EFFECT OF HARDWOODS CHARACTERISTICS ON KRAFT PULPING PROCESS: EMPHASIS ON LIGNIN STRUCTURE

Ricardo B. Santos, a  Ewellyn A. Capanema,b Mikhail Yu. Balakshin,b Hou-Min Chang,a,* and Hasan Jameel a

In an attempt to explain variations in delignification behaviors among different hardwood species, the kraft pulping delignification rates of Eucalyptus urograndis, E. nitens, E. globulus, sweet gum, maple, red oak, birch, red alder, cottonwood, and acacia were obtained and correlated with their respective lignin chemical structures. Since H-factor for hardwood is calculated based on the softwood activation energy ($E_a$) value, a comparison between softwood vs. hardwood activation energy was also performed. Lignin was isolated by a modified isolation protocol, using alkaline pretreatment of the wood prior to isolation. The lignin preparations were analyzed via quantitative $^{13}$C NMR spectroscopy. Substantial variations were found among the hardwood species studied. A linear correlation between the kraft delignification rate and the amount of syringyl units was found. Activation energy values obtained for kraft pulping of hardwoods were very similar and almost identical to the value obtained for softwood. Birch was the only species with outlier behavior.

Keywords: S/G ratio; $^{13}$C NMR; Chemical kinetics; Reaction rate constant; Activation energy; Hardwood; Kraft pulp; Lignin; Degree of condensation; Morphology

Contact information: a: Department of Forest Biomaterials, North Carolina State University, Campus Box 8005, NC 27695-8005, USA; b: Lignol Innovations Ltd., Unit 101, 4705 Wayburne Drive, Burnaby, BC, Canada V5G 3L1; * Corresponding author: hchang@ncsu.edu

INTRODUCTION

The kraft process is currently the dominant chemical pathway to produce pulp. During the process, white liquor promotes lignin dissolution and consequent fiber individualization, and the bulk phase (main delignification phase during process) is known to promote from 60% to 68% of the total delignification of the wood (Gierer 1980 and Chiang et al. 1987). The use of sodium hydroxide and sulfide during a kraft cook brings a number of advantages when compared to other processes, especially in terms of fiber strength. Disadvantages are also present, the major one being a loss in pulp yield caused by carbohydrate instability and degradation during the alkaline reaction.

In order to minimize those losses, it is important to have a good and reliable understanding of both process and raw material. Further, interactions between process conditions and utilized raw material can be critical and may require special attention.

Easier lignin breakdown during pulping may permit the use of less drastic process conditions, leading to carbohydrate preservation. When one discusses lignin vs. process conditions, it is important to note that softwood species are harder to pulp, in comparison to hardwoods. Softwood lignin appears to vary little between species (Sarkanen and Hergert 1971; Akiyama et al. 2005) and therefore fewer improvements in the process.
(related to wood) can be achieved. On the other hand, there is increasing evidence that the structure of hardwood lignin varies greatly between species. The major difference in hardwoods is the presence of syringyl lignin in combination with guaiacyl units (S/G), and the mixed system allows for the opportunity to improve process conditions. A more suitable lignin may reduce the needed alkali charge, temperature, and/or retention time. In such cases an increase in production (yield) and fiber quality is expected.

Considerable variation in kraft pulping performance of different hardwood species has been reported (Collins et al. 1990; Pinto et al. 2005; González-Vila et al. 1999; Bose et al. 2009). A study with model compounds showed indications that the β-aryl ether of syringyl lignin is cleaved much more easily than that of guaiacyl lignin (Tsutsumi et al. 1995). Since β-O-4 is a dominant structure in lignin and appears to correlate highly with the S/G ratio, there have been many studies to investigate the effect of S/G ratio on kraft pulping of hardwoods (Collins et al. 1990; Pinto et al. 2005; González-Vila et al. 1999; Bose et al. 2009; Chang and Sarkanen 1973; Gomes et al. 2008). Even within the same species of *E. globulus* wood, evidence of the influence of S/G ratio on pulp yield and ease of pulping has been reported, leading to the inclusion of lignin S/G ratio as a selection parameter in clonal breeding programs for pulpwood production (González-Vila et al. 1999; del Rio et al. 2005). Similar results were also reported for various clones of *E. grandis* and the hybrid of *E. grandis × E. urophylla* (Gomide et al. 2005; Guerra et al. 2009). The correlation was not as strong, leading to the suggestion that other lignin structural features, in addition to the S/G ratio, may also play a role (Guerra et al. 2009).

