ORIGINAL ARTICLE

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Sulfuric acid bleaching of kraft pulp III: reactivity of kraft pulping-resistant structures under acidic conditions

Abstract To investigate the bleaching mechanism, a lignin–carbohydrate complex (LCC) model compound, a vinyl ether-type lignin model dimer, and a hexeneuronic acid model compound were treated with dilute sulfuric acid of different pHs. Beech kraft pulp and red pine kraft pulp were also treated with dilute sulfuric acid and then extracted with aqueous alkali. The amount of hexeneuronic acid degradation products in acid effluents and lignin dissolved in alkali effluents were determined. It was found that the benzyl ether-type LCC bond and the vinyl ether bond in lignin were effectively cleaved under the pH where sulfuric acid bleaching of kraft pulp was effective. Hexeneuronic acid group was also effectively degraded during sulfuric acid bleaching. In beech kraft pulp bleaching, both lignin removal and hexeneuronic acid removal contributed to the kappa number reduction. In red pine bleaching, the contribution of hexeneuronic acid removal was negligible, and most of the kappa number reduction was achieved by the lignin removal.

Key words Kraft pulp · Sulfuric acid · Lignin–carbohydrate complex · Vinyl ether · Hexeneuronic acid

Introduction

In recent years environmental problems caused by the discharge of chlorinated organics substances from bleach

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plants of kraft mills have been of great concern worldwide to pulp manufacturers. As a result, the amount of elemental chlorine in use for pulp bleaching has been decreasing rapidly during the past decade. Chlorine dioxide has replaced elemental chlorine to a great extent. At the same time, oxygen-based bleaching chemicals such as oxygen, ozone, and peroxides have been used increasingly for kraft pulp bleaching.

In our earlier papers of this series,[1,2] sulfuric acid bleaching was proposed as one stage of nonchlorine bleaching sequences for kraft pulp. The results of hardwood kraft pulp bleaching and softwood kraft pulp bleaching were presented in part I. Both kraft pulps were successfully delignified with dilute sulfuric acid, keeping the pulp viscosity within acceptable levels. The delignification selectivity, which is the kappa number reduction versus viscosity loss, was greatly improved by the addition of sodium nitrate and sodium nitrite. Lignin and carbohydrates dissolved into bleach effluents were analyzed, and the results were presented in part II. Only a small amount of the hemicelluloses was disssolved during sulfuric acid bleaching even though acidolytic reactions were employed. It was also revealed that the role of the additives was oxidative degradation of lignin in the kraft pulp, which resulted in enhanced delignification.

To elucidate the bleaching mechanism, we investegated the reactions of some kraft pulping-resistant chemical structures in pulp using model compounds composed of lignin, lignin–carbohydrate complex (LCC), and hexeneuronic acid. Also investigated in this study was the relative contribution of lignin removal and hexeneuronic acid removal to the kappa number reduction of kraft pulp during sulfuric acid bleaching.
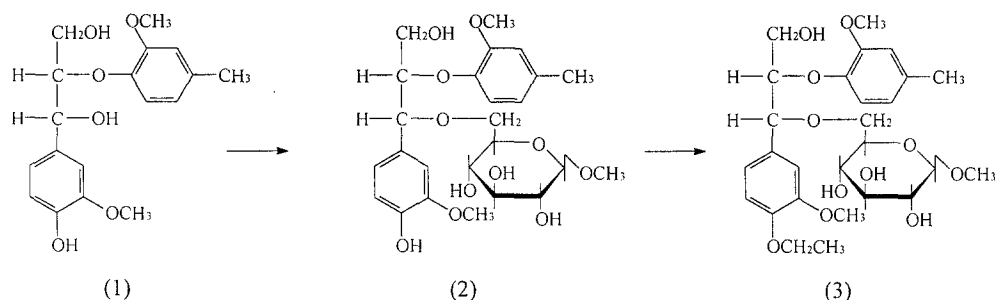
Experimental

LCC model compound

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-propan-1,3-diol (compound 1 in Fig. 1) was synthesized by the method of Hosoya et al.[3] Quinone

Fig. 1. Synthesis of lignin–carbohydrate complex (LCC) model compound

methide from compound 1 was synthesized by the method of Ralph and Young.[4] 1-(4-Hydroxy-3-methoxyphenyl)-1-methyl-β-D-glucopylanoside-2-(2-methoxy-4-methylphenoxy)-propan-3-ol (compound 2 in Fig. 1) was synthesized by the addition of methyl-β-D-glucopylanoside to the quinone methide from compound 1 by the method of Taneda et al.[5] and Tanaka et al.[6] 1-(4-Ethoxy-3-methoxyphenyl)-1-methyl-β-D-glucopylanoside-2-(2-methoxy-4-methylphenoxy)-propan-3-ol (compound 3 in Fig. 1) was synthesized by ethylation of the phenolic hydroxy group on compound 2 with diazoethane. Four isomers of compound 2 were isolated by means of high-performance liquid chromatography (HPLC), identified by nuclear magnetic resonance (^{1}H- and ^{13}C-NMR), and compared with the data reported by Taneda et al.[5] and Tokimatsu et al.[7] HPLC conditions were as follows: apparatus, Shimadzu LC-6A; column, Shimadzu Shim-pack CLC-ODS (M), 4.6 × 250mm; column temperature, 35°C; eluents, acetonitrile/water (20:80); flow rate, 0.7ml/min; detector, ultraviolet (UV) at 280nm. NMR data were recorded on a JEOL A500 (500MHz) spectrometer with tetramethylsilane as an internal standard. Compound 3 has four isomers, but their separation by HPLC was not successful. A mixture of four isomers was used for acid treatment of compound 3.

