

Characteristics of Sulfurous Acid Prehydrolysis and Its Influence on the Efficiency of Subsequent Chemical Pulping Process

Yan Shi,^a Tomoya Yokoyama,* Takuya Akiyama, Makoto Yashiro,^b and Yuji Matsumoto

The potential of sulfurous acid prehydrolysis followed by chemical pulping was examined at the laboratory scale using radiata pine. The residue obtained by sulfurous acid prehydrolysis with base addition was sufficiently delignified in a subsequent soda pulping stage, while the delignification of the residue was completely insufficient in subsequent kraft pulping. The residues prepared by prehydrolyses of hydrochloric and sulfuric acids were not delignified sufficiently regardless of the pulping method. The yield of hemicellulose-derived monosaccharides was about 90% on a theoretical basis in the optimal sulfurous acid prehydrolysis. In subsequent soda pulping under various conditions, pulps with kappa number 21 to 34, pulp yield 37 to 41%, and high cellulose content could be prepared from the residue obtained by sulfurous acid prehydrolysis with base addition. It was suggested from these results that sulfurous acid prehydrolysis with base addition in combination with subsequent soda pulping is an effective method for the utilization of wood hemicelluloses.

Keywords: Acid saccharification; Cooking; Lignin; Sugar

Contact information: Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan; a: (Current address) Department of Packaging Engineering, Tianjin University of Commerce, 300134 Tianjin, China; b: Nippon Paper Industries Co., Ltd. Chemical Division, Hitotsubashi, Chiyoda-ku, Tokyo 100-0003, Japan; *Corresponding author: yokoyama@woodchem.fp.a.u-tokyo.ac.jp

INTRODUCTION

Currently, in the kraft pulping process, about 30 to 35% of carbohydrates are lost and degraded to hydroxyl acids, such as formic, glycolic, lactic, 2-hydroxybutanoic, and 2,5-dihydroxypentanoic acids. In particular, the loss of hemicelluloses reaches about 60% or more. It would be desirable to introduce a pretreatment stage into the pulping process. The pretreatment stage should effectively extract hemicelluloses while retaining cellulose at a sufficient level in the residue to make it possible to utilize hemicelluloses as high-value oligomeric and monomeric sugars and produce a pulp suitable for dissolving pulp after subsequent chemical pulping (Hendriks and Zeeman 2009). The introduction of a dilute acid prehydrolysis stage seems to be a promising method for this purpose.

There are potentially two concerns when dilute acid prehydrolysis is introduced prior to chemical pulping: efficiency of the extraction of monosaccharides in the prehydrolysis and the influence of the prehydrolysis on the efficiency of subsequent pulping. The latter concern arises from the knowledge that pretreatments often make raw materials susceptible to chemical reactions in subsequent processes (Ohgren *et al.* 2007;

Silverstein *et al.* 2007; Xu *et al.* 2007; Misson *et al.* 2009). We have focused on sulfurous acid as an attractive reagent in prehydrolysis because the following several advantages can be considered in sulfurous acid prehydrolysis. Sulfurous acid certainly hydrolyzes polysaccharides and lignin. Sulfurous acid or the hydrogensulfite anion reacts with the carbonyl groups of liberated monosaccharides to form adducts, which may prevent the monosaccharides from undergoing acid-catalyzed conversions to further degradation products. Sulfurous acid introduces organic sulfonic acid groups, which consequently increase the system acidity, although sulfurous acid itself is a weak acid. Sulfurous acid introduces sulfonic acid groups into lignin, which can contribute to the softening of raw material and delignification in the following pulping stage.

Concerning the conversion of liberated monosaccharides to further degradation products, it was indicated in our previous study that monosaccharides are much more stable in the hydrolysis stage using sulfurous acid than in those using hydrochloric and sulfuric acids at a constant pH, suggesting that sulfurous acid prevents the acid-catalyzed conversion of monosaccharides to further degradation products (Shi *et al.* 2012). On the basis of these considerations, sulfurous acid prehydrolysis should be advantageous to utilize hemicelluloses as high-value products. In this study, the optimal conditions of sulfurous acid prehydrolysis were established and the effect of the prehydrolysis on the efficiency of subsequent chemical pulping was evaluated at the laboratory scale using radiata pine as a wood sample.

EXPERIMENTAL

Materials

Radiata pine was obtained from Nippon Paper Industries Co., Ltd. Chemical Division (Tokyo, Japan) and ground using a Wiley-mill. The prepared wood meal (passed through a 20 mesh screen and retained on an 80 mesh screen) was extracted with ethanol/benzene (1/2). The moisture content of this original wood meal was 5.5%. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

Acid Prehydrolysis

Not only sulfurous but also hydrochloric and sulfuric acids were used to evaluate whether or not the utilization of sulfurous acid is advantageous. The wood meal (2.0 g oven dry weight) was mixed with an acid solution in a 50 mL sealed cylindrical TAF-SR reactor lined with Teflon (Taiatsu Techno[®] Co., Tokyo, Japan). After overnight pre-impregnation, the reactor was immersed in an oil bath equipped with a shaker at a constant temperature, 120 °C, 130 °C, or 140 °C.