Until now, studies aimed at demonstrating the effect of S/G ratio on the ease of kraft pulping delignification have been done either by cooking to different kappa numbers at the same alkali charge or by pulping to a constant kappa number with different alkali consumption. These two methods can only give the relative ranking of the ease of kraft delignification among species or clones. These two methods may also be affected by factors unrelated to lignin structure, such as type and amount of hemicelluloses, extractives, etc. Few studies have determined the rate constant of the bulk delignification for kraft pulping of different hardwood species. To the best of our knowledge, activation energy ($E_a$) has never been determined for any hardwood. In this paper, hardwood lignin structures were evaluated and quantified by $^{13}$C NMR. In addition, hardwoods morphological aspects were also determined. An investigative study of those parameters (lignin type and wood morphology) affecting pulping delignification is presented. Activation energy was determined for commercially important hardwood species, as well as for loblolly pine as a softwood reference.

**EXPERIMENTAL**

**Raw Material**

*Eucalyptus nitens, E. globulus, E. urograndis, sweet gum (Liquidambar styraciflua), red maple (Acer rubrum), red oak (Quercus rubra), birch (Betula pendula), red alder (Alnus rubra), cottonwood (Populus trichocarpa), acacia (Acacia mangium),* and loblolly pine (*Pinus taeda*) received from different pulp and paper mills around the
world were ground and sieved as received (knots and bark were removed). The wood
meals (40 to 60 mesh) were soxhlet extracted for 24 h with benzene-ethanol 2:1 (v/v)
(TAPPI T264 om-88), dried, and used for pulping and lignin isolation.

Wood chips of *E. nitens*, *E. globulus*, *E. urograndis*, sweet gum (*Liquidambar
styraciflua*), red maple (*Acer rubrum*), red alder (*Alnus rubra*), cottonwood (*Populus
trichocarpa*), and acacia (*Acacia mangium*) were prepared using a lab chipper. The logs
had their bark manually removed and then were mechanically split into four pieces. After
chipping, each sample was separated into 3 different fractions (27 to 23 mm; 23 to 17
mm; 17 to 11 mm). The fractions were proportionally mixed in order to obtain a similar
chips size for all species and avoid size interference. They were placed in plastic bags,
and the moisture content was determined.

**Sawdust Delignification Rate Constant**

Sawdust delignification rate determination was performed at 150ºC using *E.
nitens*, *E. globulus*, *E.urograndis*, sweet gum, maple, red oak, birch, red alder,
cottonwood, acacia, aspen, and loblolly pine. Stainless steel autoclaves (50 mL) were
filled with 3 g of OD wood sawdust plus 30 mL of white liquor. An excess of white
liquor (liquor: wood ratio of 10:1) was used in order to maintain constant reagent
concentrations during the evaluation of kinetics. Therefore, the active alkaline charge was
40%, with 25% sulfidity. The autoclaves were closed and seated on the bottom of the
M&K digester. White liquor with the same ion concentration was used to heat the 50 mL
autoclaves placed inside the M&K. After the desired reaction time, the whole apparatus
was cooled down by running cold water through it. The samples were removed from the
bombs and washed with deionized water until a neutral pH was reached. Cooking yield
and lignin content (Dence and Lin 1992) were then determined for kinetics calculations.

**Chips Delignification Rate Constant**

A kinetics study on chips was performed using eight hardwoods species (*E.
globulus*, *E. nitens*, *E. urograndis*, maple, sweet gum, red alder, cottonwood, and acacia).
The species were cooked following the same approach and conditions as for sawdust. The
experiment was designed to be similar and allow comparison of the results (Fig. 1). The
only modification was in regards to the amount of sample utilized (150 g) and the direct
contact between wood sample and digester. After the kinetics experiments, the pulp was
separated from black liquors and exhaustively washed with water until a neutral pH was
reached. Pulping yield and lignin contents (Dence and Lin 1992) were determined.

