encompass 1250 species within 75 genera, most of which are relatively fast-growing, attaining stand maturity within five years, but flowering infrequently (Scurlock et al. 2000). As an industrial raw material, bamboo has been used to produce both cellulosic fibers for paper and starch granules for saccharification and production of ethanol. Bamboo shoots for food production and getting coal from the culms are also other potential uses (Beraldo and Azzini 2004). In general, the alpha-cellulose content in bamboo is 40 to 50%, which is comparable with the reported alpha-cellulose contents of softwoods (40 to 52%) and hardwoods (38 to 56%) (Dence 1992). Undoubtedly, bamboo is a potential alternative source of raw material for dissolving pulp production.

The auto-hydrolysis step has been commercially applied in the so-called pre-hydrolysis kraft pulping process, which produces dissolving pulp as a product (Liu et al. 2010). The introduction of auto-hydrolysis prior to any alkaline pulping process helps to produce pulp with a satisfactorily high content of alpha-cellulose and with low hemicellulose content, resulting from the destruction or degradation of hemicelluloses (Behin and Zeyghami 2009).

Recent literature (Liu et al. 2010) showed that the hemicelluloses may be extracted from the auto-hydrolysis liquor through its acidification and subsequent addition of ethanol, enabling the use of hemicellulose for the production of several value-added products such as biofuels, chemicals, and materials. The black liquor derived from the pre-hydrolysis kraft process, which typically contains 30 to 34% of lignin is usually burnt to provide energy for mill operations, and to recover the cooking chemicals (Wallberg et al. 2005). A fraction of this black liquor can potentially be isolated and used as the starting material for a series of useful products, such as vanillin, phenols, benzene, dispersant, emulsifying and chelating agents, antioxidants, pesticides, fertilizers, vegetal charcoal, polymers, adhesives, concrete additives, and components for resins, among others (Gargulak and Lebo 2000, Mussato et al. 2007).

In the biorefinery concept, the three main biopolymers, i.e., cellulose, hemicelluloses, and lignin, which are the dominant chemical constituents in lignocellulosic raw materials, are to be converted to the building blocks for biofuels, biochemicals, and biomaterials (Saeed et al. 2010). In this context, recovery of hemicelluloses and lignin for use in these nobler purposes in dissolving pulp production is in line with the concept of biorefinery.

This study aimed at evaluating the feasibility of using bamboo to produce dissolving pulp with a vision of utilizing left over streams for manufacturing value added products. The results are compared with traditional eucalypt dissolving pulp production by the pre-hydrolysis kraft process.

MATERIAL AND METHODS

Raw Material Preparation and Physical-Chemical Analyses

Depithed bamboo chips were provided by a paper pulp manufacturer located in the Brazilian Northeast. The eucalyptus chips were provided by a kraft pulp company located in the Brazilian Center East. The chips derived from 12, 9, 7, and 5 year old trees

in the following proportion 8:47:28:17%. Both the bamboo and the wood chips were transported to UFV Pulp and Paper Laboratory, classified according to SCAN CN 40:94 standard procedure, dried to about 15% moisture, and stored for further use. A fraction of the wood and bamboo chips were converted into sawdust, classified according to TAPPI T257-cm85 standard procedure, dried to 20% moisture, and stored in glass jars. Bamboo and wood basic densities were measured on the chips, whereas chemical analyses were done on the sawdust. Basic density, total extractives, ash, acid insoluble lignin, acid soluble lignin, and sugar composition were measured according to TAPPIT258 om-94, TAPPI T264 cm-97, TAPPI T211 om-93, Gomide and Demuner (1986), Goldshmidt (1971), and Wallis et al. (1971), respectively.

Auto-Hydrolysis (AH)

The auto-hydrolysis stages for bamboo and eucalyptus were carried out in 7 liter M/K digester equipped with a heat exchanger, circulating pump, and computer-controlled time and temperature, under the following fixed conditions: 1000 g chips, 4L/1kg liquid/fiber ratio, 170°C maximum temperature, 90 min to maximum temperature, 15 min at maximum temperature, and 2.5 to 3.0 final pH.

