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Ai, Tran Van
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

Sakai, Kokki
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University | Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

Kondo, Tamio
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

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Studies on the Holopulp

I. A Comparison of the Papermaking Properties of Holopulp and Conventional Chemical Pulp

Tran Van Ai, Kokki Sakai and Tamio Kondo

Laboratory of Wood Chemistry, Faculty of Agriculture,
Kyushu University 46-08, Fukuoka 812

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Small chip and Asplund fiber of temperate hardwood and softwood (beech and red pine respectively) as well as tropical hardwood (red lauan) were pulped by acidified chlorite and peracetic acid at laboratory-scale basis. Experimentally holopulp of these three species was made at 5-15% lower yield than theoretical value but obtained in up from 15-16% higher yield than unbleached kraft and sulfite pulps from the same species. Although having higher residual pentosan, holopulp of beech and red pine was not easy to beat as compared with chemical pulps. Nevertheless, red lauan was developed on a contrary trend. The holopulp was higher in color reversion and lower in scattering coefficient and opacity than conventional chemical pulp. Also the former had higher tensile, bursting and folding strengths but lower tearing strength than the corresponding characteristics of the latter. The physical properties of peracetic acid pulp were higher than chlorite pulp. The fact, however, happened only to the case of beech but red pine and red lauan. Limited data suggested that pentosan retention was responsible for all the above optical and physical differences.

INTRODUCTION

Wood has been used as the raw material for the manufacture of pulp and paper. The most versatile processes for making pulps were the sulfate (kraft) and sulfite. However, this raw material is becoming gradually scarce, high in price, and the pollution caused by these chemical processes is greatly concerned. Therefore the common interests nowadays are to obtain pulps having yields higher than normal chemical pulps and to eliminate simultaneously objectionable emissions to the environment. To reduce pollution, the use of sulfur chemicals is excluded. To achieve high yield pulps, the use of oxidants of holocellulose preparations is considered. Pulp obtained from the oxidative pulping is called holopulp. The chemical and physical properties of holopulp are indeed varied as compared with those of kraft or sulfite pulps. Nevertheless, little is known of to what extent this variation occurs.

The purposes of the work reported here were hence (1) to produce laboratory-scale holopulps from various wood species and (2) to investigate the variations of chemical and physical properties of these pulps as compared with those of conventional chemical pulps. As a part of the first objective the use of

sodium chlorite and peracetic acid was focussed on, of which the general procedures have been given in literature (Wise *et al., 1946;* Leopold, 1961).

Recently some papers (Silitonga and McGovern, 1975; Thompson and Kaustinen, 1964) dealt with the strength properties of holopulps prepared from acidified chlorite process but not with the physical properties of pulps from peracetic acid method. As a part of the second purpose, the strength properties as well as other properties of both chlorite and peracetic acid pulps were studied and then compared with those of conventional chemical pulps in order to understand the effect of holopulping on the wood fibers.

MATERIALS AND METHODS

Sample preparation and pulping

Samples of temperate hardwood (beech: *Fagus crenata),* temperate softwood (red pine: *Pinus densiflora*) and tropical hardwood (red lauan: *Shorea negrosensis)* were employed for the holopulping in this study. Air-dried small chips passing 10 mm screen and about 2mm in thickness or Asplund fibers were used as holopulping materials because it was believed that a higher delignification rate and a better penetration of oxidant liquors would be favored.

Two series of experiments were carried out in the holopulping. For the first series, alcohol-benzene extracted wood meals and Asplund fiber meals were used as starting materials in order to pick up the suitable conditions which would give the best yield with a less loss of carbohydrate and a maximum delignification for each technique and simultaneously each sample. Acid chlorite treatment (Wise *et al., 1946)* was carried out at 70°C for various treatment time and the best condition for each sample was shown in Table 1. The following conditions were selected as suitable for the peracetic acid delignification (Leopold, 1961) ; liquor ratio: 20, temperature: 80°C, reaction time: 2 hr and peracetic acid dosage as in Table *2*.

In the second series, when unextracted chips were delignified directly with conditions shown in Tables 1 and 2, it was found that the delignification across the chip did not take place completely and the chip did not become soft. Techniques were hence subsequently evolved by evacuating the chip at 23 milibar for 30 minutes and then under the presence of oxidant liquors for another two hours at room temperature prior to the heating in a water bath previously heated to proper temperature. The pulping runs were made in replicates of at least two. After the oxidative delignification, softened and whitened chips were washed with water and defibrated partly by hands and partly with a standard disintegrator.

