A STUDY OF LOBLOLLY PINE GROWTH INCREMENTS—PART V. EFFECTS OF CHEMICAL AND MORPHOLOGICAL FACTORS ON TENSILE BEHAVIOR OF PAPER

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ABSTRACT

Loblolly pine growth increments were divided into five fractions: two earlywood, a transition, and two latewood growth zones. Each fraction was kraft-pulped to four different time schedules, Valley beaten, made into handsheets, and investigated for tensile strength properties. Differences in tensile strength properties were related to inherent characteristics of individual tracheids. It was shown that the number of tracheids per unit volume of paper was the most important attribute to strength. Of secondary importance was the strength of the individual tracheid-to-tracheid bonds, which was influenced by residual lignin in the pulp. Using tensile energy values, the number of hydrogen bonds active in resisting tensile forces was estimated. This number was also related to the number of tracheids per unit volume as well as to residual lignin. The above variables were explained on the basis of the intraincremental chemical and anatomical properties of wood.

Keywords: Loblolly pine, growth increments, handsheets, sheet tensile strength, hydrogen bonds.

INTRODUCTION

This paper is the last of a series of publications describing the properties of loblolly pine (*Pinus taeda* L.) tracheids obtained from different zones of growth rings. The first paper in this series summarized the within-growth-ring variations in tracheid morphology and properties in loblolly pine (Ifju and Labosky 1972). In addition to fiber property variations, significant differences were found in the chemical composition of wood between earlywood and latewood (Labosky and Ifju 1972). These differences and those in tracheid morphology affected refining characteristics of pulps prepared from intraincrement growth zones (Ifju et al. 1975). In general, pulps prepared from loblolly pine latewood zones responded to beating more readily than did earlywood pulps. As a result of inherent differences in tracheid properties and their response to refining, handsheets prepared from the different growth zones showed marked differences (Labosky and Ifju 1981). Earlywood pulp sheets were stronger in tension but weaker in tear than

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TABLE 1. *Pulping properties of loblolly pine intraincremental growth zones.*

Fraction no.	Fraction name	Relative position in ring (%)	Density of wood (g/cm³)	Tracheid length (mm)	Digestion time (min) 90		105		120		180	
					Pulp yield (%)	Kappa no.	Pulp yield (%)	Kappa no.	Pulp yield (%)	Kappa no.	Pulp yield (%)	Kappa no.
1	early earlywood	12	0.425	3.58	60.2	106	57.4	92	55.4	75	54.7	61
2	late earlywood	36	0.322	3.51	54.9	98	52.7	75	50.6	65	50.2	50
3	transition wood	57	0.445	3.65	55.6	91	53.6	84	51.6	74	49.7	42
4	early latewood	76	0.644	3.94	59.5	83	57.7	87	53.6	70	50.7	44
5	late latewood	91	0.625	3.99	60.8	102	56.4	93	53.0	71	48.7	44

latewood pulps. However, refining appeared to reduce these differences as latewood pulps were modified by the beating process more significantly than earlywood pulps.

It has been recognized for some time that the most important tracheid physical property influencing sheet tensile properties is the strength of the individual tracheids (Biblis 1969; McIntosh and Leopold 1961; McIntosh 1963). Van der Akker et al. (1958) clearly showed that roughly 40% of the tracheids fail when sheets are broken in tension. It was also found that strong latewood tracheids did not necessarily produce a strong paper (Ifju and Labosky 1970), even though latewood tracheids were superior to earlywood tracheids in terms of potential bonding sites (McIntosh and Leopold 1961). Other factors such as tracheid flexibility and topochemical properties must be considered when sheet properties are analyzed.

