CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECT OF S/G RATIO ON KRAFT PULPING AND ECF BLEACHING OF SOME POPLARS AND EUCALYPTUS

GUSTAVO VENTORIM,* ERICKA F. ALVES,** LAIS S. PENNA,*** and
RAYMOND C. FRANCIS****

**Campus de Itapeva, UNESP, UniversidadeEstadualPaulista, Brazil*
*** Department of Paper and Bioprocess Engineering (PBE), SUNY College of Environmental Science and Forestry (SUNY ESF), 1 Forestry Drive, Syracuse, NY 13210, USA*
****Department of Chemical Engineering, Federal University of Viçosa (UFV), University Campus, Viçosa, MG 36570000, Brazil.*
***** Scientific Consultant, Syracuse, NY 13210, USA. On leave from PBE Department, SUNY ESF*

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The effect of syringyl:guaiacyl (S/G) ratio on kraft pulping and kraft pulping followed by O_2 delignification was investigated with six poplars grown on the same site. The results showed an improvement in the ease of delignification (EOD) when the S/G ratio was increased from a low to a moderately high value. However, above that moderately high value there was no further improvement in EOD with increasing S/G ratio. Kraft pulping followed by elemental chlorine-free (ECF) bleaching was then investigated with three Brazilian eucalypti with S/G ratio of 2.69, 2.46 and 2.41. The chips with S/G = 2.69 had superior EOD compared to the chips with S/G = 2.41. However, pulps from the S/G = 2.69 chips also contained less lignin-carbohydrate complexes (LCC) than corresponding pulps from the chips with S/G = 2.41. LCC are known to retard delignification in both alkaline pulping and ECF bleaching. The S/G ratio of eucalyptus pulp lignins was estimated by nitrobenzene oxidation (NBO) of the pulps and ^{1}H NMR or their isolated lignins. The S/G ratio decreased from a value of $\geq$2.46 for the lignin in two eucalyptus chip samples to $\leq$1.21 for the lignin in their kraft pulps. In general, S units appear to solubilize at a much higher rate than G units during kraft pulping.

Keywords: Hardwood, S/G ratio, lignin-carbohydrate complexes, kraft pulping, ECF bleaching

INTRODUCTION

It has long been known that the cleavage of the *β*-O-4 bond is the main depolymerization reaction during kraft pulping.[1,2] Two of the key dimeric lignin structures associated with the kraft pulping of hardwood are shown in Figure 1. The uncondensed *β*-O-4 structures are shown on the left and they are very reactive towards kraft liquor (NaOH + Na_2S).[3,4] On the other hand, the resinol structures on the right are very unreactive.[5,6] An uncondensed aromatic ring is defined as one not containing a C-C bond at any ring position, except for C-1 (propyl side chain in Fig. 1) nor connected to another aromatic ring by a diaryl ether linkage.[7] When uncondensed *β*-O-4 dimers (such as those in Figure 1), were treated with kraft liquor, a significantly higher rate of the *β*-O-4 cleavage was observed when one or both of the aromatic rings was syringyl (S), i.e. containing two methoxyl groups.[8,9] The number of aromatic rings without a methoxyl group (*p*-hydroxy phenylpropane of H units) is very low in hardwood lignin, typically only ~2% of all rings.[3,10,11] Literature data on the fractions of uncondensed S and G rings in hardwood lignin was recently reviewed.[7] It is believed that 60-65% of the G rings are uncondensed, while the value is believed to be >90% for S units.[7] In phenylpropane or C_9 units that are syringyl, the C-5 ring position is occupied by a methoxyl group, while ~30% of all the G units are condensed at that position.[3,12] It is believed that uncondensed rings are generally more reactive towards kraft liquor than the condensed ones.[3,13] However, this is somewhat dependent on the interunit linkages in the side chain. The resinol rings (Figure 1) are uncondensed, but they are unreactive in kraft pulping due to the β-β linkage in the side chain.

