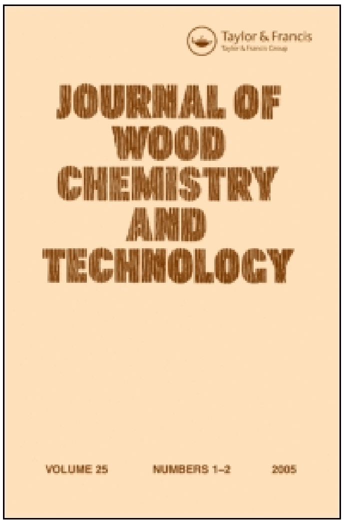

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PULPING AND BLEACHING OF PARTIALLY CAD-DEFICIENT WOOD

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ABSTRACT

Mutant loblolly pine trees that are partially deficient in cinnamyl alcohol dehydrogenase (CAD) have been studied as a possible new source of pulpwood. Young (4- and 6-year-old) partially CAD-deficient pine trees are ~20% more easily delignified (pulping and bleaching) and provide similar pulp yields to that of similarly aged normal pines grown on the same plots. Bleached pulp from a 6-year-old partially CAD-deficient pine tree displayed better strength properties than the same age normal pine tree; this probably reflects the milder pulping conditions needed in the case of the partially CAD-deficient tree. Studies also were conducted on a limited number of 14-year-old trees from a different genetic back-

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ground. In contrast to the results with young trees, no real differences in ease of delignification, pulp yields, bleached pulp strength properties, and wood specific gravities were observed with the 14-year-old trees. There would likely be no penalty if partially CAD-deficient trees were used for lumber products. The rapid growth of partially CAD-deficient trees could make them a valuable pulpwood.

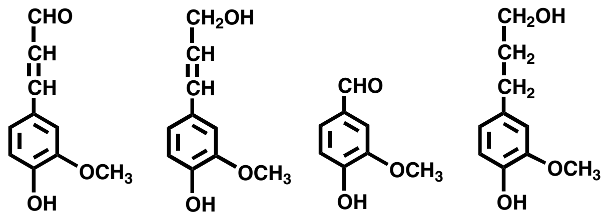
Key Words: Pulping; Bleaching; Kraft; Lignin; Cinnamyl alcohol dehydrogenase; CAD-deficient; Loblolly pine; Mutant

INTRODUCTION

Chemical pulp production involves two steps, pulping and bleaching, which are geared to remove the lignin in the wood. Opportunities exist for very large improvements in pulp production efficiency if trees contained an easily degraded lignin. Such trees could be pulped in much shorter time periods, providing pulps with less carbohydrate damage. The focus of our research is to exploit the genetic variation in lignin biosynthesis genes that occurs naturally in forests and to evaluate opportunities to select trees that contain easily degraded lignin.

By genetic selection, loblolly pine trees with substantially altered lignins have become available.[1] These trees are deficient in an enzyme, cinnamyl alcohol dehydrogenase (CAD), because of a mutant gene, the *cad-n1* allele. The CAD enzyme catalyzes the reduction of coniferaldehyde (**1**) to coniferyl alcohol (**2**).[2,3] The latter is oxidized and polymerized to give "normal" lignin. Two types of mutant trees are available: partially and totally CAD-deficient.[1,4] Lignins from totally CAD-deficient trees are built up from coniferaldehyde (**1**), vanillin (**3**), and dihydroconiferyl alcohol (**4**).[5,6] Proof of these unusual monomers is based on the analysis of milled wood lignins by NMR[4] and whole wood samples by pyrolysis-GCMS[5] and thioacidolysis.[6] The latter technique indicates that totally CAD-deficient trees contain fewer C_β-O_4 linkages and a high number of C_5-linkages.[6] In addition, the lignin in totally CAD-deficient trees is 33% lower in molecular weight and two times higher in phenol content (38% vs. 17%) than lignin from similar-aged normal trees grown in the same plot of land.[6,7] The structure of lignin in partially CAD-deficient wood is not well understood and is under investigation.[8]

Micropulping experiments were performed on two 12-year-old loblolly pine trees, one normal wood, one totally CAD-deficient, both grown on the same site from the same parents. The totally CAD-deficient tree was much