Cooking

After the pre-hydrolysis stage was completed, the digester was cooled to about 80 °C, and the residual liquor was drained and collected to determine its pH and the alkali requirement for raising the pH to 11. After removal of the residual liquor from the pre-hydrolyzed chips, the cooking liquor was added. The volume of pre-hydrolysis liquor retained by the chips was determined gravimetrically on the basis of the original feedstock dry weight; this determination was necessary to calculate the volume of cooking liquor to be injected into the system. The bamboo soda/AQ (sodium hydroxide/anthraquinone) cooking was performed under the following conditions: 30% active alkali (AA) on dry wood weight, 4L/1kg liquor/bamboo ratio, 162 °C maximum temperature, 60 min to temperature, 45 min at temperature, and 0.10% anthraquinone on dry wood weight. The eucalypt kraft (sodium hydroxide/sodium sulfide) cooking was performed under the following conditions: 17.4% active alkali, 35% sulfidity, 170 °C maximum temperature, 90 minutes to temperature and 90 min at temperature. After cooking completion, the spent liquor was drained and the cooked chips were thoroughly washed with tap water, the fiber separation was done in a 25 liter “hydrapulper”, and the pulp was screened using a laboratory 0.2 mm plate screener. The brown pulp obtained was characterized for their kappa number, viscosity and brightness, according to TAPPI T236 cm-85, T230 om-94, and T 525 om-92, respectively.

Bleaching

The bamboo AH-NaOH/AQ and the eucalypt AH-kraft pulps were bleached to full brightness with O-CCE-D-(EP)-D-P and O/O-D-(EP)-D-D sequences, respectively, where: O=single-stage oxygen delignification, O/O= double-stage oxygen delignification without inter-stage washing, CCE=cold caustic extraction, D= chlorine dioxide bleaching, (EP)=oxidative extraction reinforced with hydrogen peroxide, and P= hydrogen peroxide bleaching. Table 1 shows the conditions used for each bleaching stage.

Table 1. General Bleaching Conditions

| Conditions | Bamboo Pulp | | | | | | Eucalypt Pulp | | | | |
|--|-------------|------|-----|------|-----|------|---------------|------|------|-----|-----|
| | O | CCE | D | (EP) | D | P | O/O | D | (EP) | D | D |
| Consistency (%) | 10 | 12 | 12 | 12 | 12 | 12 | 10 | 10 | 10 | 10 | 10 |
| Temperature, °C | 105 | 40 | 60 | 80 | 80 | 80 | 95/100 | 55 | 90 | 75 | 75 |
| Time, min | 70 | 30 | 40 | 90 | 120 | 120 | 10/50 | 40 | 60 | 120 | 120 |
| Pressure, kPa | 600 | - | - | - | - | - | 500/350 | - | - | - | - |
| O ₂ , kg/t | 20 | - | - | - | - | - | 18/0 | - | - | - | - |
| ClO ₂ as Cl ₂ , kg/t | - | - | 10 | - | 30 | - | - | 15.7 | - | 11 | 1.0 |
| NaOH, kg/t | 20 | 80 | - | 10 | 5.0 | 7.0 | 20/0 | - | 12.0 | - | - |
| H ₂ SO ₄ , kg/t | - | - | 10 | - | - | - | - | 5.0 | - | - | 0.5 |
| MgSO ₄ , kg/t | 1.5 | - | - | 1.5 | - | - | 1.5/0 | - | 1.5 | - | - |
| H ₂ O ₂ , kg/t | - | - | - | 3.0 | - | 3.0 | - | - | 3.0 | - | - |
| Final pH | 11.2 | 13.5 | 2.8 | 10.8 | 4.3 | 10.3 | 11.7 | 2.4 | 11.2 | 4.4 | 4.7 |

The bleached pulps were characterized for their content of carbohydrates by high performance liquid chromatography (HPLC), using the procedure described by Wallis et al. (1996). Pulp kappa number, viscosity, brightness, α -cellulose, ash, silica, and dichloromethane extractable contents were measured according to the TAPPI T236 cm-85, T230 om-94, T525 om-92, T 203 om-93, T211 om-93, T245 cm-98, and T204 om-88 procedures, respectively. The pulp content of calcium, iron, manganese, and copper were determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 procedures. The auto-hydrolysis, cooking and bleaching yields were measured gravimetrically.

RESULTS AND DISCUSSION

Characterization of Raw Materials

The bamboo basic density was 553 kg/m³, which was higher than that of the eucalypt wood (516 kg/m³) evaluated. A high density is always favorable in pulp production because it increases pulp mill throughput, though it may penalize pulping yield due to poor white liquor penetration when conditions are not properly optimized; the AH hydrolysis treatment performed before cooking helps white liquor penetration significantly during the pulping operation. Therefore, the high density of the bamboo chips does not pose a significant problem for dissolving pulp production.