As acid solutions, 1% hydrochloric acid and 1% sulfuric acid as well as sulfurous acid were employed. Sulfurous acid solutions were prepared from a 5% sulfur dioxide (SO₂) solution, and the concentrations employed were 2.5 or 2% as SO₂. The liquor to wood ratio was 20/1 L/kg in the treatments of hydrochloric and sulfuric acids. It was 7/1 L/kg in the treatments of sulfurous acid to simulate a practical sulfite pulping process. The reaction was continued for about 1 to 5 h. In some sulfurous acid runs, magnesium hydroxide was added as a base.

Analysis of Neutral Sugar and Lignin Contents

After the acid prehydrolysis, the residue was separated using a sintered glass filter followed by thorough washing with water. The combined solution and washings were transferred into a 100 mL volumetric flask, and the volume was adjusted to 100 mL with water. An aliquot of this solution was subjected to the alditol acetate method to determine the amount of neutral monosaccharides liberated from the original wood meal into the prehydrolysis solution (Jones and Albershe 1972; Dence 1992). The quantifications of the acetates of monosaccharides were performed using gas-chromatography (GC-14B, Shimadzu Co., Kyoto, Japan) with the acetate of an internal standard compound (*myo*-inositol). Another aliquot was subjected to the post-treatment with 4% sulfuric acid for 1 h at 120 °C to hydrolyze oligosaccharides possibly present in the prehydrolysis solution. The resultant solution was also subjected to the alditol acetate method to determine the amount of neutral monosaccharides in it. The effect of the post-sulfuric acid treatment on the detected amounts of monosaccharides was examined.

The separated prehydrolysis residue was subjected to the Klason method to determine the lignin content (Borchardt and Piper 1970). The residue was hydrolyzed with 72% sulfuric acid for 4 h at room temperature and successively with 4% sulfuric acid for 1 h at 120 °C to convert carbohydrates of the residue into monosaccharides. The Klason residue was separated on a sintered glass filter, dried overnight at 105 °C, and weighed to determine the Klason lignin content. The obtained solution was subjected to UV analysis at 205 nm to determine the acid-soluble lignin content. The total lignin content was calculated as the sum of the contents of the Klason and acid-soluble lignins. The obtained solution was also subjected to the alditol acetate method to analyze the neutral sugar composition of the prehydrolysis residue.

The lignin and neutral sugar contents in the original wood meal were also analyzed by the Klason and alditol acetate methods, respectively.

Chemical Pulping of Prehydrolysis Residue

Chemical pulping of the original wood meal and prehydrolysis residues (2 g or 4 g) was conducted in a 20 mL digester (Taiatsu Techno[®] Co., Tokyo, Japan) after overnight pre-impregnation with a cooking liquor. The ranges of active alkali charge and sulfidity employed were 22 to 33% and 0 to 30%, respectively, as Na₂O. The liquor to wood ratio was 3.5/1 L/kg. The designed heating procedure was as follows: 100 °C → 150 °C for 29 min; 60 min at 150 °C; 150 °C → 160 °C for 8 min; 42 min at 160 °C; 160 °C → 170 °C for 6 min; and 20 min at 170 °C. The target H factor was 1800.

Kappa Number Determination

The Kappa number of pulps obtained after chemical pulping was determined according to the TAPPI standard T-236cm-85 (1993).

RESULTS AND DISCUSSION

Chemical Composition of Radiata Pine

Table 1 lists the composition of the original radiata pine wood meal. It was typical as a softwood species. Although the total content of the polysaccharides and lignin, 91.7%, is sufficiently high as results of the alditol acetate and Klason methods of a softwood species, it is presumed that 4-*O*-methylglucuronic acid residues in

hemicelluloses and also some intermediate residues of polysaccharides were not detected as corresponding hydrolyzed monosaccharides in the alditol acetate method. Hence, the real contents of some polysaccharides should be slightly higher than the values shown in Table 1, although the theoretical yields of the monosaccharides in the acid prehydrolyses discussed in the following sections are based on the amounts of monosaccharides calculated from the values shown in Table 1.

Table 1. Composition of the Original Radiata Pine Wood Meal Used in This Study.

	Glucan	Mannan	Xylan	Galactan	Arabinan	Rhamnan	Lignin ^c
% ^a	44.8 ± 0.1 ^b	10.9 ± 0.1	5.0 ± 0.2	2.6 ± 0.2	1.5 ± 0.3	0.2 ± 0.2	26.7 ± 0.2

^a based on the original dry wood meal

^b The analysis was repeated totally 3 times.