Vinyl ether-type lignin model compound

The vinyl ether-type lignin model compound was synthesized through alkali cooking of guaiacylglycerol-β-guaiacyl ether.[8] It was identified by ^{1}H- and ^{13}C-NMR.

^{1}H-NMR (CDCl$_3$):δ 3.87 (3H, s, aromatic-OC$\underline{H}_3$), 3.88 (3H, s, aromatic-OC$\underline{H}_3$), 3.89 (3H, s, aromatic-OC$\underline{H}_3$), 3.90 (3H, s, aromatic-OC$\underline{H}_3$), 5.54 (1H, d, cis C$_a$-$\underline{H}$), 6.28 (1H, d, trans C$_\beta$-$\underline{H}$), 6.52 (1H,d, cis C$_\beta$-$\underline{H}$), 6.99 (1H, d, trans C$_a$-$\underline{H}$), 6.77-7.60 (12H, m, aromatic H). ^{13}C-NMR (CDCl$_3$):δ 55.7 (aromatic-OCH$_3$), 55.9 (aromatic-OCH$_3$), 56.0 (aromatic-OCH$_3$), 108.1, 110.1 (cis $\underline{C}_\beta$), 111.3, 112.4, 112.6, 113.2 (trans C_β), 114.0, 114.6, 116.7, 118.0, 119.0, 120.9, 122.2, 123.7, 124.1, 127.5, 127.6, 140.5 (cis $\underline{C}_a$), 143.0 (trans $\underline{C}_a$), 144.4, 144.6, 146.2, 146.3, 146.6, 149.9, and 150.0.

Hexeneuronic acid model compound

The hexeneuronic acid model compound was obtained from oxygen-bleached kraft pulp by xylanase (*Rhizopus*

nieveus) treatment according to the procedure reported by Ishihara et al.[9] The isolated oligomer (compound 6 in Fig. 2) was identified by ^{1}H- and ^{13}C-NMR. The NMR data obtained were identical to the data in the literature.[10]

Kraft lignin and reducing sugars

Kraft lignin (Indulin AT) was purchased from Sigma. Reducing sugars were purchased from Wako.

Kraft pulping

The following conditions pertained. Species: Japanese beech (*Fagus crenata* Blume) and Japanese red pine (*Pinus densiflora* Sieb. et Zucc). Active alkali: 13.5% (beech), 18% (red pine). Sulfidity: 25%. Liquor ratio: 4l/kg. Cooking temperature and time: maximum 170°C, time to maximum 90min, time at maximum 90min. The kappa number and viscosity of the pulp were determined by the TAPPI standard method.

Acid treatment of model compounds

The LCC model compound (1.33mg) was dissolved in dioxane (0.1ml) and dilute sulfuric acid pH 1.0–3.0 (0.5ml) in a vial. This vial was then heated in am oil bath at 100°C. After the reaction, the solution was cooled in a cold bath and it was neutralized with 1N sodium hydroxide.

The vinyl ether model compound (0.93mg) was dissolved in dioxane (0.2ml) and dilute pH 1.0–4.0 sulfuric acid (0.2ml) in a vial. The reaction conditions were the same as above.

The hexeneuronic acid model compound (0.55mg) was dissolved in 0.22ml citrate buffer and adjusted to each pH (pH 1.0–6.0) by sulfuric acid in a vial. The reaction conditions were the same as above.

Identification and quantitative analysis of reaction products

1-(4-Ethoxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-propan-1,3-diol (compound 4 in Fig. 2) was subjected to HPLC directly. The HPLC conditions for compound 4 were as follows. Apparatus, Shimadzu LC-6A; column, Shimadzu Shim-pack CLC-ODS(M) (4.6 ×

