

## ORIGINAL ARTICLE

Tsutomu Ikeda · Shuji Hosoya · Yoichi Tomimura  
Kengo Magara · Isao Takano

## Sulfuric acid bleaching of kraft pulp I: Bleaching of hardwood and softwood kraft pulps\*

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**Abstract** To develop a new nonchlorine bleaching technology, hardwood and softwood kraft pulps, before and after oxygen-alkali predelignification, were treated with dilute sulfuric acid solutions (pH 1.0–1.8) at 100°C for 1 h and then extracted with aqueous sodium hydroxide at 70°C for 1 h. Hardwood kraft pulp was successfully bleached. The delignification selectivity was similar to that seen with oxygen-alkali bleaching; and it was greatly enhanced by the addition of sodium nitrate and sodium nitrite. The sulfuric acid bleaching can replace the presently adopted oxygen and chlorine stages if the additives are allowed. This bleaching process was also effective for oxygen-bleached hardwood kraft pulp, but it was less effective for softwood kraft pulp and oxygen-bleached softwood kraft pulp. The effectiveness of the addition of sodium nitrate and sodium nitrite was more apparent for softwood kraft pulp than for hardwood kraft pulp.

**Key words** Sulfuric acid · Nonchlorine bleaching · Kraft pulp · Residual lignin

### Introduction

Environmental problems are now one of the greatest concerns of the worldwide pulp and paper industry. Among these problems, the discharge of organically bound chlorine (AOX, or adsorbable organic halide) including dioxins is

the most stringent one to be solved. European countries have already stopped using elemental chlorine for kraft pulp bleaching. In the United States the cluster rule of the Environmental Protection Agency (EPA) was signed on November 14, 1997. The cluster rule includes 100% ClO<sub>2</sub> substitution, so American mills producing bleached paper-grade kraft and soda pulps no longer use elemental chlorine for bleaching after a minimum 3-year compliance interval. In the EPA cluster rule, the limitation of AOX discharge is 0.623 kg/ton of pulp. In Japan, almost all the kraft mills are now applying oxygen-alkali delignification as the pre-bleaching stage and about 20% ClO<sub>2</sub> substitution for the chlorination stage that follows. The AOX discharge in Japan is self-regulated by the industry to lower than 1.5 kg/ton of pulp. Thus, the pulp and paper industry has recently been adopting more and more nonchlorine or fewer chlorine bleaching technologies. Even though the AOX discharge is limited to 1 kg/ton of pulp, kraft mills producing 1000 tons of bleached pulp a day discharge tons of organochloro compounds into the natural environment every day. This amount is a big problem if we consider the low bio-degradability of these organochloro compounds. Accordingly, the development of economically feasible nonchlorine bleaching technologies is of significant importance for the pulp and paper industry.

This report presents sulfuric acid bleaching of kraft pulp as one stage of nonchlorine bleaching processes. The behavior of the chemical components of the kraft pulp during this acid-bleaching, including model experiments, will be reported subsequently.

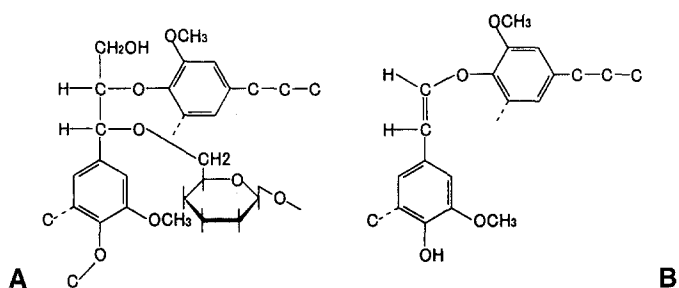
S. Hosoya ✉ · Y. Tomimura · K. Magara · I. Takano  
Wood Chemistry Laboratory, Wood Chemistry Division, Forestry  
and Forest Products Research Institute, PO Box 16, Tsukuba Norin  
Kenkyu Danchi-nai, Ibaraki 305-8687, Japan  
Tel. +81-298-73-3211, ext. 524; Fax +81-298-73-3797  
e-mail: hosoya@ffpri.affrc.go.jp

T. Ikeda · S. Hosoya  
Institute of Agricultural and Forest Engineering, The University of  
Tsukuba, Tsukuba 305-0006, Japan