All of the above is consistent with a high S/G ratio being a desired trait in kraft pulping of hardwoods. This has long been reported.[14,15] Further, some recent publications strongly support the idea.[16-18]The S/G ratio appears to be the dominant parameter governing the rate and extent of kraft cooking[16-18] and this dominance appears to be independent of species,[16] genera[17,18]and growing sites.[16-18]However, there are also a couple of recent publications showing that when the S/G ratio is increased above a moderately high value, it leads to no further improvement in the ease of delignification.[4,19]

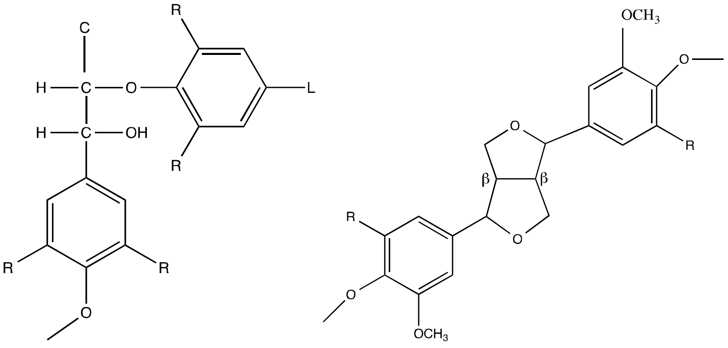

Figure 1: Structures in hardwood lignin that are relevant to kraft pulping; uncondensed β-O-4 dimeric structure (left) and resinol structure (right)

Guerra *et al.* used thioacidolysis to determine the S/G ratio of 15 *Eucalyptus globulus* clones and found absolutely no correlation between EOD and S/G ratio.[4]Interestingly however, they observed a good correlation between the yield of syringyl products from thioacidolysis degradation of β-O-4 structures with EOD.[4] The data from that research group appear somewhat counterintuitive. Their lowest S/G ratio amongst the 15 clones was 3.68.[4]If it is reasonably assumed that S and G units constitute 98% of the lignin,[3,10,11]then that S/G ratio corresponds to 77% S units and 21% G units. In general, S units are highly uncondensed[3,10-12]and most frequently connected via β-O-4 linkages.[10,11]If there is an increase in EOD with increasing yield of S thioacidolysis products and the lowest S content amongst the samples was 77%, then one would expect an increase in EOD with increasing S/G ratio. This raises two issues regarding lignin degradation methods as a means of determining S/G ratio. The first is obtaining a consistently high yield of G products and the second is application of correction factors or an overall correction factor to account for the fractions of the S and G units that are uncondensed. Generally, the yields of condensed products from these lignin degradation methods are very low.

Thiacidolysis does not appear to give a consistently high yield of uncondensed G products and frequently leads to erratic values for the S/G ratio. Methoxyl content values for eucalypti lignins are widely published and they rarely correspond to an S/G ratio >2.0.[20-23]Also, in one of the most cited paper on the composition of eucalyptus lignin, the S/G ratio of *Eucalyptus grandis* was 1.72.[10]

Nitrobenzene oxidation (NBO) appears to afford high yields of G units more consistently and if the uncondensed products are quantified as coming from the uncondensed S and G units only then the S/G ratio is close to that obtained from methoxyl analysis. This is demonstrated in Table 1 for 4 hardwood lignins with S/G varying from 1.25 to 2.11.[7,24] If it is assumed that ~63% of the G units and ~90% of the S units are uncondensed, then the yield of G products can be divided by 0.63 and yield of S products divided by 0.90. This leads to a correction factor of 0.70 (0.63/0.90). The two S products quantified in NBO are syringylaldehyde and syringic acid. The corresponding products from G units are vanillin and vanillic acid that can be abbreviated by the letter (V). The corrected S/G ratio can then be represented by equation (1).

$$\frac{S}{G} - Corr = 0.70\frac{S}{V} \qquad (1)$$

It should be noted that Santos *et al.* recently analyzed 10 different milled wood lignin (MWL) samples for S/G ratio by NBO and ^{13}C NMR.