Fig. 2. Reactions of model compounds during acid treatment
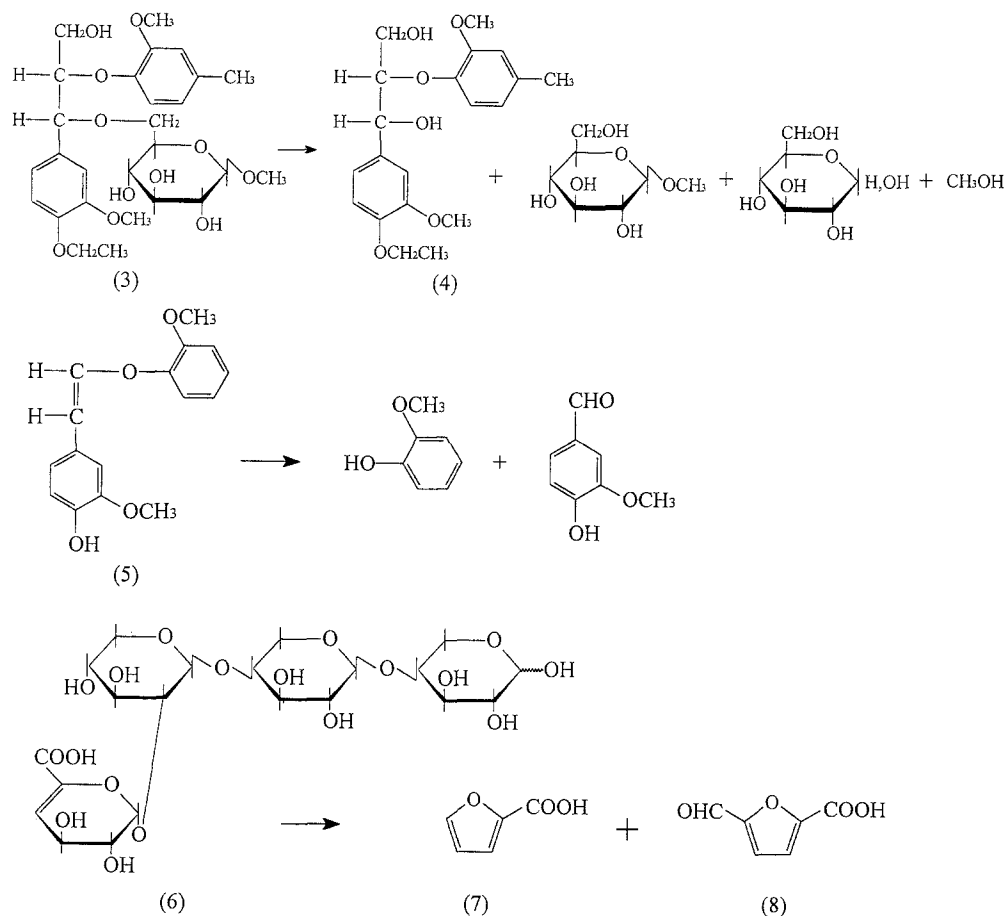
250 mm); column temperature, 35°C; eluents, acetonitrile/water (30/70), after 25 min (34/66); flow rate, 0.7 ml/min; detector, UV at 280 nm. Identification of compound 4 was performed by gas chromatography–mass spectroscopy (GC-MS). The mass spectrum was compared with the synthesized authentic compound. This authentic compound was identified by NMR and MS. MS was done on a JEOL JMS-DX303HF mass spectrometer.

^{1}H-NMR (CDCl$_3$):δ 1.46 (3H, t, -O-CH$_2$-CH$_3$), 2.33 (3H, s, aromatic-CH$_3$), 3.47 (1H, m, C $_\gamma$-H), 3.61 (1H, m, C$_\gamma$-H), 3.87 (3H, s, aromatic-OCH$_3$), 3.90 (3H, s, aromatic-OCH$_3$), 3.95 (1H, m, C $_\beta$-H), 4.09 (2H, m, -O-CH$_2$-CH$_3$), 4.97 (1H, d, C $_\alpha$-H), 6.72-7.01 (6H, m, aromatic H). ^{13}C-NMR (CDCl$_3$):δ 14.8 (-O-CH$_2$-CH$_3$), 21.3 (aromatic-CH$_3$), 55.9 (aromatic-OCH$_3$), 56.0 (aromatic-OCH$_3$), 61.0 (C $_\gamma$), 64.3 (-O-CH$_2$-CH$_3$), 74.0 (C $_\alpha$), 89.9 (C $_\beta$), 110.1, 112.4, 113.0, 119.6, 121.1, 122.0, 132.0, 134.4, 145.2, 148.2, 149.4, and 151.0. MS (trimethylsililate) (m/z) 506 (M$^+$), 279, 253 (100%), 210, 195, 180, 165.

Methanol was quantified by GC directly. The GC conditions for the methanol analysis were as follows. Apparatus, Shimadzu GC-8A; column, Chromosorb 101 (60/80 mesh) (2.6 mm × 2.0 m); column temperature, 80°–200°C at 1°C/min; carrier gas, He (196 kPa); injection temperature, 200°C.

Guaiacol was subjected to HPLC directly. The HPLC conditions for the vinyl ether-type lignin model compound

were as follows. Apparatus, column and column temperature were same as above; eluents, acetonitrile/water (35/65), after 15 min (50/50); flow rate, 1.0 ml/min; detector, UV at 270 nm.

