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https://doi.org/10.5109/23650

出版情報：九州大学大学院農学研究院紀要. 22 (1/2), pp.53-63, 1977-10. Kyushu University
バージョン：
権利関係：

J. Fac. Agr., Kyushu Univ., 22, 53-63 (1977)

Studies on the Holopulp

III. A Comparative Study of the Holopulps Prepared from Certain Woody and Non-Woody Plants

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(Received July 19, 1977)

Holopulps of rice straw (*Oryza sativa*), barley straw (*Hordeum vulgare*), bagasse (*Saccharum officinarum*), and moso bamboo (*Phyllostachys pubescens* Mazel) were prepared by chlorite and peracetic acid oxidative processes. The chemical, optical, and physical properties of the resulting holopulps were compared with the corresponding properties of the holopulps prepared from beech (*Fagus crenata*), red pine (*Pinus densiflora*), and red lauan (*Shorea negrosensis*) by the same techniques. The common characteristics of holopulps of both the woody and non-woody plants were that the yield, residual lignin, pentosan retention, beating time, brightness, light scattering coefficient, and handsheet density of the peracetic acid pulps were lower than the corresponding chemical and optical properties of the chlorite pulps prepared from the same plants. Taking the differences by the theoretical yields as a comparison basis, the holopulps of the woody plants would have higher yields than those of the non-woody plants. In the holopulps of non-woody plants, it was found that the higher the yield, the lower the brightness, and that the strength properties of peracetic acid pulps were higher than those of chlorite pulps. Such characteristics were not observed in the holopulps prepared from woody plants. Another striking difference between holopulps prepared from the two group plants is that the strength properties of pulps from non-woody plants were lower than those of pulps from woody plants. Holopulps of rice straw, in particular, had the lowest strength properties and highest optical properties.

INTRODUCTION

From the botanical viewpoint, plant species can be classified into monocotyledones and dicotyledons. Physically, the fiber structures of these two groups are quite different. Such fundamental differences are described in literatures (Clark, 1969; Rydholm, 1965 a). The fibers used in papermaking may be vascular bundle fibers from the stem or leaf of the monocotyledons or bast fibers from the dicotyledons. The physical properties of the resultant pulps depend in part on the morphological characteristics of the two groups, which are subsequently related to the growing conditions, geographic location, and state of maturity.

Till now, few of non-woody plants were used for the manufacture of pulp and corrugating board. The pulping processes prevailingly used were the soda and kraft techniques. Furthermore, a surplus of pulpwood is gradually tapered off. An examination of the non-woody plants as another fiber source, it is thought, is reasonable and timely. Use of the non-woody plants, however, is established on the fact that the species has been proved to be an acceptable material and the needed properties are conveyed to the final papers.

In this study, four non-woody plant species were used as experimental source for the preparation of holopulps. The pulping methods were the chlorite and peracetic acid techniques. The chemical, physical, and optical properties of holopulps derived from those non-woody plants were compared with the corresponding characteristics of holopulps from woody plants. By such a comparison, the variation of the papermaking properties of non-woody plants would be understandable and therefore their utilizability could be evaluated easily.

EXPERIMENTAL

1. Materials

a. Non-woody plants

The rice straw *(Oryza sativa)*, barley straw *(Hordeum vulgare)*, bagasse *(Saccharum officinarum)*, and moso bamboo *(Phyllostachys pubescens)* were used as the samples of non-woody plants. Their harvest and origin were reported earlier (Ai et al., 1977 b).

b. Woody plants

The samples representing woody plants were beech (*Fagus crenata*), red pine (*Pinus densiflora*), and red lauan (*Shorea negrosensis*). Some papermaking properties of the holopulps prepared from these species were presented in the previous work (Ai *et al., 1977* a).

2. Pulping methods

Clean rice straw and barley straw, including stalk and chaff, were chopped into chips about 5cm in length. The moso bamboo was denoded, chipped, and air-dried before use. The bagasse was not depithed, though the remaining pith would cause some disadvantages in the strength properties and brightness of resulting pulps (Clark, 1969).