^c total of the Klason and acid-soluble lignin contents

Prehydrolysis with Hydrochloric and Sulfuric Acids

Six monosaccharides, D-xylose, D-mannose, D-glucose, L-arabinose, D-galactose, and L-rhamnose, were detected in the solutions of acid prehydrolyses using hydrochloric and sulfuric acids. Figs. 1 and 2 show the yields of D-xylose, D-mannose, and D-glucose in prehydrolyses using 1% hydrochloric acid and 1% sulfuric acid, respectively. The data on L-arabinose, D-galactose, and L-rhamnose are not shown in this study because these monosaccharides are minor products and originate from side chains of hemicelluloses and pectic substances.

The results obtained in prehydrolyses using 1% hydrochloric acid are primarily discussed (Fig. 1). The maximum yields of D-xylose and D-mannose were obtained in the prehydrolyses for 3 h at 120 °C among all the reactions conducted. The reactions with longer periods at 120 °C decreased the yields. In the prehydrolyses at 130 °C and 140 °C, the shortest reaction period, 1 h, gave the maximum yields that were lower than those obtained in the prehydrolyses for 3 h at 120 °C. The yields constantly decreased upon extending the reaction period at these higher temperatures. The decrease of the yields indicates the conversion of D-xylose and D-mannose to further degradation products. Because the yield reduction was more severe for D-xylose than for D-mannose, the former should be more susceptible to acid-catalyzed further degradation. The post-treatments of the prehydrolysis solutions with 4% sulfuric acid for 1 h at 120 °C did not increase but rather decreased the yields of D-xylose and D-mannose in most cases. This result suggests that oligomeric xylan and glucomannan did not exist at considerable levels in the prehydrolysis solutions. The presence of these oligomers in the solutions should increase the yields, although it cannot completely be ruled out that the further degradations of D-xylose and D-mannose were more rapid than the productions of these monosaccharides from the oligomers in the 4% sulfuric acid post-treatments. The yields of D-glucose were almost constant in the prehydrolyses at 120 °C, while they increased upon extending the reaction period at 130 °C and 140 °C. The yield increase was significant at 140°C. It can reasonably be assumed on the basis of the yield of D-glucose at 120 °C that most D-glucose did not originate from cellulose but from a hemicellulose, galactoglucomannan. An increase of the yields in the prehydrolyses at 130 °C and 140 °C should have resulted from the hydrolysis of cellulose. The post-treatments with 4% sulfuric acid did not decrease the yields of D-glucose, suggesting the resistance of D-glucose to the post-

treatment. It is not plausible that oligomeric glucan existed in the prehydrolysis solution and the production rate of D-glucose from the oligomer was counterbalanced with the rate of the further degradation of D-glucose.

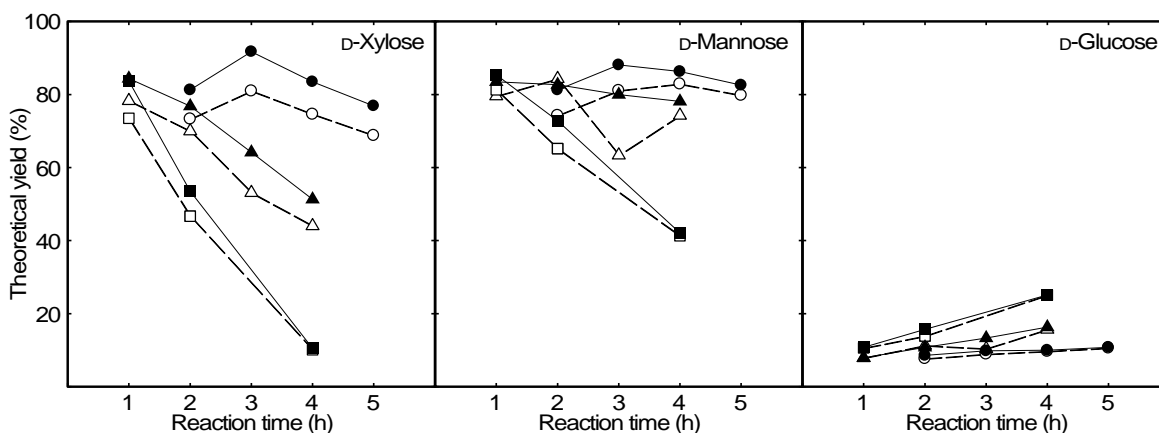


Fig. 1. Yields of D-xylose, D-mannose, and D-glucose in the prehydrolysis solutions in the prehydrolyses of the original radiata pine wood meal using 1% hydrochloric acid. Theoretical yield is based on the value listed in Table 1. Theoretical yield 100% of D-xylose, D-mannose, or D-glucose is 5.6 g, 12.1 g, or 49.8 g, respectively, when 100 g of the original wood meal was prehydrolyzed. ● ○: 120°C, ▲ △: 130°C, ■ □: 140°C, — without the post-treatment using 4% sulfuric acid, - - - with the post-treatment using 4% sulfuric acid