They arrived at a correction factor of 0.806 instead of 0.7 in equation (1).[17]

Equation (1) should be considered as semi-empirical because the uncondensed G and S fractions do vary. The reported values for the G fraction vary from ~53%[7] to ~67%,[12] while it varies from ~84%[22] to ~96%[12] for the S fraction.

The second publication showing no significant correlation between EOD and S/G ratio is much more interesting because the ten eucalyptus samples were harvested from 10 different sites. Also, NBO was used for S/G determination and product yields were high for all 10 samples.[19]

Table 1

S/G ratio of native hardwood lignins estimated by methoxyl analyses and NBO

Sample	S/G by Methoxyl	S/G-Corr[1] by NBO	Ref.
Sugar maple	1.25[2]	1.25	7
Eucalyptus	1.72[3]	1.85	24
Eucalyptus	1.72[3]	1.72	24
Eucalyptus	2.06[3]	1.98	24

[1] In accordance with equation (1)

[2] Methoxyl analysis performed in organosolv lignin

[3] Methoxyl analyses performed on woodmeal; minimum value of 7.7 wt% OCH_3 on wood

The NBO method is most accurate when a high yield of G products is obtained. When the three eucalypti with highest G product yields were compared, the S/G ratios were 2.0, 2.2 and 2.4 (corrected values, according to equation (1), of 1.4, 1.5 and 1.7). The lignin content of the three samples varied from 29.2% to 31.7%, while the hemicelluloses content varied from 20.6% to 22.0%.[19] When the 3 eucalypti were kraft delignified by the Lo-Solids cooking approach to kappa number 18.0 ± 0.3, the effective alkali required were 19.0% Na_2O, 15.5% Na_2O and 17.0% Na_2O for the S/G ratio of 2.0, 2.2 and 2.4, respectively.

This topic is of great significance to all hardwood breeding programs. The present research investigated the effect of S/G on delignification amongst poplars and eucalypti. Delignification was extended beyond kraft pulping into elemental chlorine-free (ECF) bleaching stages. It is possible that during kraft pulping, unreactive resinol structures may accumulate to varying degree amongst hardwood samples. However, most of the resinols in hardwood (>85%) contain two syringyl units[25,26] and S units are known to be more reactive towards most oxidative bleaching chemicals due to the extra electron-donating methoxyl group.[27] Also, lignin-carbohydrate complexes (LCC) are known to retard the delignitication of hardwoods in both alkaline pulping and bleaching.[6,28-31] LCC contents were quantified for the residual lignins enzymatically isolated from some eucalyptus pulps.

EXPERIMENTAL

Wood supply

Six poplars, which were previously described,[12] were harvested in Wisconsin, USA after 9.5 years of growth. Four different *E. grandis* x *E. urophylla* hybrids were harvested from three different States in Brazil. The logs were debarked and chipped in either the USA or Brazil, but all samples were screened in the PBE Department, SUNY ESF, Syracuse, NY.

Kraft pulping

All the pulps were produced by batch cooking with liquor recirculation and a 4:1 liquor to wood (L:W) ratio. For the poplars, 15% active alkali (NaOH and Na_2S added on a Na_2O basis) on chips and 25% sulfidity were used, i.e. $Na_2S/(NaOH + Na_2S)$ on a Na_2O basis. The time to reach the maximum temperature of 165°C was 90 min (H factor 77) and the duration at 165°C was 90 min (H factor 915). Various cooking profiles were used for the eucalypti. Those chips were cooked at H factor 658 and 858 corresponding to 90 min to 160°C (H factor 56), followed by 90 min at temperature (H factor 602) and 120 min at temperature (H factor 802). When cooking temperatures of 155°C and 165°C were used, the H factor to achieve maximum temperature were 29 (60 min to 155°C) and 77 (90 min to 165°C), respectively. The H factor for 1.0 h of cooking at 155°C is 260, while the value at 165°C is 610. Active alkali doses of 17%, 19% and 21% Na_2O on chips were investigated (25% sulfidity in all cases).

