Properties of extracted
Eucalyptus globulus kraft pulps

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ABSTRACT: This work was a comprehensive study of the properties of extracted Eucalyptus globulus kraft pulps. Five levels of hot water extraction were performed, each followed by kraft cooking to three different kappa numbers. As extraction took place, the hemicelluloses content of the kraft pulps was reduced from 21%-22% to 3%-4% and, conversely, the cellulose fraction increased from 73%-75% to 85%-90%. Fiber length decreased for all pulps and kink index increased greatly with extraction. The dispersive components of the surface energy for the control (unextracted) and extracted (120 min) kappa no. 15 kraft pulps, as determined by inverse gas chromatography, were found to be 30.8 and 34.9 mJ/m², respectively. The acid-base properties of the pulp surface seemed to be enhanced by the inclusion of the hot-water extraction step. We discuss the surface energy properties in terms of the chemical structure of the pulps. In addition, we report on two models able to predict the mass removal and kappa number of pulps prepared from preextracted chips.

Application: This work can give mills an understanding of the effect of hot water extraction on the properties of E. globulus kraft pulps.

Increasing concern about the environment, especially the greenhouse effect, combined with decreasing availability of cheap and accessible fossil fuels, which translates into higher costs to the consumer, has led to the first true and serious effort to find alternative and renewable energy sources. In this context, lignocellulosic materials such as wood constitute an important natural resource for the production of biofuels and biodegradable plastics and can be a component of sustainable industrial development [1]. Biofuels can help to alleviate climate change by reducing greenhouse gas emissions, and bioproducts can be used as raw materials instead of fossil-based carbon resources.

In the biorefinery concept, biomass is converted into a wide range of products that include fuel. Current pulp mills are considered precursors to modern biorefineries because they produce energy and pulp and paper from a renewable resource. Therefore, they can be adapted and converted into second-generation biorefineries that produce biofuels and/or an array of other products (e.g., acetic acid, bioplastics) while still producing paper [2-4]. The idea is to use the hemicellulose present in the wood, which is typically dissolved in the black liquor and consequently burned in the recovery process, to produce products of higher added value.

Several researchers have studied different types of hemicellulose extractions on several wood species; these types include hot water extraction (HWE, also commonly referred to as autohydrolysis), alkaline extraction, and acidic extraction [4-7]. In a study of the effect of HWE on sugar maple (Acer saccharum) pulps and Brazilian eucalypt pulps, Goyal et al. [4] found that the extracted chips were easier to pulp and bleach but the pulp had worse refi nability and strength properties in comparison to the control (unextracted) pulps. For a mass removal of up to 16.5%, they were able to produce extracted pulps from sugar maple (but not from eucalyptus) that exhibited satisfactory strength properties. Yoon and van Heiningen [7] studied the properties of loblolly pine (Pinus taeda) extracted kraft pulps and also found that the extracted pulps exhibited lower refi nability and hindered tensile strength when compared to unextracted pulps. However, no differences in pulp viscosity, zero span tensile strength, or tear index were observed with the extraction treatment, indicating that the fiber's intrinsic strength remained unaffected but the interfiber bonding decreased with extraction. Al-Dajani et al. [5] performed low-temperature alkaline extractions on aspen chips followed by a conventional kraft cook. They reported it was possible to partially remove hemicellulose from the chips without detrimentally affecting the pulp's yield or its papermaking quality.

Santos et al. [8] briefly studied the influence of hemicellulose content on the quality of bleached E. globulus kraft pulps. They produced three pulps with high, medium, and low hemicellulose content, via a normal kraft cook, an extended kraft cook, and one HWE, respectively. Pulp with hemicellulose content of 8.5% had slightly smaller fiber length and width and substantially higher kink index when compared to a pulp with hemicellulose content of 19%. As for the paper properties, they reported that the removal of hemicelluloses negatively affected tensile and tear indexes and zero span tensile strength.

In the present work, we performed five different extraction levels, each one followed by three different kraft cooks (and therefore three different kappa levels). The aim was to get deeper and broader insight on the effect of HWE on several commonly reported properties of kraft E. globulus pulps, such as

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pulp composition, fiber biometry, and papermaking potential, as well as the effect on surface properties of fibers. We present two models, the first one to predict the mass removal achieved with the preextraction stage and the second one to predict the kappa number of a pulp produced from a preextracted chip.