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### Background chemistry

Lignin in wood chips undergoes hot alkali treatment during kraft pulping. Most of the lignin is then made soluble in the aqueous alkaline solution through fragmentation reactions. There are also condensation reactions among lignin fragments during kraft pulping that form stable carbon-carbon linkages. As a result, approximately one-tenth of the native



**Fig. 1.** Alkali-stable and acid-labile linkages in residual lignin. **A** Benzyl ether type lignin-carbohydrate complex, **B** Vinyl ether

lignin in wood chips stays in the kraft pulp as the residual lignin after kraft pulping. In earlier work on the structures of the residual lignin in kraft pulp,<sup>1</sup> we showed that the lignin in kraft pulp has chemical structures between (MWL) and the dissolved kraft lignin. The resistance of the residual lignin toward delignification was explained by the possible chemical linkages between lignin and carbohydrates. One of the possible lignin-carbohydrate chemical linkages is a benzyl ether linkage (Fig. 1A) that could be formed by the addition of carbohydrates to a quinone methide intermediate in lignin during biosynthesis.<sup>2</sup> The stability of this linkage during kraft pulping, when it locates in the nonphenolic units of lignin, was experimentally confirmed in our earlier report<sup>3</sup> using a lignin-carbohydrate complex (LCC) model compound. Because benzyl ether linkages are labile to acids to some extent, it is conceivable to use acidolytic reactions for kraft pulp bleaching.

Another possible alkali-stable, acid-labile linkage in the residual lignin is a vinyl ether linkage, illustrated in Fig. 1B. This structure can be formed through liberation of the  $\gamma$ -carbon of a lignin side chain as formaldehyde. This ether linkage is known to be stable during kraft pulping and is one of the constituent structural groups of the residual lignin in kraft pulp.<sup>4</sup> Thus, because the residual lignin in kraft pulp has undergone only alkaline treatment, it consists of chemical linkages that are labile to acidic treatment. Accordingly, it is reasonable to employ acidolytic reactions for kraft pulp bleaching, although reaction conditions must be carefully chosen so as not to cleave the acid-labile glycosidic bonds in cellulose.

## Materials and methods

### Isolation and characterization of the residual lignin in oxygen-bleached kraft pulp

The residual lignin in oxygen-bleached akamatsu (Japanese red pine) kraft pulp (kappa number 14.6) was isolated by means of enzymatic digestion of the carbohydrates in pulp. To avoid enzyme contamination, the pulp was ethylated with diazoethane before enzyme digestion for the purpose of blocking the acidic functional groups in lignin. The pulp was completely dried through washing with ethanol and

then with dry ether. Diazoethane produced from 7g nitrosoethyl urea was subjected to the ethylation of 50g pulp. The ethylation was repeated six times. After the fourth ethylation run, the yellow color of diazoethane survived overnight. Ethylated pulp (20g) was treated with Meicelase (4g) in the acetate buffer (500ml, pH 4.5) for 5 days at 45°C. A few drops of toluene were added during the enzymatic digestion. The residue after enzymatic digestion was freeze-dried and then extracted with 95% dioxane. The dioxane solution was filtered and evaporated to dryness giving 166mg of the residual lignin in the pulp. The Klason lignin content of the lignin preparation was 76%, which meant that about half of the residual lignin in the pulp was isolated. Total sugar in the hydrolysate of klason lignin analysis was 8%, and the carbohydrate composition was as follows: mannose 6.1%, arabinose 8.3%, galactose 14.0%, xylose 28.0%, glucose 43.6%. Carbohydrate composition was analyzed by a Shimadzu LC-9A with Tosoh TSK-gel (AX-type). The elemental analysis of the residual lignin gave C 59.06%, H 6.45%, N 0.96%, O 39.53%. Low nitrogen content indicated no serious contamination by the enzyme.

### Acetic acid treatment of residual lignin and gel permeation chromatography analysis

The isolated residual lignin (5.4mg) was dissolved in 5ml 95% acetic acid with 0.1% hydrochloric acid (w/v) and heated at 110°C for 30 and 60min. The reaction liquors were evaporated to dryness and then acetylated with pyridine and acetic anhydride for the GPC analysis. GPC analysis was performed on a Toyo Soda HLC-8020 gel-permeation chromatograph: detector UV 280nm; column TSK gel-G.3000HXL, TSK gel-G.2500HXL, and TSK gel-G.1000HXL in series; solvent tetrahydrofuran (1 ml/min).