Chelation treatment

Q-stage: 0.2% Na_5DTPA and 2.5% SO_2 on pulp (from $NaHSO_3$), 3% consistency, 80°C for 60 min. The initial (and end) pH was adjusted to 5.0-5.2 by dilute HCl.

Bleaching conditions

O-Stage:Conducted in a Quantum Mark IV reactor at 12% consistency, 0.72 MPa of O_2, 2.0% NaOH, and 0.5% $MgSO_4.7H_2O$ on pulp at 90°C for 60 min.

P-Stage: In plastic bags at 12% consistency, 80°C, 2 h and with 0.5% $MgSO_4.7H_2O$, 2.0% H_2O_2, and 3.0% NaOH on pulp. The chemicals were mixed into the fibers at room temperature, heated to approximately 80°C in a 1.1 kW microwave oven and then placed in a water bath.

D_0-Stage: In plastic bags at 10% consistency, 70°C, 60 min with initial pH adjusted with H_2SO_4 to approximately 4.0 (before the addition of $C1O_2$) and end pH 2.6-3.0. A ClO_2 dosing factor of 0.076 (%$C1O_2$/incoming kappa number) was used on all occasions. The chemicals were mixed in at room temperature and heated in a microwave as described above.

E_P-Stage: In plastic bags at 12% consistency, 80°C, 2 h with 2.0% NaOH, 0.25% H_2O_2 and 0.1% $MgSO_4.7H_2O$ on pulp. The chemicals were mixed in at room temperature and heated in a microwave as described above. The end pH was always greater than 11.2.

D_1-Stage: In plastic bags at 10% consistency, 70°C, 3 h, and 0.5% ClO_2 on pulp. A small dose of sodium hydroxide (0.0%-0.15% on pulp) was used to ensure an end pH in the range of 3.7-4.5. The chemicals were mixed in at room temperature and heated in a microwave as described above. One-half of the pulp was bleached in this final stage and the treatment was repeated with the other half, if effluent end pH was outside of the range mentioned above.

Analyses

All wood meals (30 mesh) were toluene/ethanol extracted as previously described.[12]Lignin content determination and nitrobenzene oxidation (NBO) analysis are described in the same publication.[12] Residual lignin was isolated from pulps by the dioxane/water/HCl method of Gellerstedt *et al.*[32] Acetylation and ^1H NMR analyses were done by the methods of Lundquist, using deuteriochloroform and a 300 MHz Bruker AVANCE 300 spectrometer.[33]Pentafluorobenzaldehyde was used as an internal standard in ^1H NMR analyses.[34,35] Quantification of LCC in pulps was performed by the method of Nicholson *et al.*[6,30,31]

RESULTS AND DISCUSSION

Delignification of poplars

The lignin content and S/G ratio (corrected) of the six poplars were previously described in the literature.[12] The six poplars were kraft delignified under the standard condition (Experimental) and the results are summarized in Figure 2. It appeared that the kappa number of the unbleached pulp decreased as the corrected S/G ratio increased from 1.12 to 1.45. However, kappa number did not appear to decrease much further when the corrected S/G increased from 1.45 to 1.68.

One possibility is that even though the kappa number of the unbleached pulps with S/G ratio of 1.45 and 1.68 were nearly equal (20.4 and 19.1, respectively), the pulp made from the chips with S/G of 1.68 contained a lignin with a higher concentration of reactive S units. If that were to be the case, then that pulp should be more responsive to O_2 delignification. However, the extent of the O_2 delignification was equal for both pulps, i.e. kappa 20.4 to 9.5 or 53% for S/G= 1.45 versus 19.1 to 9.0 or 53% for S/G=1.68. The correlation between O_2 kappa number and initial S/G ratio is also shown in Figure 2 for the six chip samples. The trend is similar to that for unbleached kappa number. There was a significant decrease in O_2 kappa number going from S/G ratio of 1.12 to S/G ratio of 1.45, i.e. 14.3 to 9.5. However, for the S/G range of 1.45 to 1.68 the four O_2 kappa number values fell in the narrow range of 8.9-10.1.