EXPERIMENTAL

The eucalypt chips were obtained from a paper mill in Portugal. The chips were air dried and screened through a series of screens with circular openings of 9/8-, 7/8-, 5/8-, and 3/8-in. diameters. The chips retained in the 7/8- and 5/8-in. screens were considered accepts [9] and were used in the laboratory experiments.

The extractions and cooks were carried out in a 4.5-L laboratory digester, using 500 g o.d. chips. Distilled water was added to reach a 4:1 liquid-to-wood ratio. Extractions were carried out at 160°C, with a heating ramp time of 30 min. The time at temperature was varied, at 30, 60, 90, and 120 min. The Kraft cooks were performed with the same wood-to-liquor ratio and at the same final temperature. The white liquor had 16% active alkali (AA) and 25% sulfidity. The heating time was 60 min and the H-factor was varied to achieve three different kappa numbers: 15, 25, and 35. Cooks were performed with all the extracted chips (after extraction at 30, 60, 90, and 120 min), as well as with unextracted chips (control) for comparison. For the extracted chips, the Kraft cook was done right after the extraction and therefore the chips were never dried. However, two washing stages with distilled water at 80°C for 15 min were performed between the extraction and the cook, after collecting the extract, with the intention of simulating a more efficient counter-current extraction.

The original wood, the extracted wood, and the kraft pulp samples were all analyzed for cellulose, hemicellulose, and lignin content [1]. Proton nuclear magnetic resonance (1H NMR) spectroscopy was used to determine the cellulose and hemicellulose contents of all the wood and pulp samples. The NMR methods used in this research were developed by Kiemle et al. [10]. The samples (milled using a laboratory mill with a 60-mesh screen) were first digested to yield monomeric sugars and then analyzed using 1H NMR [11,12]. In a first digestion stage, a 50-mg o.d. sample was dispersed in 16 mL of 72% sulfuric acid at room temperature for 2 h and stirred every 15 min to ensure proper dissolution. In a second stage, 21 mL of distilled water were added to the mixture, bringing the acid content down to 40%. This mixture was then placed in a water bath at 80°C for 1 h and shaken every 15 min. The tubes were then cooled and kept in a refrigerator overnight, to allow the residual solid matter to precipitate. One mL of the clear supernatant was transferred to an NMR tube and mixed with 0.1 mL of a standard solution (a mixture of known amounts of trimethylamine hydrochloride (TMA) and glucosamine). The NMR spectra were integrated and scaled so that the glucosamine α-peak had an area of 100. The total lignin content (Klason plus acid-soluble lignin) was also determined for all the wood and pulp samples. All analyses were done at least in duplicate; the duplicated results did not differ more than 5% (relative error).

Fiber morphology was evaluated by using the OpTest HiRes Fiber Quality Analyzer (OpTest Equipment; Hawkesbury, ON, Canada) and very dilute pulp suspensions (0.04% consistency). The analysis provided information on fiber length distribution, different length averages, fines content, and fiber curl and kink. Two replicates of each pulp were analyzed; the differences between replicates were not greater than 1% for the length-weighted average fiber length and 3% for the kink index.

The viscosity of the pulps was determined according to TAPPI Standard Test Method T 230, “Viscosity of pulp (capillary viscometer method).” Because this method is only valid for lignin amounts below 4%, the pulps with kappa no. 35 were not tested. The coefficient of variation between measurements for each pulp was always lower than 4%.

