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II. Inhibitors in the Peracetic Acid Delignification of Certain Non-Woody Plants

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Rice straw (*Oryza sativa* L.), moso bamboo (*Phyllostachys pubescens* Mazel), barley straw (*Hordeum vulgare* L.), and bagasse (*Saccharum officinarum* L.) were subjected to oxidative delignification with sodium chlorite and peracetic acid. All the samples examined could be delignified almost completely by chlorite method. However, in the peracetic acid treatment, it was found that only barley straw and bagasse could be delignified. The peracetic acid delignification of rice straw and moso bamboo was unsuccessful when peracetic acid dosage was lower than 300%. Even at higher peracetic acid dosage, the delignification of rice straw could not take place, although that of bamboo was fairly accomplished. About one half of rice straw's lignin remained after peracetic acid delignification. It was found that extraction with diluted hydrochloric acid would facilitate the peracetic acid delignification of bamboo and rice straw, and that the extractable iron compound was the principal inhibitor. Bamboo contained 0.02% of extractable Fe^{2+} compound and rice straw 0.02% of Fe^{2+} and Fe^{3+} in approximately equal amounts. In addition to iron compound, manganese salt was found to be the co-inhibitor of rice straw's peracetic acid delignification. Such inhibitors played the role of catalysts in the decomposition of peracetic acid.

INTRODUCTION

It is reported in the previous work (Ai et al., 1977) that holopulps prepared from wood chips and Asplund fibers were slow to beat and had higher strength properties than conventional chemical pulps prepared from the same materials. It is also known that straws are not heavily lignified and can be pulped under less drastic conditions than wood. Besides, the loose structure of straws allow easy diffusion and penetration of chemicals. These significant phenomena made it desirable to extend the study of holopulp to other natural fibrous materials than woody fibers.

In the present study, materials of four non-woody plants, namely, rice straw, bamboo, barley straw, and bagasse were subjected to holopulping using sodium chlorite and peracetic acid as delignification reagents. It was observed that barley straw, bagasse, and moso bamboo could be delignified with both chlorite and peracetic acid methods. Rice straw, on the other hand, could be delignified only with chlorite and not with peracetic acid. About one half of rice straw's

lignin remained after the peracetic acid treatment.

As far as known, there is no work pointing out any chemicals or substances preventing the delignification of woody or non-woody plants by peracetic acid since this oxidant was first used in 1948 (Poljak, 1948) as a means of preparing holocellulose.

The purposes of the work reported here were thus: (1) to look for a suitable reagent for the pretreatment of rice straw, which would facilitate its post peracetic acid delignification and (2) to deal with the reason of why rice straw could not be delignified with peracetic acid.

EXPERIMENTAL

1. Materials

The rice straw (*Oryza sativa* L.) and moso bamboo (*Phyllostachys pubescens* Mazel) originated from the farm and the forest of Kyushu University, respectively. The rice straw was received in the autumn of 1975 and the moso bamboo, older than two years in age, in the spring of 1976. The barley straw (*Hordeum vulgare* L.) was the product of Fukuoka prefecture. The bagasse (*Saccharum officinarum* L.) originated in Okinawa and was not depithed. Both were taken in the spring of 1976. All the materials were ground in a Wiley mill, extracted with alcohol-benzene, air-dried, and denoted as original samples.

2. Oxidative delignification

Chlorite treatment was based on Wise method (Wise *et al.*, 1946). Temperature was 70°C.

Conditions of peracetic acid treatment were: liquor ratio, 30 ; temperature, 80°C ; pH, 3.75 (CH₃CO₂Na as buffer). Peracetic acid dosage was varied from 50 to 500%.

3. Pretreatment of rice straw

Prior to the peracetic acid treatment, rice straw was treated with various neutral, acidic, and alkaline reagents at a relatively high temperature for a short period. Conditions of these pretreatments are given in Table 1. From the results of preliminary experiments, the suitable concentration of each pretreatment reagent was, as shown in Table 3, based on the selection of a minimum concentration which would give a high delignification percentage and a

Table 1. Pretreatment conditions of rice straw.