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more easily delignified, but the pulp yields were relatively low (~33%) in comparison to the normal pine tree (48%).[7] Our findings suggest that tremendous benefits are possible by developing forests of trees that contain modified lignins. However, totally CAD-deficient loblolly pine trees do not appear to be the ideal wood raw material because of poor pulp yields and poor tree growth. [These characteristics may be a result of extensive inbreeding.] Partially CAD-deficient loblolly pines, on the other hand, show an increase of 14% in debarked volume after four years of growth in comparison to normal trees.[9]

RESULTS AND DISCUSSION

Pulping of Young Trees

We identified partially CAD-deficient and normal loblolly pine trees among two open-pollinated families with the same maternal genetic background by using DNA fingerprinting of the *cad* gene locus. The fingerprinting used haploid genomic DNA isolated from the megagametophyte removed from each seedling in the nursery.[9] The first family was comprised of 4-year-old trees; its fingerprinting has been previously described.[9] The second family was comprised of 6-year-old trees grown on a different site. For both families, several trees from each genotypic class (partially CAD-deficient and normal) were chipped together to form mixtures of chips representing each class.

We conducted over three dozen kraft cooks of the 4- and 6-year-old trees. Data examples are shown in Figs. 1 and 2. Figure 1 compares a mixture of three 4-year-old trees/set and Fig. 2 a 6-year-old partially CAD-deficient tree to two normal trees. The kappa number (lignin content) was significantly lower for partially CAD-deficient wood vs. normal pine. Roughly 25% less H-factor (energy) was needed to reach a 30-kappa pulp in the case of the partially CAD-deficient wood. There was no significant difference in pulp yields between the two types of wood.

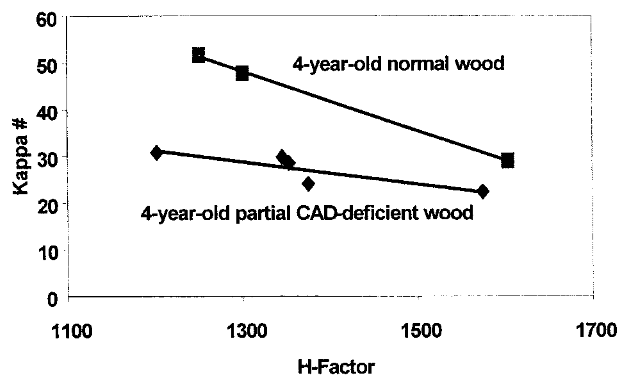

Figure 1. Delignification comparison of kraft cooking of pooled partially CAD-deficient and normal pine wood.

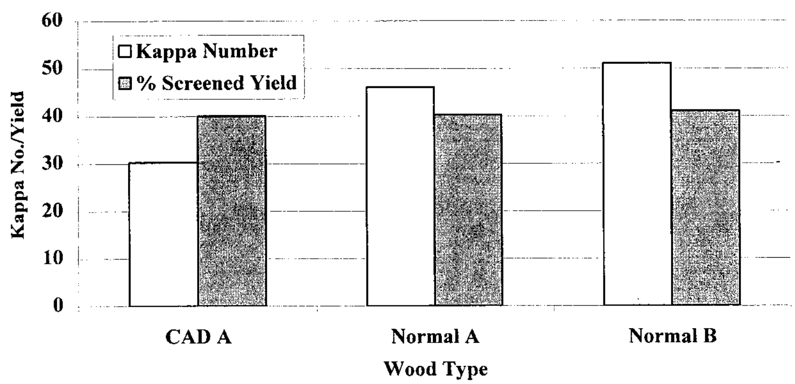

Figure 2. Delignification comparison of kraft cooking of pooled partially CAD-deficient and normal pine wood.

To further investigate the impact of genotype on pulping, we performed several kraft cooks on individual partially CAD-deficient and normal-type wood. The 6-year-old trees were pulped with 18% alkali and 25% sulfidity to a 1300 H-factor. Four trees from each genotype were pulped. On average the partially CAD-deficient wood had a kappa number seven units lower than the normal control (Table 1).