Two pulp samples were also analyzed by inverse gas chromatography (IGC): (1) a control pulp obtained by cooking eucalypt wood chips to kappa no. -15 and (2) a pulp obtained after HWE of the wood chips during 120 min followed by cooking to kappa no. -15. Inverse gas chromatography is a powerful technique for studying the thermodynamics of adsorption and the surface properties of organic and inorganic materials [13]. The IGC technique is based on the physical adsorption of a well-known probe by a solid surface. The London dispersive component of the surface energy [14,15] and the acid-base surface properties of the stationary phase [16,17] may be determined from the retention time (and the peak shape) of an elution peak. For the IGC analysis, the samples were previously milled in a laboratory mill using a 60-mesh screen. A DANI GC 1000 digital pressure control gas chromatograph (DANI Instruments; Milan, Italy), equipped with a hydrogen flame ionization detector, was used for the IGC data collection. Stainless-steel columns, 0.5 m long and 0.4 cm inside diameter, were washed with acetone and dried before packing. A vacuum pump was used to pack 1.6–1.8 g of sample into the gas chromatograph columns. The columns were shaped in a smooth “u” to fit the detector/injector geometry of the instrument. The packed columns were conditioned overnight at 105°C under a helium flow, before any measurements were made. This procedure was used to remove any volatiles, including water molecules, adsorbed on the stationary phase surface and that, consequently, could affect the retention of the probe molecules. Experiments were carried out at a column temperature of 40°C with the injector and detector kept at 180°C and 200°C, respectively. Helium was used as carrier gas; its flow was selected to ensure that neither absorption nor diffusion of the probes would occur inside the column stationary phase. Small quantities of probe vapor (<1 µL) were injected into the carrier gas flow to ensure that the experiments took place at infinite dilution. The probes, methane, n-hexane (C6), n-heptane (C7), n-octane (C8), n-nonane (C9), n-decane (C10), trichloromethane (TCM), acetone, tetrahydrofuran (THF) and ethyl acetate (ETA) were of chromatographic grade and were used as received (Sigma-Aldrich; St. Louis, MO, USA). The retention
times ($t_e$) were the average of at least three injections and were
determined at the peak maximum for symmetrical peaks or
by the recommended Conder and Young method [15-18] for
the less-symmetrical chromatograms (observed with TCM,
acetone, THF and ETA). The coefficient of variation between
runs was not larger than 3%. The theory behind IGC for the
calculation of the dispersive component of the surface energy
($\gamma_d$) and the works of adhesion with the polar probes is
detailed elsewhere [13]. The physical properties of the probes
used in this work ($a$ and $w^*$) can be found in Kamdem et al.
[19] and Santos and Guthrie [13].

The x-ray photoelectron spectra were obtained using a ES-
CALAB 200A (VG Scientific; East Grinstead, UK) with PICSBS
software (Dayta Systems; Bristol, UK). A monochromatic Al
(Ko) x-ray source operating at 15kV (500 mA) was used. The
spectrometer, calibrated with reference to Ag 3d$_{5/2}$ (368.27
eV), was operated in constant analyzer energy mode with 20
eV pass energy. Spectra analysis was performed using peak
fitting with Gaussian-Lorentzian peak shape and Shirley-type
background subtraction. Samples were analyzed in duplicate
using pellets of about 1 cm diameter.

To assess papermaking properties of the pulps, handsheets
were prepared according to TAPPI Standard Test Method T 205,
"Forming handsheets for physical tests of pulp." Only not-
extracted pulps (control pulps) and 120-min extracted pulps
(for all kappa levels) were used for paper testing. TAPPI Standard
Test Methods were followed for every property tested.

RESULTS AND DISCUSSION

Table I shows the impact of HWE on wood mass and chemical
composition. A significant mass loss occurred as HWE
took place, reaching a maximum of up to 22% for 120-min
extraction. This was mainly due to the removal of hemicelluloses.
In fact, HWE can remove a significant amount of hemicelluloses (about 65%) and a modest amount of lignin (about
17%) from the original wood, while keeping the cellulose
mass almost unaffected. Therefore, in terms of the wood
weight percentage (wt %), the hemicelluloses content diminishes,
the lignin content remains virtually unchanged, and the
cellulose content is augmented after HWE. A model for the
mass removal, considering first-order kinetics for the dissolu-
tion of hemicellulose, previously developed for sugar maple
[20,21], was also applied in this study to E. globulus (Eq. (1)):

$$M = a[1 - \exp(-b \times t)]$$

where $M$ is the mass removal, $t$ is time, and $a$ and $b$ are fitting
coefficients. The coefficient $a$ quantifies the maximum dis-
solvable fraction of wood (mostly made up of hemicellulose
with a small fraction of lignin), and coefficient $b$ is a pseudo
first-order reaction rate constant (at 160°C). This model was
used to fit the data, with a very high correlation coefficient
(0.9998). All parameters of Eq. (1), valid within the range of
the experimental conditions used in this work, are shown in
Fig. 1.

After HWE, the wood samples were kraft cooked.

