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Chemical Study of the Variation in the Bleaching and Pulping Response of Predominantly Juvenile and Mature Northern Black Spruce Fractions

Douglas G. Mancosky,[†] Weiping Ban,[‡] and Lucian A. Lucia*[,§]

Hydro Dynamics, 8 Remond Court, Rome, Georgia 30165, Institute of Paper Science and Technology, Georgia Institute of Technology, 500 Tenth Street, NW, Atlanta, Georgia 30332-0620, and Department of Wood and Paper Science, North Carolina State University, 3108 Biltmore Hall, Campus Box 8005, Raleigh, North Carolina 27695-8005

A difference in the absolute brightening response was observed between predominantly juvenile and mature kraft fibers of a Northern black spruce following oxygen and peroxide bleaching. Although the initial brightness from the digester for the two wood fiber types is approximately the same (36.8 vs 36.5 for juvenile and mature, respectively), it is interesting to note that the juvenile wood has a lower brightening response than the mature wood. A potential source for the brightness difference may be the increased amount of compression wood found in the juvenile wood. Another potential source for the brightness difference may be the chemical characteristics of the lignins. The juvenile and mature pulp lignins display substantial differences in methoxyl content; the mature lignin sample possessed a greater number of methoxyl units. The methoxyl group would be expected to increase the activation energy of the aromatic rings to addition reactions in both peroxide and oxygen bleaching reactions. Further lignin differences included a higher amount of aliphatic hydroxyl groups in the juvenile lignin, while mature lignin contained a greater amount of carboxylic acid groups. Metal data from inductively coupled plasma measurements indicated that the juvenile wood is richer in manganese and iron, perhaps related to lignin functional differences that may account for inefficient consumption of peroxide.

Introduction

The properties of wood-derived paper products are mainly dependent upon the physical and chemical attributes of the wood fibers from which they are manufactured; thus, the manufacturing process must be optimized to address final customer demand. However, in-house calculations demonstrate that the single largest component affecting the economics of paper product manufacture is fiber cost.[1] It is therefore imperative that the industry efficiently utilize its fiber resources to offset increasing wood costs and diminishing wood resources.

To address the issues of wood costs and diminishing wood resources, intensive forest management and silvaculture are two methods currently being practiced in many parts of the world that have offered significant promise. Nevertheless, given the increasing wood demands and diminishing resources, an increased use of thinnings (juvenile wood trees) has been witnessed.[2] Also, it has been shown that while wood supply from natural forests continues to decline, supplies from maintained plantation forests have increased and plantation wood fiber has become the important component in the global wood supply.[2] China, for example, has plantations that are characterized by a faster growth rate and a shorter rotation age than natural stands.[3] It is known that at age twenty most of the hardwoods in these plantations possess 80−100% juvenile wood, while at age sixty only 25% is juvenile wood.[4] Several of the plantation hardwood species can be harvested quickly (10−15 years) despite wider growth rings (lower density) and higher juvenile wood content.[5]

In general, juvenile wood is a type of fiber that differs in a number of properties from mature wood.[6] It is generally defined as the wood formed near the pith. Juvenile wood is generally considered inferior to mature wood due to shorter fiber length, lower density, thinner wall thickness, and lower microfibril angle.[3] This wood is generally more pronounced in conifers such as the Northern black spruce.[4] In many instances, thinning or clearing operations have produced a higher than average proportion of juvenile wood for mill furnishes, which can influence pulping, bleaching, and papermaking operations in a variety of ways.[7] For example, the shortage of hardwood in the Southeast United States may be potentially compensated by shorter, more pliable juvenile fibers, the properties of which are similar to hardwood in opacity, smoothness, and bulk. Also, certain lightweight paper grades require high burst, but only moderate tear (found in Northern softwoods, but not Southern), which are found in juvenile wood.

Therefore, a better understanding of the physical and chemical differences in the components of wood as they relate to final fiber characteristics is essential to optimize papermaking operations. These characteristics affect the response of the fiber to pulping and bleaching. For example, a number of studies examining the pulping and bleaching response of juvenile wood have pointed to pronounced differences. Work by Kirk has shown that juvenile wood has lower pulp yields, by as much as 10−15% per unit volume of green weight compared to normal wood, a fact mainly due to the loss in cellulose.[7]

* To whom correspondence should be addressed. E-mail: lucian.lucia@ncsu.edu.
[†] Hydro Dynamics.
[‡] Georgia Institute of Technology.
[§] North Carolina State University.

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Table 1. Process Conditions Used for the Kraft Batch Pulping of Northern Black Spruce[a]

	juvenile wood (normal)	mature wood (normal)	juvenile wood (compression)	mature wood (compression)
H−factor (actual)	1703	1703	1703	1703
cook Temperature, °C	172	172	172	172
ramp time to temp., min.	90	90	90	90
liquor-to-wood ratio	4:1	4:1	4:1	4:1
percentage active alkali applied (as Na_2O)	18.5	18.5	18.5	18.5
total yield, % (unscreened)	49.8	56.6	51.1	37.8
rejects, %	0.2	0.1	0.5	0.0
screened yield, %	49.6	56.5	49.6	37.8
lignin content, %	3.5	4.3	3.9	4.9

[a] Wood chips used for pulping were air-dried.