2-Furancarboxylic acid (compound 7 in Fig. 2) and 5-formyl-2-furancarboxylic acid (compound 8 in Fig. 2) were subjected to HPLC directly. The HPLC conditions for the hexeneuronic acid model compound were as follows. Apparatus, column and column temperature were the same as above; eluents, acetonitrile/phosphoric acid buffer 20:80 pH 2.5; flow rate, 0.5 ml/min; detector, UV at 265 nm.
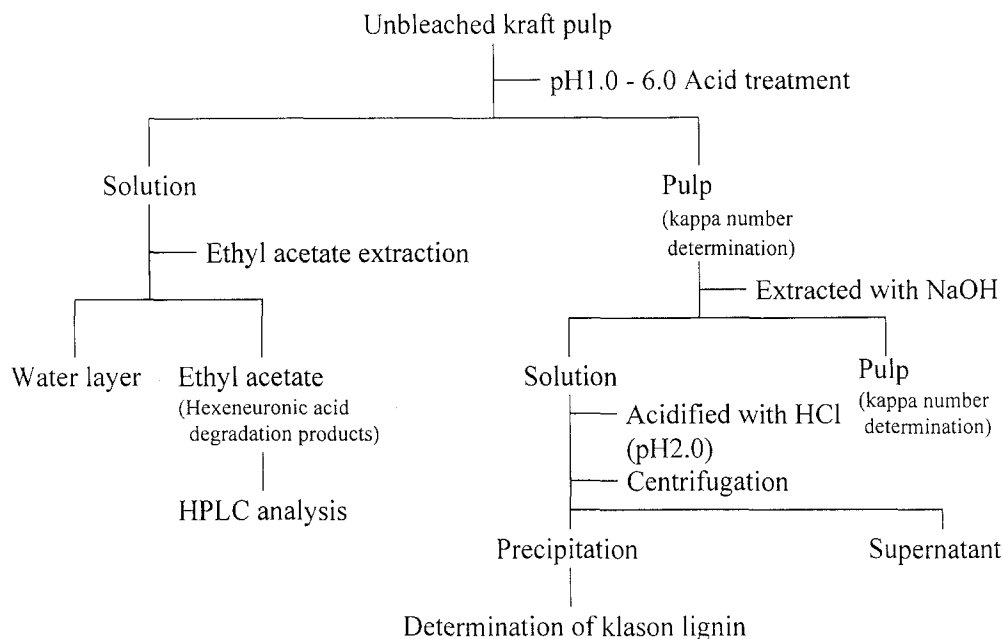
Permanganate treatment of kraft lignin and reducing sugars

Kraft lignin was dissolved in 0.05 N sodium hydroxide solution, and the kappa number of this solution was measured. Glucose, cellobiose, and the hexeneuronic acid model compound were dissolved in water, and the kappa number of each solution was measured. The kappa number was determined according to the TAPPI standard method.

Acid treatment of kraft pulp

The acid treatment and alkali extraction of kraft pulps and the analytical scheme for the degradation products are

Unbleached kraft pulp

— pH1.0 - 6.0 Acid treatment

Solution | Pulp (kappa number determination)

— Ethyl acetate extraction

— Extracted with NaOH

Water layer | Ethyl acetate (Hexeneuronic acid degradation products)

Solution | Pulp (kappa number determination)

— Acidified with HCl (pH2.0)

— Centrifugation

HPLC analysis

Precipitation | Supernatant

Determination of klason lignin

shown in Fig. 3. Kraft pulp was placed in a plastic bag, and acidic buffer (pH 1.0–6.0) was added to make the pulp consistency 10%. The plastic bag was then placed in a boiling waterbath for 1 h. The pulp was filtered and the effluent collected for analysis of hexeneuronic acid degradation products.

Alkali extraction

The kraft pulp treated with acidic buffer was then washed with water and placed in a plastic bag again and extracted with aqueous sodium hydroxide solution at 70°C for 1 h. The alkali charges were 3% and 4% on pulp for beech kraft pulp and red pine kraft pulp, respectively. The pulp consistency was 10%. The extracted kraft pulp was then filtered and washed with water. The alkali extraction liquor was collected for lignin analysis.

Analysis of hexeneuronic acid degradation products

Acid effluents were adjusted to pH 2.0, and *p*-hydroxybenzoic acid was added as an internal standard. After extraction of this liquor with ethylacetate, the ethylacetate phase was evaponated, and 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid in the ethylacetate phase were subjected to HPLC. The HPLC conditions were the same as described above.

Lignin analysis

Alkali extraction liquors were adjusted to pH 2.0 and centrifuged. The residue after centrifugation was hydrolyzed with 3% sulfuric acid solution in an autoclave at 120°C for 1 h. It

was then filtered by a 1G4 filter, and the Klason lignin content was determined.