In addition, kraft cooks were conducted of a single partially CAD-deficient tree and single normal tree, both six years old, at different H-factors (Fig. 3). A trend similar to the pooled cooks (Fig. 1) was observed. At a low H-factor large differences in kappa number were observed. As the H-factor

Table 1. Kappa Number of Individual Tree Kraft Cooks at 1300 H-Factor

Tree #	CAD-Deficient	Normal
1	29.9	35.9
2	31.4	41.5
3	34.1	37.3
4	30.7	38.2
Average	31.3	38.2

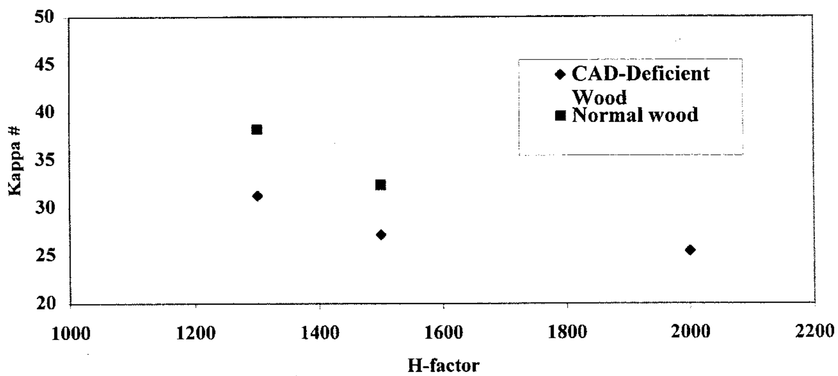

Figure 3. Delignification comparison of individual partially CAD-deficient and normal trees; 800 g of Chips, 18% A.A., and 25% sulfidity; 4 : 1 L/W ratio.

Table 2. Kappa Number and Yield Data Comparison of Soda/AQ Cooking of 4-Year-Old Partially CAD-Deficient and Normal Pinewood at ∼2080 H-factor

Wood Type	% Screened Yield	Kappa #
CAD-deficient	36.3	27.1
CAD-deficient—Duplicate	37.9	27.1
Normal	33.2	28.7

was increased, the kappa difference decreased. The data further indicate the easier delignification that exists with the partially CAD-deficient wood.

Soda/AQ cooks also provided encouraging results. While only a few cooks were done, it appears that delignification is more extensive and yields are much better in the partially CAD-deficient wood case (Table 2).

Table 3. Comparison of the Bleaching of 4-Year-Old Normal and Partially CAD-Deficient Pulps

Pulp	Stage	Temp. (°C)	Time (min)	Cons. (%)	ClO_2 (%)	NaOH (%)	Kappa	Brightness
Normal							29.1	
	Do	50	30	3.0	0.2 K.F.			
	(EO)	75	60	12		1.4	6.25	
	D_1	70	120	10	0.6	0.15		71.1
	E	70	60	10		0.3		
	D_2	70	180	10	0.4	0.1		84.8
CAD							32.7	
	Do	50	30	3.0	0.2 K.F			
	(EO)	75	60	12		1.4	6.23	
	D_1	70	120	10	0.6	0.15		74.6
	E	70	60	10		0.3		
	D_2	70	180	10	0.4	0.1		86.4

The delignification difference was not large; possibly the H-factor was too high and the partially CAD-deficient cook had already reached the slow residual phase. The kappa difference might have been much larger at shorter times. The observed low yields reflect the use of immature wood.

Bleaching and Strength Properties of Pulps from Young Trees

With identical applications of bleaching chemicals, pulp obtained from pulping a mixture of 4-year-old partially CAD-deficient wood was 3.5% and 1.5% ISO higher in brightness after the D_1 and D_2-stages, respectively, than a similar kappa normal pulp (Table 3).

The bleached partially CAD-deficient pulp was stronger (Fig. 4), mostly because of a better tensile strength. Tear and burst strength were similar. It appears that the milder cook has benefited the pulp strength in the partially CAD-deficient case.

Pulping of 14-Year-Old Trees

We used DNA fingerprinting techniques to identify partially CAD-deficient and normal (devoid of CAD deficiency) among nineteen full-sib-4-year-old loblolly pine trees, supplied to us by International Paper Company.