In addition, although juvenile wood fibers contain more lignin than their mature fiber counterparts, we have found that the pulping of Northern juvenile softwood leads to higher kappa numbers (lignin content) despite lower pulp yields.[8] With respect to yield, the unbleached pulp yield of juvenile wood compared to mature wood shows a strong positive correlation with specific gravity. Juvenile wood fibers generally have a lower specific gravity than roundwood and since mill digester capacity is usually a limiting factor in pulp production, the weight of wood per unit volume determines the maximum pulp production capacity of the mill. Thus, juvenile wood will tend to restrict mill production capacity.

With respect to the bleaching of these fibers after they exit the digester, our studies have demonstrated phenomenological differences. For example, the predominantly juvenile and mature fibers of Northern black spruce display different brightness responses after oxygen and hydrogen peroxide bleaching.[9] In fact, mature wood fibers tend to brighten better than their juvenile counterparts by as much as 5 points from similar starting brightness. This result likely originates in several key features of the wood, including lignin structural components, metal levels, and differing levels of quinone and methoxyl functionalities.

The overarching goal in this paper was to obtain a chemical basis for the observed differences in pulping and bleaching response between predominantly juvenile and mature Northern black spruce fibers. The specific objectives of the work described in this paper are as follows: (1) Pulp under the same conditions a series of mostly juvenile and mature wood sections that are separated according to normal and compression wood characteristics, (2) bleach these samples equivalently, and (3) examine the fundamental chemical lignin structure, metal contents, and viscosity of both the predominantly juvenile and mature pulp samples in order to address the overarching goal of this paper. Obtaining an understanding of the pulping and bleaching responses for these general classes of wood types is critical for improving the use of diminishing regional wood supplies to address wood costs and obtain optimum properties of final paper products.

Experimental Section

Black Spruce Pulp Manufacture. A whole, defect-free black spruce that was approximately 40 years old was obtained courtesy of Consolidated Papers, Inc., (currently Stora Enso) from Wisconsin Rapids, WI and shipped to the Institute of Paper Science and Technology at the Georgia Institute of Technology in Atlanta, Georgia, for chipping at the industrial chipper. The tree sections were separated into predominantly juvenile and mature fiber sections by segregating the top 2.5 m of the tree (primarily juvenile fiber) from the thick breast height bolus. The sections were debarked by hand and split into approximately 30-cm cords for chipping. After chipping, all chips were screened for undersized and oversized rejects; all accepts were 2−8-mm chip fractions that were shipped to Potlatch Company in Duluth, MN (now SAPPI) for standard kraft batch pulping in a 10-L digester. The pulping conditions and final pulp properties are shown in Table 1.

Parallel to the pulping at Potlatch, pulping on a smaller scale (sub-L) was carried out in a multi-unit stainless steel bomb digestive system that was home-built at the in-house pulping and bleaching labs. Eight different samples could be manipulated simultaneously, and the cooking protocol was exactly the same way that the larger runs were done at Potlatch. Cooking procedures were controlled by a computer-programmed oil bath that regulated a 1.2 °C/min temperature ramp. A 50-g batch of wood chips (based on oven-dried mass) was loaded into each bomb which was the only difference between these runs and the larger scale runs (all other conditions and chemicals were scaled down appropriately for a 50-g run). All runs were done in triplicate since the amount of available pulp was much smaller than that used for the large cooks and hence a larger window of error existed for final pulp property measurement.

Black Spruce Bleaching Experiments. All bleaching was done using Kapac polyethylene bags by directly adding the pulp and chemicals (either 1.5% or 3% relative to pulp mass of a 23% H_2O_2 solution). NaOH (10%) was added to increase the pH to 11−12 while the additives (EDTA, $MgSO_4$) were added at 1% concentration relative to pulp mass. When iron was used, it was added to pulps as iron filings in 50 ppm levels relative to the pulp mass. All pulps had a solid concentration (consistency) of 10% relative to the water. The pulps were heated to temperature (70° or 90 °C) in a hot bath for 60 min. Pressurized oxygen bleaching was performed in a PARR 4282 reactor at 10% consistency. The caustic concentration by weight of pulp was 2.5% for all runs and all final pH values were 11. The oxygen pressure in the reactor was set at 90 psi and reactions were run for 60 min at 90°C.

Measurement of Hexenuronic Acid Levels in Pulps. The spectroscopic technique for the measurements of HexA content in wood fibers was done as follows: 22 mmol/L (0.6%) mercuric chloride and 0.7% sodium acetate were used to make a hydrolysis solution. A known amount of wood fibers was added to a vial that contained the above solution. The vial was then placed in a water bath with a temperature range of 60−70 °C for 30 min. After the solution was allowed cooled to room