**13C-NMR for Lignin Structure Quantification**

13C-NMR analysis was performed according to Capanema et al. (2007). 13C-
NMR spectra of the lignin preparations in DMSO-d6 were recorded on a Bruker
AVANCE 300 MHz spectrometer at 300 K using a 90º pulse width, a 1.4 s acquisition
time, and 1.7 s relaxation delay. MWL was isolated according to the modified protocol,
(Capanema et al. 2007) in which all samples are extracted with 0.3% NaOH for 1 hour to
remove tannins. The ball milled wood was extracted with 96% aqueous dioxane, in
accordance with the method of Bjorkman (1956). The targeted milled wood lignin yield
was 27%. Chromium (III) acetylacetonate (0.01 M) was added to the lignin solution to provide complete relaxation of all nuclei. A total of 20,000 scans were collected.

![Figure 1. Apparatus for kraft kinetics study using sawdust or chips](image)

**Carbohydrate Analysis**

The samples’ carbohydrate composition was determined by acid hydrolysis. 0.1 g of sample was hydrolyzed with 1.5 mL of 72% H₂SO₄ at room temperature with occasional stirring for 2 hrs. The mixture was then diluted to 3% H₂SO₄ using deionized water, transferred to a vial, sealed, and heated to 120°C for 1.5 hrs. The resulting suspension was filtered, and the filtrate was analyzed for monomeric sugar. Fucose was added as internal standard.

The monomeric sugar content was determined by injecting 2.5 mL samples into a high-performance anion-exchange chromatography system with pulsed amperometric detection (HPAE-PAD) with a Dionex IC-3000 chromatograph. Sugars were separated using a Carbo-Pac PA1 guard and analytical columns connected in series. Water was used as eluent at the flow rate of 1.0 mL/min, and the column temperature was 18°C. A post-column base 40 mM NaOH was added in to improve detection by pulsed amperometry. The post-column flow rate was 1.0 mL/min.

**Quantitative Wood Anatomy**

Eight hardwood species were selected for quantitative anatomical evaluation. Four chips of each species were cut to obtain transverse microtomes, and a 1% aqueous safranin solution was used to enhance contrast of the sections. Next, the samples were washed with deionized water and placed on a warm plate at 75±5°C to dry. Each section was fixed on a glass slide with Permount, and anatomical properties were measured using a light microscope (Nikon E200), 3CCD color video camera (Sony DXC-390), and an Image-Pro Plus 4.5 software. From each slide, four 546 μm x 410 μm-sized images at x200 magnification and four 273 μm x 205 μm-sized images at x400 magnification were
taken randomly at 640x480 pixels resolution. On the lower magnification images, vessel number, vessel lumen diameter (μm), and vessel lumen area fraction (%), were measured. Fiber lumen area fraction (%) and double cell wall (μm) were measured on the higher magnification images.

Fiber Quality Analysis

The same species used for quantitative wood anatomy were also analyzed using a Fiber Quality Analyzer (FQA). Samples for FQA evaluation were obtained by isolating holocellulose from 1 g of extractive-free 20 min. kraft pulps. 20 mg of oven-dried holocellulose was suspended in 20 mL of deionized water and defibrillated for 8 minutes. The liberated fibers were placed into 300 mL of deionized water, stirred, and placed in the equipment. The beaker was filled with water 3 times to guarantee that all fibers were counted. The ranges used for the analysis were the following: fines (L = 0.05 to 0.20 mm), mean fiber length (L = 0.20 to 10.00 mm), mean fiber width (W = 7 to 60 μm), and vessels (0.10 < L < 2.00 mm W>100.00 mm).

RESULTS AND DISCUSSION

Samples Characterization

Species’ chemical characterization and lignin isolation yield are given in Table I. Among the ten hardwoods, lignin content varied from 22% to 28%. The yield of MWL was rather constant, varying from 24% to 29%, and was independent of the lignin content. These results are consistent with the finding that yield of MWL depends only on the extent of ball milling (Fujimoto et al. 2005). Total carbohydrate content ranged from 57% to 63%, with glucan and xylan as the major components. Glucans composed 37% to 49% of the total wood composition, while xylan ranged from 11% to 20%. S/G, as determined based on NMR measurements, was found to differ widely among the species. It varied from 1.18 for acacia, to up to 3.15 for birch. As expected, Eucalyptus and red oak are among the species with high syringyl content.