The chemical characteristics of bamboo and eucalyptus chips are presented in Table 2, where it is seen that bamboo glucans content (49.3%) was higher than that of eucalypt (47.9%). The bamboo xylan content (19.5%) was also higher than that of

eucalypt (11.2%), and was compensated by its lower lignin content (22.4%); typically, lignin and xylan compensate each other in the chemical composition of biomass secondary wall, with the glucan content varying only slightly among different raw materials. The high glucan and xylan contents of bamboo render this raw material interesting for production of dissolving pulp, associated with subsequent use of the extracted xylan and xylan derivatives for biorefinery purposes. These can be recovered through collection and processing of the auto-hydrolysis liquor, after separation of the small fraction of lignin (Liu et al.2010; Danielsson 2007). Bamboo showed very high extractive (16.2 %) and mineral (1.5%) contents in relation to the eucalypt (4.1 % extractives and 0.3% minerals). The high extractive and mineral contents is quite challenging for dissolving pulp production. Besides causing a variety of operational problems (scaling, corrosion, pitch deposition, chemical degradation during bleaching, recovery boiler plugging, etc.), minerals and extractives may cause severe difficulties during utilization of the dissolving pulp for production of cellulose derivatives, if not properly removed during the process

Table 2. Quantitative Chemical Composition of *Bamboo and Eucalypt*, Expressed in Weight Basis Percentage of Extractive-Free* Dry Raw Materials

| Results | Glu. (%) | Xyl. (%) | Gal. (%) | Ara. (%) | Man. (%) | Acetyl (%) | Uronic Acid (%) | Total Extractives** (%) | Ash** (%) | Total Lignin (%) |
|----------|----------|----------|----------|----------|----------|------------|-----------------|-------------------------|-----------|------------------|
| Bamboo | 49.3 | 19.5 | 0.6 | 0.8 | 0.3 | 3.0 | 0.9 | 16.2 | 1.5 | 22.4 |
| Eucalypt | 47.9 | 11.2 | 0.9 | 0.1 | 0.9 | 2.0 | 5.9 | 4.1 | 0.3 | 26.6 |

*TAPPI T264 cm-97

**on total wood

Auto-Hydrolysis

The auto-hydrolysis (AH) resulted in significant xylan removal for both bamboo and eucalypt, with the process being more effective for the latter. The bamboo xylan content decreased by 9.9%, from its original 19.5% in the original material to 18.5% in the AH chips, taking into account the 5% yield loss, whereas the eucalypt xylan decreased by 29.3%, from 11.2% in the wood to 8.9 % in the AH chips, taking into account the 11.1% yield loss (Table 3). The auto-hydrolysis of bamboo was less effective in the removal of xylans than in the case of eucalypt, even though the bamboo acetyl group content was higher than that of eucalypt. This fact may be explained by bamboo's high calcium and extractives content (particularly starch), which likely hindered the chip impregnation in the auto-hydrolysis and neutralized the acetic acid released, thus minimizing the acid hydrolysis; the pH dropped to 4.4 only.

Another explanation is the condensation of the bamboo lignin during the AH process which may have impaired the xylan release since xylan is linked to lignin. In a recent study with another grass material (sugarcane bagasse) it was observed that under acidic conditions there occurs significant lignin condensation (Alves 2011). The bamboo and eucalypt lignin H:S:G ratio were 1:2:2.1 and 0.1:2:1, respectively, which already indicates a higher level of condensation in the bamboo lignin in relation to that of eucalyptus.

Table 3. *Bamboo and Eucalypt* Chip Auto-Hydrolysis (AH) Results

| AH Results | Yield, % | Xylans, % on wt. | Xylans Removal, % | Lignin, % on wt. | Spent liquor pH | Hydrolyzate solids, % |
|-----------------|----------|---------------------|----------------------|---------------------|--------------------|--------------------------|
| <i>Bamboo</i> | 95.1 | 18.5 | 9.9 | 23.2 | 4.4 | 4.0 |
| <i>Eucalypt</i> | 88.9 | 8.9 | 29.3 | 27.6 | 2.8 | 2.4 |

Another factor that could explain the lower auto-hydrolysis efficiency for bamboo in relation to eucalypt could be the porous structure differences of these two raw materials. The lower “openness” of the bamboo material may hinder the acid hydrolysis liquor penetration into the chips, thus decreasing the hemicelluloses removal rate. The AH treatment increased bamboo and eucalypt chip lignin content slightly, from 22.4 and 26.6% lignin in the original wood to 23.2 and 27.6% in the auto-hydrolyzed chips, respectively. This increase is explained by the partial removal of xylans.