### Sulfuric acid bleaching and caustic extraction of kraft pulps

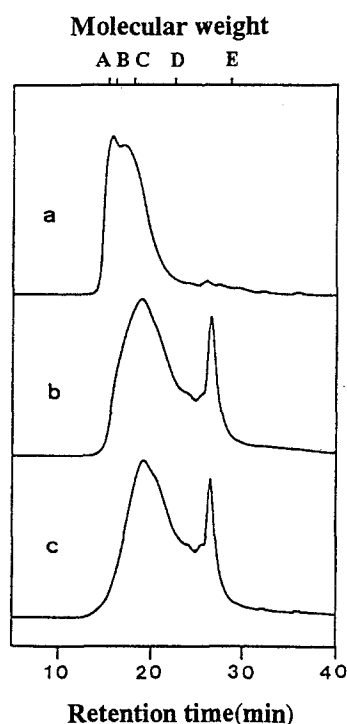
Hardwood (mixed species) kraft pulp and softwood (mixed species) kraft pulp and their oxygen-alkali bleached pulps were obtained from the mill. The pulps were immersed in water overnight and then washed thoroughly in our laboratory. The pulps with a moisture content of approximately 70% were kept in a refrigerator before use. The kappa number and the viscosity of each pulp are shown in the respective table of bleaching results. The kraft pulp (15g o.d.) was put in a plastic bag (polyvinylidene chloride), and sulfuric acid of various pH was added to make the pulp consistency 10% (w/w). The desired amount of additives was also added to the plastic bag. The plastic bag was then placed in a boiling waterbath and kept for 1h with periodic stirring (10-min intervals). The pulp was washed with water and then placed in a plastic bag again with an appropriate amount of aqueous sodium hydroxide and subjected to caustic extraction (1h 70°C). The pulp consistency was 10%. The pulp was then washed with water. The kappa

number and the viscosity of the pulp were determined according to the Tappi standards.

## Results and discussion

### Reactivity of the residual lignin in kraft pulp

To examine the possibility of employing acidolytic reactions for kraft pulp bleaching, the residual lignin isolated from oxygen-bleached kraft pulp was treated with 95% acetic acid containing 0.1% hydrochloric acid by weight. The reaction conditions are similar to those of the atmospheric acetic acid pulping proposed by Nimz et al.<sup>5</sup> Changes in molecular weight distributions of the residual lignin during the acidolytic treatment are shown in Fig. 2. Drastic changes toward lower-molecular-weight regions were observed even after a 30-min reaction time. Because the main reactions of the acetic acid pulping are ether cleavage reactions, the result shows that the residual lignin in oxygen-bleached kraft pulp contains appreciable numbers of interunit ether linkages. It is well known that the main fragmentation reactions of lignin during kraft pulping are  $\alpha$ - and  $\beta$ -ether cleavage reactions. It was shown that the residual lignin in kraft pulp still contains acid-labile ether linkages. Thus, it was suggested that the acidolytic reactions could be employed for bleaching kraft pulp.



**Fig. 2.** Gel permeation chromatography analysis of the residual lignin after acidolytic treatment. **a** Original residual lignin. **b** After acetic acid (0.1% HCl) treatment for 30 min. **c** After acetic acid (0.1% HCl) treatment for 60 min. Molecular weights of polystyrene standards: A, 42 800; B, 16 700; C, 6 200; D, 890; E, 124 (guaiacol)

### Sulfuric acid bleaching of hardwood kraft pulp

Considering the industrial application, sulfuric acid was chosen as an acid for kraft pulp bleaching. To achieve more satisfactory delignification, sodium nitrate with a small amount of sodium nitrite as a reaction initiator was added to a sulfuric acid solution. Because lignin is not soluble in acidic water, caustic extraction was applied after the sulfuric acid treatment. The results of sulfuric acid bleaching of hardwood Kraft pulp (LKP) are summarized in Table 1.