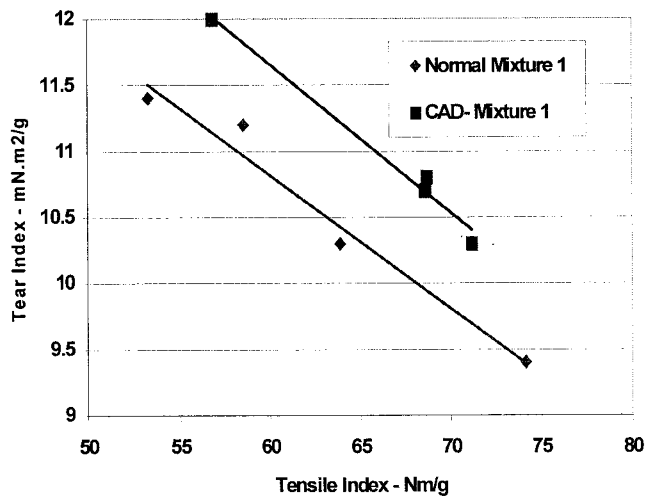

Figure 4. Tear index vs. tensile index comparison of bleached pulps from 4-year-old wood mixtures.

The trees came from six blocks within a single progeny test established near Georgetown, SC. We were able to conclusively identify seven normal and three partially CAD-deficient trees. We selected three normal trees that were from the same plot, or a closely related plot, to compare with the three identified partially CAD-deficient trees.

The results of pulping 14-year-old trees were significantly different than those observed for the young trees. Figure 5 shows the kappa numbers obtained after kraft pulping at 15.8% A.A. of the two wood types (three of each type) at two H-factors; a duplicate was done in the case of partially CAD-deficient wood source 3 to show the reproducibility of the results. The average kappa numbers obtained for the two wood types were nearly the same at 1450 H-factor; the average at 1300 H-factor appeared higher for the partially CAD-deficient wood. A set of kraft cooks at 18.5% A.A. produced the data shown in Fig. 6. Here, the kappa number across 1150–1450 H-factor was fairly flat for both woods and 2.5–4.0 lower in the CAD case; however, the values observed for duplicates raise some doubts on the degree of differences. The average pulp yields and screened yields for roughly 20 cooks of each wood were 0.9% (45.1 vs. 44.2) and 0.6% (43.5 vs. 42.9) higher, respectively, for the partially CAD-deficient compared to the normal woods.

A limited number of cooks were also conducted using 22% active alkali. Both wood types gave the same kappa number at 1300 H-factor;

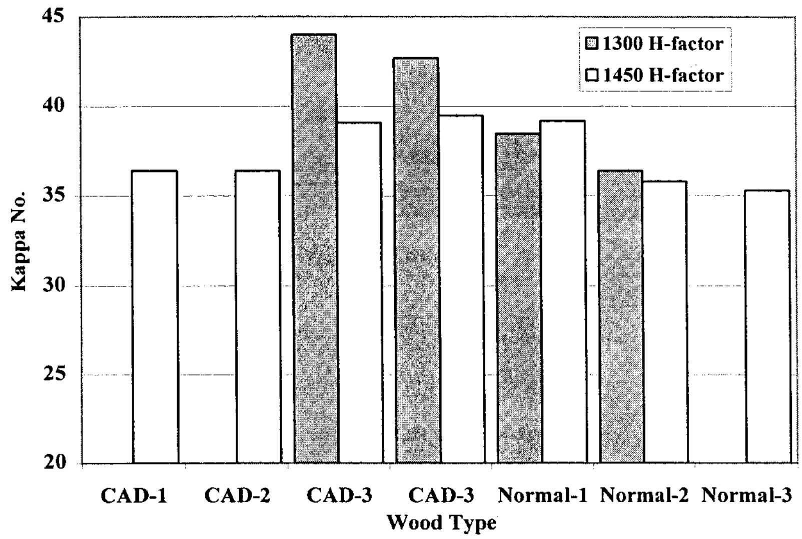

Figure 5. Comparison of the kappa numbers obtained with pulping the different wood species at two different H-factors for 1 kg cooks at 15.8% A.A. and 30% sulfidity.