<table>
<thead>
<tr>
<th>Components</th>
<th>Extraction Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Total wood mass</td>
<td>100 (100)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>42.7 (42.7)</td>
</tr>
<tr>
<td>Glucuronoxylan$^b$</td>
<td>22.0 (22.0)</td>
</tr>
<tr>
<td>Glucomannan$^c$</td>
<td>2.5 (2.5)</td>
</tr>
<tr>
<td>Other hemicelluloses</td>
<td>1.7 (1.7)</td>
</tr>
<tr>
<td>Total hemicelluloses</td>
<td>26.2 (26.2)</td>
</tr>
<tr>
<td>Total lignin</td>
<td>25.9 (25.9)</td>
</tr>
<tr>
<td>Other components$^a$</td>
<td>5.2 (5.2)</td>
</tr>
</tbody>
</table>

$^a$Within brackets is (component weight/wood weight) x 100
$^b$Corrected with furfural
$^c$Assumes xylose:acetyl:xyluronic ratio of 10:7:1
$^d$Assumes mannose:glucose ratio of 2:1
$^e$Calculated by difference — includes ash, degradation products such as hydroxymethylfurfural (HMF), methanol, acetic acid, and formic acid.

I. E. globulus wood composition before and after hot water extraction.
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<table>
<thead>
<tr>
<th>Extraction Time (min)</th>
<th>H-factor</th>
<th>Kappa Number after Cooking</th>
<th>Screened Total Yield (%)</th>
<th>Screened Cooking Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>699</td>
<td>15.7</td>
<td>54.6</td>
<td>54.6</td>
</tr>
<tr>
<td>30</td>
<td>308</td>
<td>27.3</td>
<td>56.2</td>
<td>56.2</td>
</tr>
<tr>
<td>60</td>
<td>234</td>
<td>38.4</td>
<td>58.3</td>
<td>58.3</td>
</tr>
<tr>
<td>90</td>
<td>327</td>
<td>15.4</td>
<td>46.4</td>
<td>52.4</td>
</tr>
<tr>
<td>120</td>
<td>181</td>
<td>24.5</td>
<td>46.9</td>
<td>53.0</td>
</tr>
<tr>
<td>183</td>
<td>100</td>
<td>32.5</td>
<td>48.8</td>
<td>55.2</td>
</tr>
<tr>
<td>183</td>
<td>88</td>
<td>24.1</td>
<td>44.4</td>
<td>53.4</td>
</tr>
<tr>
<td>174</td>
<td>48</td>
<td>35.5</td>
<td>45.1</td>
<td>54.3</td>
</tr>
<tr>
<td>174</td>
<td>48</td>
<td>26.5</td>
<td>41.2</td>
<td>51.9</td>
</tr>
<tr>
<td>180</td>
<td>48</td>
<td>26.5</td>
<td>42.3</td>
<td>53.1</td>
</tr>
<tr>
<td>48</td>
<td>31</td>
<td>34.1</td>
<td>43.2</td>
<td>54.2</td>
</tr>
<tr>
<td>180</td>
<td>48</td>
<td>26.0</td>
<td>41.2</td>
<td>52.8</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>36.5</td>
<td>42.3</td>
<td>54.2</td>
</tr>
</tbody>
</table>

*All rejects were between 0% and 2%

II. E. globulus cooking results.

Table II shows the yield data for all the eucalypt pulps. There was a noticeable drop in the total yield from the inclusion of the extraction step, which was mostly due to the mass removal during the HWE stage. On the other hand, the drop in the cooking yield (i.e., digester yield) was not very significant, especially when taking into account that all cooks were performed using the same cooking liquor as a typical kraft cook. Therefore, the cooks were not optimized for the extracted chips, which behave quite differently than the control chips.