Results and discussion

Reaction of LCC model compound

As discussed in our earlier paper,[1] the background chemistry of sulfuric acid bleaching is to cleave acid-labile bonds in the residual lignin of kraft pulp. A benzyl ether bond between lignin and carbohydrates is one of the possible acid-labile bonds in the residual lignin. The possibility of this bond forming during the biosynthesis of lignin was suggested by Tanaka et al.[6] through model experiments. Furthermore, Yamasaki et al.[11] characterized residual lignin in kraft pulp and reported that the resistance of the residual lignin toward kraft pulping could be explained by the presence of an LCC bond. Later, the stability of this bond during kraft pulping was confirmed by Taneda et al.[5] using an LCC model compound (compound 3 in Fig. 2). Figure 4 shows the reaction products from the LCC model compound after acidic treatment. The main reaction products were 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-propan-1,3-diol (compound 4 in Fig. 2) and methyl-β-D-glucoside, which showed that the main reaction that occurred during sulfuric acid treatment of the LCC model compound was acidolytic cleavage of the benzyl ether bond. Glucose and methanol were also obtained, but the glucose yield was low and the methanol yield was 10% (pH 1.6, 100°C, 60 min) under the reaction conditions, adopted here. In our earlier reports on the sulfuric acid bleaching of kraft pulps,[1,2] it was observed that the pulp viscosity dropped depending on the bleaching conditions,
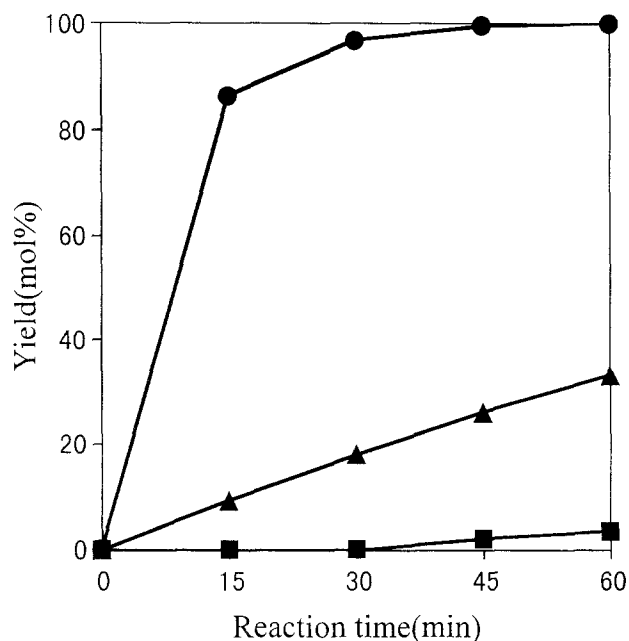
Fig. 4. Yield of the lignin model dimer (compound 4 in Fig. 2) on acid hydrolysis of the LCC model compound (compound 3 in Fig. 1) under different acidities. *Squares*, pH 3.0; *triangles*, pH 2.0; *circles*, pH 1.0
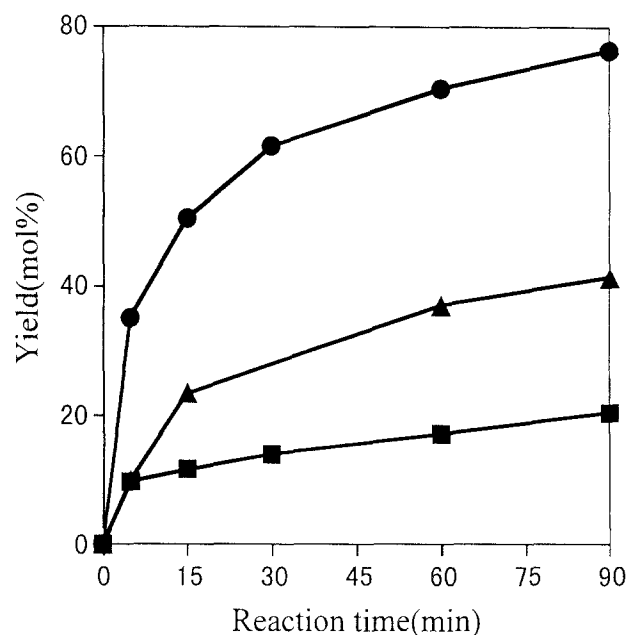

Fig. 5. Yield of guaiacol on acid hydrolysis of the vinyl ether-type lignin model dimer (compound 5 in Fig. 2) under different acidities. *Squares*, pH 4.0; *triangles*, pH 2.0; *circles*, pH 1.0

although it was controllable within acceptable levels. These results of model experiments and pulp bleaching were in good agreement with each other. No reaction products were obtained that showed cleavage of the β-ether linkage in the lignin moiety of the LCC model compound. It was shown that the β-ether linkages in lignin were stable during sulfuric acid bleaching, which is probably why the lignin that dissolved in the alkali extraction effluent during sulfuric acid bleaching of kraft pulp without additives was of comparatively high molecular weight, similar to milled wood lignin (MWL) (see part II[2]).

Figure 4 shows the reactivity of the LCC model compound under different pH conditions. If the reaction time and the reaction temperature were fixed at 1 h and 100°C, respectively, the pH needed to cleave the benzyl ether linkage in the LCC model compound was 1.0–2.0. This is in accord with the results of kraft pulp bleaching reported in our earlier paper.[1] The delignification during sulfuric acid bleaching of kraft pulp was quite pH-dependent within the range of pH 1.0–2.0. These results indicate that cleavage of the benzyl ether-type LCC bond plays an important role in the sulfuric acid bleaching of kraft pulp.