All the samples prepared were subjected to holopulping using sodium chlorite and peracetic acid as cooking oxidants. Procedures of the two techniques were reported previously (Ai *et al.*, 1977a). However, some modifications were carried out in the pulping of non-woody plants as described briefly below.

The barley straw and bagasse were evacuated for one half hour and then again under the presence of oxidative liquors for two hours. Total evacuation time was two and half hours. The mixture was then heated in a water bath at a proper temperature. After the delignification treatment, the barley straw and bagasse were fiberized in distilled water with a high-speed propellor mixer and then flat-screened.

Preliminary runs showed that the rice straw and bamboo would yield relatively low accepts and high rejects if the procedure used for the barley straw and bagasse was followed. The rice straw and bamboo were therefore soaked in distilled water overnight, fiberized with mixer, and then delignified with chlorite or peracetic acid. Such procedures gave higher accepts and lower rejects than the previous techniques.

All the holopulps prepared were chemically analyzed. If the residual lignin content was found to be higher than 1 %, the holopulps were treated further with oxidants until the residual lignin was below 1 %.

Methods of chemical analysis of the resulting holopulps, beating procedure, handsheet formation, measurement techniques of the optical and physical properties were reported elsewhere (Ai et *al.*, 1977 a).

3. **Analysis**

The analytical methods, including solubilities in alcohol-benzene, cold water, hot water, and 1 % NaOH, and the determinations of ash, silica, Klason lignin, and pentosan were described previously (Ai et *al.*, 1977 b).

RESULTS AND DISCUSSION

Included in Table 1 is the analytical data of the woody and non-woody plants examined. It is evident that the solubilities in alcohol-benzene and cold water of straws were higher than those of the bagasse and bamboo and the woody species. Lower solubilities in hot water and 1 % NaOH of the woody plants as compared with the non-woody plants suggested an easier dissolution of pentosan and lignin of the latter than the former. Also, the ash and silica contents of the latter were higher than those of the former. The lignin content of the straws was found to be the lowest among the samples studied. This fact coincides with their high ash and silica contents. This may be related to the mechanical strength of the straws being supported mostly by silica and partly by their lignin. The role of lignin in lignified material is known to give the plant mechanical strength and to protect the cellulose fibers from the attack of microorganisms (Brauns and Brauns, 1960). The pentosan content of the non-woody plants was clearly higher than that of the temperate softwood (red pine) and tropical hardwood (red lauan) but was not different much from that of the temperate hardwood (beech).

Although the lignin content of rice straw was the lowest and that of bamboo was the same as that of red pine, their holopulp yields were the lowest among the holopulps prepared (Table 2). The low yields of holopulps prepared from rice straw and bamboo were probably due to their inhibitors interfering with their delignification processes (Ai *et al.*, **1977** b). Therefore a large amount of oxidants was consumed and their fibers were consequently damaged greatly. In comparison with the theoretical yield of each species, it was found that total yield of the rice straw was 30% lower. For the barley straw, bagasse, and moso bamboo, their total yields were 16, 13, and 18 % lower, respectively. To sum up, the total yields of the non-woody plants were 13 to 30% lower than their theoretical yields. On the other hand, the total

Table 1. Analytical data on the woody and non-woody plants.

Samples	Extractives (%) in				Ash (%)	Silica (%)	Lignin* (%)	Pentosan (%)
	Alcohol-benzene	Cold water	Hot water	1% NaOH				
Rice straw	7.0	14.2	14.4	48.9	15.2	13.9	14.7	26.5
Barley straw	7.2	10.7	12.5	44.8	6.7	3.9	18.7	23.3
Bagasse	1.5	3.3	4.3	37.2	1.2	2.1	21.7	27.3
Bamboo	3.8	0.7	1.7	23.3	0.3	0.3	27.3	22.1
Beech	4.2	3.6	4.7	13.0			23.9	26.1
Red pine	3.9			13.0	0:3		27.4	12.6
Red lauan		0:6	1:1	13.7	0.4		33.2	15.2