Reagents	Temp. (°C)	Time (min)	Liquor ratio	Conc. (%)
HCl	70	60	50	0.01 -0.2
NaOH	70	10	80	0.005-0.2
NaHCO ₃	70	20	50	0.01 -0.2
(COONH ₄) ₂	80	60	50	0.1 -0.5
CH ₃ COOH	70	60	50	0.01 -0.2
Hot water	80	60	10	

minimum loss of holocellulose yield resulting from the peracetic acid treatment of pretreated rice straw.

4. Fractionation of HCl extract

The HCl extract of rice straw was neutralized with mild sodium hydroxide, concentrated under reduced pressure and then centrifuged. The supernatant was dialyzed for 24 hrs. The fractionation scheme is shown in Figs. 3 and 4. Each resulting fraction was mixed with HCl-extracted rice straw and those mixtures were treated with peracetic acid with a dosage of 400%.

5. Determination of inhibitory-effect

In the present study, the inhibitory-effect of hydrochloric acid extract or heavy metals was determined as follows: five grams of rice straw were extracted with 250ml of 0.05 % HCl solution at 70°C for 1 hr and then filtered. The filtrate was concentrated under reduced pressure to about 20ml. The concentrated filtrate, or, the heavy metal weights calculated from five grams of rice straw meal, were mixed with two grams of alcohol-benzene extracted beech (*Fagus crenata*) wood meal. Such mixtures were treated with peracetic acid (dosage, 150%) at 80 °C for 2 hrs. The residual lignin content of the resultant holocellulose was regarded as the inhibitory-effect of hydrochloric acid extract or heavy metals on the peracetic acid delignification of rice straw.

6. Analysis

Solubilities in alcohol-benzene, cold water, hot water, and 1 % NaOH, and ash determination were conducted according to the methods presented in Tappi standards (Browning, 1967). Silica determination followed the procedure of Tappi standard T224 su-70. Lignin content was determined as ash-free Klason lignin. Pentosan was determined as phloroglucinol furfural.

Iron, manganese, and copper were measured by colorimetric and atomic absorption (Shimadzu Atomic Absorption Flame Photometer AA-610) methods. Ignition was carried out at 700-800°C in an electric furnace.

RESULTS AND DISCUSSION

1. Analyses

Included in Table 2 are analytical data of the non-woody plants examined. It is evident that the solubilities in alcohol-benzene, cold water, hot water, and 1 % NaOH, and the ash and silica contents of straws were higher than those of moso bamboo and bagasse. The straws, however, had lower lignin contents than bamboo and bagasse. Rice straw, especially, had the highest silica content and the lowest lignin content when compared with three other samples.

2. Oxidative delignification behaviours

The degrees of chlorite delignification of the four samples studied here are given in Fig. 1. It was observed that the delignification percentages of rice straw were lower than those of the three other samples. However, it seemed

Table 2. Analytical data on the non-woody plants.

Constituents	Rice straw	Barley straw	Moso bamboo	Bagasse
Alcohol-benzene ext. (%)	7.0	7.2	3.8	1.5
Cold water ext. (%)	14.2	11.2	3.3	0.7
Hot water ext. (%)	14.4	15.3	4.3	2.5
1% NaOH ext. (%)	48.9	44.8	23.3	37.2
Ash (%)	15.2	6.7	0.3	2.8
Silica (%)	13.9	3.9	0.3	2.1
Lignin (corrected for ash, %)	14.7	18.7	27.3	21.7
Pentosan (%)	26.5	23.3	22.1	27.3

Fig. 1. Degree of chlorite delignification of four non-woody plants.

likely that the chlorite method was widely suitable to all the samples examined because their delignification degrees were more than 80% at the end of the third treatment hour.

In contrast to the chlorite method, peracetic acid did not seem to be suitable to the delignification of rice straw and bamboo as seen from Fig. 2. At a peracetic acid dosage of 200 %, the degrees of delignification of rice straw and bamboo were 40.2 and 60.8 % respectively. At a peracetic acid dosage of 400%, while 94.1% of bamboo's lignin were removed, only 52.4 % of lignin in rice straw were removed. Thus about one half of rice straw's lignin remained after its peracetic acid treatment. By that reason it was believed that there were inhibitors in rice straw which inhibited its peracetic acid delignification.