It was decided to switch from poplars to Brazilian eucalypti, decrease the number of chip samples and investigate a broader range of lignin characteristics and pulping and bleaching conditions. The lignin characterization would include quantification of LCC.

Delignification of eucalypti

The lignin content and NBO results for four eucalypti are presented in Table 2. The NBO product yield was >40 mole% for all samples, with the minimum yield of G products being 11.9 mole%. The S and G products are shown in Figure 3. There was no correlation between S/G ratio and lignin content for the four samples. Lignin content varied from 25.6% to 27.9%, while uncorrected S/G ratio varied from 2.41 to 2.69 (1.68-1.88 corrected). The two samples with highest and lowest S/G ratio (A and B) were chosen for detailed investigation, as related to their pulping and bleaching characteristics. Later on, Sample C was investigated to see if there was evidence for a correlation between S/G and EOD amongst three samples.

All of the kraft pulping results are summarized in Table 3 and it does appear that sample A (S/G = 2.69) delignified easier than sample B (S/G= 2.41). The first set of experiments was with a high alkalinity (21% Na_2O on chips) and a low H factor (658). This was to aid the sample with the lower S/G ratio (higher G content). Alkaline condensation occurs primarily between G units[13] and the rate of lignin-lignin condensation appears to be higher at lower alkalinity.[36] Lignin-lignin condensation should be minimal at the high alkalinity and low H factor that were used. There was no difference in EOD between chip samples A and B under these cooking conditions (alkalinity and H factor) at 155°C, 160°C or 165°C (Table 3). There was also no difference in EOD between the two chip samples when the Na_2O dose was decreased to 19.0% on chips at H factor 658. However, when the Na_2O dose was decreased to 17.0% on chips, sample A achieved kappa number 18.7, while sample B achieved a value of 19.6. Both pulps were oxygen delignified in duplicate and sample A achieved an average kappa number of 10.4 (average of 10.1 am 10.6), while sample B achieved an average value of 10.8 (10.7 and 10.9) (Table 3).

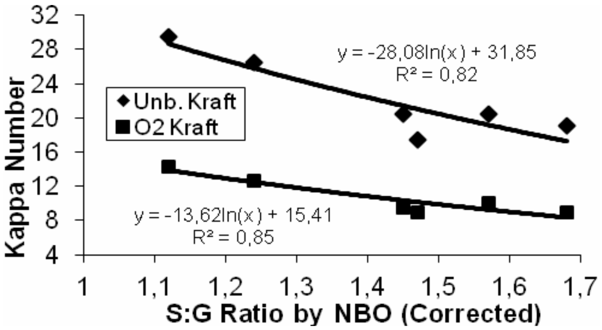

Figure 2: Effect of S/G ratio on the delignification of six poplars harvested from the same site

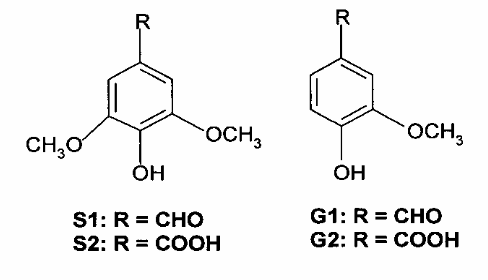

Figure 3: Major products from nitrobenzene oxidation (NBO) of hardwood lignin

Table 2
Lignin content and S/G ratio of four Brazilian eucalypti

Sample	Lignin content, %	Yield from NBO[1] S1+ S2	Yield from NBO[1] G1+ G2	S/G	S/G-Corr.[2]
A	26.9	35.2	13.1	2.69	1.88
B	26.5	29.6	12.3	2.41	1.68
C	27.9	30.0	12.2	2.46	1.72
D	25.6	31.1	11.9	2.61	1.83