Not only are the individual tracheid properties important in paper strength evaluations, but such paper characteristics as the number of tracheids per unit volume must be considered (Giertz 1962; Clark 1970). Among intraincremental growth zones, the most important morphological tracheid properties in this regard are cross-sectional dimensions and cell-wall thickness. Biblis (1969) reported that average radial diameter of loblolly pine earlywood tracheids ranges from 55 μm to 60 μm. These differences in tracheid dimensions indicate that they might influence sheet properties through the number of tracheids and intertracheid contacts.

More recently Kellogg and Thykeson (1975) attempted to relate fiber characteristics to sheet properties. They found that sheet bulk could be predicted from fibril angle and fiber coarseness, and bulk was highly correlated with other sheet properties. Matolcsy (1975) also found highly significant correlations between sheet properties and such fiber characteristics as fiber length, fiber diameter, lumen width, cell-wall thickness, and fiber strength. However, he stated that it was impossible to predict accurately the physical properties of paper from fiber dimension ratios.

The objectives of this paper were to bring together the results of the earlier studies and to relate inherent variations in tracheid morphology, chemical properties, and refining characteristics to paper sheet properties. The purpose was also

TABLE 2. *Bulk and tensile strength of pulps in relation to digestion time and beating time in five growth zones within rings.*

Frac-tion no.	Fraction name	Beat-ing time (min)	Digestion time (min)															
			90				105				120				180			
			Bulk		Tensile strength		Bulk		Tensile strength		Bulk		Tensile strength		Bulk		Tensile strength	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	early	15	2.00	.03	22.6	1.9	1.93	.02	32.2	1.0	1.78	.02	42.0	2.7	1.96	.02	30.6	0.9
	earlywood	35	1.70	.02	39.8	1.1	1.67	.02	44.6	2.9	1.63	.01	50.8	2.9	1.58	.01	51.8	0.4
2	late	15	1.70	.01	37.0	2.7	1.53	.01	52.9	2.8	1.54	.01	54.9	1.5	1.63	.01	44.3	1.1
	earlywood	35	1.50	.02	55.4	1.7	1.42	.01	63.8	2.1	1.48	.01	60.7	3.1	1.40	.02	66.4	3.6
3	transition	15	1.92	.05	27.8	0.8	1.89	.02	31.7	1.3	1.76	.02	40.4	1.2	1.90	.02	31.2	1.4
	wood	35	1.66	.02	41.3	0.7	1.61	.02	44.8	1.9	1.64	.02	47.3	1.9	1.57	.01	48.8	0.7
4	early	15	—	—	—	—	2.10	.03	19.8	2.5	1.98	.07	19.9	5.2	2.03	.03	23.5	0.5
	latewood	35	1.83	.04	25.7	1.2	1.68	.01	35.6	1.4	1.78	.03	34.1	2.1	1.64	.02	37.1	2.4
5	late	15	—	—	—	—	—	—	—	—	1.97	.03	24.0	1.7	1.72	.05	36.6	1.4
	latewood	35	1.84	.02	26.6	0.9	1.75	.02	33.4	1.4	1.79	.02	33.9	1.8	1.44	.04	58.0	1.7

Mean: based on 10 observations.
Bulk: cm^3/g.
Tensile strength: MPa.