3. Evidences showing the presence of inhibitors

Usually rice straw was delignified by peracetic acid at a pH of 3.75. How-

Fig. 2. Degree of peracetic acid delignification of four non-woody plants.

ever, in order to study the effect of the pH of peracetic acid solution on the delignification of rice straw, this material was delignified at pH 6 with other conditions unchanged. The residual lignin content of rice straw after delignified at pH 6 was 8.8% or the delignification degree was 40.1%. Thus the result indicated that at pH 6 rice straw was more difficult to be delignified than at pH 3.75. This is probably due to the greater decomposition rate of peracetic acid at pH 6 than at lower pH.

Rice straw was then treated with various reagents prior to its usual peracetic acid delignification (see Experimental section). The peracetic acid dosage was 400 %, and the delignification percentages were determined in order to compare the effects of various pretreatment reagents. It is evident from Table 3 that 0.05 % HCl was the best pretreatment medium because the degree of delignification of rice straw treated sequentially with 0.05 % HCl and peracetic acid was the highest (82 %). This percentage was nearly the same as that attained by the chlorite method, about 84%.

The above results suggest that rice straw contains something which may interfere with the peracetic acid delignification of rice straw and is extractable with diluted hydrochloric acid.

To verify this conclusion, the HCl extract was fractionated as shown in Fig. 3. Fractions H1, H2, and H3 were mixed again with HCl-extracted rice straw prior to its peracetic acid treatment (peracetic acid dosage, 400 %). Residual lignin was then determined (Table 4). In comparison with residual lignin

Table 3. Effect of various pretreatment reagents on the peracetic acid delignification* of rice straw.

Reagents	Untreated	Hot water	CH ₃ COOH	(COONH ₂),	NaHCO ₃	NaOH	HCl
Conc. (%)	—	—	0.2	0.4	—	—	—
Res. lignin (%)	7.0	5.6	4.4	3.8	0.05	0.005	0.05
Degree of delignification (%)	52.4	61.9	70.1	74.2	75.5	78.9	82.3

* Peracetic acid dosage was 400%.

Fig. 3. Fractionation of 0.05% HCl extract from rice straw.**Table 4.** Residual lignin after the peracetic acid treatment of rice straw.

Samples*	Residual lignin (%)	Degree of delignification (%)
S	7.0	52.4
R	2.6	82.3
R+H1	5.8	60.5
R+H2	4.2	71.4
R+H3	3.6	75.5

* See Fig. 3.

of peracetic acid treatment of HCl-extracted rice straw (2.6%), it seemed that the inhibitory-effect was almost recovered in fraction H1, and dispersed into fractions H2 and H3. As mentioned above, rice straw contained a large amount of ash and the ash content of the Klason lignin was consequently up to 60%, based on the lignin weight. It should therefore be noted that the experimental errors in the ash determination of Klason lignin influenced largely the calculation of residual lignin of peracetic acid treated rice straw. In order to avoid these errors, the concept of "inhibitory-effect" (see Experimental section) was introduced and determined. Alcohol-benzene extracted beech wood meals (2g) were impregnated with fractions H1, H2, and H3 prior to the peracetic acid treatment. Peracetic acid dosage for beech was 150%. Fractions H1, H2, and H3 were seen clearly to inhibit the peracetic acid delignification of beech wood meal (Table 5).

Table 5. The inhibitory-effect of various fractions in Fig. 3.

Fractions	Degree of delignification (%)	Inhibitory-effect (%)
H1		
H2	51.5 24.3	11.6 18.1
H3	46.9	12.7
Control	95.0	1.2

Fig. 4. Further fractionation of 0.05% HCl extract from rice straw.

4. Characterizations of inhibitors

It was evident therefore that the HCl extract of rice straw contained inhibitors prohibiting the peracetic acid delignification of rice straw. However, it could not be known whether such inhibitors were high or low molecular and organic or inorganic matters. Therefore, further fractionation of HCl extract was carried out (Fig. 4). The inhibitory-effect of each resultant fraction, namely RM, RP, RA, H1A, RPa, RMn, and RMda, was recorded in Table 6. Sodium chloride formed from the neutralization of HCl extract was also included. Obviously, sodium chloride was not the inhibitor because it did not inhibit the peracetic acid delignification of beech wood meal. All other fractions, except RMn, did contain of forbidding materials whose existences and intensities were marked with + in Fig. 4. This can explain why fractions H2 and H3 had the same inhibitory-effect against the peracetic acid delignification of beech wood meal. Since there was precipitate in fraction H2 and, as given in Table 6, precipitate has showed inhibitory-effect, it was therefore made understandable the above phenomena.