As shown in Table III, the inclusion of the HWE stage reduced significantly the amount of hemicelluloses remaining in the fibers after cooking for a predetermined kappa level. For instance, O-acetyl-4-O-methylglucuronoxyolan (glucuronoxylan) accounted for 20%–22% of the unextracted pulps’ composition; that amount decreased to 3%–4% if a previous extraction of 120 min was carried out. Also, in general, the differences in the extent of hemicelluloses removal decreased with extraction time. In fact, the difference in glucuronoxylan content from the 90-min to the 120-min extracted pulps was less than 0.5% (absolute values), whereas the difference between 60-min and 90-min extraction exceeded 1% and the difference between 30-min and 60-min extraction exceeded 3% for all kappa levels. In addition, in each kappa series all the pulps were cooked to the same kappa level (±2) and the lignin content was fairly constant along each series; therefore, it was mostly the amount of cellulose that increased with the decrease of the glucuronoxylan content. It is also worth mentioning that the fraction of the other hemicelluloses (such as glucomannan) was virtually insignificant in both the control and extracted pulps, never surpassing 0.5%.

By looking in more detail at the chemical composition values and yields shown in Tables I–III, we calculated that, under the kraft cooking conditions applied, only about 3% of the cellulose and 54% of the hemicelluloses in unextracted wood were degraded. On the other hand, for the extracted wood, the majority of hemicelluloses still present in the extracted chips was lost during the cook (83% on average for the 120-min extracted pulp), and a significant part of the cellulose was also degraded (19% on average for the 120-min extracted pulp). These results confirm the different behavior of the extracted versus control chips under similar kraft cooking conditions. Therefore, it should be possible to increase the cooking yield for the extracted chips by employing different cooking conditions (e.g., lower alkalinity) to have lower degradation and loss of cellulose and hemicelluloses in the extracted chips. However, our purpose was to evaluate the consequences of HWE and not to optimize the cooking conditions.

A model for estimating the kappa number of a pulp produced from an extracted wood chip was previously developed [20]. This model, given by Eq. (2), assumes that kappa number and lignin are linearly proportional and correlates kappa number with H-factor and P-factor (used as a reaction coordinate by Testova et al. [22], Sixta [23], and Tunc et al. [24] and with a similar algebraic expression to the H-factor):

\[ k = aL_0 \exp\left[\left(\frac{bH + cP + dH \cdot P}{2}\right)\right] \]  

where \( k \) is the kappa number and \( aL_0, b, c, \) and \( d \) are empirical constants used to fit the data. Table IV gives these coefficients, and Fig. 2 shows how the predicted values correlated with the experimental values.

Regarding fiber length (Fig. 3), the length-weighted aver-


III. Composition of pulps for all extraction times and kappa numbers.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Estimate</th>
<th>Standard Error of Estimated Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa number</td>
<td>a, L₀</td>
<td>44.096</td>
<td>1.1406</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>1.446x10⁻³</td>
<td>3.308x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>2.292x10⁻⁴</td>
<td>3.261x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>1.172x10⁻⁴</td>
<td>1.799x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.8694</td>
<td></td>
</tr>
</tbody>
</table>

IV. Coefficients in Eq. (2) via multiple linear regression and standard errors of regression estimates.

2. Comparison of the predicted versus measured kappa number for extracted eucalypt pulps.

The average fiber length of the cooked pulps decreased (approximately 10%–13%) for each kappa level as extraction took place. This was in accordance with the trend noticed by Santos et al. [8]. Another interesting observation was that at each extraction time, the differences between fiber lengths were lower than those between the unextracted pulps (0 min), where the fiber length seemed to decrease with decreasing kappa (more extended cook), as expected. This was due to the fact that the fibers became more exposed to the white liquor after the extraction stage. Thus, the incorporation of the extraction stage seemed to make pulps with different kappa numbers more uniform. It was also interesting to notice the great increase (about 270%) of the kink index with extraction time (Fig. 4). This, along with the lower hemicelluloses content (translated into a lower hydrophilicity), might be one of the reasons why other authors are observing that preextracted kraft fibers do not refine properly [8,25].

Figure 5 shows that viscosity increased significantly with HWE of 30 min, but decreased steadily as extraction proceeded. Santos et al. [8] also noticed an increase in viscosity from 950 to 1320 cm²/g when the hemicelluloses content decreased from 19% to 8.5%. That finding is in reasonable agreement with the variation of 44.4 cP to 71.3 cP observed in our
study for the kappa no. 15 control pulp and the corresponding 30-min extracted pulp. The behavior of viscosity was, most likely, not only due to the hemicelluloses removal but also to a side effect on the cellulose chains if compared to the control (unextracted) pulp. In fact, as the extraction time was increased (beyond 30 min), the cellulose became more and more exposed to the action of the cooking chemicals; thus, it started to degrade and consequently the viscosity decreased. Nonetheless, the effect of the hemicelluloses removal seemed to be always superior to that of the cellulose depolymerization, since the viscosity of the extracted pulps was always superior to that of the control pulps.