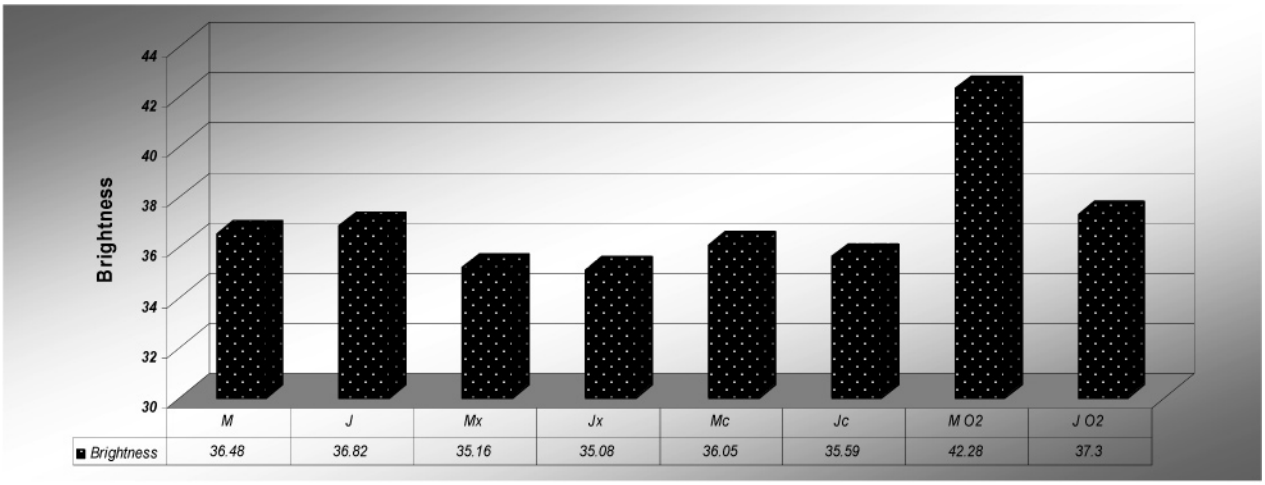

Figure 1. Brightness levels in the mature (M) and juvenile (J) pulp samples for a series of pulps whose conditions of manufacture (with a subscript) are described in the Experimental Section: oxygen delignified (O_2), chelated (c) before a hydrogen peroxide stage, and extraction (X) of extractive content after the pulping.

temperature, spectroscopic measurements of the absorption of the solution at 260 and 290 nm were conducted. The measured absorbances were used for HexA content calculations. Detailed descriptions of the mathematical methods can be found in the literature.[10]

Physical and Chemical Testing. Pulp samples were analyzed for lignin content (kappa) and viscosity using analysis methods based on TAPPI standard test methods (see T 236 cm-85 for kappa, T 230 om-94 for viscosity), while yield and rejects (nonpulped wood levels) were calculated gravimetrically based on mass balance. Brightness of the pulps was obtained by forming a handsheet using TAPPI test method T 205 sp-95 and then collecting its brightness at 457 nm (TAPPI test method T 452 om-98), a commonly used term for sample reflectance collected a very specific way and calibrated according to a magnesium oxide standard (see method for specific details) that can range from 0 to 100.

Methoxyl Measurement. The methoxyl measurement was conducted in accordance with TAPPI test methods 209 m-45 and T 2 m-60. The techniques are essentially iodine titrations that are very versatile since they can be conducted on pulp, wood, or extracted lignin.

Lignin, Extractive, and Carbohydrate Analyses. Klason lignin analyses were done in accordance with TAPPI Standard T-222 om-85. Extractives on wood chips were determined gravimetrically by Soxhlet extracting the extractives with acetone over a 24-h period. Carbohydrates (cellulose and hemicelluloses) were determined by conducting an acid hydrolysis followed by standard capillary electrophoresis. Specific gravity was determined by the maximum moisture content method.[11]

NMR Analyses. Lignin samples were isolated from the pulps according to a method previously described.[12] The pulp samples were extracted by acetone refluxing for 24 h in a Soxhlet extractorh, washed with deionized water, and air-dried. The residual lignin was isolated by refluxing with an acidic dioxane solution (0.1 M HCl in a 9:1 dioxane/water solution) for 2 h, after which the mixture was filtered, and the filtrate was neutralized to pH 6.0 with a saturated sodium bicarbonate solution. The dioxane was removed under reduced pressure. Lignin was precipitated by adding 1.0 M HCl solution at pH 2.0. The acidic mixture was transferred to centrifuge bottles and frozen to allow for lignin coalescence. Then the samples were thawed, centrifuged, and decanted. After this washing procedure, all of the lignin samples were freeze-dried. The yield of residual lignin was 60−70% based on the kappa numbers of the pulps before and after acidic hydrolysis.

The samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2 dioxaphospholane and analyzed by ^{31}P NMR following the procedure described in previous reports.[13,14] NMR spectral acquisition and analyses were controlled by a Bruker XWinNMR 2.1 software running on a SGI (Silicon Graphics Indigo) server under the Irix 7.0 operating system.