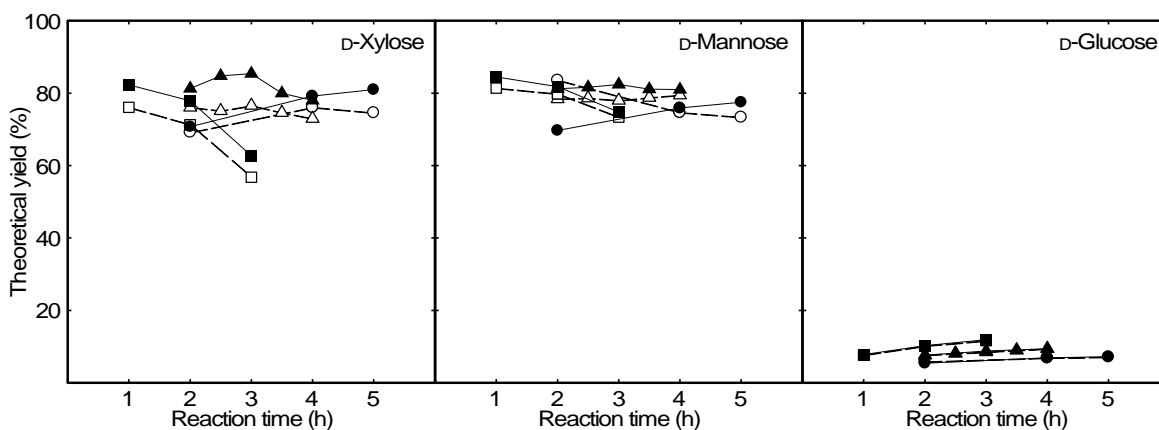


Fig. 2. Yields of D-xylose, D-mannose, and D-glucose in the prehydrolysis solutions in the prehydrolyses of the original radiata pine wood meal using 1% sulfuric acid. ● ○: 120 °C, ▲ △: 130 °C, ■ □: 140 °C, — without the post-treatment using 4% sulfuric acid, - - - with the post-treatment using 4% sulfuric acid

The prehydrolyses using 1% sulfuric acid for 3 h at 120 °C or for 1 h at 140 °C gave the maximum yield of D-xylose or D-mannose, respectively (Fig. 2). Because the molar concentration of 1% sulfuric acid is lower than half that of 1% hydrochloric acid, and sulfuric acid acts mostly as a monoprotic acid at the pH range employed (the pK_a value of hydrogensulfate anion is 1.99), prehydrolysis with 1% sulfuric acid can be regarded as an acid treatment weaker than that with 1% hydrochloric acid. This is a reason for the result that the maximum yield of each monosaccharide was slightly lower in the prehydrolyses with 1% sulfuric acid than in those with 1% hydrochloric acid.

Instead, the monosaccharides liberated from the original wood meal to the solutions were more stable in the former prehydrolyses than in the latter. The production of D-glucose from cellulose seems to have been effectively suppressed. It will be examined in future work whether or not sulfuric acid prehydrolysis gives yields of D-xylose, D-mannose, and D-glucose comparable to those in the 1% hydrochloric acid prehydrolysis, when the molar concentrations of the two prehydrolyses are the same.

It was indicated that about 90% of hemicelluloses are obtained as monosaccharides by the prehydrolyses using hydrochloric and sulfuric acids without significant hydrolysis of cellulose under the optimal conditions.

Prehydrolysis with Sulfurous Acid

Because sulfurous acid is weaker as an acid than hydrochloric and sulfuric acids, the conditions applied to sulfurous acid prehydrolysis were different from those used in the hydrochloric and sulfuric acid prehydrolyses. The concentration and temperature employed were 2.5% as SO_2 and 140 °C, respectively. In spite of this difference in the conditions, comparison of the yields of the monosaccharides between the prehydrolyses using these three types of acid should be meaningful. Magnesium hydroxide was used as a base in some sulfurous acid prehydrolyses. The same six monosaccharides as those obtained in the hydrochloric and sulfuric acid prehydrolyses were detected in the sulfurous acid prehydrolyses. The data on L-arabinose, D-galactose, and L-rhamnose are not shown.

