

CHEMICAL DEGRADATION OF WOOD: THE RELATIONSHIP BETWEEN STRENGTH RETENTION AND PENTOSAN CONTENT¹

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ABSTRACT

This investigation resulted from a prior study on the effect of acids and alkalis on wood. In that study, indirect support was given the contention that a low original pentosan content in wood favors resistance to chemical degradation. In the present study, the relationship of pentosan content and its retention to the resistance of wood to chemical attack is quantitatively established. A low original pentosan content and a high pentosan retention correlate well with resistance to acid degradation as measured by strength retention. The relationship between these two pentosan values and alkaline degradation is weaker, but still significant. Hemicellulose retention is a better indicator of the behavior of wood with respect to alkaline attack. The most useful result is the fact that, through chemical analysis for pentosans in a wood, resistance to chemical degradation can be indicated.

The use of wood in chemical processing and for the storage of corrosive chemicals is well established, and wood is generally regarded as possessing a high degree of resistance to degradation by numerous chemicals. Wood is most severely attacked by strong acidic and caustic solutions, representing the extremes in pH values, and by powerful oxidizing agents (Browning 1963). In a prior study by one of the authors (Wangaard 1966), the effect of acids and alkalis on wood was subjected to a comprehensive investigation. That publication also contained a review of the literature pertaining to the chemical degradation of wood resulting from the action of these chemicals. Another recent review of the effect of chemicals on wood is that of Thompson (1969).

Different woods vary greatly in their resistance to chemical degradation, but on the whole, softwoods display more resistance than do hardwoods (Campbell and

Bamford 1939, Wangaard 1966, Thompson 1969). Most investigators (Campbell and Bamford 1939, Baechler 1954, Kollmann 1951, Wangaard 1966) ascribe this difference in resistance between the two wood types to basic differences in chemical composition. Wangaard (1966) also considers inaccessibility as another major contributing factor in resistance to acidic, hydrolytic degradation.

The loss of hemicellulosic material from wood during chemical attack is considerable, and there is a good correlation between strength retention and hemicellulose retention (Wangaard 1966). Since the primary hemicellulose of hardwoods is a pentosan—xylan—and hardwoods are more susceptible to chemical attack, there may be a relationship between the two. In the study by Campbell and Bamford (1939), which involved considerable chemical analysis, it was revealed that acidic treatment reduced the pentosan content severely. According to Wise and Jahn (1952), the amount of hemicelluloses in wood is considerably reduced on alkaline treatment; and pentosans are isolated directly from hardwoods with aqueous alkaline solutions

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(Timell 1964). That the pentosan content and its retention in wood might be important factors in chemical degradation was also given additional favorable support through the work of Wangaard (1966).

A definite demarcation between hardwoods and softwoods in their resistance to chemical attack is not always true when tropical hardwoods are compared to softwoods. Campbell and Bamford (1939) and Wangaard (1966) have reported instances of similarly good resistance to chemical degradation. The two woods—teak (*Tectona grandis*) and jarrah (*Eucalyptus marginata*) were as resistant as some softwoods to acidic attack, and their pentosan content was not significantly higher than that of softwoods (Campbell and Bamford 1939). The chemical composition of fourteen tropical woods was determined by Wise et al. (1951, 1952), and both the hemicellulose and pentosan values were lower than those of temperate-zone hardwoods. If there is a relationship between pentosan content and resistance to chemical attack, then tropical hardwoods should be superior to temperate-zone hardwoods. The work of Wangaard (1966) seems to verify this contention in comparing ten tropical hardwoods to white oak (*Quercus alba*).

The present study was undertaken to quantify the role of pentosans in the chemical degradation of wood through acidic and caustic solutions. The purpose of the project also included the establishment of an indicator for predicting resistance to chemical attack. Primarily two relationships were investigated: (1) strength retention (a measure of resistance to degradation) versus original pentosan content and (2) strength retention versus retention of pentosans.