Discussion

Differences in the Bleaching Response of the Juvenile and Mature Wood Fractions. Early evidence that a difference existed for the pulping and bleaching chemistry of the two wood fiber types showed a dramatic difference in the brightness of the pulps after oxygen and hydrogen peroxide bleaching. Figure 1 shows the difference in brightness between the fiber types as a function of various treatments. The subscripts denote the treatment for the pulps: the chelation (c) treatment was done before a hydrogen peroxide stage, the oxygen (O) treatment was stand-alone after pulping, the extraction (X) was stand-alone after pulping, and the nontreated samples are designated without subscripts. The differences in brightness varied as much as 5 points (TAPPI) and were found to be independent of scattering differences. Thus, this brightening difference was attributed to absorbance (chromophore) variations arising from lignin and/or carbohydrate components. This effect was persistent even after chelation with EDTA and acetone extraction of the pulps as shown in Figure 2 which demonstrates the brightness differences between the juvenile and mature pulps as a function of various additions during two levels of hydrogen peroxide bleaching. Interestingly, we found that the mature pulp displayed higher brightness values despite chelation or chemical addition, with the exception of the addition of iron. The addition of iron inverted the brightness difference that was in effect for all of the previous conditions, a phenomenon that will be analyzed later in this discussion. Hexenuronic acid, a hemicellulose component that has been suggested to be impli-

Table 2. Chemical Composition and Specific Gravity for the Mature and Juvenile Wood (Unpulped) Samples Used in This Study

	%					
	extractives	lignin	cellulose	hemicellulose	methoxyl group	specific gravity
mature	1.11	26.16	38.9	19.1	17.8	0.384
juvenile	1.47	25.71	39.3	18.4	17.4	0.364

Table 3. General Physical Pulp Properties for the Mature and Juvenile Pulp Fibers Used in This Study

sample	brightness (ISO)	freeness (mL)	breaking length (km)	viscosity (cP)	length (mm)	coarseness (mg/m)
mature	36.48	710	15.38	22.96	2.367	0.139
juvenile	36.82	710	13.66	24.89	2.227	0.127

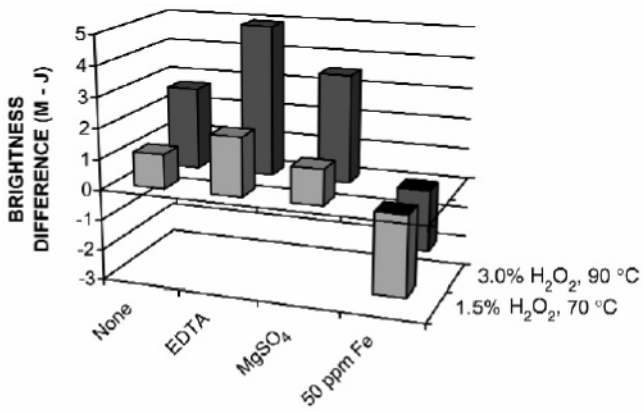

Figure 2. Peroxide bleaching differences between the juvenile (J) and mature (M) pulp samples as a function of additives during two different bleaching runs.

cated in brightness differences since it can sequester metals efficiently, was found to be similar (<0.2%) between the two wood sections.[15] We attempted to find a literature basis for the brightness differences between the two general fiber types, but found limited data, despite the fact that thinnings (juvenile wood) are becoming a greater part of the furnish in pulping operations.

Important baseline measurements were next taken on each of the wood and fiber substrates. The fiber quality data was obtained on an OpTest Equipment fiber quality analyzer (FQA). It is shown in Table 2 that the mature wood had a higher specific gravity, and methoxyl, lignin, and hemicellulose contents, whereas the juvenile wood was higher in extractives and cellulose content. All data were averaged from triplicate runs if not mentioned otherwise. After pulping the woods, the fiber qualities of the pulps were obtained, and these are shown in Table 3. In general, the mature pulp compared to the juvenile wood has a higher strength and possesses longer and thicker fibers, facts that inherently qualify these wood fibers as more "mature."

Inductively coupled plasma (ICP) analyses were run to obtain metal ion profiles, and the results for the juvenile and mature pulps before and after chelation are shown in Table 4. Of special interest is the fact that the pulps do not chelate evenly. This is probably due to differences in lignin structure, which will also be discussed later in this article. The iron levels of the pulp are more similar after chelation, but the manganese and magnesium levels are different. It was found that chelation had little to no effect on the starting brightnesses, although differences were found after bleaching. Part of the explanation for the differences can be attributed to the variation in iron content. The juvenile fibers are 42% more enriched in iron and more likely to

Table 4. Distribution of Metals (ppm) for the Juvenile and Mature Pulp Samples

metal	juvenile	mature	juvenile chelated	mature chelated
Ba	24.2	24.2	5.8	19.3
Ca	1295.0	1290.0	233.0	512.0
Cu	19.8	19.6	3.9	6.6
Fe	32.7	19.0	10.5	11.8
Mg	189.0	170.0	40.1	122.5
Mn	191.0	150.0	4.7	25.5

give rise to colored charge-transfer (CT) iron complexes between catechol or biphenyl-type structures. The metal-to-ligand CT phenomenon has been documented in the literature[16−19] and receives support from ^{31}P NMR spectra which indicate an approximate 13% greater abundance of phenolic sites for iron coordination in juvenile fibers.