* Lignin content of the non-woody plants was determined as ash-free Klason lignin.

yields of holopulps prepared from the woody plants were 5 to 15 % lower than their theoretical yields (Ai **et al.,** 1977 a). Thus, if taking the difference by the theoretical yield as a comparison basis, it would be observed that the yields of the holopulps prepared from the wood chips were higher than those of the holopulps prepared from the non-woody plants. It could therefore be concluded that on the same basis of the residual lignin content (below 1 %), the carbohydrates of non-woody plants were degraded by oxidants more easily than those of woody plants, consequently resulting in lower yields of holopulps of the former than the latter (Fig. 1).

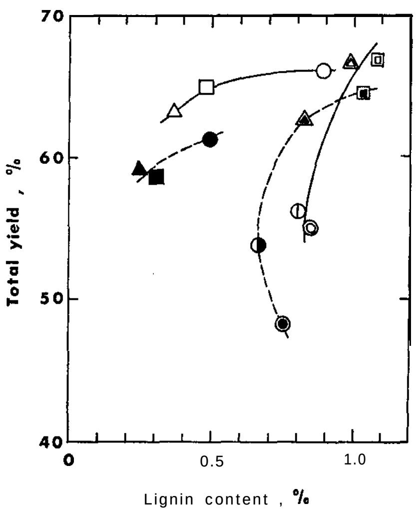

Fig. 1. Total yield vs. lignin content.
△ ,▲ beech ; ○,● red pine; □ ,■ red lauan ;
◎ ,◉ rice straw; ◐ ,◑ bamboo ; ❑ ,▣ barley straw ;
◬ ,◭ bagasse.

In each species, the first symbol represents the chlorite pulps and the second the peracetic acid pulps, The common characteristics of both holopulps prepared from the wood chips and non-woody plants are that the total yield, residual lignin, and pentosan content of the chlorite pulps were higher than those of the peracetic acid pulps. It is evident, therefore, that peracetic acid would degrade the carbohydrates more than would chlorite. Another common characteristic is that the brightness of the latter was lower than that of the former (Table 2). This fact is probably due to the peracetic acid pulp's higher density than that of the chlorite. The high density of a given pulp will be decreased in brightness because of its increase in transparency. Thus, there are fewer interfaces for the reflection of light but a greater opportunity for the absorption of light (Casey, 1961). On the other hand, it was found that for the holopulps of the

Table 2. Analytical data on the holopulps prepared from the woody and non-woody plants.

Samples	Pulp type	Theoretical yield (%)[1]	Yield (%)	Lignin (%)[2]	Pentosan (%)	Ash (%)	Silica (%)	Brightness (%)	Density (g/cm³)
Rice straw	PaP[3]	85.3	48.2	0.75	11.2	6.76	6.57	64.0	0.57
	ChP[4]	85.3	57.1	0.85	13.2	8.22	7.70	65.6	0.55
Barley straw	PaP	81.3	64.4	1.03	14.5	3.34	2.93	54.1	0.65
	ChP	81.3	66.a	1.08	16.5	2.75	2.27	59.2	0.59
Bagasse	PaP	78.3	62.6	0.82	13.7	1.10	0.87	49.0	0.64
	ChP	78.3	66.7	0.96	15.4	1.37	0.82	54.7	0.61
Bamboo	PaP	72.7	53.8	0.66	12.2	0.35	0.17	59.5	0.53
	ChP	72.7	57.a	0.80	13.7	0.77	0.17	64.2	0.49
Beech	PaP	76.1	58.9	0.25	16.6			71.3	0.68
	ChP	76.1	63.3	0.38	17.0			71.9	0.50
Red pine	PaP	72.6	61.1	0.49	7.5			70.1	0.71
	ChP	72.6	66.1	0.79	8.3			70.1	0.67
					7.4			55.9	0.59
Red lauan	ChP	67.8	[illegible]	[illegible]	9.9			69.0	0.58

[1] Theoretical yield $= 100 -$ lignin content in samples. [2] Lignin content of holopulps prepared from the non-woody plants was determined as ash-free Klason lignin. [3] Peracetic acid pulps. [4] Chlorite pulps.