MATERIALS AND EXPERIMENTAL METHODS

Thirteen wood samples were used: two softwoods, Douglas-fir (*Pseudotsuga menziesii*) and Caribbean pine (*Pinus caribaea*); one temperate-zone hardwood, white oak (*Quercus alba*); and ten tropical hard-

woods. All of the wood samples for chemical analysis and all of the strength data were obtained from the prior study (Wangaard 1966). The wood samples for chemical analysis were obtained from a set of beams previously used in obtaining the strength data. Each sample consisted of control, acid-treated, and alkaline-treated material. The acid-treated wood had been soaked in 10% HCl solution and the alkaline-treated in 10% NaOH solution. In both treatments, the small beams were submerged for 32 days at 20 C and then washed with cold tap water overnight before being tested for strength properties. The strength testing was completed in June 1962, and the pentosan determinations were initiated in February 1967. During this time interval, the tested beams were dried and stored in the air-dry condition at room temperature. It has been assumed that changes in chemical composition would be negligible under these conditions of storage.

The wood samples were prepared for chemical analysis by grinding in a Wiley mill to pass a 40-mesh screen. Approximately five grams of wood meal were sealed in nylon bags and extracted, using a Soxhlet extraction apparatus. The material was extracted, using the following sequence: 8–10 hr with a 95% ethyl alcohol-benzene mixture (1:2), 2–3 hr with 95% ethyl alcohol; and 20 hr with hot water. The wood meal was removed from the nylon bags, air-dried, and stored in stoppered glass bottles until needed.

The procedure used for the chemical analysis is that described in Technical Association Pulp and Paper Industry (1950). The method involves hydrolysis of the pentosans in wood and formation of furfural from the resulting sugars by the action of hot 12% HCl. The furfural is distilled and precipitated with phloroglucinol, and the precipitate is determined gravimetrically. All results were calculated on the extractive-free weight basis of the wood, and data for the treated material were adjusted to the original extractive-free wood basis.