Figure 3 shows the difference in methoxyl content measured in juvenile and mature pulps before and after bleaching. Vanillin, which has a 20% methoxyl content of the total phenolic units, was utilized as a control. The mature pulp for the bleaching studies had 30% more methoxyl groups when compared to the juvenile pulp. These differences were eliminated after oxygen bleaching and were not as great after peroxide bleaching. The difference in methoxyl content for the unbleached pulp is important since the methoxyl group can activate the ring for peroxide and oxygen bleaching. This could serve as a potential explanation for the brightness differences observed in bleaching. Interestingly, it was found that juvenile and mature oxygen delignified pulps have approximately equal methoxyl content compared with the original kraft pulps. This may suggest that the lignin methoxyl groups are robust and resist elimination during oxygen delignification. Therefore, there should be a higher level of methoxyl groups content in the residual lignin of oxygen delignified pulp, especially for mature wood.

The data shown in the preceding Figures 1 and 3 was more fully investigated by obtaining ^{31}P NMR and fiber quality data. All spectroscopic NMR data employing ^{31}P NMR sample preparation and spectral collection parameters have been previously published.[20] The NMR data are shown in Figure 4. We discovered that the chemical characteristics of juvenile lignin differ from mature lignin, principally in the level of lignin acid and aliphatic hydroxyl functionalities. Most importantly, the juvenile lignin had a higher level of acid groups by almost 20%. As displayed in Figure 2, the addition of 50 ppm of iron caused the brightness difference to become inverted. The juvenile pulp is therefore brighter than the mature pulp by 3 units of brightness. To rationalize a chemical basis for this phenomenon, the NMR data discussed above are critical. The mature

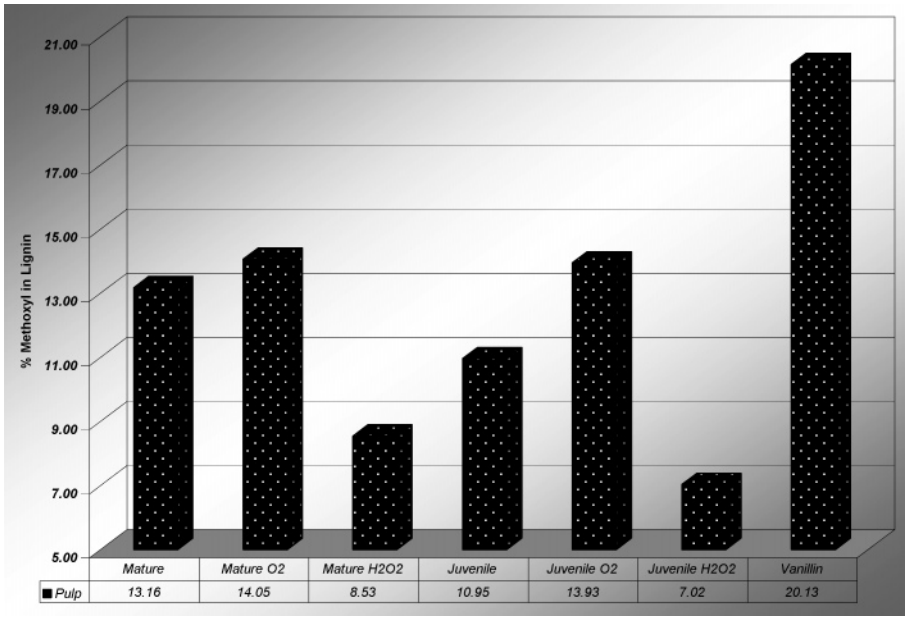

Figure 3. Methoxyl content for pulps as a function of the conditions listed in Figure 1.

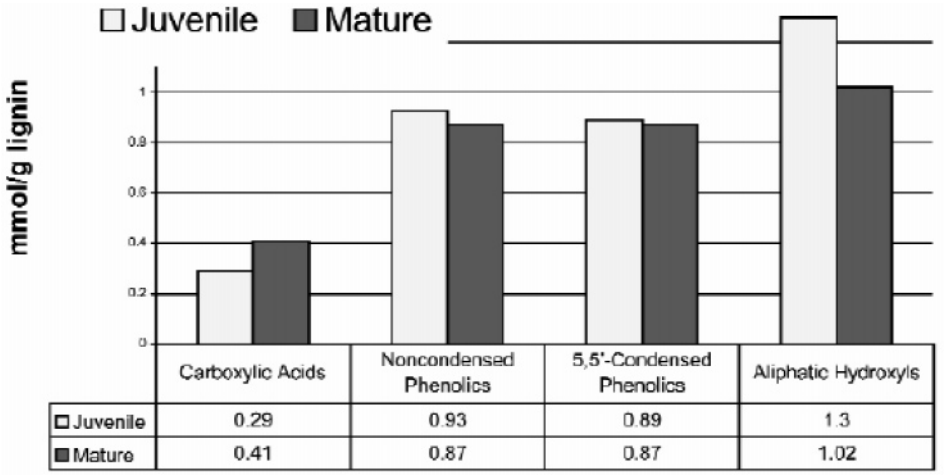

Figure 4. ^{31}P NMR functional groups in the juvenile and mature pulp fractions.

lignin has almost one-third more carboxylic acid groups than the juvenile lignin. This acid-enriched lignin is ideal for the selective chelation of multivalent iron ions.[21] Clearly, the disparity in acid levels leading to iron chelation is among the important factors underlying the brightness inversion phenomenon between the mature and the juvenile fibers.