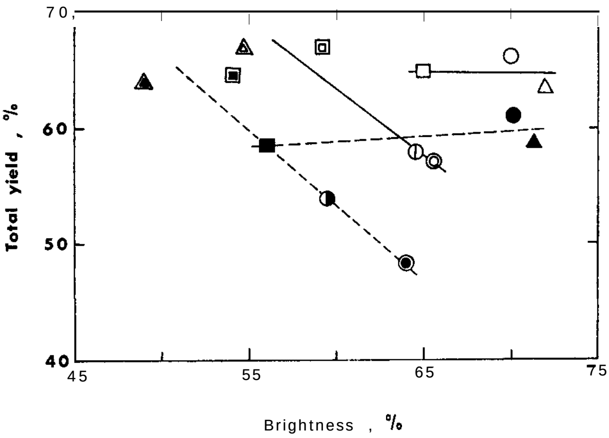

Fig. 2. Total yield vs. brightness (symbols as in Fig. 1).

non-woody plants, the higher the total yield, the lower the brightness. This characteristic was, however, not found in the holopulps prepared from the wood chips (Fig. 2). Although the holopulps of various woody plants had almost the same yield, their brightnesses varied greatly. The above facts can be explained as follows. It is known that the fiber content of woody plants is from 70% (for hardwoods) to 90 % (for softwoods) while non-woody plants contain about 50% fibers and other 50% are composed of parenchyma cells, vessels, and epidermic cells (Rydholm, 1965 a). High yield holopulps of non-woody plants thus contained more parenchyma cells, vessels, and epidermic cells than low yield ones and consequently have higher transparency which results in their low brightness. Holopulps of wood chips, on the other hand, were composed mostly of fibers. Their variations in brightness are thus influenced by other factors than by their morphological structure.

There was a definite relationship between the total yield and the scattering coefficient (Fig. 3). Such a relationship is seen clearly for the holopulps of non-woody plants but obscurely for those of woody plants. It is also evident that a high yield pulp would have a low scattering coefficient value, and *vice versa.* Since the total yield of holopulps from both the two group plants is almost in the same range, the fact is probably caused by the different numbers of fibers per unit weight. Light scattering coefficient is an indication of the extent of intra- and interfiber bonding.

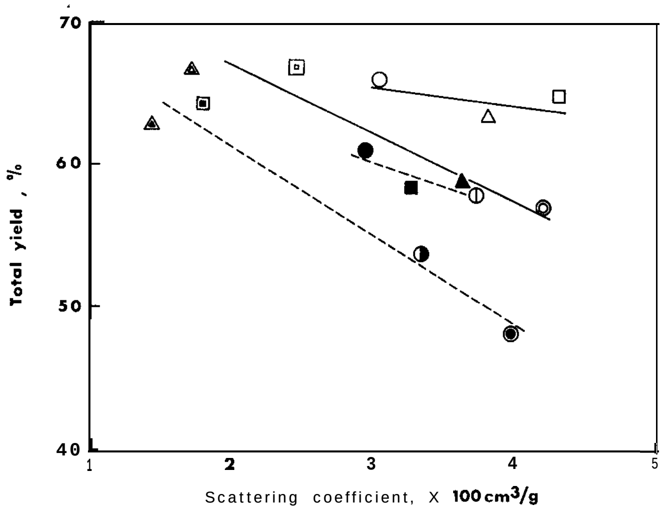

Fig. 3. Total yield vs. scattering coefficient (symbols as in Fig. 1).