Reaction of vinyl ether-type lignin model dimer

Acidolytic cleavage of the β-ether linkage of the vinyl ether-type lignin model compound (compound 5 in Fig. 2) gave guaiacol in good yield, but only small amounts of polymeric materials was obtained. The yields of guaiacol under different pH conditions are shown in Fig. 5. Again, a pH of 1.0–2.0 was found to be necessary for cleavage of the vinyl ether at 100°C.
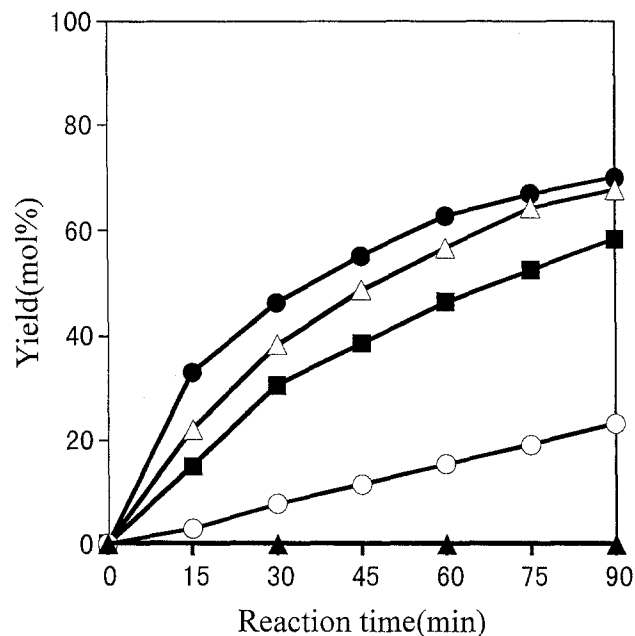
Fig. 6. Yield of degradation products (compounds 7 and 8 in Fig. 2) on acid hydrolysis of the hexeneuronic acid model compound (compound 6 in Fig. 2) under different acidities. *Filled triangles*, pH 6.0; *open circles*, pH 4.0; *filled squares*, pH 3.0; *open triangles*, pH 2.0; *filled circles*, pH 1.0

Reaction of hexeneuronic acid model compound

As illustrated in Fig. 6, Teleman et al.[10] and Vuorinen et al.[12] have reported that 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid were the main reaction products

from hexeneuronic acid on acidolytic reactions. The hexeneuronic acid model compound (compound 6 in Fig. 2) was treated with dilute sulfuric acid of different pH, and the total yields of these two reaction products were plotted in Fig. 6. It was shown that a pH below 3.0 was necessary for the acidolytic degradation of this compound at 100°C. Accordingly, it can be said that the sulfuric acid bleaching of kraft pulp reported in our earlier papers, where a pH below 2 was applied, includes hexeneuronic acid removal as well as lignin removal.
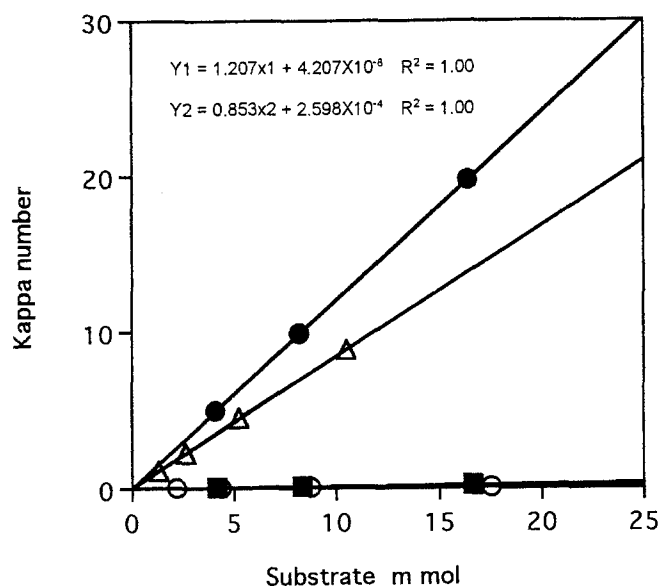
Fig. 7. Kappa number response of lignin, hexeneuronic acid, and reducing sugars. *Filled circles*, lignin; *open triangles*, hexeneuronic acid; *filled squares*, glucose; *open circles*, Cellobiose $Y1$, response of kappa number and lignin; $x1$, Klason lignin (millimoles) in Tables 1 and 2; $Y2$, response of kappa number and hexeneuronic acid; $x2$, sum of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid (millimoles) in Tables 1 and 2