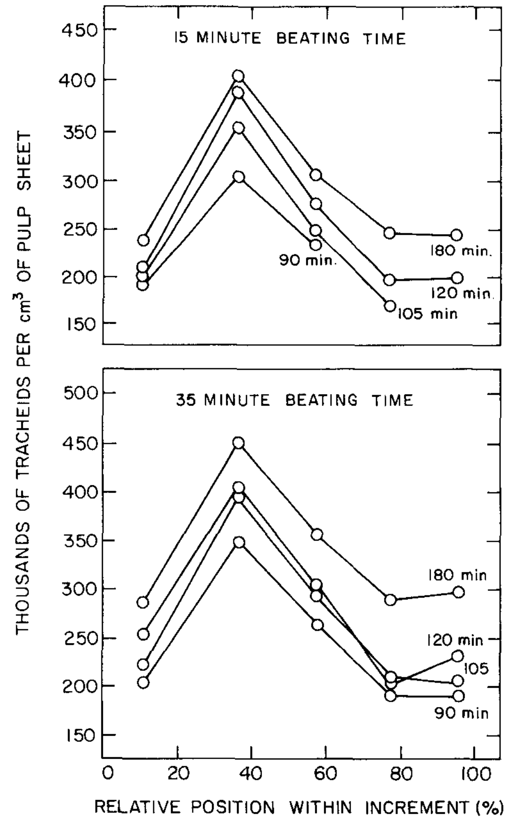

FIG. 1. Number of tracheids per unit volume of pulp sheet as a function of within-growth-ring source, kraft digestion times of 90, 105, 120, and 180 min, and beating times of 15 and 35 min.

to find the fundamental reasons for the differences in the properties of handsheets prepared from intraincremental growth zones of loblolly pine.

EXPERIMENTAL PROCEDURES

Material and procedures for this series of publications have been reported in the first four papers. The following is a summary of the procedures. Loblolly pine growth rings were carefully separated into five growth zones: early earlywood (fraction 1), late earlywood (fraction 2), transition wood (fraction 3), early latewood (fraction 4), and late latewood (fraction 5). The material from each growth zone was converted to pin-chips, kraft digested according to four different schedules. These were 90, 105, 120, and 180 minute digestions at 173 C with 18% chemical charge and 25% sulfidity. The twenty batches of pulp from the five growth zones and four cooks were Valley beaten, made into handsheets, and tested for tensile strength properties according to Tappi standard procedures.

In Part I (Ifju and Labosky 1972) of this series of papers, the preparation of the material and the morphological characteristics of tracheids and wood were given. In Part II (Labosky and Ifju 1972), the pulping procedure and pulp yield results were reported. In Part III (Ifju et al. 1975), the refining characteristics for

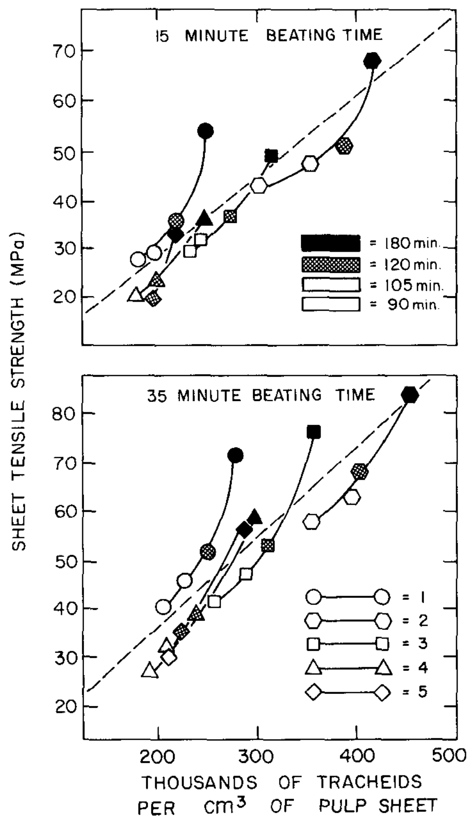

FIG. 2. Relationship between sheet tensile strength and number of tracheids per unit volume of pulp sheet after two beating periods (15 and 35 min) for five intraincrement fractions (1–5) after four cooking times (90–180 min).

each growth zone at four different pulp yields were reported. In Part IV (Labosky and Ifju 1981), handsheet strength evaluations were published.

Earlywood and latewood tracheid radial diameter values were used to calculate the number of tracheids per unit volume of paper produced (Biblis 1969). Assuming a hollow bar shape for individual tracheids, their volume could be calculated from length and cross-sectional dimensions. From the volume, the average weight of individual tracheids of the five growth zones was calculated using wood density values.