[1] Mole% based on lignin with assumed C_9 molecular weight of 212; S and G products shown in Fig. 3
[2] Corrected in accordance with equation (1)

Table 3
Kraft cooking conditions and outcomes for three eucalypti

Chip sample	Active alkali, % Na_2O	Temperature, °C	H-factor	Total yield, %[1]	Rejects, %[1]	Kappa number
A	21.0	155	658	50.6	0.6	14.6
A	21.0	160	658	50.3	0.3	13.9
A	21.0	165	658	50.0	0.6	14.5
A	19.0	160	658	51.5	0.6	16.1
A	17.0	160	658	52.2	1.1	18.7 (10.4)[2]
A	17.0	155	858	50.9	0.1	15.7

A	17.0	165	858	50.4	0.1	15.5
B	21.0	155	658	51.4	0.8	14.6
B	21.0	160	658	51.5	0.5	14.2
B	21.0	165	658	51.0	0.7	14.6
B	19.0	160	658	51.9	0.7	16.2
B	17.0	160	658	52.9	1.2	19.6 (10.8)[2]
B	17.0	155	858	51.6	0.1	16.6
B	17.0	165	858	51.0	0.1	16.0
C	17.0	160	658	51.9	0.8	19.3
C	17.0[3]	160	658	52.3	0.6	18.7

[1]% on chips

[2]Average kappa number after duplicate O stages

[3]Duplicate cook

Table 4

QPD_0EpD_1bleaching of eucalyptus kraft pulps

	A, 155°C	A, 165°C	B, 155°C	B, 165°C
Unbleached				
Kappa number	15.7	15.5	16.6	16.0
After QP stages				
Kappa number	8.4 (8.6)[1]	8.5 (8.3)	9.0 (9.2)	8.7 (9.1)
After D_0Ep stages				
Brightness, % Elrepho	--	88.1 (88.3)[1,2]	--	86.9 (87.3)[1,3]
D_1 stage				
Brightness, % Elrepho	--	92.8 (93.1)[1]	--	92.0 (92.3)[1]

[1] Duplicate result

[2] Bleaching performed on mixture of 8.5 and 8.3 kappa number pulps

[3] Bleaching performed on mixture of 8.7 and 9.1 kappa number pulps

At a later date, sample C with S/G ratio of 2.46 was kraft delignified in duplicate under this cooking condition (17.0% Na_2O on chips). The average kappa number was 19.0 (Table 3), which is in-between the 19.6 value for S/G= 2.41 and 18.7 for S/G= 2.69. Although the data set is too limited for any conclusions to be drawn, the data show a decrease in kappa number with an increase in S/G ratio.

Samples A and B were delignified with 17.0% Na_2O on chips, but the H factor was increased from 658 to 858. Sample A achieved a kappa number of 15.7 and 15.5 at 155°C and 165°C, respectively. The corresponding values for sample B were 16.6 and 16.0 (Table 3). Bleaching results for these four samples are presented in Table 4 and the sequence started with QP stages instead of O_2. The Q stage would have normalized, to some degree, the transition metal content of the 4 samples. The full sequence was QPD_0EpD_1. Sample A achieved duplicate QP kappa numbers of 8.4 and 8.6 for the 155°C pulp and 8.5 and 8.3 for the 165°C pulp. The corresponding values for sample B were 9.0 and 9.2 for 155°C and 8.7 and 9.1 for 165°C. Sample A appeared easier to bleach. The two QP samples from the 165°C pulps were mixed and brightened by D_0EpD_1 treatment. An average kappa number of 8.4 was assumed for sample A (8.5 and 8.3 from above), while 8.9 (8.7 and 9.1 from above) was assumed for sample B. The average final brightness for sample A was 93.0% Elrepho for sample A and 92.2% for sample B (Table 4).