Regarding the surface properties, the dispersive component of the surface energy of the pulps under study was determined at 40°C on the basis of the retention times obtained for a series of n-alkanes (C6, C7, C8, C9, and C10). From the plots of RTln(V0) as a function of 2Nα(γd)5/3, depicted in Fig. 6, the values calculated for γd were 30.8 and 34.9 mJ/m² for the control and extracted E. globulus kraft pulps, respectively. These values were slightly lower than the 41 mJ/m² obtained at 37°C for an E. globulus kraft pulp with kappa no. 13.4 [26]. Recently, red maple (A. rubrum) wood samples also underwent HWE [27,28]. The authors found values for γd at 40°C of 38–39 mJ/m² after HWE at 160°C for 90 min, whereas those of the control samples were 36–37 mJ/m² (at 20°C, the values obtained by Paredes et al. [27] for γd were about 44 and 39 mJ/m² for the extracted and control samples, respectively).

The increase of the dispersive component of the pulp surface energy by the inclusion of HWE, as previously observed for red maple wood samples, is likely to be related mostly to the removal of hemicelluloses and other components such as extractives and lignin from the pulp surface. To get more information about the surfaces of the pulps, x-ray photoelectron spectroscopy (XPS) was performed on the same two pulps analyzed by IGC. The main results obtained after the deconvolution of the XP spectra are presented in Table V. The extracted pulp presented a slightly lower amount of C1 groups and a larger amount of C2 groups than the control pulp. Typically, C1 is the major spectral component for lignin and extractives while C2 is the dominant component for cellulose/hemicelluloses [26,29,30]. Therefore, a lower amount of extractives/lignin can be anticipated at the surface of the extracted pulp in comparison to the control pulp, which contributes to the increase of γd because those components exhibit lower γd than cellulose [26,29]. Moreover, considering the much lower amount of glucuronoxylan in the chemical composition of the extracted pulp in comparison to the control pulp and the fact that cellulose presents a much larger chain than glucuronoxylan, it may be proposed that the intensity of the London forces between the chemical groups present at the surface of the materials and the non-polar probes should be higher for the pulp enriched with cellulose (i.e., the extracted pulp), thus also contributing to the higher value of the dispersive component of the surface energy in the latter, at the same temperature. It should be noted that the γd values of bleached E. globulus kraft pulps (38–45 mJ/m²) [30–32] are slightly lower than those of purified α-cellulose fibers (around 47 mJ/m²) [29,33].

The acid-base properties of the pulps’ surfaces were evaluated on the basis of calculations of the specific components
of the work of adhesion ($W_a$) between the surfaces and several polar probes, namely acidic (TCM), basic (THF), and amphoteric (acetone, ETA) probes. The results obtained are presented in Fig. 7. For both the control and extracted eucalypt pulps, the $W_a$ values followed the order acetone > ETA and THF > TCM. Those values indicate a higher interaction of the pulps’ surfaces with amphoteric probes and suggest, therefore, that the materials are of amphoteric nature. In addition, a greater affinity of the pulps’ surfaces with a basic probe (THF) than with an acidic one (TCM) indicates that both pulps have a more acidic than basic character, in agreement with the dominant presence of OH groups (and also COOH groups, though to lesser extent) in the macromolecular structure of glucuronoxylan and cellulose.

The values of the specific components of the work of adhesion with all evaluated polar probes increased when going from the control to the extracted pulp, which meant that the acid-base properties were enhanced in the extracted pulps. Because hemicellulose is more hydrophilic (and polar) than cellulose, this result was somewhat unexpected in view of the large removal of hemicelluloses (mainly glucuronoxylan) caused by the HWE stage. However, as shown by the XPS surface analysis results, the partial removal of extractives/lignin at the pulp surface from the control to the extracted pulp could unblock some high-energy sites, mainly from cellulose chains, which would expose them to interaction with the polar probes and enhance the acid-base properties of the pulp surface. Overall, because IGC is sensitive only to the highest-energy sites, it can be concluded that the amount of those active sites increased from the control to the extracted pulp.