Because fractions RM, RMd, RA, RMda, and RPa were involved in the inhibition of the peracetic acid delignification of beech wood meal, it could then be concluded, in part, that such inhibitors were inorganic matters and soluble partly in water. It was also observed that H1A, RA, RMda, and RPa had more inhibitory-effect than H1, RM, RMd, and RP. This is probably due to their increasing activities upon ignition.

Table 6. The inhibitory-effect of various fractions in Fig. 4.

Fractions	Degree of delignification (%)	Inhibitory-effect (%)
H1	28.9	17.1
RM	24.3	18.0
RP	16.3	20.0
RMd	38.1	14.8
RMn	98.3	0.4
H1A	19.7	19.2
RA	1a. 0	19.6
RPa	15.1	20.3
RMda	20.9	1a. 9
Control*	95.0	1.2

* Original lignin content of beech: 23.9%

H1A, RA, RPa, RMda were ashes of H1, RM, RP, RMd, respectively.

Fig. 5. Decomposition rate of peracetic acid.

5. Identification of inhibitors

Attempts were made to identify the function of inhibitors in the course of the peracetic acid delignification. Peracetic acid was then mixed with rice straw or HCl extract or ash from HCl extract at pH 3.75 and the decomposition rate of such peracetic acid mixtures was measured at 80°C (Fig. 5). It is evi-

dent that the decomposition rate of the mixture of peracetic acid with HCl extract or ash from HCl extract was the highest. Therefore inhibitors have acted as catalysts in the increase of decomposition rate of peracetic acid and hence rice straw's peracetic acid delignification was not accomplished completely. It is interesting to note that ash of HCl extract gave a reddish color during the early moment of the reaction with peracetic acid and a reddish-purple color at the end of the reaction.

Since inhibitors were inorganic matters as mentioned above, the resistances of various metals were investigated. Metal dosage was arbitrarily chosen as 4.8%, a percentage equal to the ash content of HCl extract. Preliminary runs showed that Mg, Ca, K, Al, P, Zn, Pb, and Na had no inhibitory-effect upon the peracetic acid delignification of beech wood meal. Fe^{2+} , Fe^{3+} , Cu^{2+} , Mn^{2+} , and Si (as water glass), however, exhibited a clear resistance to the peracetic acid delignification of beech wood meal with their intensities decreased in that order. In the above experiment, MnSO_4 was used as the sample of manganese because it was reported that manganese was likely to be absorbed by plants as the divalent cation (Adams, 1965).

Table 7. Delignification degree of the HCl-extracted non-woody plants at peracetic acid dosage of 100%.

Samples	Degree of delignification (%)		
	Unextracted	HCl-extracted	Gain
Rice straw	23.1	64.0	40.9
Bamboo	31.5	84.3	52.8
Barley straw	67.4	81.3	13.9
Bagasse	80.2	91.7	11.5

Besides, HCl-extracted bamboo, rice straw, barley straw, and bagasse showed a perfect delignification with peracetic acid (Table 7). Moreover, only the HCl extracts of rice straw and bamboo indicated the inhibitions against the peracetic acid delignification of beech wood meal (Table 8). By combining these facts, the contents of Fe^{2+} , Fe^{3+} , total iron, copper, manganese, and silica in the HCl extracts of four non-woody plants examined were determined (Table 8). Beech wood meal was then mixed with an amount equal to the determined percentage of each inhibitory-effect-having-metal of rice straw's HCl extract prior to its peracetic acid treatment. Results indicated that only iron inhibited the peracetic acid treatment of beech (Table 9). Hence, it could be concluded that the reason why rice straw was not delignified satisfactorily by peracetic acid was fundamentally due to its extractable iron compound (0.020%) which existed as both Fe^{2+} and Fe^{3+} in about half amount each.

It was experimentally found out that under 0.01% limit, iron would not inhibit the peracetic acid treatment. Above this limit, peracetic acid delignification would be decreased markedly (Fig. 6).

Also it was observed that HCl-soluble iron content of bamboo was the same as that of rice straw (Table 8). Hence, bamboo was found to be difficult to

Table 8. Metal content and inhibitory-effect of the HCl extracts of four non-woody plants.