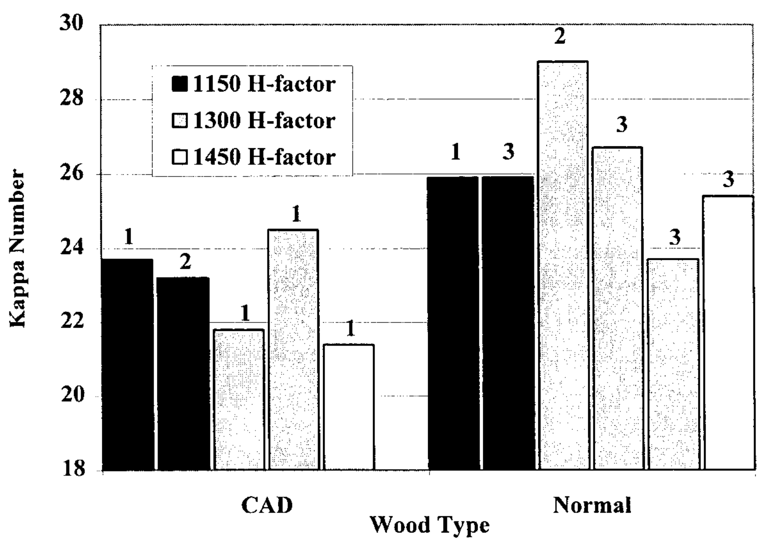

Figure 6. Comparison of the kappa numbers obtained with pulping the different wood species at different H-factors for 1 kg cooks at 18.5% A.A. and 30% sulfidity. Numbers 1, 2, and 3 refer to specific trees within the set.

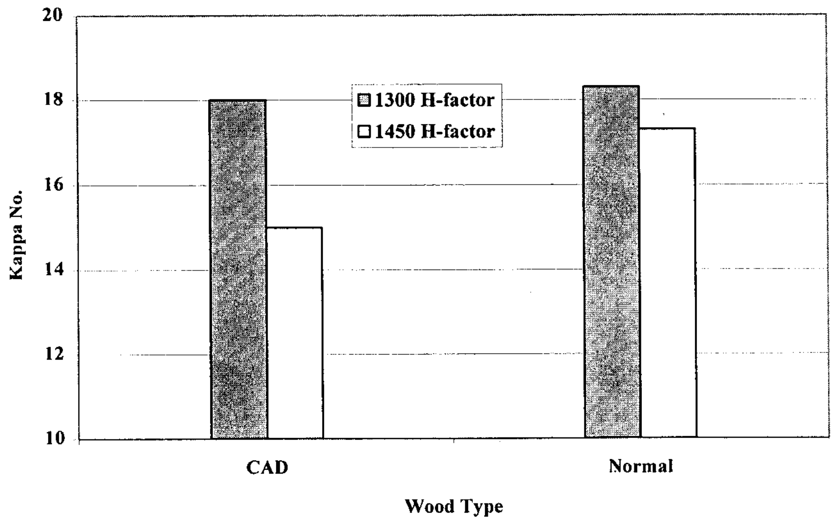

Figure 7. Comparison of the kappa numbers obtained with pulping the different wood species at two different H-factors for 1 kg cooks at 22% A.A. and 30% sulfidity.

however, the partially CAD-deficient wood pulped to a lower kappa number (15 vs. 17) when using a 1450 H-factor (Fig. 7).

Bleaching and Strength Properties of Pulps from 14-Year-Old Trees

Two pulps of similar kappa number, one from pulping a normal tree and one from a partially CAD-deficient tree, were bleached by a D(EO)DED sequence under identical conditions. The data in Table 4 clearly show that the CAD pulps were slightly easier to bleach. Figure 8 compares the brightness response to using different levels of ClO_2. The partially CAD-deficient pulp gave 1–2% ISO higher brightness with the same application of bleaching chemicals or required 0.2% less ClO_2 in the D_2-stage to give the same brightness. The latter is apparent by comparing the results (last row of Table 4) of duplicate bleaching experiments aimed at producing pulps of the same brightness. A comparison of the strength properties of two 87% ISO pulps indicated that the partially CAD-deficient pulp had slightly lower strength values, which might not be statistically different, for tear, tensile, burst, and zero span at four different degrees of refining (freeness). A comparison of tear versus tensile is shown in Fig. 9.