The physical properties of the pulps were also tested by using standard CED viscosity measurements to evaluate degradation during the brightening reactions. All viscosity information was converted to the appropriate degree of polymerization (DP) which was compared to the original DP (DP_o) to yield a chain scission count ($[1/DP - 1/DP_o]DP_o$) that reflects the integrity of the cellulose chains. The larger numbers are indicative of greater chain damage. Figure 5 illustrates the degradation in the fibers as a function of selected conditions.

For the juvenile fibers, the most obvious damage was obtained with iron doping. Chain scissions of up to 0.29 were found compared to 0.03 under "mild" conditions (low temperature and hydrogen peroxide charge) with no doping. As shown in Figure 5, the effect of increasing peroxide concentration and temperature induces more damage, but the damage is not as precipitous as that found with iron doping. The underlying factor contributing to this response may be the nature of the pulp. In juvenile tree sections, it is known as confirmed in this work that there is a greater abundance of compression wood that is more difficult to pulp or bleach due to higher levels of lignin.[22] The influence of additives such as EDTA and $MgSO_4$ was not apparent until more

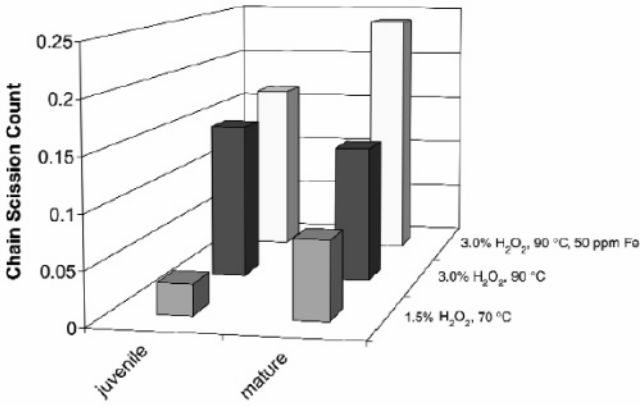

Figure 5. Chain scission count for the juvenile and mature fibers as a function of bleaching conditions.

forcing conditions (high temperature and high hydrogen peroxide charge) were used, in which case the chain scission was increased by up to 50%. The manganese ion was likely redox stabilized by inclusion in an isomorphic magnesium complex and EDTA was able to effectively compete for copper and manganese in solution.[23] Despite the efficacy of the above additives, degradation is still a concern since iron is known to undergo self-hydrolysis, chelates very strongly, and is difficult to completely remove, allowing it to engage in Fenton-type reactions that damage the pulp physical properties.

The mature pulp has a very similar response to the juvenile pulp as seen in Figure 5, but under iron doping, it has an approximately 2-fold drop in the scission count. Neither $MgSO_4$ nor EDTA is as effective for controlling viscosity as observed in the juvenile pulp. As indicated earlier (vide infra), the mature pulp has a much higher level of acids that tend to promote chelation of iron. To investigate the distribution of iron on the fiber surface, independent time-of-flight secondary-ion-mass spectroscopy (TOF SIMS) was employed for surface profiling. We found that iron tends to agglomerate in scattered pockets that form on the coarse fiber surface upon iron doping. Since it is known that the self-hydrolysis of iron disfavors EDTA trapping, the response of the mature pulp was expected, with a significant loss in pulp integrity after increasing the iron content by almost 3-fold. What was most surprising was that $MgSO_4$ was not as effective for pulp protection as witnessed in the juvenile pulp.

The juvenile fibers had a lower tensile strength (approximately 13 km) versus the mature fibers, which had breaking lengths of about 15 km. This difference was maintained throughout the bleaching runs. Wet pressing physical tests of the pulp handsheets were run in tandem and demonstrated that good bonding was observed in the fibers despite their high freeness. Since commercial sheets typically exhibit failure due to defects in individual fibers instead of relative bonded area, these studies were primarily concerned with fiber strength and evaluating how the fiber degradation associated with bleaching could be minimized.[24]

Pulping Differences in the Juvenile and Mature Wood Fractions. Pulping studies were also conducted in which compression wood was separated from "normal" wood in order to eliminate differences from a higher level of compression wood that is normally found in juvenile wood.[21] Juvenile wood had a higher percentage of compression wood than the mature wood as found from a statistical analysis of wood sections of the same length. Interesting pulping differences were observed between the compression wood and normal wood of both the juvenile and mature sections. Figure 6 illustrates the comparison of pulp yields separately derived from both compression and normal wood chips in juvenile and mature wood. Surprisingly, the juvenile compression wood provided the same-screened pulp yield as normal wood. But a tremendous difference was observed in mature wood where the compression wood exhibited almost a 20-percentage point lower screened pulp yield compared to normal wood.