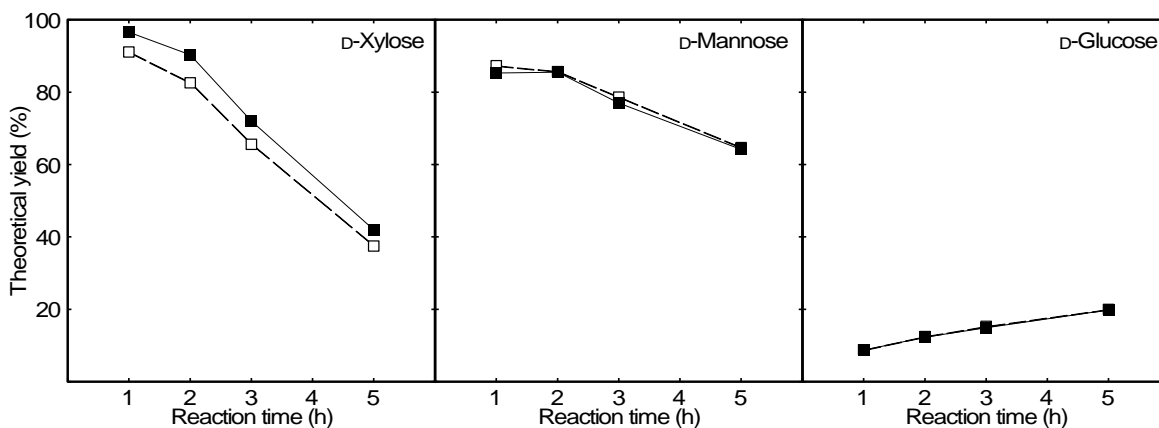


Fig. 3. Yields of D-xylose, D-mannose, and D-glucose in the prehydrolysis solutions in the prehydrolyses of the original radiata pine wood (140 °C) meal using sulfurous acid (2.5% as SO_2) without base addition. — without the post-treatment using 4% sulfuric acid, - - - with the post-treatment using 4% sulfuric acid

Figure 3 shows the yields of D-xylose, D-mannose, and D-glucose in the sulfurous acid prehydrolyses without base addition. The maximum yield of D-xylose obtained by the 1 h prehydrolysis (more than 95% as the theoretical basis) was somewhat higher than the maximum yields of D-xylose in the hydrochloric and sulfuric acid prehydrolyses. The maximum yield of D-mannose, also obtained by the 1 h prehydrolysis (about 88% as the theoretical basis) was similar to and higher than the maximum yields of D-mannose in the hydrochloric and sulfuric acid prehydrolyses, respectively. On the other hand, the liberation of D-glucose was suppressed in the sulfurous acid prehydrolysis to a degree similar to those in the hydrochloric and sulfuric acid prehydrolyses. It was shown that

sulfurous acid prehydrolysis affords amounts of hemicellulosic monosaccharides larger than hydrochloric and sulfuric acid prehydrolyses and damages cellulose on a level similar to hydrochloric and sulfuric acid prehydrolyses, and hence the former prehydrolysis is more advantageous as an acid prehydrolysis stage than the latter two. The post-treatments with 4% sulfuric acid slightly increased the yield of D-mannose in the sulfurous acid prehydrolyses, which suggests the existence of oligomeric glucomannan in the solutions.

A base is always added in practical sulfite pulping processes to attain sufficient delignification. Therefore, sulfurous acid prehydrolysis with base addition was also examined. Magnesium hydroxide was used as a base. The amount of added base is commonly expressed as TA/CA (total acid/combined acid) in practical sulfite pulping processes. TA is the weight percentage of the amount of added sulfurous acid (or SO_2). CA is equal to the weight percentage of the amount of sulfurous acid (or SO_2) that is converted to sulfite anion by base addition, supposing that sulfurous acid always works as a diprotic acid. The concentration of sulfurous acid and temperature employed in this kind of experiment were the same as those applied to the sulfurous acid prehydrolyses without base addition (2.5% as SO_2 and 140 °C, respectively). It was shown that the ratio TA/CA should be greater than 4/1 to attain sufficient delignification (Hart 1985). Figure 4 shows the yields of D-xylose, D-mannose, and D-glucose in the sulfurous acid prehydrolyses with base addition under conditions simulating those of a practical sulfite pulping process, where relatively small TA/CAs and a long reaction period were employed (TA/CA = 4.5, 4, and 3.5 for 5 h at 140 °C) to simulate practical acid sulfite pulping processes. Figure 5 shows the results obtained in the sulfurous acid prehydrolyses with base addition, where the conditions employed were TA/CA ratios larger than and a reaction period shorter than those applied in Fig. 4 (TA/CA = 15, 10, and 8 for 1.5 h at 140 °C). The yields of the monosaccharides were examined under these reaction conditions, which were different from those for a common sulfite pulping process, because it was desirable to decrease the amount of added base and shorten the reaction period without influencing the yield of monosaccharide.