The time taken to beat holopulps of the woody and non-woody plants to a freeness of 350ml CSf is given in Fig. 4. Generally, the beating time of chlorite pulps was longer than that of peracetic acid pulps. Except for the peracetic acid pulp of barley straw, the beating time of peracetic acid pulps prepared from the non-woody plants was shorter than that of the corresponding pulps from woody plants. On the other hand, the variation in the time taken to beat chlorite pulps from the woody and non-woody plants to a freeness of 350ml CSf was similar. However, no striking differences in the beating time of holopulps of the two group plants could be found.

It was observed that the pentosan content of chlorite pulps was higher than that of peracetic acid pulps (Table 2), this fact could not, nevertheless, be used to explain the longer beating time of the former pulps. A pentosan rich pulp is known to be rapid to beat because pentosan swells more in water than does cellulose (Casey, 1952). The flexibility of fibers, which is related to the ratio of fiber length to fiber diameter (Dinwoodie, 1966), can not also be used to explain the variation in the beating time of pulp types of the two group plants. The ratio of fiber length to fiber diameter of the non-woody plants is higher than that of the woody plants (Aronovsky, 1951). The longer beating time of chlorite pulps than peracetic acid pulps is therefore probably due to the amount of beating-resisting outer layers remaining larger in the former than in the latter. The hardness of beating of a given pulp is believed to be caused by the outer layers of cell wall (Hägglund and Webjörn, 1949). Such an assumption will indicate that the degree of attack on the cell wall in the delignification process is different between chlorite and peracetic acid.

Compared with the other non-woody species, holopulps of the barley straw were relatively slow to beat. This fact is probably due to the weak attack of oxidants, e. g. chlorite and peracetic acid, on the cell wall of the barley straw during cooking process.

The beating behaviour of the woody and non-woody plants will be examined further in greater detail.

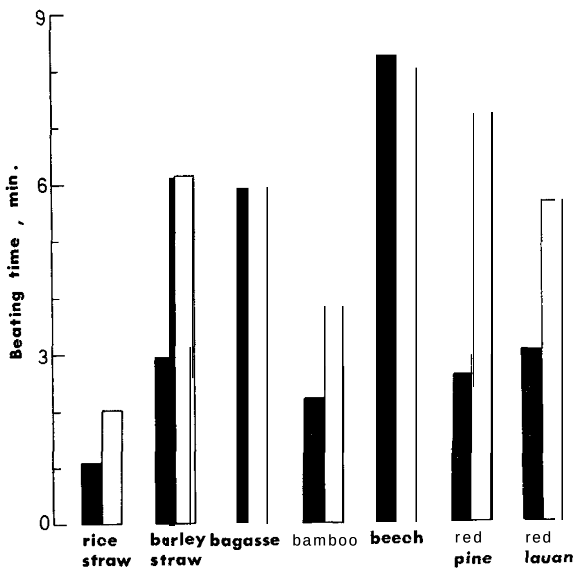

Fig. 4. The time of beating of holopulps from the woody and non-woody plants. Filled column, peracetic acid pulps ; Voided column, chlorite pulps.

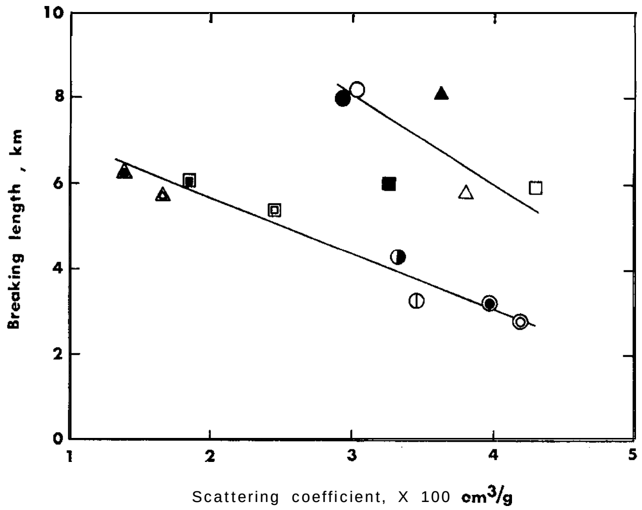

Fig. 5. Breaking length vs. scattering coefficient (symbols as in Fig. 1).