Pulping Results

In order to cook the auto-hydrolyzed bamboo and eucalypt wood chips to kappa number 10-11 and 16-17, respectively, alkali charges of 30 and 17.4% as NaOH were required (Table 4). Pulp viscosity was quite satisfactory for both bamboo and wood, with a higher value for the wood one, reflecting its lower active alkali requirement. The choice of a higher kappa number for the eucalypt raw material was based on its easiness of subsequent bleaching in relation to the bamboo.

Table 4. Kraft Pulping Results for Auto-Hydrolyzed *Bamboo and Eucalypt* Chips (from Table 3)

| Cooking Results | Active Alkali, % as NaOH | Kappa No. | Pulping Yield, % | AH + Pulping Yield, % | Pulp Viscosity, mPa.s | Xylans, % on wt. | BLS, % |
|-----------------|-----------------------------|-----------|------------------|-----------------------|-----------------------|---------------------|--------|
| <i>Bamboo</i> | 30 | 11.2 | 43.4 | 41.2 | 46.8 | 8.4 | 16.5 |
| <i>Eucalypt</i> | 17.4 | 17.4 | 44.6 | 40.5 | 61.1 | 3.3 | 15.3 |

The cooking screened yields were determined on the basis of the auto-hydrolyzed wood chip weight, and they were 43.4 and 44.6% for bamboo and wood, respectively. Hence, the xylan removal from raw material by AH significantly decreased subsequent kraft pulping yield. The screened yield found by Vu et al (2004) and Guo et al (2010) for bamboo to a kappa number target similar to the one of this study was 45.0% and 46.0%, respectively. For the eucalypt, Santiago and Neto (2007) found a screened yield of 56.0% for a kappa number around 17. The overall yield, including auto-hydrolysis (AH) plus pulping were 40.2 and 40.5% for bamboo and eucalypt, respectively. The low stability of the carbohydrates remaining in the raw materials after the AH treatment towards kraft cooking may be explained by two factors: (1) the xylans remaining in the auto-hydrolyzed chips are very sensitive to kraft cooking conditions because they are severely degraded, possessing very low molecular weight (high content of reducing end groups) and being largely soluble in alkali; and (2) the cellulose chains become more susceptible to kraft cooking because the xylan layer existing over the cellulose fibrils is partially removed, exposing the cellulose to alkali attack with consequent decrease in molecular

weight (increased number of reducing end groups) and increased polydispersity (Colodette et al. 2011). The xylan retained in the pulps derived from bamboo and eucalypt were 8.4% and 3.3%, respectively, after the pulping operation.

The eucalypt pulp containing only 3.3% xylan can be used for dissolving pulp applications grades after bleaching. However, the bamboo pulp containing 8.4% xylans finds little application in the dissolving pulp industry due to its high xylan content, in spite of the harsh pulping conditions used. For this pulp a subsequent xylan removal step is required during the bleaching operation.

Oxygen Delignification and Bleaching

The double-stage (O/O) oxygen delignification efficiencies of pulps derived from auto-hydrolyzed bamboo and eucalypt chips were 66.1 % and 66.7%, respectively. The oxygen delignification efficiency is calculated on the basis of kappa number before and after the O/O-stage. The viscosity drop was higher for the bamboo pulp and resulted in lower O/O-stage selectivity for this pulp. The brightness for the bamboo pulp was comparable to that of the eucalypt pulp. In general, the performance of the oxygen delignification was quite high for both pulps if compared, for example, with conventional kraft wood pulps.