The chip sample with higher S/G ratio definitely had superior EOD, but since only two samples were extensively compared it was though necessary that the lignin in the unbleached pulps should be analyzed. For example, NBO and/or methoxyl analyses would show if S units are indeed solubilized at a higher rate during kraft cooking. These two analyses were performed; NBO was performed on pulp directly, while ^1H NMR was used to determine the methoxyl content of the isolated lignin, as described in the Experimental section.

NBO was the first approach attempted and the three A samples made with 21.0% Na_2O at 155°C, 160°C and 165°C were analyzed. At a later date, the duplicate pulps from sample C were mixed (kappa number 19.0 assumed) and analyzed. The results are summarized in Table 5 and it can be seen that for sample A, uncorrected S/G ratio fell from 2.69 in the chips to values of 1.10, 0.91 and 0.88 for 155°C, 160°C and 165°C, respectively. When pulp C was analyzed, the S/G ratio fell from 2.46 in the chips to 1.21 in the pulp. These results would suggest that S units are solubilized to a much higher degree than G units. However, the credibility of NBO for S/G determination in pulps is not yet well established.

Table 5
Analyses of lignin in eucalyptus kraft pulps by NBO

Sample	Kappa number	Yield from NBO[1] S1+S2	Yield from NBO[1] G1+G2	S/G[2]
A, 155°C	14.6	7.9	7.2	1.10
A, 160°C	13.9	6.4	7.0	0.91
A, 165°C	14.5	6.0	6.8	0.88
C, 160°C	19.0[3]	9.3	7.7	1.21

[1] Mole% based on lignin with assumed C_9 molecular weight of 212

[2] Uncorrected S/G

[3] Average for two pulps in Table 3 with kappa numbers 19.3 and 18.7

Lignins were isolated from the same four samples, acetylated and analyzed for methoxyl content by ^1H NMR. A typical spectrum for the pulp lignins is shown in Figure 4. The three peaks of main interest[33] were fairly well resolved on all occasions. Those peaks are protons from aliphatic acetates (1.8-2.2 ppm), aromatic acetates from phenolic hydroxyl groups (2.2-2.4 ppm) and methoxyl groups (3.6-4.0 ppm). All of the pulps contained ~0.5 phenolic hydroxyl (PhOH) and ~0.8 aliphatic hydroxyl groups per C_9 units. The ~0.5 PhOH value is typical for lignin isolated from kraft pulps by dioxane/water/HCl.[37] The methoxyl contents for the sample A pulps made at 155°C, 160°C and 165°C were 1.29, 1.23 and 1.14 OCH_3/C_9, respectively. The value for pulp C lignin was 1.14 OCH_3/C_9. All of these values correspond to an S/G ratio <1.0. If it is assumed that S and G units comprise 98% of hardwood lignin, then an S/G ratio of 1.0 would correspond to 1.47 OCH_3/C_9, i.e. 0.49 (from G units) + 2 x 0.49 (from S units).

Both the NBO and ^1H NMR results would suggest that S units are much more reactive that G units in kraft cooking; so much so that there should be an unambiguous correlation between S/G ratio and EOD. However, this was not seen when the poplar samples were analyzed. Could it be that above a certain critical value of the S/G ratio, the difference in EOD is due to other lignin characteristics? We decided to investigate the LCC contents of the pulps. This decision was based on the fact that we had a repeatable and reproducible method already developed for the LCC quantification[6,30,31] and a substantial amount of data showing that the LCC content correlates with EOD in both alkaline pulping[30] and bleaching with O_2, H_2O_2 and ClO_2.[31] In the method, cellulase and hemicellulase enzymes are used to degrade and solubilize almost all of the carbohydrates. The residual lignin containing only the strongly bound sugars is then recovered by precipitation in dilute acid. The residual or enzymatic lignin (EL) is then treated with 4% H_2SO_4 at 121°C to liberate the carbohydrates and convert them to monomers.