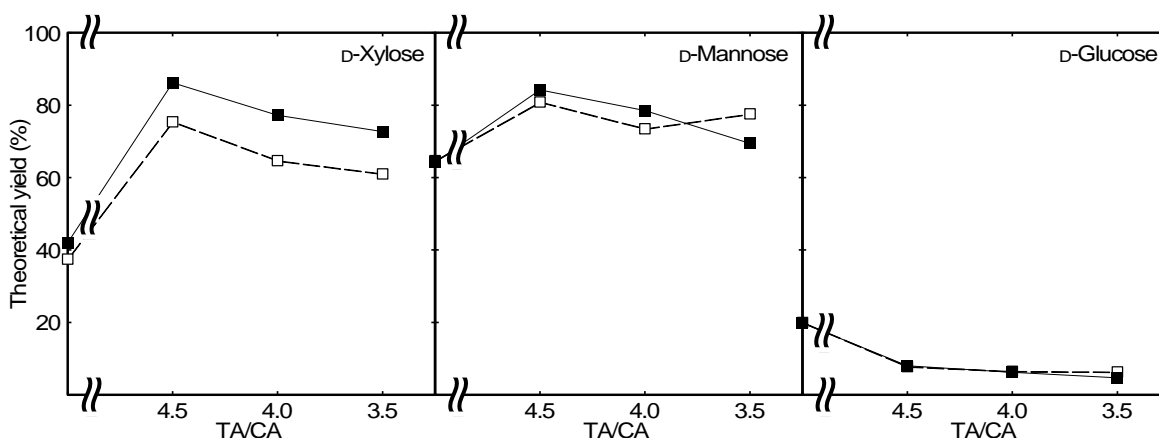


Fig. 4. Yields of D-xylose, D-mannose, and D-glucose in the prehydrolysis solutions in the prehydrolyses of the original radiata pine wood (5 h, 140 °C) meal using sulfurous acid (2.5% as SO_2) with base addition. — without the post-treatment using 4% sulfuric acid, - - - with the post-treatment using 4% sulfuric acid

As can be seen from Fig. 4, the addition of the base (TA/CA = 4.5) increased the yields of the hemicellulosic monosaccharides, D-xylose, and D-mannose, while the addition of larger amounts of the base (TA/CA = 4.0 and 3.5) decreased their yields. The yield of D-glucose decreased with increasing amount of added base. It was suggested that the hydrolysis of cellulose is suppressed by base addition. It was indicated that the largest TA/CA is the best among the three TA/CAs examined as a prehydrolysis process under the conditions simulating a practical sulfite pulping process. The maximum yields of D-xylose and D-mannose were about 84% and 87% as the theoretical basis, respectively. The lignin removal in these sulfurous acid prehydrolyses was about 85%. The larger TA/CAs and shorter reaction period shown in Fig. 5 gave yields of the monosaccharides similar to or higher than those described in Fig. 4. The yields of D-xylose and D-mannose were about 89% and 97% as the theoretical basis, respectively. The lignin removal in these cases was about 20%. Because the degree of lignin removal is not very important in the prehydrolysis stage owing to the presence of a subsequent pulping process for delignification, it is suggested that the amount of added base can be reduced and the reaction period can be shortened in sulfurous acid prehydrolysis.

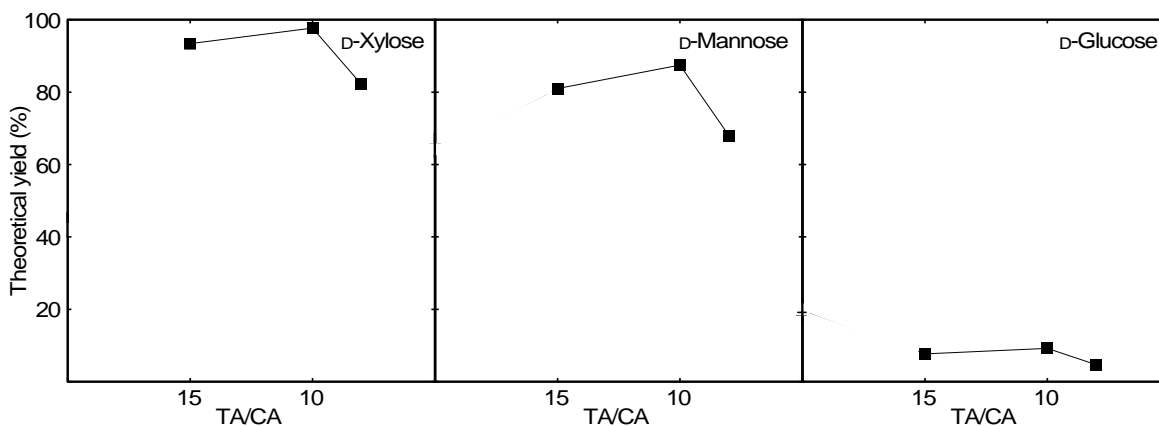


Fig. 5. Yields of D-xylose, D-mannose, and D-glucose in the prehydrolysis solutions in the prehydrolyses of the original radiata pine wood (1.5 h, 140 °C) meal using sulfurous acid (2.5% as SO₂) with base addition. — without the post-treatment using 4% sulfuric acid