At 40°C, the ratio $W_a$(THF)/$W_a$(TCM) was 3.5 and 2.6 for the control and extracted pulps, respectively. Thus, acidity increased less than basicity when going from the control to the extracted pulp. This result for the E. globulus pulps is in line with those obtained for red maple wood samples after undergoing HWE [27, 28] and is in agreement with the partial removal of glucuronoxylan, which typically exhibits more pronounced Lewis-acid character than cellulose.

The physical properties of handsheets were investigated by comparing those prepared from the highest extracted pulps (120 min) with those prepared from the control pulps, for all kappa levels. As seen in Fig. 8, a significant decrease in the tensile index occurred when comparing the 120-min extracted eucalypt pulps and the unextracted pulps, for all kappa levels. Furthermore, as expected, as the lignin content of the pulps increased the tensile index decreased. The handsheets of the extracted pulps, which were more affected by the white liquor, lost slightly less tensile index over the kappa range (15%) than those of the control pulps (19%), as evidenced by the slope of the plotted regression line. Similar conclusions can be drawn from the bonding index (ratio of tensile strength [N/m] to zero span tensile strength [N]) results (Fig. 8). Overall, the handsheets produced with the ex-
Extracted pulps had lower bonding index than those produced with the control pulps (30%-36% smaller) due to their lower hemicelluloses content. The values of the other physical properties were also lower for the extracted pulps, with the exception of air resistance (TAPPI Standard Test Method T 460 om-11, 'Air resistance of paper [Gurley method]'), as shown in Fig. 9. This was mostly due to the higher fines content resulting from the extraction.

**CONCLUSIONS**

Hot water extraction has a serious effect on several *E. globulus* pulp properties and consequently on the paper produced from these pulps. The pulp composition is the first and most important parameter that is affected. As extraction took place, hemicelluloses are preferentially removed, dropping from 21%-22% in the control (0-min extraction) to 3%-4% at the highest extraction level (120-min extraction). Significant degradation of the cellulose occurred in the extracted chips under typical Kraft cook conditions; therefore, it is conceivable that there is room for optimization of the cook conditions to minimize such degradation.

The dispersive component of the surface energy of the pulps increased with the inclusion of HWE, and the acid-base character was more pronounced for the extracted pulps when compared to the unextracted pulps. That was attributed mainly to the lower amount of extractives/lignin at the surface of extracted pulps, as determined by XPS. The lower amount of glucuronoxyl in the extracted pulps should also contribute to the higher value of the surface energy (dispersive component) for the extracted pulps. In addition, the acidity increased less than the basicity from the control to the extracted pulp, mainly as a consequence of the partial removal of glucuronoxyl that exhibits more pronounced Lewis-acid character than cellulose.

Generally, handsheets properties decreased, except for Gurley air resistance. Therefore, papers produced from the extracted pulps will exhibit weaker properties.

Two models, one for the estimation of the overall mass removal during extraction and the other for the estimation of the kappa number, were applied with very satisfactory fitting to the experimental results.

**LITERATURE CITED**


ABOUT THE AUTHORS

Worldwide, hemicellulose extraction is a promising area of development in the pulp and paper biorefinery industry, in which eucalypt pulps play an increasingly relevant role.

This research was performed in the framework of Duarte's doctoral thesis. The work complements other previously published studies, namely at SUNY-ESF. A systematic approach to the hemicellulose removal procedure and some additional techniques were used to gain new insights on the effects of HWE.

Our systematic experimental approach required a huge amount of experimental laboratory work. Therefore, our biggest challenge was to analyze and interpret the large set of results generated. The findings confirmed that the effects of HWE on other species found in previous studies were also valid for *E. globulus* and also showed the overall effect of HWE on surface chemistry of pulps. Furthermore, we developed and presented two models, one for the estimation of the overall mass removal during extraction and the other for the estimation of the kappa number.

Although research in this area is in the early stages, our work may be used as a stepping stone to an eventual revamping of a pulp and paper mill to an integrated biorefinery.

On the pulping side, the next step would be to optimize the (chemical) cooking conditions to enhance the hemicellulose extraction with less degradation of the cellulose chains. On the paper side, the next step would be to find a suitable and cheap substitute to the binding effect of hemicellulose.

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