Asplund fibers needed no such evacuation and were converted easily into holopulps when the oxidative delignification was over.

Kraft and sulfite pulps were prepared and bleached with conditions often used in this laboratory (Sameshima *et al.,* 1974). Kraft pulps were bleached with CEDED sequence and sulfite pulps with CEHD sequence (Chang and Kondo, 1971).

Table **1.** Conditions for chlorite pulp preparation.

Materials	Treatment time (hr)		
	beech	red pine	red lauan
Wood	5		6
Asplund fibers	4.5	47.5	4.5

Table 2. Conditions for peracetic acid pulp preparation,

Materials	Peracetic acid dosage (g/g of sample)		
	beech	red pine	red lauan
Wood	1.5	2.5	1.5
Asplund fibers	1.00	1.75	1.25

Both holo- and chemical pulps were evaluated by analyzing residual lignin, pentosan retention, Kappa number and brightness. Pulps were also beaten in a PFI mill at 10 % consistency and at a load of 1.8 kg/cm. The beating would be stopped when freeness was fallen into the range of 300 to 350 ml CSF and the beating time was recorded. Handsheets were then made for the optical and physical tests.

Analytical

The analyses carried out in this study included the determination of Klason lignin, pentosan (as phloroglucinol furfural) (Nakano, 1956), and sugar components (Borchardt and Piper, 1970).

Brightness was recorded with a Hunter spectrophotometer fitted with a blue filter. Opacity and scattering coefficient were measured with a green filter. Color reversion tests were conducted in dry conditions at 105°C for 60 hours. Effects of aging were calculated on PC number basis. Paper tests were carried out according to the general procedures given in Tappi standard (Tappi 220 m-60).

RESULTS AND DISCUSSION

Wood analyses, yield, Kappa number, and evacuation stage

1) Wood analyses

The analytical results of the samples taken are given in Table 3. As seen in this table, the analytical values of the Asplund fibers are generally lower than that of wood meals. It is evident that the chemical components of wood chips have been undergone some modifications during the Asplund process. Those modifications have affected further on the properties of pulps prepared from Asplund fibers as shown in the following part of this study. In general, the properties of pulps from Asplund fibers are inferior to those of pulps prepared from wood chips of the same species.

Table 3. Analytical data on the samples taken.

Materials / Constituents	Wood meals			Asplund fibers		
	beech	red pine	red lauan	beech	red pine	red lauan
Klason lignin	23.9	27. 4	33.2	23.2	25.5	32.3
pentosan	26.1	12.6	15.2	25.8	12.4	15.2
arabinan	1.3	1.7	1.5	1.5	1.1	0.6
xylan	24.9	11.2	13.7	23.2	10.9	12.8
mannan	2.7	9: 6	3: 9	2.4	13: 6	3.5
galactan	0.4	1.4	0.6	0.5	0.7	0.2
glucan	49.8	48.7	48.6	47.2	47.9	47.9

All percentages based on extractive-free samples.

2) ***Yield***

Included in Table 4 are analytical values of the holo- and chemical pulps prepared. It is seen that holopulps were made at lower yields of, in comparison with theoretical values of each species, 12-17 %, 7-9 %, and l-9 % for beech, red pine, and red lauan, respectively. However, holopulps of these three species were obtained in up to the following corresponding values of 12-17 %, 14-18 %, and 12-20 % higher yields than unbleached chemical pulps of the same plant (Fig. 1).

On the same basis of residual lignin content, differences in carbohydrate compositions are existed between chlorite and peracetic acid pulps (Table 4). Therefore the yield of the former was higher than the latter. Results also suggest that it is not facile to prepare holopulp from wood chip by peracetic acid technique.