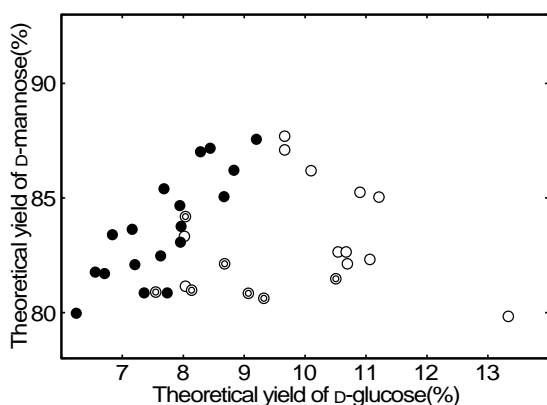


Fig. 6. Correlation between the yields of D-glucose and D-mannose in the prehydrolyses conducted. Theoretical yield of each monosaccharide is based on the maximum yield calculated from the value listed in Table 1. ●: sulfurous acid, ○: 1% hydrochloric acid, ⊙: 1% sulfuric acid

Because D-mannose is the main hemicellulosic monosaccharide in the case of radiata pine, it is desirable as a prehydrolysis stage that D-mannose and D-glucose are obtained with yields as high and as low as possible, respectively. Figure 6 shows the correlation between the yields of D-glucose and D-mannose in the prehydrolyses conducted in this study. It is clearly recognized that sulfurous acid prehydrolyses afford higher yields of D-mannose than hydrochloric and sulfuric acid prehydrolyses when these three different acids give the same yields of D-glucose as one another. These results indicate that sulfurous acid is advantageous as a prehydrolysis reagent.

Chemical Pulping of Prehydrolysis Residues and Original Wood Meal

Lots of prehydrolysis runs were conducted under various conditions using three acids to prepare prehydrolysis residues undergoing subsequent chemical pulping. Ten prehydrolysis residues listed in Table 2 were selected as those that should undergo subsequent chemical pulping because the total yields of six monosaccharides in these 10 prehydrolyses were sufficiently high, 23.0 to 24.9 g based on 100 g of original dry wood meal. Among the 10 prehydrolyses, the yields of D-glucose were lower in most of the sulfurous acid prehydrolyses than in the hydrochloric and sulfuric acid prehydrolyses. The 10 prehydrolysis residues were primarily subjected to the alditol acetate method to determine their polysaccharide compositions. The alditol acetate methods for most of the sulfurous acid prehydrolysis residues gave yields of D-glucose higher than those for the hydrochloric and sulfuric acid prehydrolysis residues. This result suggests that the sulfurous acid prehydrolysis residues, especially those with base addition, contained cellulose at levels higher than those in the hydrochloric and sulfuric acid prehydrolysis residues.

Table 2. Prehydrolysis Conditions Applied to the Preparation of 10 Prehydrolysis Residues Undergoing Subsequent Pulping ^a

No.	Prehydrolysis conditions ^b				Yield from 100 g dry wood meal (g)				
					Hydrolyzate		Prehydrolysis residue		
	Acid	Temp	Time	TA/CA	Glucose	Total ^d	Residue	Glucose	Lignin
1	1% HCl	120°C	3 h	—	4.8	24.9	68.4	42.9±0.3	24.0±0.2
2	1% HCl	140°C	1 h	—	5.4	24.2	66.9	42.2	23.3±0.3
3	1% H ₂ SO ₄	140°C	1 h	—	4.0	22.8	67.3	40.8	22.7±0.4
4	1% H ₂ SO ₄	140°C	2 h	—	5.2	23.0	66.8	42.5	23.0±0.3
5	2.5% H ₂ SO ₃ ^c	140°C	1 h	—	4.1	24.0	65.7	43.5	20.1±0.5
6	2.5% H ₂ SO ₃	140°C	1.5 h	10	4.6	24.7	64.1	43.3	21.3±0.4
7	2.5% H ₂ SO ₃	140°C	5/3 h	10	5.3	24.8	63.0	43.3	21.2±0.4
8	2.5% H ₂ SO ₃	140°C	2 h	10	5.3	24.8	61.9	43.8±0.3	20.4±0.4
9	2% H ₂ SO ₃	140°C	1.5 h	15	4.2	24.4	62.9	45.5	19.2±0.3
10	2% H ₂ SO ₃	140°C	2 h	10	4.1	24.2	61.9	44.7	17.6±0.3

^a The analysis was repeated 2 times in those with the standard deviations.