Table 5. Oxygen Delignification Performance for Pulps Derived from Bamboo and Eucalypt Auto-Hydrolyzed (AH) Chips

| Oxygen Delignification Results | Kappa drop, % | Viscosity drop, % | Brightness out, % ISO | Selectivity* |
|--------------------------------|---------------|-------------------|-----------------------|--------------|
| <i>Bamboo</i> | 66.1 | 62.2 | 47.2 | 1.1 |
| <i>Eucalypt</i> | 66.7 | 50.2 | 47.1 | 1.3 |

*Selectivity=kappa drop (%) / viscosity drop (%)

The oxygen delignified pulps derived from bamboo and eucalypt AH chips were further bleached to $\geq 92\%$ ISO brightness with the CCE-D-(EP)-D-P and D-(EP)-D-D sequences, respectively (Table 6). A fixed kappa factor was applied in the first chlorine dioxide stage, and variable chlorine dioxide doses were applied in the second D-stage. The total chlorine dioxide dose required to produce full brightness was calculated by the sum of the ClO_2 applied in the D_0 Stage (kappa factor) plus the optimum ClO_2 dose obtained in the D_1 stage, which produced the target brightness. More detailed information about the operating conditions used in each bleaching stage is given in the footnotes of Table 6 and Table 1. The brightness obtained for the bamboo bleached pulp (92.4 %) is acceptable for acetate grade (He et al. 2008). The total active chlorine demand was higher for the bamboo pulp (52.5 kg Cl_2 /odt pulp) in relation to that for the eucalypt one (34 kg Cl_2 /odt pulp). Note that the bamboo pulp had a kappa number of 3.8 after oxygen delignification, while that of the eucalypt had a kappa of 5.8; these differences in kappa number after the O/O-stage reflected the differences in kappa number after pulping, which were 11.2 and 17.4 for the bamboo and eucalypt, respectively. Hence, the higher active chlorine demand of the bamboo pulp in relation to *Eucalyptus* can only be explained by the more condensed nature of the bamboo lignin, particularly that fraction coming from p-hydroxyphenyl type lignin, which was significant in the original bamboo

raw material (H:S:G = 1:2:2.1). The p-hydroxyphenil type structures are difficult to remove during bleaching with oxygen-derived chemicals, for example (Akin et al. 2001). Furthermore, such structures are exclusively oxidized to quinones (not muconic acids/ester structures) in the chlorine dioxide bleaching stages, since they do not contain methoxyl groups (Gierer 1986). These quinone structures are not reactive towards chlorine dioxide and thus resist to bleaching difficult besides contributing to brightness reversion. Bleachability differences could not be explained by differences in pulp hexenuronic acids (HexA), since their contents were very low in both bamboo (5.5 mmol/kg) and eucalypt (8.5 mmol/kg) pulps. The HexA levels were low due the pulping technologies used for both raw materials, which included an auto-hydrolysis step prior to kraft pulping. In addition, for the bamboo pulp, a cold caustic extraction stage (CCE) was used during bleaching.

Another significant contributor to the bleaching differences between bamboo and eucalypt pulps was the cooking process used. Soda/AQ pulps are more difficult to bleach than their kraft counterparts (Bose et al. 2009); hence, the poorer bleachability of the bamboo pulp, which was produced by the AH-soda/AQ process, in relation to the eucalypt one, produced by the AH-kraft process, may be also explained by differences in cooking technology. It is worth noting that the choice of the soda/AQ and kraft cooking technologies for bamboo and eucalypt, respectively, was based on real commercial practice. The small size of industrial operations with grass type raw materials makes the soda/AQ process more attractive in relation to the kraft due to black liquor recovery and environmental issues. Processes using eucalypt wood are usually large scale, making the kraft process much more viable.

The yield loss across bleaching was higher for the bamboo pulp. The bamboo pulp also presented lower brightness stability and viscosity than the eucalypt one. The low viscosity (6.2 mPa.s) of the bleached bamboo pulp somewhat limits its applications for certain dissolving grade applications such as acetate and nitrate; but it could be useful for production of viscose rayon and CMC derivatives. According to Henriksson et al. (2005) and Kvarnlöf et al. (2006), during the viscose process it is necessary to decrease the viscosity (200–300 dm³/kg or 3.5–4.5 mPa.s) by a pre-aging stage, since a high viscosity affects the cellulose processability. Considering that the largest viscosity loss of the bamboo pulp occurred in the oxygen delignification stage, the use of magnesium salts in such a stage could mitigate the problem to some extent. The eucalypt pulp viscosity (16.3 mPa.s) is quite acceptable for most dissolving pulp applications.