3) ***Kappa number***

It is generally accepted that there would be a straight line relationship between Kappa number and lignin content of pulp. This is the cases of chlorite, kraft, and sulfite but peracetic acid pulps (Fig. 2). The relationship be-

Table 4. Analytical data on

Materials	beech						
	chips				Asplund fibers		
Pulps	ChP	PaP	KP	SP	ChP	PaP	KP
accepts	59.8	57.3			64.7	59.8	
rejects	3.5	1.6			0.5	0.5	
total yield	63.3	58.9			65.2	60.3	
bleached pulp			45.5	43.7			46.1
pentosan	17.0	16.6	12.6		19. 4	16.8	10.6
Kappa number	4.6	1.2	3.2	[illegible]	5.3	1.4	2.6
brightness	71.9	71.3	85.7	[illegible]	72.9	72.0	86.4
arabinan	0.7	0.5	0.4				
xylan	16.4	16.1	10.8				
mannan	1.9	1.8	[illegible]	[illegible]	[illegible]	0.7	0.4,
galactan	+	+	+	[illegible]	0.4	[illegible]	+
glucan	43.7	42.3	30.7	33.6	42.2	[illegible]	31.8

All percentages based on original samples. +, trace; —, nil. ChP, chlorite pulp;

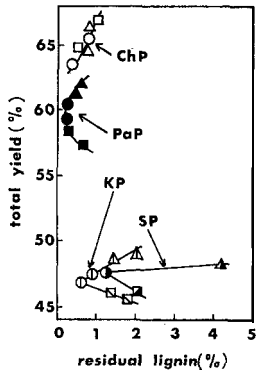


Fig. **1.** Total yield vs. residual lignin.
○ △ □ Chlorite pulp;
. ▲ ■ Peracetic acid pulp;
◐ ◭ ◨ Kraft pulp;
◑ ◮ ◪ Sulfite pulp.
Circle, Beech ;
Triangle, Red pine;
Square, Red lauan.

tween Kappa number and lignin content of peracetic acid pulp showed a convex curve. The slope of the lines showing such relationships is largest for kraft and then reduced gradually to sulfite and chlorite. It should be noted that the relationship was investigated over the lignin range of 0 to 5 % and beyond this range nothing is known about.

4) ***Evacuation stage***

As mentioned in the experiment part, wood chip was evacuated prior to holopulping. In order to understand the influence of evacuation stage upon the

holo- ***and*** chemical pulps.

red pine							red lauan						
chips				Asplund fibers			chips				Asplund fibers		
ChP	PaP	KP	SP	ChP	PaP	KP	ChP	PaP	KP	SP	ChP	PaP	KP
-63.5	56.6			64.4	61.1		61.6	56.6			65.4	57.1	
2.6	4.5			0.2	0.5		3.2				1.5	0.2	
66.1	61.1			64.6	61.6		64.8	58.1			66.9	57.3	
		45.5	44.3			46.7			43.6	43.4			43.9
a. 3	7. 5	5.4	3.1	6.5	6.1	3.2	9.9	7.4	5.8	2.3	10.1	8.3	3.5
5.9	11.0	3.0	3.7	5. a	12.5	2.8	4.9	1.4	4.1	3.4	8.1	9.2	3.4
70.1	70.1	84.2	81.0	56.6	62.7	86.3	65.0	55.9	84.5	88.6	77.0	56 7	86.1
0.9	1.0	0.4	0.2	0.7	0.6	0.2	0.9	1.1	0.5	0.4		...	0.4
8.2	6.1	4.5	3.7	7.0	5.0	2.8	9.1	6.4	4.9	2.1	9.8	7.0 4	2.8
9.5	8.8	3.0	6.6	8.1	6.0	3.3	2.7	2.8	1.2	2.3	2.4	3.3	3.1
0.4	0.4	+	+	0.3	0.3	0.1	0.3	0.3	+	—	+	+	—
46.8	44.5	35.8	32.8	47.2	47.1	40.5	48.2	47.2	32.8	37.1	46.8	44.9	34.2

PaP, peracetic acid pulp; KP, kraft pulp; SP, sulfite pulp.