^b liquor to wood ratio: 20 L/kg in the reactions of HCl and H₂SO₄, 7 L/kg in the reactions of H₂SO₃

^c as SO₂, ^d total of the detected 6 monosaccharides

The 10 above-described prehydrolysis residues and the original wood meal were pulped under various conditions. Table 3 lists the yields, kappa numbers, and amounts of D-glucose liberated in the alditol acetate methods of the obtained pulps. The original wood meal was sufficiently pulped under kraft pulping conditions of 33% active alkali charge and 25% sulfidity. No pulping sufficiently delignified the hydrochloric and sulfuric acid prehydrolysis residues. However, the soda pulpings produced pulps with sufficiently low kappa numbers and high pulp yields from the prehydrolysis residues obtained by the sulfurous acid treatments with base addition, although the same residues were not sufficiently delignified by the kraft pulpings.

Table 3. Pulping Conditions Applied to the Preparation of Pulps from the 10 Prehydrolysis Residues and Quality of the Obtained Pulps ^a

No.	Pulping conditions		Pulp yield ^c	Kappa number	Glucose yield ^d
	Active alkali ^b	Sulfidity ^b			
Wood meal	23%	30%	52.3%	41.1±0.5	—
	29%	0%	41.6%	34.1±0.3	—
	29%	25%	48.9%	33.6±0.4	—
	29%	30%	50.2%	34.1±0.5	—
	31%	0%	43.2%	42.1±0.4	—
	33%	0%	40.0%	34.0±0.4	86.7±0.3 g
	33%	20%	50.3%	40.8±0.4	—
	33%	25%	48.3%	24.6±0.5	82.9±0.2 g
	33%	30%	50.0%	36.0±0.5	—
1	33%	0%	35.8%	146.7±0.5	—
	33%	10%	40.4%	159.6±0.4	—
	33%	25%	38.0%	120.1±0.5	—
2	33%	0%	36.3%	170.1±0.4	—
3	33%	0%	38.3%	140.1±0.5	—
	33%	10%	43.9%	155.5±0.4	—
	33%	25%	40.6%	118.8±0.6	—
4	33%	0%	40.4%	210.4±0.4	—
5	33%	0%	34.0%	85.9±0.5	—
	33%	10%	44.6%	193.3±0.5	—
	33%	25%	50.4%	216.3±0.4	—
6	29%	0%	41.6%	41.6±0.5	—
	33%	0%	40.8%	20.5±0.4	89.7±0.3 g
	33%	10%	47.7%	46.6±0.4	—
	33%	20%	43.2%	53.6±0.4	—
	33%	25%	45.8%	54.6±0.5	—
7	21%	0%	37.8%	26.6±0.3	—
	33%	0%	39.5%	34.0±0.4	92.8±0.2 g
8	29%	0%	36.9%	22.1±0.4	—
	31%	0%	36.6%	20.1±0.4	91.6±0.2 g
	33%	0%	36.0%	32.6±0.5	—
	33%	10%	40.0%	57.2±0.6	—
	33%	25%	43.8%	73.4±0.5	89.0±0.2 g
9	33%	0%	38.2%	55.4±0.4	89.6±0.3 g
	33%	10%	46.8%	137.7±0.5	—
10	33%	0%	36.4%	86.7±0.5	—
	33%	10%	44.9%	144.9±0.5	—
	33%	20%	44.1%	153.9±0.6	—

^a The analysis was repeated 2 times in those with the standard deviations.

^b based on the dry wood meal or prehydrolysis residue as Na₂O

^c based on the dry wood meal or prehydrolysis residue

^d obtained from the 100 g dry pulp in the alditol acetate method

No pulping prepared pulps with sufficiently low kappa numbers from the prehydrolysis residues obtained by the sulfurous acid treatments without base addition. The yields of D-glucose were about 90 g or more when 100 g of the pulps with sufficiently low kappa numbers and high pulp yields were subjected to the alditol acetate method. This result shows that the cellulose content in these pulps was fairly high. It was indicated that sulfurous acid prehydrolysis with base addition followed by soda pulping affords a pulp with sufficiently high yield, low kappa number, and high cellulose content.

CONCLUSIONS

1. Sulfurous acid prehydrolyses of radiata pine wood meal with and without base addition afforded hemicellulosic monosaccharides, D-mannose and D-xylose, with yields similar to or better than those obtained by hydrochloric and sulfuric acid prehydrolyses sufficiently suppressing cellulose hydrolysis. It was indicated that sulfurous acid prehydrolysis with base addition is advantageous as a pre-treatment stage of chemical pulping.
2. Subsequent soda pulping of the residues of sulfurous acid prehydrolysis with base addition produced pulps with sufficiently low kappa numbers, high pulp yields, and high cellulose contents. It was shown that sulfurous acid prehydrolysis with base addition followed by soda pulping is a good method for efficient utilization of wood polysaccharides.

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