TABLE 1. Comparison of changes in chemical composition and strength resulting from acidic and alkaline treatments of woods¹

Species	Treatment	Weight retention ²	Hemi-cellulose content %	Hemi-cellulose retention ²	Pentosan content %	Pentosan retention ²	Modulus of rupture retention ²	Work-to-max. load retention ²
Douglas-fir (1)	Control	—	31.1	—	7.1	—	—	—
(<i>Pseudotsuga menziesii</i>)	Acidic	97.6	31.0	100	6.1	86	76	38
	Alkaline	94.0	24.8	80	7.0	99	39	69
Caribbean pine (10)	Control	—	26.5	—	7.4	—	—	—
(<i>Pinus caribaea</i>)	Acidic	94.4	27.6	104	5.7	77	72	71
	Alkaline	96.0	22.0	83	6.8	92	53	77
White oak (2)	Control	—	36.7	—	24.6	—	—	—
(<i>Quercus alba</i>)	Acidic	85.4	21.4	58	14.1	57	39	12
	Alkaline	88.2	16.4	45	20.0	81	20	27
Teak (3)	Control	—	31.8	—	14.8	—	—	—
(<i>Tectona grandis</i>)	Acidic	94.2	24.9	78	10.6	72	59	34
	Alkaline	86.8	15.3	48	11.0	74	26	52
Lignum-vitae (4)	Control	—	27.3	—	18.3	—	—	—
(<i>Guaiacum officinale</i>)	Acidic	90.9	20.0	73	12.5	68	42	18
	Alkaline	85.8	13.1	48	14.3	78	29	44
Vera (5)	Control	—	31.6	—	22.3	—	—	—
(<i>Bulnesia arborea</i>)	Acidic	91.9	23.5	74	16.3	73	54	22
	Alkaline	93.9	17.8	56	19.2	86	26	22
Bannia (6)	Control	—	27.0	—	14.2	—	—	—
(<i>Swartzia bannia</i>)	Acidic	93.3	21.3	79	11.8	83	70	72
	Alkaline	88.0	13.0	48	9.9	70	20	39
Copaia (7)	Control	—	32.7	—	12.5	—	—	—
(<i>Jacaranda copaia</i>)	Acidic	94.9	21.3	65	9.2	74	48	9
	Alkaline	88.3	15.6	48	9.1	73	34	44
Cedro granadino (8)	Control	—	29.6	—	13.2	—	—	—
(<i>Cedrela tonduzii</i>)	Acidic	99.0	21.0	71	9.8	74	60	19
	Alkaline	83.2	11.0	37	7.4	56	16	61
Yekoro (9)	Control	—	30.5	—	14.9	—	—	—
(<i>Ocotea schomburgkiana</i>)	Acidic	92.1	23.3	76	10.5	70	62	33
	Alkaline	88.6	14.7	48	10.5	70	25	47
Mora amarilla (11)	Control	—	31.6	—	18.7	—	—	—
(<i>Chlorophora tinctoria</i>)	Acidic	95.9	22.4	71	16.9	90	64	30
	Alkaline	87.3	15.7	50	15.9	85	20	43
Marishiballi (12)	Control	—	25.5	—	15.1	—	—	—
(<i>Licania buxifolia</i>)	Acidic	96.1	21.7	85	10.1	67	59	33
	Alkaline	98.2	16.5	65	14.5	96	35	50
Acapu (13)	Control	—	30.7	—	17.9	—	—	—
(<i>Vouacapoua americana</i>)	Acidic	91.9	18.7	61	14.3	80	54	28
	Alkaline	86.3	12.4	40	13.4	75	19	19