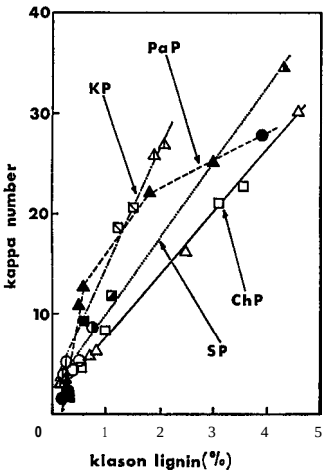
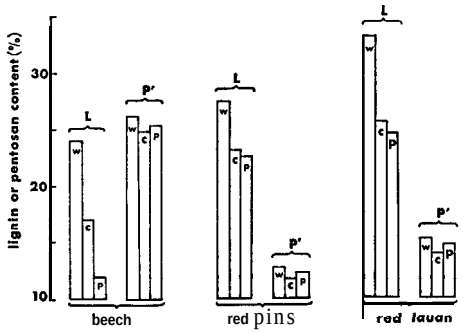


Fig. 2. Kappa number vs. Klason lignin. (Symbols as in Fig. *1)*



Pig. 3. Effect of the evacuation stage. w, chip; c, chlorite ; p, peracetic acid; L, lignin ; P′, pentosan.

chemical composition of chips, Klason lignin and pentosan contents of evacuated chip were determined and the results are shown in Fig. 3. It is evident that both chlorite and peracetic acid have reduced lignin and pentosan of wood chip. The delignification rate was faster with peracetic acid than chlorite while pentosan was reduced in a contrary way. The fact indicates that evacuation has acted not only as the improvement stage of the cooking liquor penetration into chips but also as a pre-cooking stage.

Beating

It is well known that freeness has been used to determine the degree of beating and also a measure of the rate of drainage of the pulp. In this study Canadian Standard Freeness was used as the measurement of pulp drainage and PFI mill as beater because of their availabilities for laboratory tests. The resulting time of beating of holo- and chemical pulps is shown in Fig. 4.

It is evident from Fig. 4 and Table 4 that for holo- and chemical pulps of

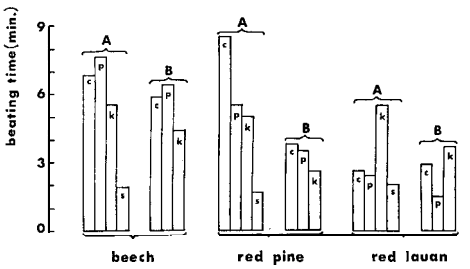


Fig. 4. Beating time required to 350ml CSF for various pulps.
c, ChP; p, PaP; k, KP; s, SP; A, pulps from wood chips; B, pulps from Asplund fibers.

temperate hardwood (beech) and temperate softwood (red pine), the higher the pentosan retention the longer the beating time. It is worthy to note that their residual lignins were smaller than 1%. The relationship between pentosan content and beating time of tropical hardwood (red lauan), however, developed in a different way. The kraft pulp of this species has a longer beating time than the holopulp. In every case studied, the time of beating of the sulfite pulp is the shortest as compared with other pulps. The variation of beating time of pulps prepared from Asplund fibers is the same as that of pulps derived from wood chips and always shorter.

In holopulps prepared from beech, beating time of peracetic acid pulp was longer than chlorite pulp. On the contrary, beating time of chlorite pulp from red pine and red lauan was longer than peracetic acid pulp from the same species. Holopulps of three species studied here were observed to be higher in residual pentosan content (Table 4) than conventional chemical pulps. The higher contents of arabinan and galactan in holopulps than in sulfite and kraft pulps support that a larger amount of primary wall was retained intact during the holopulping than in the chemical pulping since there were much evidences strongly suggesting that arabinan and galactan have been located principally in the primary wall (Meier and Wilkie, 1959 ; Meier, 1961). The characteristics of easy-to-swell of pentosan and difficult-to-bulge of primary wall can not explain completely the differences in beating time of various pulps derived from these three species. It is thus thought that the fact was probably lied in the differences of morphological and physicochemical properties of fibers prepared from different pulping processes, i. e. holo-, kraft, and sulfite. These problems will be examined further in more detail.

Color reversion

Included in Fig. 5 are results of the heat aging tests of beech. Red pine and red lauan had the same trends as that of beech. It is found in both beaten and unbeaten pulps prepared from wood chip and Asplund fiber, that kraft pulps were aged at a slow rate as compared with chlorite, peracetic acid and sulfite pulps. It would indicate that the acidity of three latter pulps was responsible for the larger decrease in their brightnesses upon heating. Also, since hemicelluloses are known to cause greater brightness reversion when hypo-

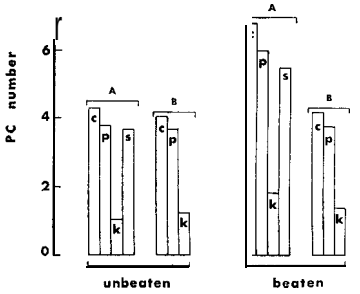


Fig. 5. Color reversion of beech by heat aging. (Symbols as in Fig. 4)

chlorite is included in bleaching (Histed, 1967), it seems likely that the large drop in brightness of sulfite pulp is due to the hypochloritc stage in the CEHD sequence which this pulp underwent.