The EL were isolated from the four pulps made at the H factor 858 (Table 3) and their bound sugars were hydrolyzed by sulfuric acid and quantified by ^1H NMR.[6,30,31] Two of the pulps were from chip sample A (155°C and 165°C),while the other two were from chip sample B (155°C and 165°C). The concentration of sugars hydrolyzed from the ELs is presented in Table 6. The two pulps from chip sample B pulp contained ~50% more bound glucan and xylan than the corresponding pulps from chip sample A.

In prior research using a 61.4 kappa number kraft pulp from sugar maple (*Acer saccharum*), it was observed that lignin oligomers containing glucan-rich LCC accumulated in the fibers when they were delignified by O_2 and QP under alkaline conditions and ClO_2 at the end pH 4.0, 2.9 or 2.1.[31] For example, when the unbleached pulp was delignified with ClO_2 (end pH 2.9), then extracted with 2.0% NaOH on pulp (E stage), the kappa number decreased from 61.4 to 24.2. However, when their ELs were isolated and analyzed, the EL from the unbleached pulp contained 0.15% glucan, while that from DE pulp contained 0.39% glucan[31] It is still unclear whether the glucan in the LCC was native to the wood or generated by condensation reactions during cooking. However, based on the prior results,[31] the differences in glucan contents in Table 6 should have retarded the bleachability of sample B, as compared to sample A.

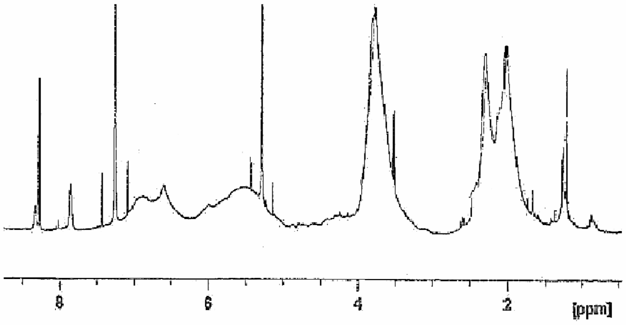

Figure 4: Typical ^{1}H NMR spectrum for acetylated lignin isolated from hardwood kraft pulps by dioxane/water/HCl

Table 6
Sugar concentrations hydrolyzed from ELs from unbleached eucalypti pulps

Sample	Kappa No.[1]	Glucan[2]	Xylan	Arabinan	Galactan
A, 155°C	15.7	0.25, 0.24[3]	0.87, 0.85	0.04, 0.04	0.30, 0.29
A, 165°C	15.5	0.21	0.88	0.04	0.28
B, 155°C	16.6	0.37	1.24	0.04	0.21
B, 165°C	16.0	0.33	1.15	0.06	0.19

[1] Pulps made with 17.0% Na_2O on chips, H factor 858
[2] Wt% on EL
[3] Duplicate sugar analyses from one EL

CONCLUSION

The effect of S/G ratio on kraft pulping and kraft pulping followed by O_2 delignification of poplars was investigated. The results showed no additional improvement in EOD when the S/G ratio was increased above a moderately high value. Kraft pulping followed ECF bleaching to>90% brightness was then investigated with two Brazilian eucalypti with S/G ratios of 2.69 and 2.41. The pulp with the higher S/G ratio had superior EOD. However, this pulp also contained less LCC, which are known to retard delignification. It is unclear as to whether the superior EOD was due to the higher S/G ratio or less LCC. More research is needed and it can't be concluded that S/G ratio is a dominant parameter governing EOD. The S/G ratio of eucalyptus pulp lignins were estimated by NBO of the pulps and ^{1}H NMR or their isolated lignin. The S/G decreased from a value of ≥ 2.46 for the lignin in two eucalyptus chip samples to ≤ 1.21 for the lignin in their kraft pulps. In general, S units appear to solubilize at a much higher rate than G units during kraft pulping.

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