Kappa number responses of kraft lignin, hexeneuronic acid, and reducing sugars

To evaluate the relative contribution of lignin and hexeneuronic acid removal to the kappa number reduction of kraft pulp during sulfuric acid bleaching, the kappa number responses of kraft lignin and hexeneuronic acid were determined. Reducing sugars, glucose, and cellobiose were also examined. The results are shown in Fig. 7, where the kappa number was plotted against the millimoles of each substance in the solution. For convenience, a molecular weight of 183 was used for one C6-C3 unit of lignin. Surprisingly, on molar bases, hexeneuronic acid consumed as much as 70% permanganate compared to kraft lignin, although it has only one double bond in its molecule. Vuorinen et al.[12] reported somewhat higher permanganate consumption by hexeneuronic acid. Their data were calculated on the basis of the determination of hexeneuronic acid degradation products and kappa number reduction by acid treatment of kraft pulp. The difference might be explained by lignin removal during their acid treatment of kraft pulp. It was also found that there was almost no permanganate consumption by the reducing sugars.

Contribution of lignin and hexeneuronic acid removal to kappa number reduction of kraft pulp during sulfuric acid bleaching

As illustrated in Fig. 3 beech kraft pulp and red pine kraft pulp were treated with dilute sulfuric acid of different pH (1.0–6.0), and the pulps were then subjected to alkali extraction. The kappa numbers after acidic treatment and after alkali extraction were determined. The amount of hexeneuronic acid degradation products in acid effluent and the amount of lignin dissolved in the alkali extraction liquor were also determined. The results were summarized in Table 1 (beech kraft pulp) and Table 2 (red pine kraft pulp). The kappa number reduction (Δ KN) was estimated from the amount of hexeneuronic acid degradation products and

Table 1. Kappa number reduction of beech kraft pulp and the yield of lignin and hexeneuronic acid degradation products during sulfuric acid bleaching

Condition	Results at pH 1.0–6.0					
	1.0	2.0	3.0	4.0	5.0	6.0
KN after acid treatment	10.2	11.9	12.8	13.6	14.9	15.3
KN reduction on acid treatment	6.4	4.7	3.8	3.0	1.7	1.3
2-Furancarboxylic acid (mmol)[a]	2.7	2.4	1.8	1.1	0.26	0.23
5-Formyl-2-furancarboxylic acid (mmol)[a]	0.30	0.40	0.30	0.20	–	–
ΔKN estimated from hexeneuronic acid[b]	2.6	2.4	1.8	1.1	0.22	0.20
KN after alkali extraction	6.1	8.8	10.4	11.0	12.4	13.1
KN reduction on alkali extratction	4.1	3.1	2.4	2.6	2.5	2.2
Klason lignin (mmol)[a]	2.5	1.5	1.2	0.8	0.8	0.5
ΔKN estimated from lignin[c]	3.1	1.8	1.5	0.9	1.0	0.7

Original kappa number (KN) is 16.6
[a] Based on 100 g kraft pulp
[b] ΔKN was calculated from the sum (mmol) of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid using the formula shown in Fig. 7
[c] ΔKN was calculated from the Klason lignin content (mmol) using the formula shown in Fig. 7

Table 2. Kappa number reduction of red pine kraft pulp and the yield of lignin and hexeneuronic acid degradation products during sulfuric acid bleaching

Condition	Results at pH 1.0–6.0					
	1.0	2.0	3.0	4.0	5.0	6.0
KN after acid treatment	23.1	23.1	23.8	23.9	25.0	25.0
KN reduction on acid treatment	2.4	2.4	1.2	1.1	0.5	0.5
2-Furancarboxylic acid (mmol)[a]	0.59	0.46	0.34	0.25	0.22	–
5-Formyl-2-furancarboxylic acid (mmol)[a]	0.08	0.03	0.03	0.02	–	–
ΔKN estimated from hexeneuronic acid[b]	0.57	0.42	0.31	0.23	0.19	–
KN after alkali extraction	17.8	20.1	22.1	22.5	23.4	23.8
KN reduction on alkali extratction	5.3	3.0	1.7	1.4	1.6	1.2
Klason lignin (mmol)[a]	4.7	2.8	2.5	2.2	2.0	1.6
ΔKN estimated from lignin[c]	5.7	3.4	3.0	2.7	2.4	1.9

Original kappa number (KN) is 25.5
[a] Based on 100 g kraft pulp
[b] ΔKN was calculated from the sum (mmol) of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid using the formula shown in Fig. 7
[c] ΔKN was calculated from the Klason lignin content (mmol) using the formula shown in Fig. 7

the amount of klason lignin using the data in Fig. 7. These results also are shown in Tables 1 and 2.