In order to calculate the number of tracheids per unit volume of the pulp sheets, all tracheid weights were reduced according to pulp yield. Using these corrected weights and the bulk values in cm^3/g of handsheets, the number of tracheids in one cm^3 of pulp sheet could be obtained as follows:

$$\text{Number of tracheids/cm}^3 \text{ of paper} = \text{Bulk} \times \frac{1}{\text{Weight of tracheid}}$$

It is apparent from the above calculations that not only the original dimensions

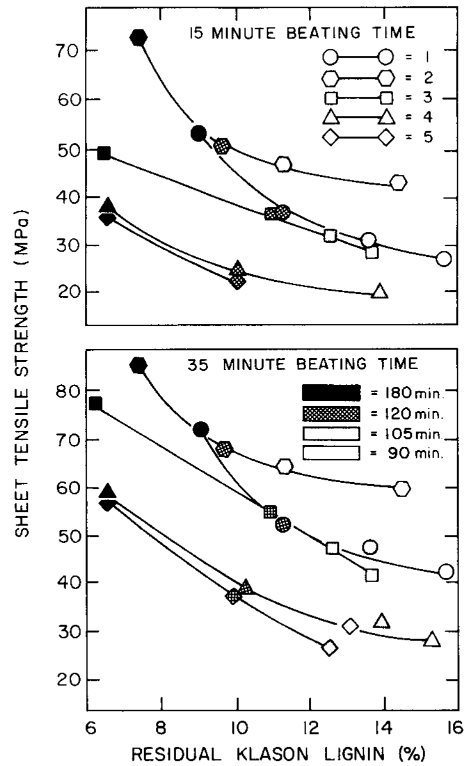

FIG. 3. The influence of residual Klason lignin on the tensile strength of pulp sheets from five incremental growth zones (1–5) following four digestion times (90–180 min) and two beating periods (15 and 35 min).

of the tracheids influence the number per unit volume of paper but also the pulping process and yield, which modify the original weight of tracheid. In addition, refining had a marked effect on sheet density; thus it further changed the number of tracheids per cm^3 of paper.

RESULTS AND DISCUSSION

Pulping properties of the five within-growth-ring zones are shown in Table 1. Although density of the latewood zones was significantly higher than that of the earlywood zones, it did not seem to have an effect on yield. However, handsheet properties showed marked differences with respect to growth zones (Table 2). In order to find the fundamental reasons for these differences, the possible influence of certain tracheid characteristics was closely examined.

The number of tracheids calculated for each pulp showed that late earlywood pulp (relative position at 36%) was computed to have twice the number of tracheids in a unit volume as did latewood pulps (Fig. 1). It may also be seen that as digestion time (minutes) increased, the number of tracheids per unit volume increased. This could be expected since long digestion times should result in a more complete tracheid separation from the middle lamella resulting in improved

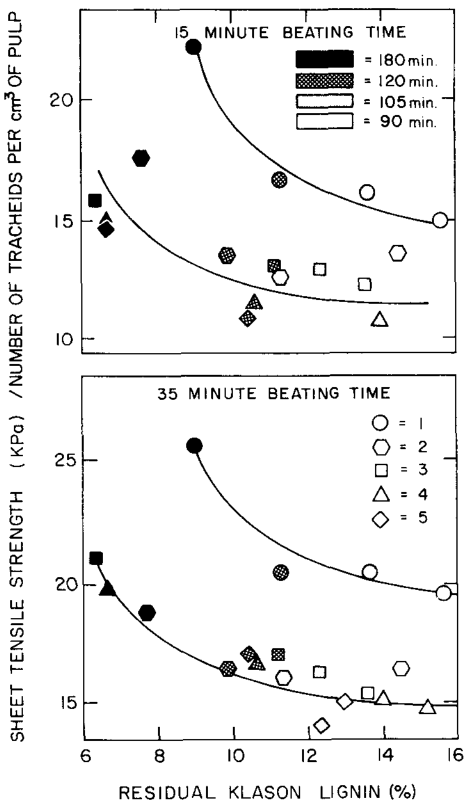

FIG. 4. Influence of residual Klason lignin, intraincrement fraction (1–5), and beating time (15 and 35 min) on the contribution of individual tracheids to sheet tensile strength after four cooking times (90–180 min.).

papermaking properties. The same observation may be made regarding refining—that is, the number of tracheids increased as beating increased because of further tracheid separation and delamination.