Table 4. Comparison of Bleaching Results for Partially CAD-Deficient and (Normal) Pulps

Stage	% ClO_2	% NaOH	Final pH	Kappa	Brightness
Brown Stock				36.4 (35.8)	
D_0	2.77 (2.72)		2.1		
(EO)		2		6.0 (7.2)	
D_1	0.6	0.15	3.6 (4.0)		72.6 (74.0)
E		0.5	11.3		
D_2	0.3	0.015	4.5		86.2 (84.2)
D_2	0.5	0.15			87.0 (85.8)
D_2	0.7	0.2	3.6 (3.5)		87.6 (86.3)
D_2	0.5 (0.7)	0.15 (0.2)	3.5 (3.3)		87.1 (87.2)

D_0: 0.20 kappa factor, 3.5% consistency, 50°C, and 45 min.
E stages: 10% consistency, 70°C, and 60 min; EO stage has 60 psig O_2.
D_1 and D_2: 10% consistency, 70°C, and 120 min.

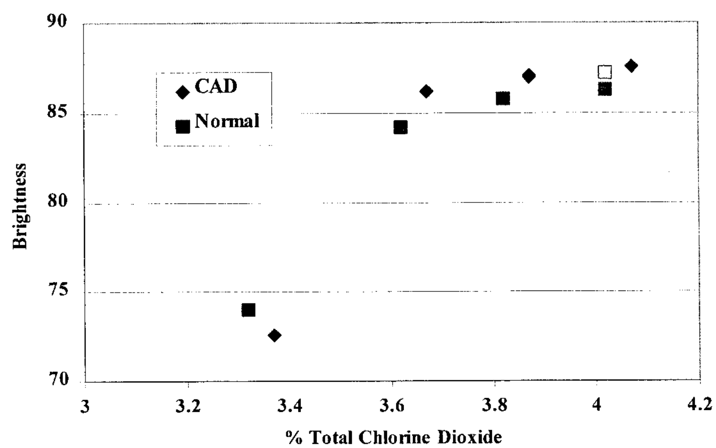

Figure 8. Comparison of the brightness response of partially CAD-deficient and normal pulps to using different levels of ClO_2.

Wood Physical Properties

Since wood specific gravities relate to lumber quality,[10] we measured specific gravities of individual and mixtures of 4-year-old partially CAD-deficient and normal pine chips. The values were nearly the same (0.34); the low value probably reflects the thin-wall fibers in these juvenile

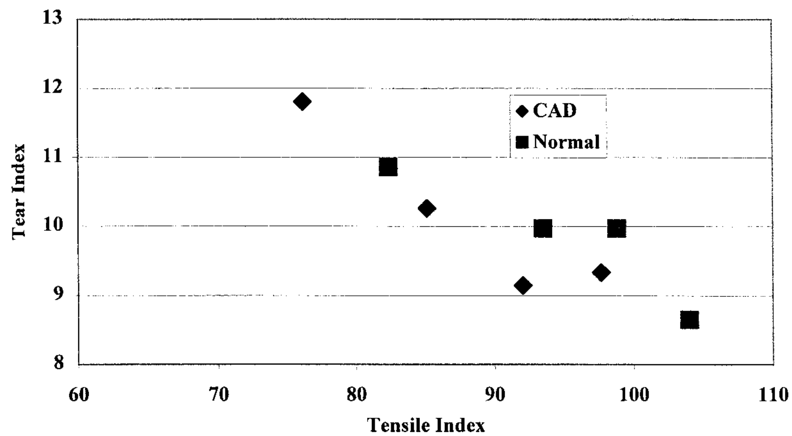

Figure 9. Comparison of the tear versus tensile indexes of 87% ISO partially CAD-deficient and normal pulps.

pines. The average specific gravities of three 6-year-old trees of each type were exactly the same (0.39). The average specific gravities, determined by using disk specific gravities of a basal area weighted average of the individual ring specific gravities, gave the following values for two samples each of 14-year-old trees: partially CAD-deficient 0.435 and normal 0.427. These are within the experimental measurement error of being the same.

Tree Growth Issues

It was previously shown that 4-year-old partially CAD-deficient pines had a 14% increase in debarked volume in comparison to normal trees.[9] While only a limited, not statistically significant, set of 14-year-old trees was examined, it *appears* that the earlier noted growth difference continues as the tree ages (Table 5).