Regarding the sulfuric acid bleaching of beech kraft pulp (Table 1), it can be said that the kappa number reduction due to hexeneuronic acid removal was marked when the pH was below 4.0, whereas the reduction due to lignin removal became marked at a pH below 2.0. These results were in accord with the results of model experiments described above. The results of the bleaching at pH 1.0 (Table 1) showed that the overall kappa number reduction was 10.5, and the contribution of hexeneuronic acid removal was calculated to be 2.6 (25%) and that of lignin removal 3.1 (30%). The rest of the kappa number reduction was mostly achieved during the acid treatment because the kappa number reduction on acid treatment was 6.4, and only 2.6 was explained by the removal of hexeneuronic acid. The difference could not be simply explained by the leaching effect, as the kappa number reduction by bleaching at pH 6.0 was small (1.3). Furthermore, it was reported in our earlier paper[2] that there was only a negligible amount, in terms of kappa number reduction, of lignin in the acidic effluent. It could be assumed that there is some unknown acid-soluble substance dissolved in the acidic effluent, the behavior of which might be similar to that of hexeneuronic acid.

As for the bleaching of red pine kraft pulp (Table 2), the kappa number reduction became notable when the pH of the sulfuric acid was below 2.0. In comparison with the bleaching of beech kraft pulp (Table 1), the contribution of hexeneuronic acid removal was small even at low pH. Most of the kappa number reduction was explained by lignin removal during the alkali extraction after acidic treatment. The hexeneuronic acid structure in pulp is known to originate from the 4-O-methylglucuronic acid group in xylan. The xylan contents in both pulps were reported in our earlier paper[2] and were about 2.5 times higher for beech kraft pulp than red pine kraft pulp. The frequency of the 4-O-methylglucuronic acid group in xylan has been reported to be about twofold more for softwood than hardwood. Hence the big difference in the amount of hexeneuronic acid group between the two kraft pulps could not be explained by the

difference in 4-O-methylglucuronic acid content in original wood. It could probably be explained by the more severe kraft cooking conditions for red pine, under which the hexeneuronic acid structure is not stable.

Conclusion

Both lignin removal and hexeneuronic acid removal contribute to the kappa number reduction of beech kraft pulp during sulfuric acid bleaching, whereas the contribution of hexeneuronic acid removal is negligible in red pine kraft pulp bleaching. The hexeneuronic acid groups once formed during kraft cooking of red pine chips seem to be degraded because of the more severe cooking conditions for red pine chips than for beech chips during kraft cooking. Cleavage of benzyl ether-type LCC bonds and vinyl ether bonds in kraft residual lignin plays an important role in the sulfuric acid bleaching of kraft pulp.

References

1. Ikeda I, Hosoya S, Tomimura Y, Magara K, Takano I (1999) Sulfuric acid bleaching of kraft pulp I: Bleaching of hardwood and softwood kraft pulps. J Wood Sci 45:233–237
2. Ikeda I, Tomimura Y, Magara K, Hosoya S (1999) Sulfuric acid bleaching of kraft pulp II: Behavior of lignin and carbohydrate during sulfuric acid bleaching. J Wood Sci 45:313–318
3. Hosoya S, Kanazawa K, Kaneko H, Nakano J (1980) Synthesis of guaiacylglycerol-β-guaiacyl ether (in Japanese). Mokuzai Gakkaishi 26:118–121
4. Ralph J, Young RA (1983) Stereochemical aspects of addition reactions involving lignin model quinone methides. J Wood Chem Technol 3:161–181
5. Taneda H, Nakano J, Hosoya S, Chang HN (1987) Stability of α-ether type model compounds during chemical pulp process. J Wood Chem Technol 7:485–498
6. Tanaka K, Nakatsubo F, Higuchi T (1976) Reactions of guaiacylglycerol-β-guaiacyl ether with several sugars. I. Mokuzai Gakkaishi 22:589–590

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7. Tokimatsu T, Umezawa T, Shimada M (1996) Synthesis of four diastereomeric lignin carbohydrate complexes (LCC) model compounds composed of a β-O-4 lignin model linked to methyl β-D-glucoside. Holzforschung 50:156–160
8. Yaguchi T, Hosoya S, Nakano J, Nomura Y, Satoh A, Nakamura M (1979) Studies on reaction mechanism of quinone in alkaline cooking. Part 2. Mechanism of rapid delignification during alkaline cooking (in Japanese). Jpn TAPPI 33:666–672
9. Ishihara M, Nojiri M, Hayashi N, Niahimura T, Shimizu K (1997) Screening of fungal β-xylanases for production of acidic xylooligosaccharides using in situ reduced 4-O-methylglucuronoxylan as substrate. Enzyme Microb Technol 21:170–175
10. Teleman A, Hausalo T, Tenkanen M, Vuorinen T (1996) Identification of the acidic degradation products of hexeneuronic acid and characterization of hexeneuronic acid-substituted xylooligosaccharides by NMR spectroscopy. Carbohydr Res 280:197–208
11. Yamasaki T, Hosoya S, Chen CL, Gratzl JS, Chang HM (1981) Characterization of residual lignin in kraft pulp, vol 2. The Ekman-Days, Stockholm, June 9–12, pp 34–42
12. Vuorinen T, Telman A, Fagerström P, Buchert J, Tenkanen M (1996) Selective hydrolysis of hexeneuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. Presented at the International Pulp Bleaching Conference, Atlanta, April 14–18, Book 1, pp 43–51