Table I. Sugar Composition, Lignin Content, and Structure

<table>
<thead>
<tr>
<th>Species</th>
<th>Sugar, %</th>
<th>Lignin, %</th>
<th>S/G</th>
<th>MWL, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ara</td>
<td>Rha</td>
<td>Gal</td>
<td>Glc</td>
</tr>
<tr>
<td>E.nitens</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>41.8</td>
</tr>
<tr>
<td>E.urograndis</td>
<td>0.2</td>
<td>0.3</td>
<td>0.8</td>
<td>48.5</td>
</tr>
<tr>
<td>E.globulus</td>
<td>--</td>
<td>--</td>
<td>1.2</td>
<td>46.1</td>
</tr>
<tr>
<td>Cottonwood</td>
<td>0.4</td>
<td>0.3</td>
<td>0.6</td>
<td>44.8</td>
</tr>
<tr>
<td>Acacia</td>
<td>--</td>
<td>--</td>
<td>0.7</td>
<td>46.9</td>
</tr>
<tr>
<td>Red alder</td>
<td>0.3</td>
<td>0.4</td>
<td>0.7</td>
<td>40.8</td>
</tr>
<tr>
<td>Maple</td>
<td>0.7</td>
<td>0.4</td>
<td>0.6</td>
<td>43.5</td>
</tr>
<tr>
<td>Sweetgum</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
<td>37.8</td>
</tr>
<tr>
<td>Red oak</td>
<td>--</td>
<td>--</td>
<td>0.6</td>
<td>41.6</td>
</tr>
<tr>
<td>Birch</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>37.4</td>
</tr>
<tr>
<td>Pine</td>
<td>--</td>
<td>1.8</td>
<td>2.3</td>
<td>41.9</td>
</tr>
</tbody>
</table>

--: not detected
Sawdust Delignification Rate Constant

Since the greatest proportion of the lignin removal takes place during the kraft bulk phase, the kinetics experiments were designed to investigate the effect that lignin structure has on this phase of pulping. As polymers such as carbohydrates and extractives consume part of the alkaline solution, an excess in alkali charge was necessary in order to isolate those reactions that made it possible to conduct the experiment without their interference. Lignin reactivity with the kraft liquor was measured at 150°C at four different points in time (20, 30, 45, and 60 minutes).

Figures 2 to 4 show sawdust delignification curves obtained for the kinetics experiments.

Figure 2. Red alder, E.globulus and cottonwood delignification curves

Figure 3. E.urograndis, acacia, E.nitens and red oak delignification curves
Birch, loblolly pine, maple and sweetgum delignification curves

There was a very good correlation between cooking time and percentage of lignin removal during the kinetics. The delignification rate constant value was calculated using the exponential function. Each of the species studied presented a pseudo-first order reaction, in agreement with similar studies (Wild and Daleski 1965; Kleinert 1966).

A wide range of reaction rate constants were obtained among the hardwoods (Fig. 5). A high rate constant represents a higher delignification rate and therefore a more reactive lignin. In general, eucalyptus species presented the highest delignification rates. The highest values were assigned for *E. globulus*, followed by *E. nitens* and, *E. urograndis*. The lowest value was obtained for maple wood.

Sawdust delignification rate constant

**Figure 4.** Birch, loblolly pine, maple and sweetgum delignification curves

**Figure 5.** Sawdust delignification rate constant
Figure 5 can be divided into three different zones: the first zone contains easily delignifiable species (*Eucalyptus*), the second zone is composed of intermediate species (from red oak to acacia), and the third zone contains low delignification rate species (red alder and maple). Softwood’s rate of delignification was not even half that of the lowest hardwood value (maple), showing the dominance that hardwood species have in regards of pulping performance.

**S/G vs. Delignification Rate Constant**

In order to explain differences in rate of delignification among the species, lignin structure obtained from $^{13}$C-NMR was correlated with the rate constant values. A substantial variation of syringyl and guaiacyl content among the species was found, and those values strongly correlated with the delignification rate constant. As shown in Fig. 6, a straight line was found ($R^2 = 94\%$), indicating a high influence of syringyl lignin on the kraft pulping delignification process. As syringyl lignin increases, condensed lignin structure decreases and $\beta$-O-4 linkages increase (Santos et al. 2011). These findings are very important and confirm the benefits of high S/G ratio for the kraft process. Moreover, the use of species with high syringyl lignin content may reduce pulping reagent use and consequently diminish fiber degradation, increasing fiber strength. Species having high S content can also be suitable for cellulosic bioethanol processes that have an alkaline stage as pretreatment.

Only one of the species had an unexpected behavior during the study. Birch, which has the highest S/G ratio (3.15), was expected to have the highest rate of delignification. Instead birch delignification was slow and comparable to acacia, with a value of 1.65, 1/min (x100). Further investigation for this species is required, and it will be done as future work.