¹ All values based on extractive-free weight.² Per cent of control.

RESULTS AND DISCUSSION

The results of the pentosan determinations and additional pertinent information obtained in the prior study (Wangaard 1966) are tabulated and shown in Table 1. The pentosan content of the two softwoods averaged 7.25%, that of the oak was 24.6%, and the average value for the ten tropical hardwoods was 16.2%. All of these values are slightly high when compared with aver-

age values given in the literature (Browning 1963, Timell 1964, Wise et al. 1951, 1952). This discrepancy is probably due to lack of a correction for the uronic anhydride content of the wood, which was not determined. The uronic acids also yield furfural under the pentosan analysis conditions, to the extent of about 0.35 mole per equivalent of uronic anhydride (Browning 1967). The magnitude of such a correction would

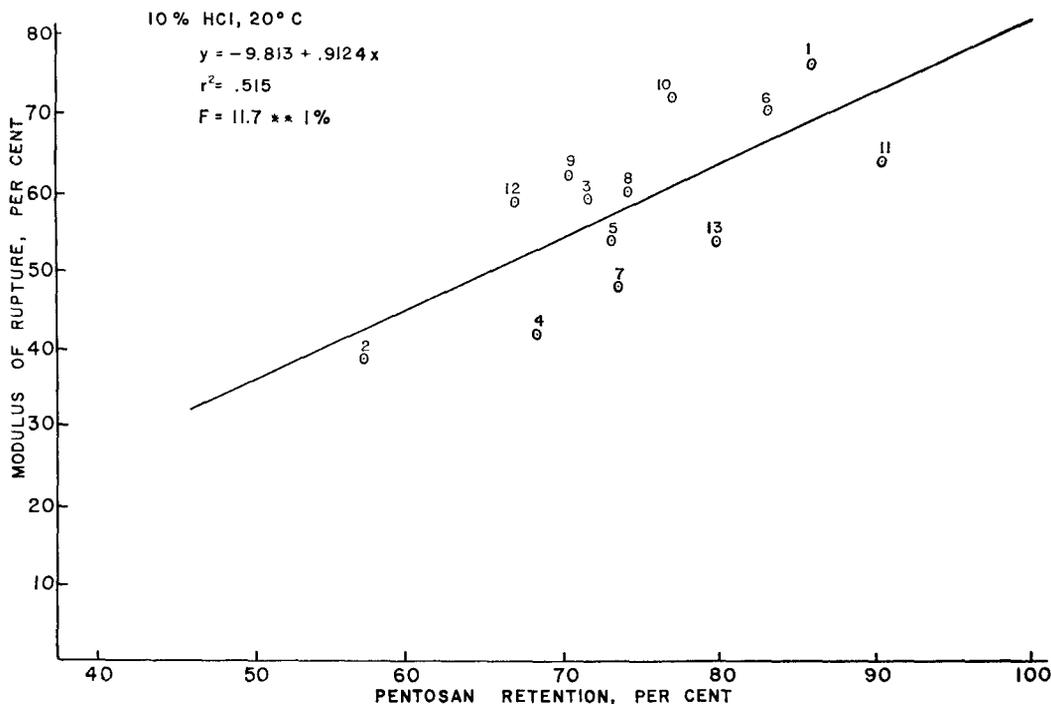


FIG. 1. Relationship between pentosan retention and modulus of rupture retention following treatment with 10% HCl for 32 days at 20 C. Individual species are identified by number in Table 1.

be such as to nullify the apparent difference in values.

The hemicellulose content of the control specimens also appears high, especially for the tropical hardwoods. The average hemicellulose value given for fourteen tropical hardwoods by Wise et al. (1952) was 19.0%; that of four Amazon Basin woods by Lauer (1958) was 22.2%, while the average of the tropical hardwoods listed in Table 1 is 29.8%. All of these values were determined and calculated in essentially the same manner: the difference between holocellulose and α -cellulose, based on the weight of extractive-free wood. Reasons for this discrepancy are not readily apparent. If it is assumed that the principal hemicellulose of tropical species is similar to that of temperate-zone hardwoods, then 70–80% of the total hemicellulose content should be accounted for in the pentosan value. The data presented by Wise et al. (1952) seem to support this assumption;

but the values given in Table 1 do not agree. The hemicellulose values in this study are higher than would be expected.

Acidic Treatment

With the exception of the two softwood species, the hemicellulose content was reduced when wood was attacked by acid. Although the pentose content was also reduced during the acid attack, there was no consistency between pentosan retention and hemicellulose retention. At first this may appear unusual since the hemicelluloses of hardwoods are primarily xylan, a pentosan; however, the procedure by which the hemicelluloses are determined explains the problem. An unknown amount of cellulosic material is undoubtedly determined as "hemicellulose" after degradation during the acidic treatment, which results in fragments that are soluble in aqueous 17½% NaOH solution. This would explain the high hemicellulose values for the two acid-