Figure 7 illustrates the pulp kappa numbers. Not surprisingly, the pulp produced from juvenile compression wood displayed a higher kappa number than pulp produced from normal juvenile wood. Yet, both the compression and normal mature wood had a significantly higher kappa number, by over five kappa units (almost 1% more lignin mass) than their respective juvenile wood counterparts. The given data unequivocally demonstrate that both the compression and normal sections of juvenile wood pulp similarly. Although a much lower pulp yield was obtained using mature compression wood, a simultaneously higher kappa number also was observed, almost as much as 4 points higher than the normal pulp. The kappa data for this portion of the study run contrary to the kappa data obtained in the pulping for the bleaching work. A key difference, however, is the fact that the normal and compression wood were separated for the pulping work. This allows for a more homogeneous cook for the juvenile wood due to its high compression wood content. Compression wood usually contains more lignin and lower amounts of cellulose as compared to normal wood and it would be reasonable to obtain a lower yield and a higher kappa number pulp from compression wood pulping. The high density of this wood may reduce the efficiency of cooking liquor penetration and slow delignification, but a negligible amount of rejects from mature compression wood pulping indicated that the denser compression wood structure did not affect pulping. The main reason for poor delignification in compression wood can be ascribed to inherent lignin structural characteristics.[25]

Figure 8 illustrates the comparison of pulping selectivity for various pulp samples. Pulping selectivity,

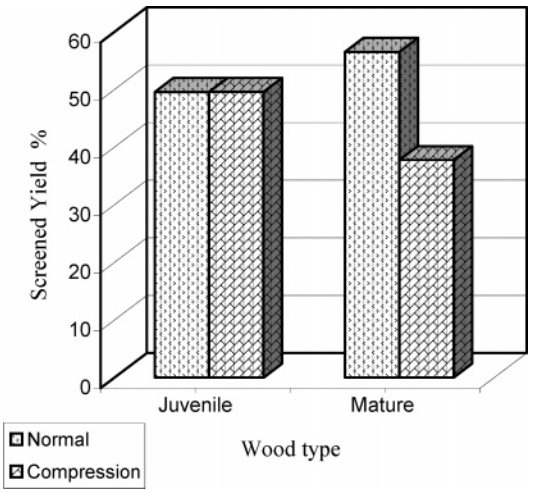

Figure 6. Comparison of pulp yield between the juvenile and mature pulp samples.

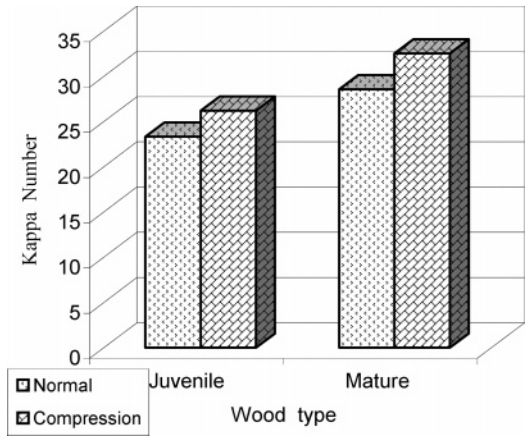

Figure 7. Comparison of kappa numbers for normal and compression wood in the pulp samples.

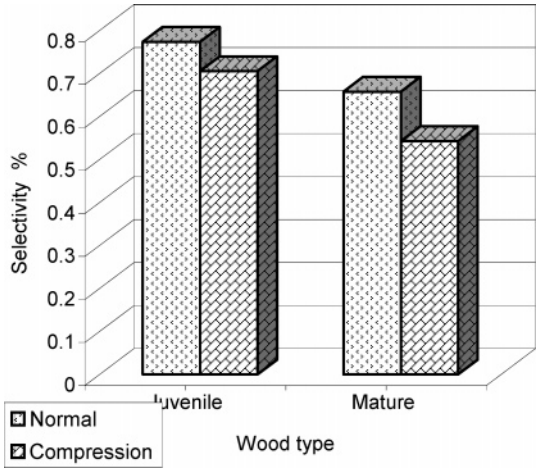

Figure 8. Comparison of pulping selectivities.

defined as the ratio of viscosity to kappa number, compares the level of carbohydrate retention to lignin removal during the pulping process. Overall, the pulping selectivity from mature wood in the case of both normal and compression is lower than that of juvenile wood, which indicates that the mature lignin structures become more difficult to delignify during the pulping process. On the other hand, the compression wood showed a lower selectivity than normal wood. In the case of juvenile wood, its compression wood showed a lower pulping selectivity (8.8% lower) than normal wood. The selectivity difference between compression and normal wood increased to 17.5% in the mature wood case. Furthermore, an interesting comparison was obtained from a simple analysis of the juvenile and mature woods: the selectivity in the normal and compression pulped wood decreased 15% and 23.1%, respectively, an 8-percentage point difference. The compression and normal comparisons in both the juvenile and mature woods showed a pulping selectivity decrease of 8.8% and 17.5%, respectively, an 8.7-percentage point difference. Thus, the close pulping selectivity difference data imply that a change in the lignin structure of compression wood from juvenile to mature may be a critical factor for reducing pulping efficiencies.

Conclusions

The physical and chemical characteristics of predominantly juvenile and mature fibers obtained from the same black spruce tree (*P. mariana*), have been shown to differ in their pulping and bleaching responses. Factors that may account for such differences include metals distribution, methoxyl content, lignin functional group characteristics, and specific gravity. Mature fibers, in general, after either hydrogen peroxide bleaching or oxygen delignification, display a greater propensity to brighten, but also tend to degrade at a faster rate than the juvenile fibers. The 30% more methoxyl groups in the mature wood could serve to activate the ring to peroxide and oxygen bleaching. This result may be a function of the differing metal distribution found in the fibers or the lignin structural characteristics.