The CCE stage was included in the bleaching of bamboo pulp in order to meet the low hemicelluloses and extractives requirements of such pulps. The efficiency of conversion of cellulose into specific derivatives is dependent upon hemicelluloses content of the dissolving pulp (Christov et al. 1998). Hemicelluloses are undesirable impurities in dissolving pulps, affecting the cellulose processability, e.g. the filterability and the xanthanation in the viscose process, and properties of the cellulose- end products such as the viscose strength (Christov and Prior 1993). In this study, a bamboo bleached pulp containing 5.1% xylan was achieved (Table 6), a value which is acceptable for may dissolving pulp applications (Christov et al. 1998).

The bamboo bleached pulp presented an ash content higher than that of *Eucalyptus* (Table 6). In a study realized by Barba et al. (2002), for synthesis of

carboxymethylcellulose (CMC) from non-wood fibers, an ash content was obtained that was about six times greater than that found for pulp the bamboo bleached pulp of this work. Despite the higher ash content, Barba et al. concluded that the non-woods studied were suitable to prepare cellulose derivatives such as CMC. A detailed study (Table 6) of the bamboo ash showed that it is mainly composed of calcium, iron, manganese, copper, and silica. The α -cellulose content found (94.9 %) is in agreement with the values (>90%) reported in the literature for viscose grade pulps (Christov et al. 1998; Behin and Zeyghami 2009, Ibarra et al. 2010). However, the bamboo α -cellulose content (94.9 %) was lower than that of the eucalypt pulp (96.3%).

The dichloromethane (DCM) extractive content of bamboo pulp obtained was 0.041% (Table 6). Recent literature (He et al. 2008) found that DCM extractive content for acetate and viscose grade bamboo pulp were 0.08% and 0.22%, respectively. This shows that the proposed cooking and bleaching method, including a CCE stage, was effective in removing the extractives from the bamboo chips.

Table 6. Bleaching Results for Bamboo and Eucalypt Pulps Derived from Reference and Auto-Hydrolyzed Chips

| Conditions | Bamboo Pulp | | | | | | Eucalypt Pulp | | | | |
|--|-------------|------|----------------|------|----------------|-------|---------------|------|------|----------------|----------------|
| | O | CCE | D ₀ | (EP) | D ₁ | P | O/O | D | (EP) | D ₁ | D ₂ |
| Reagent Consumed, % | - | - | 98.4 | 100 | 99.3 | 100 | - | 100 | 100 | 100 | 100 |
| Kappa Number | 3.8 | 3.5 | - | - | - | - | 5.8 | - | 1.2 | - | - |
| Brightness, % ISO | 47.2 | 45.4 | 71.7 | 81.1 | 91.5 | 92.4 | 50.5 | 74.7 | 84.9 | 91.3 | 92.0 |
| Brightness Reversion, % ISO | - | - | - | - | - | 2.4 | - | - | - | - | 1.5 |
| Viscosity, mPa.s | 17.7 | 23.3 | - | 6.9 | 6.8 | 6.2 | 30.4 | - | 20.5 | 19.4 | 16.3 |
| Yield, % | - | - | - | - | - | 92.7 | - | - | - | - | 95.6 |
| Xylans, % | - | - | - | - | - | 5.1 | - | - | - | - | - |
| Alpha-Cellulose | - | - | - | - | - | 94.9 | - | - | - | - | 96.3 |
| Ash, % | - | - | - | - | - | 0.13 | - | - | - | - | 0.08 |
| Ca, ppm | - | - | - | - | - | 277 | - | - | - | - | - |
| Fe, ppm | - | - | - | - | - | 25.5 | - | - | - | - | - |
| Mn, ppm | - | - | - | - | - | 1.7 | - | - | - | - | - |
| Cu, ppm | - | - | - | - | - | 4.3 | - | - | - | - | - |
| SiO ₂ , ppm | - | - | - | - | - | 24 | - | - | - | - | - |
| Extractable in dichlorometahne, % | - | - | - | - | - | 0.041 | - | - | - | - | - |
| ¹ Total Active Chlorine, kg/bdt | | | 52.5 | | | | | 34 | | | |
| ² Yield loss, % | | | 7.3 | | | | | 4.3 | | | |

***Bamboo:D₀-stage:**12% consistency, 60°C, 40 min, Kappa Factor 0.20, 2.8 end pH; **D₁-stage:**12% consistency, 80°C, 120 min, 4.5 end pH and 10, 15, 20 and 30 kg/bdt ClO₂; **Eucalypt:D₁-stage:**10% consistency, 75°C, 120 min, Kappa Factor 0.27, 4.5 end pH; **D₂-stage:**10% consistency, 75°C, 120 min, 4.5 end pH and 1, 2, 4 and 6 kg/bdt ClO₂.