The color reversion of unbeaten and beaten pulps from wood chip and Asplund fiber of all species examined was thus found in the following order: chlorite $\geq$ peracetic acid $\geq$ sulfite $\geq$ kraft. The reason that holopulps were more yellowed than chemical pulps is likely due to their higher pentosan content (Fig. 6). However, what kind of sugar in pentosan is responsible for this result is not known clearly. The PC number of beaten pulps were always large as compared with unbeaten pulps. This demonstrated that there was a greater influence of heat aging on the former than on the latter.

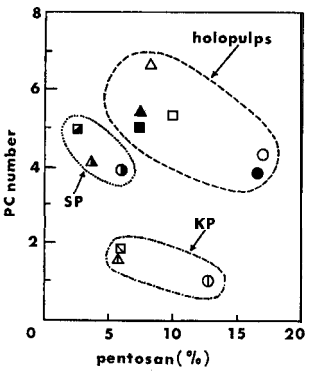


Fig. 6. PC number vs. pentosan. (Symbols as in Fig. 1)

Brightness of holopulp prepared just after the oxidative delignification was finished was as high as a corresponding bleached chemical pulp. However, it was not stable because after some process such as screening or beating, it was dropped rapidly. More works are necessary to stabilize brightness of holopulp.

Optical properties

Scattering coefficient is known as an expression of the opacity of a given pulp and decreases rapidly with increasing delignification. A relationship

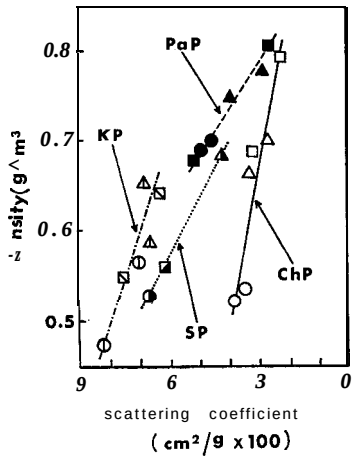


Fig. 7. Density vs. scattering coefficient. (Symbols as in Fig. **1)**

between sheet density and scattering coefficient is shown in Fig. 7. Sheet density of chemical pulp was generally lower than that of holopulp, and corresponded to a higher scattering coefficient. Lower optical properties of holopulp were probably due to their higher pentosan content (Fig. 9). Since it is known that by beating the hemicellulose-rich holopulp is increased more in the fiber bonded area than the pcntosan-poor chemical pulp, their fiber-air area, which is responsible for the scattering of light, would be therefore decreased. Also holopulp was observed to have a higher color reversion and simultaneously a lower scattering coefficient than chemical pulp (Fig. 8). This is another characteristic of the holopulp.

Physical properties

The physical properties of handsheets from holo- and chemical pulps were

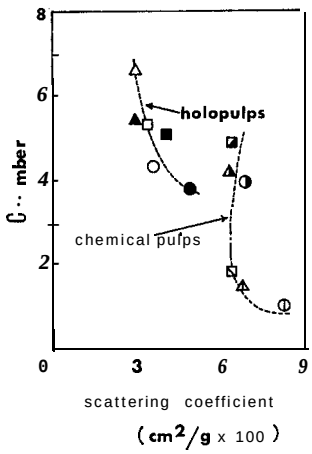


Fig. 8. PC number vs. scattering coefficient. (Symbols as in Fig. 1)

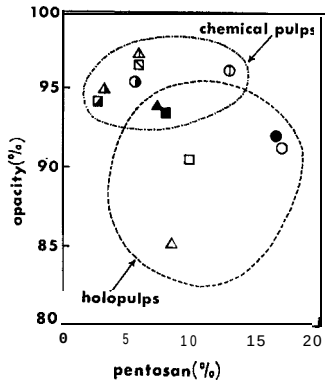


Fig. 9. Opacity vs. pentosan. (Symbols as in Fig. 1)

recorded in Figs. 10, 11, and 12. It is remarkable that at equal residual lignin content, holopulp has tensile, bursting, and folding strengths superior to the corresponding properties of chemical pulp. Tearing strength of holopulp is, however, lower than that of kraft pulp but higher than that of sulfite pulp. The strength values of Asplund fiber derived pulp were not included in Figs. 10, 11, and 12 because these figures would become intricate. However, these pulps had generally lower strengths than pulps from wood chips. Pentosan is believed to be responsible for the differences in strength properties of holo- and chemical pulps (Figs. 10, 11, and 12).