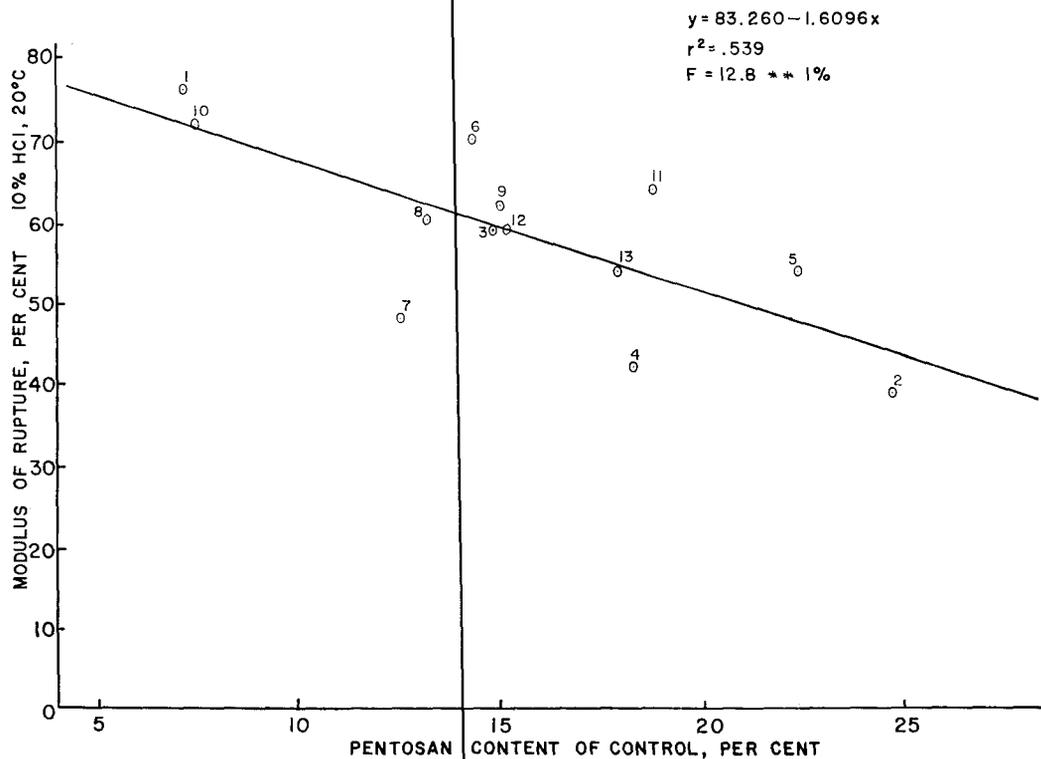


FIG. 2. Relationship between original pentosan content and modulus of rupture retention following treatment with 10% HCl for 32 days at 20 C.

degraded softwood samples. Caribbean pine, with a hemicellulose retention of 104%, had only an 81.5% α -cellulose retention (Wangaard 1966).

Following acid treatment, pentosan retention and hemicellulose retention both gave a significant correlation with retention of modulus of rupture. The relationship between strength retention, as indicated by retention of the modulus of rupture, and pentosan retention is shown in Fig. 1. This regression has a coefficient of determination (r^2) = 0.515. This relationship is actually slightly poorer than that found for strength retention versus hemicellulose retention where the coefficient of determination (r^2) = 0.598. Several of the tropical hardwoods had pentosan retentions comparable to that of the two softwoods. These species, as shown in Table 1, are Mora amarilla, with the highest retention of any wood, and

Bannia and Acapu. White oak had the lowest pentosan retention and also the lowest strength retention.

When the original pentosan and hemicellulose contents are compared with strength retention after acid degradation, only the pentosan values show a significant correlation. This relationship is shown in Fig. 2, where the regression had a coefficient of determination (r^2) = 0.539.

Alkaline Treatment

The modulus of rupture was more severely reduced in the alkaline treatment than in the acidic treatment; however, the average pentosan retention was slightly higher. The better pentosan retention under alkaline treatment is to be expected, as is indicated by a similar retention under alkaline pulping conditions (Rydholm 1965). An appreciable amount of alkaline-modified