When sheet tensile strength was related to the number of tracheids per unit sheet volume, an approximate linear relationship was observed (Fig. 2). These results support earlier observations in that the largest number of tracheids should have the greatest probability of interweaving and forming more tracheid-to-tracheid bonds. However, certain morphological or chemical interactions occurred as may be evidenced by the higher strength values for the early earlywood growth zone. This observation suggests that pulps from a given species containing more fibers per unit volume should produce paper with the strongest tensile strength properties.

A slight curvilinear relationship may be observed for each growth zone with respect to digestion time as shown in Fig. 2. Three data points, corresponding to the shorter digestions, appear to fall on a straight line. The fourth point corresponding to the 180-minute cooking time deviates from the straight line relationship for each growth zone. This observation suggests that for short digestions, an increase in tensile strength is due to an increase in the number of tracheids

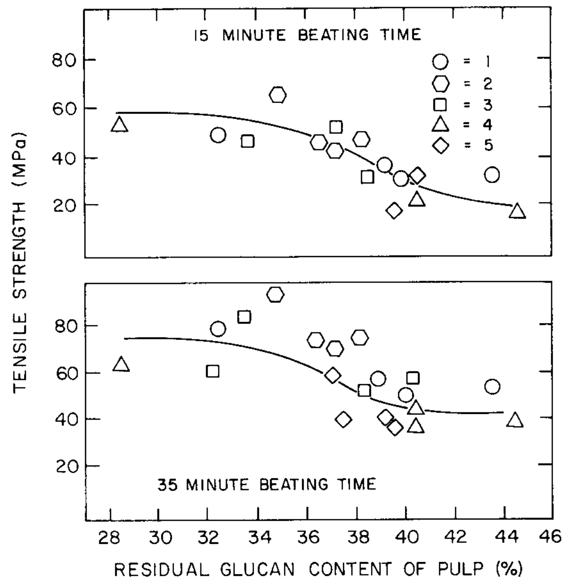

FIG. 5. Relationship between sheet tensile strength and residual glucan in pulps from five intraincrement fractions at two beating times (15 and 35 min).

per unit volume which, in turn, increases the number of tracheid-to-tracheid bonds. It appears that reduction of lignin has only a minor effect, but increased fiber flexibility is most important. For the 180-minute cook, however, the large increase in tensile strength cannot be accounted for by an increase in number of the tracheids alone. The increase in the strength of the individual tracheid-to-tracheid bonds is important here. Only when a critical amount of lignin has been removed do more hydrogen bonds between tracheids appear to develop.

The above conclusion is supported when sheet tensile strength is plotted against residual lignin content of the pulps (Fig. 3). A curvilinear relationship is observed with a slight break occurring towards the 180-minute digestion time for several fractions. An increase in bond strength develops when lignin content drops to approximately 10%. As beating time increases, there is a corresponding increase in tensile strength for all growth zones.

In order to remove the effect of the number of tracheids per cm^3 on tensile strength, the ratio of these two variables was calculated and plotted against residual Klason lignin. A curvilinear relationship was again observed (Fig. 4). Two distinct patterns may be observed in Fig. 4 with fractions 2, 3, 4, and 5 showing a similar response whereas fraction 1 was significantly stronger in tensile strength.