Although various plant species and holopulp types were studied here, a direct relationship between the scattering coefficient and breaking length was obtained for each group plant, e. g. woody and non-woody plant (Fig. 5).

Breaking length values were decreased with increasing in scattering coefficient values. A high scattering coefficient indicates a low amount of fiber bonding. Since fiber bonding is known to have influence on the breaking length, a low scattering coefficient will therefore correspond to a high breaking length. For a given scattering coefficient value of 300 to 400 cm^3/g, breaking length of the woody holopulps is greater than that of the non-woody holopulps by 2 to 4km. Though the fiber length is another factor affecting the breaking length (Rydholm, 1965 b), it can not be used to explain rationally the lower breaking length of the non-woody holopulps because the fiber length of non-woody plants (about 1.5 mm) is between of those of hardwoods (about 1 mm) and softwoods (about 3 mm) (Aronovsky, 1951; Casey, 1960). It is also observed that the pulp yields of the non-woody plants were generally lower than those of the woody plants (Table 2). Thus, it is natural that the handsheet of the non-woody holopulps will contain a larger number of fibers per gram than that of the woody holopulps. Rationally, there will be larger opportunities for the fiber to fiber bonding in the former than in the latter. However, since the breaking length of the non-woody holopulps was lower than that of the woody holopulps, this fact can not hence be demonstrated by the differences in the numbers of fiber per gram.

As seen in Fig. 5, breaking length of the rice straw holopulps was lowest when compared with those of the other species. An explanation for this fact and also for the difference in breaking length of the woody and non-woody holopulps could not possibly be based on the high silica content of rice straw pulps, in particular, or of non-woody holopulps in general (Table 2), although it was believed in the past that a pulp containing high silica content would

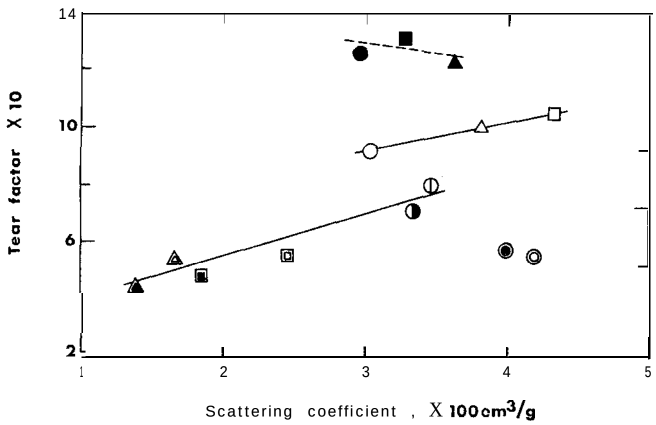

Fig. 6. Tear factor vs. scattering coefficient (symbols as in Fig. 1).

result in low physical strengths (Schenck and Kurth, 1941). Among the holopulps prepared from non-woody plants, the bamboo pulps had lowest silica content although their breaking lengths were lower than those of the barley straw and bagasse pulps.

In contrast to the breaking length, the tearing strength of the holopulps studied here can be divided into four groups : the rice straw, the three other non-woody plants, the woody chlorite pulps, and the woody peracetic acid pulps (Figs. 6 and 7). Normally, the tear factor is increased with an increase in the scattering coefficient (Fig. 6) or is decreased with an increase in the breaking length (Fig. 7). For a given scattering coefficient value or at a given breaking length value, the tear factor of woody peracetic acid pulps is always the highest as compared with the others.

One of the most striking differences observed in the comparison of the physical properties of holopulps from the woody and non-woody plants is that, only in pulps from the non-woody plants, the strength characteristics of peracetic acid pulps are higher than those of chlorite pulps (Fig. 7). This is a characteristic which was not found in the comparison of the physical properties of peracetic acid and chlorite pulps prepared from the woody plants.