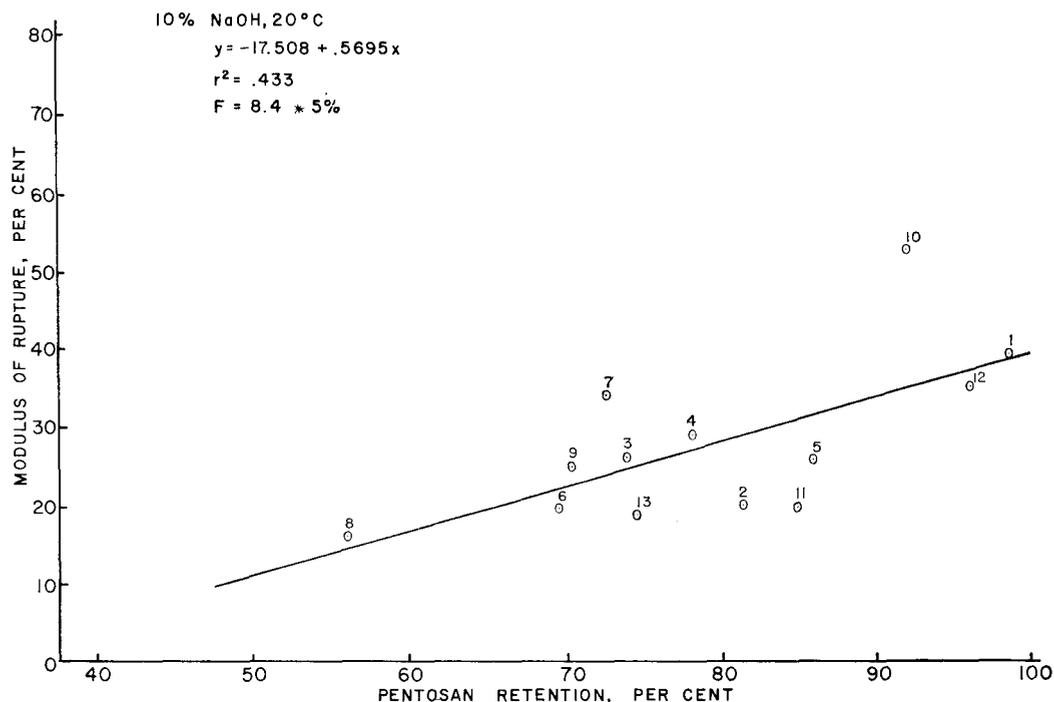


FIG. 3. Relationship between pentosan retention and modulus of rupture retention following treatment with 10% NaOH for 32 days at 20°C.

pentosan actually increases the α -cellulose content by reduced solubility in 17½% NaOH. This was indicated in the prior study (Wangaard 1966) in which the α -cellulose retention of the wood after alkaline treatment was often over 100%.

As seen in Fig. 3, a weaker relationship was found between strength retention and pentosan retention after alkaline treatment than was found after acid treatment. The relationship, however, between modulus of rupture retention and hemicellulose retention is good, the regression having a coefficient of determination (r^2) = 0.792. This good correlation was also shown in the prior study (Wangaard 1966) where averaging of two temperature series also gave a highly significant coefficient of determination (r^2) = 0.763.

An evaluation of modulus of rupture retention after alkaline degradation versus original pentosan content revealed a weaker relationship than that found after acid

degradation. Nevertheless, as seen in Fig. 4, it was significant, while the hemicellulose data did not reveal any relationship of significance. Interestingly, retention of work-to-maximum load following alkaline treatment showed a good correlation with original pentosan content. This relationship is illustrated in Fig. 5, the regression having a coefficient of determination (r^2) = 0.735. No such relationship exists between original pentosan content and work-to-maximum load when the woods are subjected to an acidic treatment.

CONCLUSIONS AND SUMMARY

Acidic Treatment

When wood is given an acidic treatment, it is in essence being subjected to the catalytic action of the hydrogen ion. The effect on the carbohydrate portion of the wood is hydrolysis of the glycosidic linkages within the polysaccharide chains. The effect on the lignin is the initiation of con-