Another explanation for the significant increase in tensile strength after the 180-minute digestion may lie in the change in properties of the carbohydrate framework of tracheids after prolonged digestion. As would be expected, carbohydrate analyses showed a decrease in carbohydrate content with increasing digestion time (Labosky and Ifju 1972). These results suggest that fiber flexibility is related to carbohydrate removal, more specifically, removal of glucan, the sugar associated mostly with framework carbohydrates.

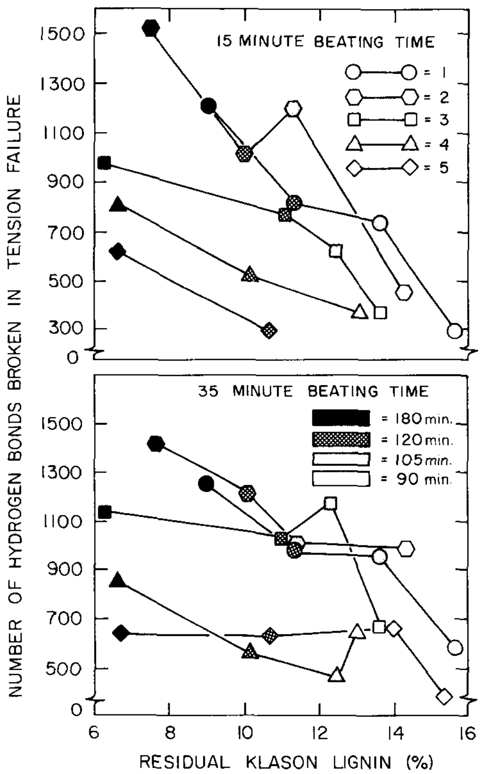

FIG. 6. Hypothetical number of hydrogen bonds broken in paper sheets in tension as a function of residual Klason lignin and beating times (15 and 35 min) for the five fractions and four digestion times (90–180 min).

The relationship between tensile strength of pulp sheets and residual glucan content at two levels of refining shows that the important range of glucan retention occurs between 33 and 40% where tensile strength appears to change most rapidly (Fig. 5). On the basis of these data, it may be concluded that retention of glucan beyond 40% or its removal beyond 33% results in very little change in tensile strength.

Removal of hemicelluloses associated with matrix substances did not seem to affect tensile properties in this study. The only hemicellulosic carbohydrate that gave some indication of influencing strength was xylan. Data reported earlier indicated that some xylan redeposition had occurred toward the longer digestions (Labosky and Ifju 1972). It is possible that only after a sufficient amount of lignin is removed from the tracheids can redeposition of xylan-type hemicelluloses readily occur resulting in an increase in bond strength among tracheids.

Properties of pulps from the early earlywood deserve further discussion, since this early growth zone was shown to have produced unexpectedly high pulp yields. One might argue that during pin-chip preparation, latewood contamination from the adjacent growth ring may have occurred and contributed to the higher pulp yields. However, a comparison of yields (Table 1) and pulp sheet properties (Figs. 1, 2, and 4) clearly shows that this did not occur. For example, this growth zone

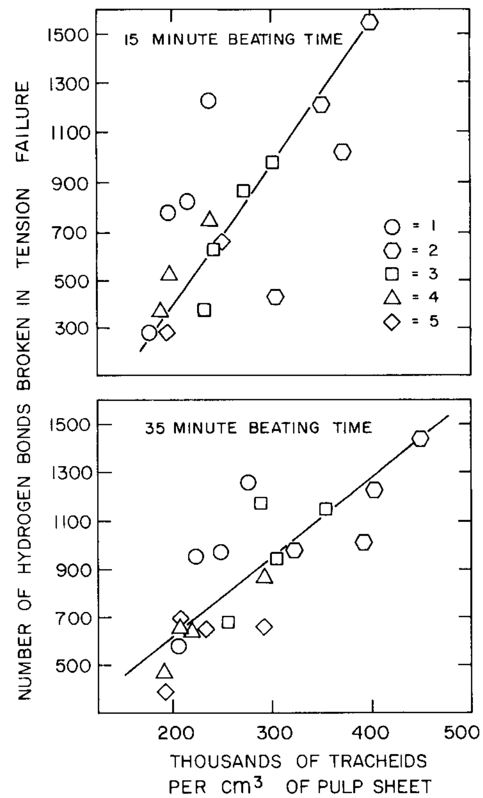

FIG. 7. The influence of the number of tracheids per unit volume, fractions (1-5) and beating time (15 and 35 min) on the number of hydrogen bonds broken in paper sheets in tension.