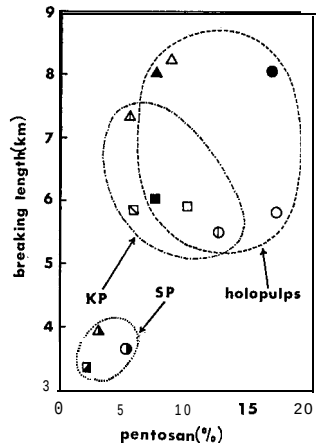


Fig. 10. Breaking length vs. pentosan. (Symbols as in Fig. 1)

The physical strengths of red pine pulps were generally higher than those of hardwood pulps (beech and red lauan). On the other hand, the mechanical properties of peracetic acid pulp were superior to those of chlorite pulp when beech wood were used as a raw material, but such the differences could not be observed with red pine and red lauan pulps.

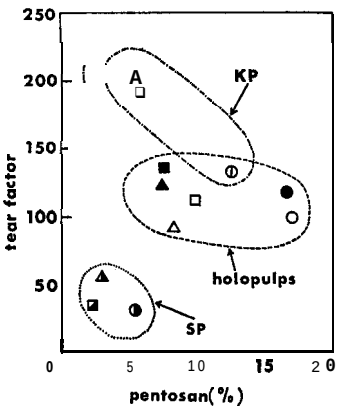


Fig. 11. Tear factor vs. pentosan. (Symbols as in Fig. 1)

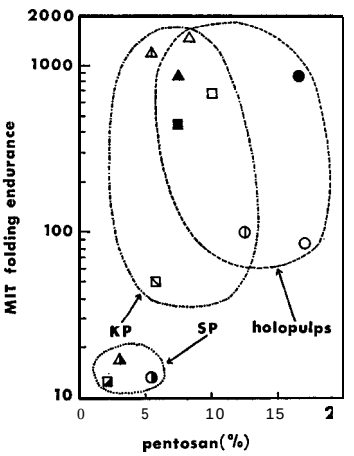


Fig. 12. Folding endurance vs. pentosan. (Symbols as in Fig. 1)

Other factors than chemical components such as fiber density, fiber length, and fiber strength (Dinwoodie, 1965, 1966) which are believed to be related to paper strengths will be examined and testified in further works.

SUMMARY AND CONCLUSIONS

It is possible to prepare holopulp from wood chip and Asplund fiber of temperate hardwood and softwood (beech and red pine respectively) as well as tropical hardwood (red lauan) at laboratory-scale basis by acidified chlorite and peracetic acid.

Generally holopulp of these three species was made at 5 to 15 % lower yield than theoretical value but in up from 15 to 16 % higher yield than unbleached kraft and sulfite pulps.

A lower chemical component of peracetic acid pulp than chlorite pulp sug-

gested that the former was more degraded than the latter and it is thus appeared more difficult to prepare peracetic acid pulp than chlorite pulp.

Holopulp was higher in color reversion upon heat aging and lower in scattering coefficient and opacity than chemical pulp. High percentage of pentosan of the former was believed to contribute to their lower optical properties.

Results of beating test of holo- and chemical pulps indicated that although having high pentosan content the beating time of the former of beech and red pine was much longer than the latter of 'the same species. Reating time of red lauan was developed on a. contrary way.

Evaluation of handshcets prepared from holo- and chemical pulps showed the former had lower tearing strength but higher tensile, bursting, and folding strengths than the corresponding strengths of the latter. Pentosan was thought to be responsible for these developments of holopulp.

It is concluded that at even higher yields, the holopulping has produced pulp having higher paper strengths and lower optical properties than pulp from conventional chemical pulping. Pulp fibers prepared in a shape nearly the same as that in the plant may be difficult to beat than wood fibers modified by chemical processes.

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