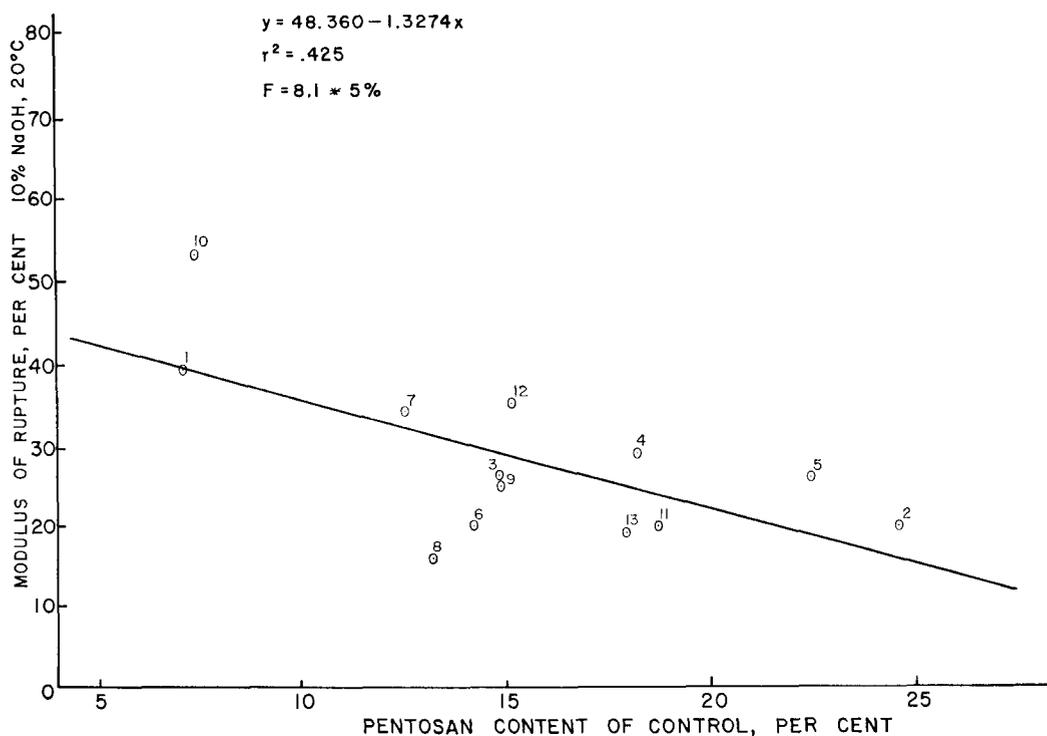


FIG. 4. Relationship between original pentosan content and modulus of rupture retention following treatment with 10% NaOH for 32 days at 20 C.

condensation reactions. The extreme situation occurs in wood saccharification or the formation of acid-insoluble lignin.

The degree to which wood is affected by acids is determined by the hydrogen ion concentration, temperature, and inaccessibility and chemical constitution of the wood. That the chemical constitution of the wood is important was shown by the two softwoods, which were the most acid resistant of all wood species. That inaccessibility is of considerable importance was shown in the prior study (Wangaard 1966), in which, for the hardwoods only, this factor versus strength retention was most significant, $r^2 = 0.830$. Differences in behavior of the ten tropical hardwoods under acidic attack should be primarily the result of differences in accessibility.

The differences in both hemicellulose and pentosan retentions, under identical acidic treatment, for the various tropical

woods should be considered due to differences in inaccessibility. Not only are the hemicelluloses in the less-well-ordered regions of the cell wall and, therefore, more readily available for acidic attack, but the primary hemicellulose, the xylan, is considerably more sensitive to acids than the other wood polysaccharides. The rate of hydrolysis of xylose glycosides is approximately 4.5 times that of glucose glycosides (Wolfrom and Thompson 1957), and this same rate should apply in comparing xylan and cellulose.

The effectiveness of wood in resisting acidic attack is therefore indicated by the hemicellulose and pentosan retention values. The critical acidic degradation of the wood with respect to its strength retention is most probably lowering of the degree of polymerization of the cellulose. The effect of lowering the degree of polymerization of cellulose upon the strength retention of