¹Total active chlorine (kg/bdt) = ClO₂(kg/bdt)*2.63 + H₂O₂(kg/bdt)*2.09;

²Includes yield loss across oxygen delignification stage

CONCLUSIONS

The chip autohydrolysis process applied to dissolving pulp production improves the xylan removal but decreases pulp yield. The AH-NaOH/AQ pulping process and the O/O-CCE-D-(EP)-D-P bleaching sequence proved suitable for production of dissolving pulp from bamboo and resulted in bleached pulp of 94.9% α -cellulose, 92.4 % brightness, 6.2 mPa.s viscosity, 5.1% xylans, 0.04% DCM extractives, and 0.13% ash, which are acceptable specifications for many dissolving grade pulps. The low viscosity limits the applications of the bamboo pulp for certain dissolving grades applications such as acetate and nitrate; but it is useful for production of viscose rayon and CMC derivatives. When compared to eucalypt dissolving pulp, the bamboo pulp is of slightly lower quality and more costly to produce.

ACKNOWLEDGMENTS

Financial support offered by National Council for Scientific and Technological Development (CNPq), Minas Gerais State Research Foundation (Fapemig) and the European Commission (LIGNODECO project) is greatly appreciated.

REFERENCES CITED

- Akin, L. G., Colodette, J. L., and Argyropoulos, D. S. (2001). "Factors limiting oxygen delignification of kraft Pulp," *Canadian Journal of Chemistry* 9, 201-210.
- Alves, E. F. (2011). "Simultaneous production of paper-making fibers and potential bio-products from sugarcane bagasse," State University of New York: College of Environmental Science and Forestry. Syracuse, 2011.
- Barba, C., Montané, D., Rinaudo, M., and Farriol, X. (2002). "Synthesis and characterization of carboxymethylcelluloses (CMC) from non-wood fibers I. Accessibility of cellulose fibers and CMC synthesis," *Cellulose* 9, 319-326.
- Behin, J., and Zeyghami, M. (2009). "Dissolving pulp from corn stalk residue and waste water of Merxunit," *Chemical Engineering Journal* 152, 26-35.
- Beraldo, A. L., and Azzini, A. (2004). *Bambu: Características e Aplicações*, Livraria Editora Agropecuária, Guaíba, Rio grande do Sul, 180 pp.
- Bose, S. K., Omori, S., Kanungo, D., Francis, R. C., and Shin, N.-H. (2009). "Mechanistic differences between kraft and soda/AQ pulping. Part 1. Results from wood and chips," *J. Wood Chem. Technol.* 29, 214-226.
- Christov, L. P., Akhtar, M., and Prior, B. A. (1998). "The potential of bisulfite pulping in dissolving pulp production," *Enzyme Microb. Technol.* 23, 70-74.
- Christov, L. P., and Prior, B. A. (1993). "Xylan removal from dissolving pulp using enzymes of *Aureobasidium pullulans*," *Biotechnol. Lett.* 15, 1269-1274.
- Colodette, J. L., Loungue Jr., D., Pedrazzi, C., Oliveira, R. C., Gomide, J. L., and Gomes, F. J. B. (2011). "Pulpability and bleachability of xylan-depleted eucalyptus wood chips," *Ind. Eng. Chem. Res.* 50, 1847-1852.