![Figure 6. Sawdust delignification rate constant vs S/G ratio](image)
Activation energy

Activation energy ($E_a$), which defines the energy that must be overcome in order for a chemical reaction to occur, was calculated for four hardwood species and one softwood. An activation energy experiment was performed to show possible differences between hardwood and softwood species. It is well known that the activation energy for softwood is around 140 kJ/mol (Sjöström 1981), but to the best of our knowledge, no activation energy experiment using hardwoods had been done before.

Figure 7 shows the coefficients used to calculate activation energy, and Table II brings the calculated activation energy.

Activation energy for the bulk phase of the kraft pulping process presented almost the same value for hardwood and softwood. This confirmation is important, since softwood activation energy value has been applied routinely to calculate hardwoods’ H-factor for process control until now.

Chip Delignification Rate Constant

Because of the high activation energy value obtained, no other influence rather than chemical is expected during the kinetics reaction. To ensure this statement and to create a more tangible industrial scenario, kinetic tests with chips were also performed.
Figures 8 and 9 show the curves obtained from chip kinetics experiments. There was also a strong correlation between cooking time and percentage of lignin removal during the reaction. As for sawdust, delignification rate constant value was calculated using an exponential function. The reaction followed pseudo-first order kinetics.

![Figure 8](image1.png)

**Figure 8.** Chip delignification curves for *E. urograndis*, *E. globulus*, sweetgum, and acacia

![Figure 9](image2.png)

**Figure 9.** Chip delignification curves for red alder, cottonwood, *E. nitens*, and maple

Figure 10 shows a comparison between sawdust and chip rates. The rates for chips were slightly higher for the eight species studied. This could be due to the use of sawdust inside stainless steel autoclaves and a consequent delay in heat transfer from the
liquid being heated by the digester to the sample inside the autoclave. Also, when chips are cooked, the circulation provided by this type of digester (M&K) might result in a better homogenization of the system and slightly better lignin removal. These two factors would raise the rate values. Nevertheless, the tendency obtained was the same (Fig. 11). The S/G ratio was found to govern chips’ rate of reaction, in a similar manner as observed in the case of sawdust.

**Figure 10.** Sawdust and chip delignification rate constant

**Figure 11.** Chip delignification rate constant vs S/G ratio.
Wood Morphology vs. Rate of Delignification

Wood morphological features have been mainly reported as determinants of pulp properties (Kayama 1968; Amidon 1981; Ona et al. 2001), and scarce information is found in regards to their influence on pulpability (Ramírez et al. 2009). Looking at the morphological results obtained in this study (Table III), some highlights can be made.

In terms of fiber length, sweetgum presented the highest value, followed by red alder. On the other hand, *Eucalyptus nitens* had the lowest value. Fiber diameter was found to be very close among the Eucalyptus fibers. Cottonwood and red alder had the highest value for that feature. In terms of cell wall thickness, all the species presented a similar value, except sweetgum and acacia, which had, respectively, the highest and lowest values. In terms of vessel characterization, the three *Eucalyptus* and acacia were found to have the highest vessel diameter. Sweetgum and cottonwood had the highest percentage of vessels, and acacia the lowest.

However, even with the wide variations found among the species, no wood morphological feature was found to interfere during chip and/or sawdust kinetics (Table IV); these findings demonstrate that the kinetics are based on chemical reactions. Statistical analysis was performed using Person product-moment correlation coefficient (r) which evaluates the linear dependence between two variables and gives value between +1 to -1. The correlation matrix for the variables in discussion was created using a p-level for highlighting of 0.05. Significant t-tests containing p ≤ 0.05 is shown as highlighted color in the results tables.