Samples	Total iron (%)		Fe ²⁺	Fe ³⁺	Mn ²⁺	Cu ²⁺	Si*	Inhibitory-effect (%)
	Color	AA	(%)	(%)	(%)	(%)	(%)	(%)
RS extract	0.019	0.020	0.0091	0.010	0.071	+	1.40	18.1
BB extract	0.018	0.019	0.013	0.005	0.0032	0.0005	0.08	16.3
BS extract	0.009	0.0087	0.0075	0.0015	0.0012	0.0017	0.70	2.0
BG extract	0.007	0.0082	0.0061	0.001	0.0015	0.0003	0.30	2.2

RS, rice straw; BB, bamboo ; BS, barley straw ; BG, bagasse ; Color, colorimetric method; AA, atomic absorption method.

+: trace

* Determined as the difference of the silica content in original and HCl-extracted samples.

Table 9. Inhibitory-effect of iron and its mixtures on the peracetic acid delignification of beech wood meal.

Metals	Dosage (%)	Inhibitory-effect (%)	
		Before ignition	After ignition
FeSO ₄	0.007		ND
FeSO ₄	0.009	2.3	ND
FeSO ₄	0.020	16.7	0.2
FeCl ₃	0.020	15.8	0.3
MnSO ₄	0.071	0.6	0.7
Water glass	1.40	0.6	ND
FeSO ₄ +MnSO ₄	0.020+0.071	18.2	13.5
FeSO ₄ +FeCl ₃	0.011+0.009	13.4	0.4
FeCl ₃ +MnSO ₄	0.020+0.071	14.7	9.6
FeSO ₄ +FeCl ₃ +MnSO ₄	0.011+0.009+0.071	18.3	7.8
FeSO ₄ +MnSO ₄ +Water glass	0.020+0.071+1.40	18.7	0.5
FeSO ₄ *	0.020	4.1	ND
FeSO ₄ +MnSO ₄ *	0.020+0.071	11.8	ND

ND, not determined.

* Peracetic acid dosage was 400%. The others were carried out at peracetic acid dosage of 150%.

delignify at low peracetic acid dosages ($\leq 300\%$) (Fig. 2). However, since it could be delignified successfully at high peracetic acid dosages ($\geq 400\%$), it should be said that other factors must be involved in the inhibition of the peracetic acid delignification of rice straw. In other words, extractable iron compound was merely a principal inhibitor of the peracetic acid delignification.

As mentioned above, HCl extract of rice straw contained of manganese salt and silica (Table S), though these metals alone did not inhibit the peracetic acid delignification of beech wood meal at their determined percentages.

However, a mixture of iron and manganese or iron, manganese, and silica showed a higher hindrance effect upon the peracetic acid delignification than did iron alone (Table 9).

At peracetic acid dosage of 400 %, the delignification percentage of a mix-

Fig. 6. Inhibitory-effect of FeSO_4 dose against the peracetic acid delignification of beech.

ture of ferrous sulfate and beech wood meal was 80 % (Table 9). This was generally the same as that of moso bamboo's delignification percentage (94.1%) at the same peracetic acid dosage. Therefore, it is understandable why bamboo was delignified difficultly at low peracetic acid dosages. Also, since the delignification percentage of beech wood meal mixed with ferrous sulfate and manganese sulfate at a peracetic acid dosage of 400 % was 50 % (Table 9), a similar percentage to that of rice straw at the same peracetic acid dosage, it can certainly be said that manganese salt was a co-inhibitor of the peracetic acid delignification of rice straw. Such a conclusion was supported by the fact that a combination of ferrous sulfate and manganese sulfate did show a clear inhibition against the peracetic acid delignification of beech wood meal even after ignition, while other metals did not (Table 9). This result may explain, in part, why fractions H1A, RA, RMda, and RPa had higher inhibitory-effect on the peracetic acid delignification than fractions H1, RM, RMd, and RP, as already mentioned above. Hence it was thought that manganese has played a great role in the survived inhibitory-effect of ignited iron.

From the above results, it would be concluded that iron compound was the principal inhibitor of the peracetic acid delignification of rice straw and bamboo. Manganese salt, in particular, was the co-inhibitor in addition to iron compound, of the peracetic acid delignification of rice straw.

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