Mature and juvenile fibers also pulped differently. The results demonstrate that juvenile compression wood has pulping characteristics similar to those of juvenile normal wood, except slightly lower delignification selectivity. On the other hand, mature compression wood exhibited poorer pulping properties such as a lower pulp yield, a higher kappa number, and lower delignification selectivity.

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Literature Cited

(1) Baum, G. A. Fiber Engineering: The Key to Industry Change. *Solutions!* **2002**, 42.

(2) Robertson, D.; Hamel,-M. P. *North American Wood/Fiber Supplies and Markets: Strategies for Managing Change*; Forest Products Research Society: Madison, WI, 1987.

(3) Cooper, R. J. Changing Patterns of Global Wood and Fiber Supplies. *Chem. Process. Wood Plant Fibrous Mater.* **1996**, 13.

(4) Bao, Z. H. Differences in Wood Properties between Juvenile Wood and Mature Wood in 10 Species Grown in China. *Wood Sci. Technol.* **2001**, *35*, 363.

(5) Bhat, K. M.; Priya, P. B.; Rugmini, P. Characteristics of Juvenile Wood in Teak. *Wood Sci. Technol.* **2001**, *34*, 517.

(6) Bao, Z. H. Studies on the Properties of Wood from Fast-Growing Forest Plantation. *World For. Res.* **1994**, *7*, 340.

(7) Zobel, B. S. *Juvenile Wood in Forest Trees*. Springer: Berlin, 1998.

(8) Kirk, L. G.; Zobel, B. J. A Pulping Evaluation of Juvenile Loblolly Pine. *TAPPI J.* **1972**, *55*, 1600.

(9) Ban, W.; Mancosky, D.; Lucia, L. A. Evaluation of the Pulping Response of Juvenile and Mature Black Spruce Compression Wood. *Cell. Chem. Technol.* **2004**, in press.

(10) Chai, X.-S.; Zhu, J. Y.; Li, J. A Simple and Rapid Method to Determine Hexenuronic Acid Groups in Chemical Pulp. *J. Pulp Paper Sci.* **2001**, *27* (5), 165.

(11) Mancosky, D. G.; Lucia, L. Use of TOF-SIMS for the Analysis of Surface Metals in H_2O_2-Bleached Lignocellulosic Fibers. *Pure Appl. Chem.* **2002**, *73*, 2047.

(12) Gellerstedt, G.; Pranda, J.; Lindfors, E.-L. Structural and Molecular Properties of Residual Birch Kraft Lignins. *J. Wood Chem. Technol.* **1994**, *14*, 467.

(13) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignin. *J. Agric. Food Chem.* **1995**, *43*, 1538.

(14) Argyropoulos, D. S. Quantitative Phosphorus-31 NMR Analysis of Lignin, a New Tool for the Lignin Chemist. *J. Wood Chem. Technol.* **1994**, *14*, 45.

(15) Smith, D. M. *Maximum Moisture Content Method for Determining Specific Gravity of Small Wood Samples*; U.S. Department of Agriculture: Madison, WI, 1954.

(16) Granstrom, A.; Gellerstedt, G.; Eriksson, T. On the Chemical Processes Occurring during Thermal Yellowing of a TCF-Bleached Birch Kraft Pulp. *Nord. Pulp Pap. Res. J.* **2002**, *17*, 427.

(17) Ghosh, A.; Ni, Y. Metal Ion Complexes and Their Relationship to Pulp Brightness. In *9th International Symposium on Wood and Pulping Chemistry*; TAPPI Press: Atlanta, GA, 1997.

(18) Meshitsuka, G.; Nakano, J. Effect of Metal Ion on Color of Lignosulfonate and Thiolignin. *TAPPI J.* **1973**, *56*, 105.

(19) Polcin, J.; Rapson, W. H. Sapwood and Heartwood Groundwood of Western Hemlock and Jack Pine. III. Influence of Solvent Extraction on the Bleaching of Pulps. *Pulp Pap. Can.* **1972**, *73*, 86.

(20) Jiang, Z. H.; Argyropoulos, D. S. 2-Chloro-4, 4, 5,5-Tetramethyl-1,3,2-dioxaphosolane. A Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43*, 1538.

(21) Werner, J.; Ragauskas, A. J.; Jiang, J.-E. Intrinsic Metal Binding Capacity of Kraft Lignins. J. *Wood Chem. Technol.* **2000**, *20*, 133−145.

(22) Wadenback, J.; Clapham, D.; Gellerstedt, G.; Von Arnold, S. Variation in Content and Composition of Lignin in Young Wood of Norway Spruce. *Holzforschung* **2004**, *58*, 107.

(23) Líden, J.; Ohman, L.-O. Redox Stabilization of Iron and Manganese in the +II Oxidation State by Magnesium Precipitates and Some Anionic Polymers: Implications for the Use of Oxygen-Based Bleaching Chemicals. *J. Pulp Pap. Sci.* **1997**, 2*3*, 193.

(24) Page, D. H.; Seth, R. S. *TAPPI J.* **1988**, *71*, 182.

(25) Timell, T. E. Studies on Opposite Wood in Conifers. (1). Chemical Composition. *Wood Sci. Technol.* **1969**, *7*, 1.

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