### Table 3. Species’ Morphological Features

<table>
<thead>
<tr>
<th>Species</th>
<th>Fiber Length mm</th>
<th>Fiber Diameter µm</th>
<th>Fiber/lumen %</th>
<th>Cell wall µm</th>
<th>Coarseness mg/m</th>
<th>Fines, %</th>
<th>Vessel Diameter µm</th>
<th>Vessel %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E.nitens</em></td>
<td>0.78</td>
<td>7.9</td>
<td>41.6</td>
<td>2.4</td>
<td>0.05</td>
<td>1.8</td>
<td>122.9</td>
<td>9.0</td>
</tr>
<tr>
<td><em>E.urograndis</em></td>
<td>1.01</td>
<td>7.6</td>
<td>36.3</td>
<td>2.6</td>
<td>0.08</td>
<td>1.0</td>
<td>118.9</td>
<td>16.0</td>
</tr>
<tr>
<td><em>E.globulus</em></td>
<td>0.88</td>
<td>7.8</td>
<td>32.4</td>
<td>3.1</td>
<td>0.07</td>
<td>1.4</td>
<td>127.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Cottonwood</td>
<td>0.94</td>
<td>13.7</td>
<td>46.9</td>
<td>2.8</td>
<td>0.15</td>
<td>2.4</td>
<td>70.2</td>
<td>23.4</td>
</tr>
<tr>
<td>Acacia</td>
<td>0.78</td>
<td>8.5</td>
<td>58.3</td>
<td>1.9</td>
<td>0.07</td>
<td>2.4</td>
<td>129.9</td>
<td>7.8</td>
</tr>
<tr>
<td>Red alder</td>
<td>1.10</td>
<td>11.9</td>
<td>44.0</td>
<td>3.0</td>
<td>0.22</td>
<td>2.8</td>
<td>55.8</td>
<td>19.3</td>
</tr>
<tr>
<td>Maple</td>
<td>0.88</td>
<td>9.0</td>
<td>42.1</td>
<td>2.6</td>
<td>0.14</td>
<td>2.2</td>
<td>42.7</td>
<td>16.6</td>
</tr>
<tr>
<td>Sweetgum</td>
<td>1.48</td>
<td>6.5</td>
<td>18.2</td>
<td>6.6</td>
<td>0.23</td>
<td>4.1</td>
<td>54.6</td>
<td>35.9</td>
</tr>
</tbody>
</table>

### Table 4. Correlation Matrix of Species’ Morphological Features vs. Reaction Rate

<table>
<thead>
<tr>
<th>Variable</th>
<th>Delignification rates, 1/min (x100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sawdust</td>
</tr>
<tr>
<td>Length, mm</td>
<td>-0.34</td>
</tr>
<tr>
<td>Diameter, µm</td>
<td>-0.64</td>
</tr>
<tr>
<td>Fiber/lumen, %</td>
<td>-0.26</td>
</tr>
<tr>
<td>Cell wall, µm</td>
<td>-0.15</td>
</tr>
<tr>
<td>Coarseness, mg/m</td>
<td>-0.67</td>
</tr>
<tr>
<td>Fines, %</td>
<td>-0.67</td>
</tr>
<tr>
<td>Vessel diameter, µm</td>
<td>0.17</td>
</tr>
<tr>
<td>Vessel, %</td>
<td>-0.51</td>
</tr>
</tbody>
</table>
Nevertheless, the knowledge of the different species’ anatomical structures can be used as database for future studies aimed at understanding final product quality (paper) attributes based on the original wood and fiber structures.

CONCLUSIONS

1. This study used an investigational approach to explain the effect of hardwood lignin structure during the kraft pulping process. Ten industrially important hardwood species were compared in terms of delignification performance, and a wide range of delignification rate constants were obtained for the various species. These variations indicate how easy or difficult the delignification process for each species shall be. Eucalyptus were established as the easiest species to delignify. Even though birch presented a high S/G ratio, its delignification rate was rather low. The species was considered an outlier, and further evaluation will be done.

2. Hardwood lignin structure analysis revealed substantial variation in terms of syringyl and guaiacyl units content. Eucalyptus had the highest syringyl content when compared to the other species (except birch). A linear correlation was found when S/G ratio was plotted against bulk delignification rate constant. This confirms the importance of syringyl units in pulping, due to its higher reactivity with alkaline liquor, the presence of lower condensed linkages, and higher β–O-4 content.

3. Hardwood activation energy, which is a key value for process control calculations, was found to be the same as for the hardwoods as for softwood (≈ 135 kJmol). This is an important confirmation, since the H-factor has been historically calculated based on data obtained for softwood.

4. Rates of delignification for sawdust and chips were found to be similar. No wood morphological interference during chip kinetics was found, showing that the kinetics mechanism is controlled by chemical reactions.

5. During the course of this study, interference from carbohydrates, extractives, hexenuronic acids, and reagent concentration was avoided. This was achieved by the use of high alkaline charge and by measuring pulp residual Klason lignin, instead of kappa number.

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