- Danielsson, S. (2007). *Xylan Reactions in Kraft Cooking. Process and Product Considerations*, Doctoral Thesis. Royal Institute of Technology. School of Chemical Sciences and Engineering. Department of Fibre and Polymer Technology. Stockholm, 73 pp.
- Dence, W. (1992). "The determination of lignin," In: *Methods of Lignin Chemistry*, Lin, S. Y., and Dence, C. W. (eds), Springer-Verlag, Berlin, 33-61.
- Gargulak, J. D., and Lebo, S. E. (2000). "Commercial use of lignin-based materials," In: *Lignin: Historical, Biological, and Materials Perspectives*, Glasser, W. G., Northey, R. A., and Schultz, T. P. (eds.), American Chemical Society, Washington, 305-320.
- Gierer, J. (1986). "Chemistry of delignification. Part 2: Reactions of lignin during bleaching," *Wood Sci. Technol.* 20, 1-33.
- Goldschmid, O. (1971). "Ultraviolet spectra," In: *Lignins: Occurrence, Formation, Structure and Reactions*, Sarkanen, K. V., and Ludwig, C. H. (eds), Wiley-Interscience, New York, 241-266.
- Gomide, J. L. (1979). *Polpa de Celulose – Química dos Processos Alcalinos de Polpação*, Viçosa, Univ. Federal, 50 pp.
- Gomide, J. L., and Demuner, B. J. (1986). "Determination of lignin content in woody material: Modified Klason method," *O Papel* 47(8), 36-38.
- Gue, S., Heijnesson-Hulten, A., Basta, J., Wang, Q., and Germgard, U. (2010). "Optimum bamboo kraft cooking – The influence of the cooking conditions on the pulp and fibre properties," *O Papel* 71(7), 63-76.
- He, J., Cui, S., and Wang, S. (2008). "Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate," *Journal of Applied Polymer Science*; 107(2), 1029-1038.
- Henriksson, G., Christiernin, M., and Agnemo, R. (2005). "Monocomponent endoglucanase treatment increases the reactivity of softwood sulphite dissolving pulp," *Journal of Industrial Microbiology and Biotechnology* 32, 211-214.
- Ibarra, D., Köpcke V., and Ek, M. (2010). "Behavior of different monocomponent endoglucanases on the accessibility and reactivity of dissolving-grade pulps for viscose process," *Enzyme and Microbial Technology* 47, 355-362.
- Kvarnlöf, N., Germgård, U., Jönsson, L., and Söderlund, CA. (2006). "Enzymatic treatment to increase the reactivity of a dissolving pulp for viscose production," *Appita Journal* 59, 242-246.
- Liu, Z., Fatehi, P., Jahan, M. S., and Ni, Y. (2010). "Separation of lignocellulosic materials by combined processes of pre-hydrolysis and ethanol extraction," *Bioresource Technology*, doi:10.1016/j.biortech.2010.08.049.
- Mezzomo, L. X. (1996). *Potencialidade de Eucalyptus cloeziana S. Muell, E. citriodora Hook, E. urophylla St. Blake e E. urophylla x grandis, cultivados na Bahia, para produção de celulose solúvel*. Master's degree Thesis. Federal University of Santa Maria. Rio Grande do Sul, 99 pp.
- Mussatto, S. I., Fernandes, M., and Roberto, I. C. (2007). "Lignin recovery from brewer's spent grain black liquor," *Carbohydrate Polymers* 70, 218-223.
- Neogi, A. N., Sealey, J. E., Harvey Persinger, W., Luo, M., and Roscelli, V. A. (2001). "Alkaline pulp having low average degree of polymerization values and method of producing the same," *United States Patent*, No. 574538.

- Saeed, A., Jahan, M. S., Li, H., Liu, Z., Ni, Y., and van Heiningen, A. (2010). "Mass balances of components dissolved in the pre-hydrolysis liquor of kraft-based dissolving pulp production process from Canadian hardwoods," *Biomass and Bioenergy*, doi:10.1016/j.biombioe.2010.08.039.
- Santiago, A., and Neto, C. P. (2007). "Assessment of potential approaches to improve *Eucalyptus globulus* kraft pulping yield," *J. Chem. Technol. Biotechnol.* 82, 424-430.
- Scandinavian Pulp, Paper and Board Testing Committee. Scan Test Methods, 1993.
- Scurlocka, J. M. O., Dayton, D. C., and Hamesb, B. (2000). "Bamboo: An overlooked biomass resource?," *Biomass and Bioenergy* 19, 229-244.
- Technical Association of the Pulp and Paper Industry, TAPPI Standard Methods, Atlanta: TAPPI, 2000.
- Vu, T. H. M., Pakkanen, H., and Alén, R. (2004). "Delignification of bamboo (*Bambusa procera*). Part 1. Kraft pulping and the subsequent oxygen delignification to pulp with a low kappa number," *Industrial Crops and Products* 19, 49-57.
- Wallberg, O., Linde, M., and Jonsson, A. S. (2006). "Extraction of lignin and hemicelluloses from kraft black liquor," *Desalination* 199, 413-414.
- Wallis, A., Wearne, R., and Wright, P. (1996). "Chemical analysis of polysaccharides in plantation eucalypt woods and pulps," *Appita Journal* 49(1), 258-262.

Article submitted: March 18, 2011; Revised version accepted: December 9, 2011;
Published: December 13, 2011.