CONCLUSIONS

Our data with young trees clearly show that partially CAD-deficient wood is superior to normal wood for pulp production; this conclusion is based on easier pulping and bleaching and better resulting pulp strength

Table 5. Comparison of Tree Sizes and Weights

Wood Type	Rep.[a]	Tree[b]	Diameter (in) at 4.5 ft	Height (ft)	Ht. of Live Crown (ft)[c]	Calc. wt. (Kg) Above 4.5 ft[d]
Part. CAD-	1	1	10.5	59.9	33.0	292
normal	1	3	9.2	59.7	34.5	236
Part. CAD-	3	3	9.7	62.7	34.5	262
normal	3	5	8.6	58.0	34.8	208
Part. CAD-	5	5	11.8	67.0	41.4	477
normal	6	3	10.3	66.5	37.3	323
CAD-Average			10.7	63.2	36.3	344
Normal Average			9.4	61.4	35.5	256

[a]Plot number; [b]Arbitrarily assigned tree number within a plot; [c]From the ground up to the first branch; [d]A rough calculation for the logs removed and transported; the volume was calculated using the diameter at each end of each 4-foot log harvested; wet weight was calculated using a constant estimated density of 0.9 for both woods.

properties. The better strength properties probably reflect the milder pulping conditions needed in the partially CAD-deficient wood case. The delignification trends do not hold up with older trees, where partially CAD-deficient wood appears to be only slightly easier to delignify. The strength properties appear to be a little lower in the case of 14-year-old partially CAD-deficient wood as compared to normal wood. These conclusions are based on limited comparisons; more studies are needed of wood grown on different sites.

Further research is needed to explain the big rate differences for delignification of partially CAD-deficient and normal pinewood for young vs. older trees. Possibly, in the case of partially CAD-deficient pine trees, lignin biosynthesis involves a balance between taking a normal and an abnormal pathway. For young trees, where growth is very rapid, both paths are taken and some abnormal lignin is produced. Then, as the rate slows, the normal path is preferred. If the transformation from partially abnormal to normal takes place somewhat early in the plant's development, the older tree will have dominance of normal lignin. We are presently performing a ring-by-ring analysis of lignin structure to determine if lignin differences change with tree age.

Factors influencing early-year lignin structure may also be causing a spurt in growth that carries through to the older trees. Even if there are no real delignification differences for older partially CAD-deficient versus normal pine trees, the former type may be a preferable pulpwood because of their faster growth and ability to supply more wood/acre for trees of a similar age. There appear to be no differences in the densities of partially

CAD-deficient versus normal pine trees; thus, the former will likely be a good source of wood for lumber uses.

EXPERIMENTAL

Pulping

Logs were debarked and chipped in a 4 foot Carthage chipper. The chips were screened on a Rader thickness screen and the 2–8-mm fractions collected and used for pulping. All pulping was done in a 10-L M/K Digester with external liquor circulation and electric heating. The cook schedule and H-factor were controlled by a process computer. The chip charge was either 800 or 1000 o.d. g. and the final liquor:wood ratio was 4 : 1. White liquor was made from stock solutions of NaOH and Na_2S. Cooked chips were disintegrated in an agitated tank, then screened on a flat screen with 0.006 inch slots. The screen accepts and rejects were collected and the screened yield, % rejects, and total yield were calculated. Kappa numbers were measured on the screen accept pulp according to TAPPI UM 246.

Bleaching

All D and E stages were done in sealed plastic bags in a water bath. (EO) stages were done in a pressurized mixer with a horizontal mixing shaft. Chlorine dioxide (ClO_2) was made in the lab from sodium chlorite ($NaClO_2$) and H_2SO_4. The NaOH was added as a 1 N solution. Brightness values were determined according to TAPPI T525.

Handsheet Strength

Pulps were refined at four levels in a PFI mill according to TAPPI T248. Handsheets were made at a basis weight of 60 g/m^2 according to TAPPI T205 and the strength measured according to TAPPI T220.

Wood Properties

The chip density of the 4- and 6-year-old samples was determined by water displacement of a saturated chip sample to determine the green volume followed by oven drying at 105°C to determine the weight. The densities of the 14-year-old samples were determined by cutting radial strips from disks and measuring the growth ring density by X-ray densitometry. The average density was calculated from the ring density data as the basal area weighted average.

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