Since the breaking length of the rice straw and bamboo was relatively low when compared with that of the other species, it is thought that this fact was probably due to their inhibitors decomposing peracetic acid and hence resulting in the formation of radicals which further degraded the cellulose. In testing this assumption, the rice straw and bamboo were therefore extracted with 0.05% HCI for one hour at 70°C before they were subjected to peracetic acid or chlorite treatment. It was interesting to observe that the peracetic acid dosage needed for HCl-extracted rice straw (200 %) or bamboo (125 %) was lower than that used for unextracted rice straw (250 %) or bamboo (150 %). However, the amount of chlorite needed was the same for both the extracted and unextracted materials. Some results of the peracetic acid pulps prepared from the HCl-extracted and unextracted rice straw and bamboo are given in

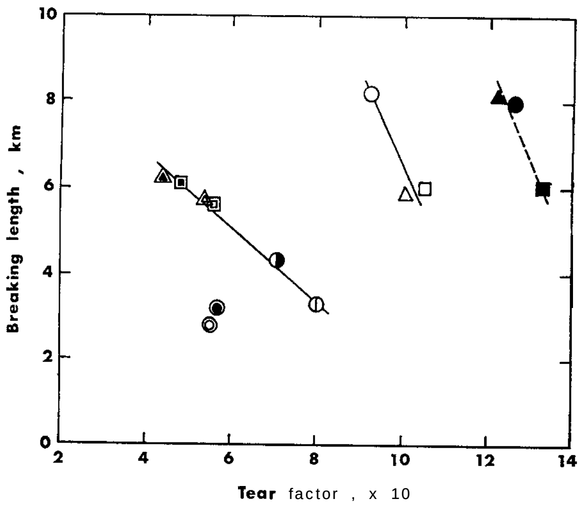

Fig. 7. Breaking length vs. tear factor (symbols as in Fig. 1).

Table 3. Analysis and physical properties of peracetic acid pulps prepared from the HCl-extracted and unextracted rice straw and bamboo.

Constituents	Rice straw		Bamboo	
	unextracted	HCl-extracted	unextracted	HCl-extracted
Rejects (%)	3. 9	0. 5	6. 1	3. 1
Accepts (%)	44. 3	55. 4	47. 7	48. 7
Total yield (%)	48.2	55. 9	53. a	51. a
Ash (%)	6. 76	a. 00	0.35	0.44
Silica (%)	6. 57	6.95	0. 17	0.17
Brightness (%)	64.0	60. 7	59. 5	69. 0
Beating time (min)	1.04	0. 50	2. 15	1. 52
Density (g/cm³)	3. 27	3. 23	0. 53	0.50
Breaking length (km)	56. 6	47. 6	4.3	5.2
Tear factor	...		70.7	91.3
Folding endurance	18	12'	38	99

Table 3. Results of the chlorite pulps of the extracted samples were not described here because there were no differences between the unextracted and extracted materials.

It is evident from Table 3 that the accepts were increased markedly, especially with the rice straw. The total yield of the HCI-extracted rice straw was quite higher than that of the unextracted rice straw. However, no difference in yield of the unextracted and extracted bamboo was observed. The beating time and brightness of the HCI-extracted rice straw were lower than those of the unextracted one.

In compensation for the increase of yield and the shortened beating time, the physical properties of the HCl-extracted rice straw were almost unchanged.

On the other hand, there was a marked augmentation of brightness and a slight increase of strength properties of the HCl-extracted bamboo. However, the increased strength properties of the extracted bamboo pulps are still lower than those of the barley straw, bagasse, and woody plants. The low strength properties of the rice straw and bamboo are therefore independent of the effect of their inhibitors.

The HCl extraction consequently affects to some extent the yield and the physical properties of peracetic acid pulps prepared from the rice straw and bamboo.

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