produced higher yields even after 120 min of digestion compared to either of the two latewood zones. A striking separation of early earlywood appears on Fig. 4. Here again, a mere intermixing of tracheids cannot account for the unusual behavior. It is felt that the mechanism of earlywood formation postulated by Wilson (1964) may explain the anomalous behavior of early earlywood. According to Wilson, the overwintered xylem mother cells produce tracheids that resemble chemically to latewood but morphologically to earlywood. Apparently, the unique properties and behavior of this first-formed earlywood is related to the ontogeny of this growth zone.

FUNDAMENTAL ENERGY RELATIONSHIPS IN TENSILE TESTING OF PAPER

The energy required to break a pulp sheet in tension should be directly related to the number of tracheid-to-tracheid bonds and to the number of tracheids broken. The area under the stress-strain diagrams in tensile tests is a measure of the total energy spent in breaking the material. Assuming that all bonds broken are hydrogen bonds, including those associated with intratracheid bonds, theoretical calculations may be made to determine the number of hydrogen bonds broken. Here it is postulated that although primary ether bonds are involved in tracheid failure, their contribution to the overall energy is of negligible importance.

Such an analysis was performed in an attempt to correlate tensile strength to the overall intra- and intertracheid hydrogen bonding potential of pulps. The area under representative stress-strain diagrams was measured with a planimeter, and the total work to failure in cm kg/cm^3 was calculated. Since the energy of one cm kg/cm^3 is equivalent to 10^6 ergs/cm^3 and a hydrogen bond represents 3×10^3 ergs of work, the energy values could be converted to total number of hydrogen bonds.

A negative trend is observed between the hypothetical number of hydrogen bonds broken in a unit volume of paper in tension and residual lignin content of pulps refined to two time intervals (Fig. 6). Here again the importance of lignin removal and/or the development of fiber flexibility through carbohydrate removal may be noted. For each growth zone (fractions 1–5) the relationship is such that with increasing yield and decreasing cooking time, which are associated with increasing residual lignin content and increasing glucan retention, the hypothetical number of active hydrogen bonds participating in the resistance of the sheet to tensile stresses decreases. A slight indication of a critical lignin content may be noted for some pulps in Fig. 6; however, it is not as evident and consistent as it appears in Figs. 2 and 3.

These results may be explained on the basis of differences in the number of tracheids per unit volume of pulp sheets made from the various growth zones. Figure 7 clearly supports the above conclusion—that is, as the number of tracheids increases per unit volume, sheet strength increases because of an increase in number of hydrogen bonds. The first-formed earlywood again showed superior tracheid-to-tracheid bonding as was shown earlier in Fig. 4.

CONCLUSIONS

From the results of this study the following conclusions may be drawn:

1) Number of tracheids per unit volume of paper is one of the most important single variables affecting sheet properties.
2) Number of tracheids per unit volume of paper is influenced most significantly by tracheid morphology inherent in coniferous growth zones.
3) Digestion time and refining influence sheet properties through affecting the number of tracheids per unit volume.
4) Tensile properties of pulp sheets are affected by residual lignin in the tracheids through limiting the available bonding sites between tracheids.
5) Framework carbohydrate removal improves tracheid flexibility which, in turn, influences sheet tensile strength.
6) Tensile energy values can be converted into a value of number of effective hydrogen bonds in a sheet resisting tensile forces. This number gives a new insight into sheet formation.

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