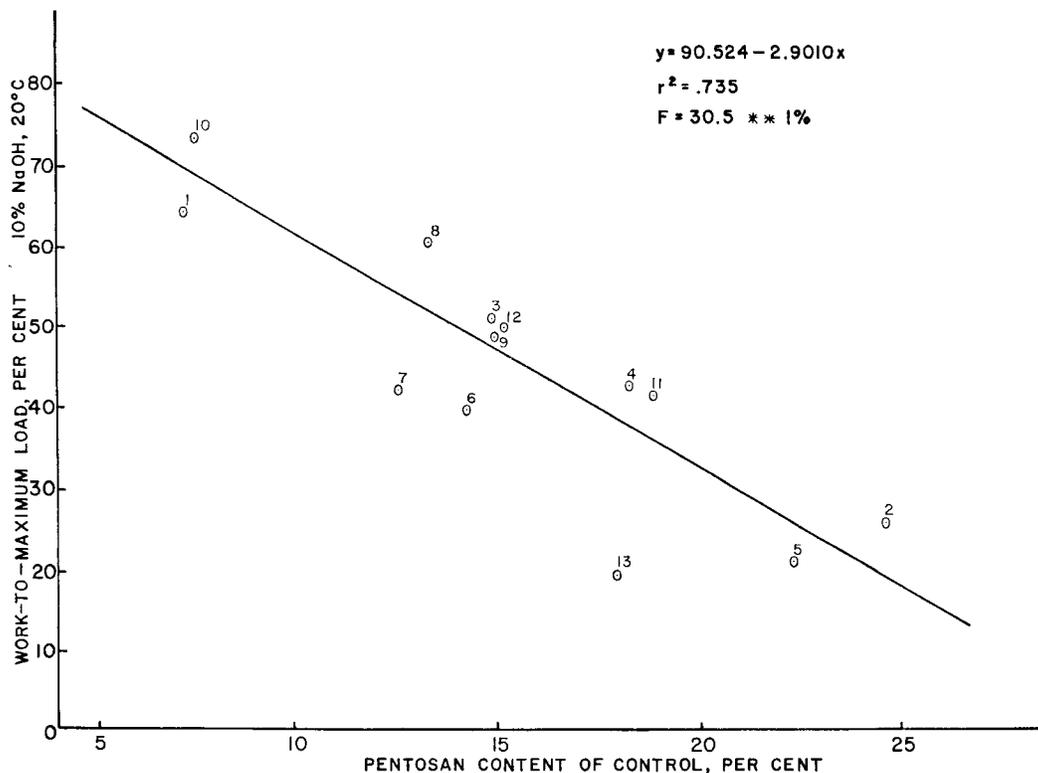


FIG. 5. Relationship between original pentosan content and work-to-maximum load retention following treatment with 10% NaOH for 32 days at 20 C.

wood has been shown by Ifju (1964). Although the hemicelluloses undoubtedly contribute to the strength of wood, it would be unwarranted not to consider the cellulose in wood of prime importance.

The significant relationship between the original pentosan content of the wood and modulus of rupture retention is important in that it gives a means for determining through chemical analysis the behavior of a wood sample with respect to acidic treatment. The assumption that a high pentosan content indicates low acid resistance has been given quantitative verification.

Alkaline Treatment

The primary effect of alkaline solutions on wood is one of causing increased swelling or increased accessibility. The glycosidic bonding of wood polysaccharides is resistant to alkaline cleavage below normal

pulping temperatures (Rydholm 1965). Some lignin is soluble in alkali as was indicated in the prior study (Wangaard 1966); the amount, however, is small in comparison to the loss of hemicellulose. The degree to which the hemicellulosic material is lost can be considered a measure of the degree of alkaline-induced accessibility. Where the concentration and temperature of the alkaline treatment are kept constant and the woods treated are all of a similar type, the extent of retention of hemicellulose could be a measure of the individual wood's ability to resist swelling by alkali. Increased accessibility resulted in a lowering of resistance to degradation, as indicated by a reduction in strength retention.

Pentosan retention under alkaline treatment does not give as good a correlation as does hemicellulose retention; however, it is still significant. Pentosan retention is a

more complex factor due to enhanced retention that results from alkaline-induced modification of the polysaccharide.

As with the acidic treatment, there is a significant relationship between the original pentosan content of wood and modulus of rupture retention after alkaline treatment. There is also a good relationship between original pentosan content and work-to-maximum load retention. The importance of these relationships is that they permit determination of the behavior of wood under alkaline treatment. As was the case in situations with acidic treatment, a high pentosan content indicates low resistance to degradation. The implication is that a low pentosan content of wood is an indicator both of good inherent inaccessibility and resistance to alkaline-induced accessibility.

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