The results showed that sulfuric acid bleaching was effective for the hardwood kraft pulp. Without additives (exps. 1, 4, 7), the delignification selectivities (delignification versus viscosity loss) were similar to those of oxygen-alkali bleaching. The delignification selectivities were greatly improved by the addition of sodium nitrate and sodium nitrite. This improvement in selectivity was caused by enhancement of delignification to a great extent, whereas the viscosity was affected by the additives to only a minor extent. The pH of the acidic treatment liquor was also found to be an important bleaching condition. The kappa number decreased with the decreasing pH, but the viscosity of the bleached pulps also decreased with the decreasing pH of the bleaching liquor. The increase in the amount of additives from 2.7% to 4.5% on pulp did not show any notable decrement in kappa number especially in the lower pH region (exps. 2, 3). It was also shown that the caustic extraction following the acidic treatment effectively reduced the kappa number, whereas the viscosity of the pulp was not affected. Sodium nitrate was added for the purpose of applying some oxidative reactions to the lignin in the pulp in addition to acidolytic reactions during sulfuric acid bleaching. The use of nitrogen compounds (nitrogen dioxide<sup>6</sup> or sodium nitrite<sup>7</sup>) has been reported as pretreatment for oxygen-alkali bleaching, although the bleaching systems were different from ours. The role of sodium nitrite in our bleaching system is to initiate the reaction. In the separate experiments, it was observed that without sodium nitrite addition no effective delignification was obtained even with enough sodium nitrate. Similar phenomena were reported for the nitric acid oxidation of lignin model compounds.<sup>8</sup> This is often the case in nitric acid oxidation reactions in general, although the reaction mechanism has not yet been identified.

To summarize the results of sulfuric acid bleaching of LKP, it can be said that delignification is controlled by both the pH of the bleaching liquor and the amount of sodium nitrate. The viscosity of the bleached pulp is controlled only by the pH of the aqueous sulfuric acid at constant temperature and time.

### Sulfuric acid bleaching of oxygen-alkali-bleached hardwood kraft pulp

Because the kappa number and viscosity of oxygen-alkali-bleached hardwood kraft pulps (LKOP) are lower than those for LKP, somewhat milder bleaching conditions

**Table 1.** Sulfuric acid bleaching of LKP

Exp. no.	pH	NaNO <sub>3</sub> (%)	NaNO <sub>2</sub> (%)	Kappa number <sup>a</sup>		Viscosity (cP) <sup>b</sup>	
				Before alkali extr.	After alkali extr.	Before alkali extr.	After alkali extr.
1	1.0	0	0	13.7	8.3	21.9	20.4
2	1.0	2.7	0.9	7.6	3.3	18.9	19.8
3	1.0	4.5	0.9	6.7	3.3	18.6	19.0
4	1.2	0	0	13.3	9.4	25.1	25.4
5	1.2	2.7	0.9	9.2	4.8	23.9	24.8
6	1.2	4.5	0.9	8.3	4.3	24.1	24.6
7	1.4	0	0	14.5	9.9	31.7	30.1
8	1.4	2.7	0.9	10.7	7.0	30.2	29.8
9	1.4	4.5	0.9	10.0	5.7	31.3	31.2

Acid treatment conditions: 100°C and 60 min. Alkali extraction conditions: 70°C, 60 min, 3% NaOH on pulp LKP, hardwood kraft pulp

<sup>a</sup>Original kappa number: 19.8

<sup>b</sup>Original viscosity: 47.4

**Table 2.** Sulfuric acid bleaching of LKOP

Exp. no.	pH	NaNO <sub>3</sub> (%)	NaNO <sub>2</sub> (%)	Kappa number <sup>a</sup>	Viscosity <sup>b</sup> (cP)
10	1.2	0	0	5.4	14.4
11	1.2	0.9	0.9	3.7	14.4
12	1.2	1.8	0.9	3.4	14.7
13	1.2	2.7	0.9	3.5	14.9
14	1.2	3.6	0.9	3.3	14.7
15	1.4	0	0	5.9	17.5
16	1.4	0.9	0.9	4.6	17.1
17	1.4	1.8	0.9	4.0	17.0
18	1.4	2.7	0.9	4.1	17.7
19	1.4	3.6	0.9	3.9	17.0
20	1.6	0	0	6.2	19.9
21	1.6	0.9	0.9	5.0	20.0
22	1.6	1.8	0.9	5.0	22.2
23	1.6	2.7	0.9	5.0	21.6
24	1.6	3.6	0.9	4.6	20.9
25	1.8	0	0	6.5	22.8
26	1.8	0.9	0.9	5.4	23.2
27	1.8	1.8	0.9	5.3	24.6
28	1.8	2.7	0.9	5.8	24.8
29	1.8	3.6	0.9	5.1	23.0

Acid treatment conditions: 100°C, 60 min. Alkali extraction conditions: 70°C, 60 min, 3% NaOH on pulp

LKOP, oxygen-alkali bleached hardwood kraft pulp

<sup>a</sup>Original kappa number: 10.5

<sup>b</sup>Original viscosity: 32.2

**Table 3.** Sulfuric acid bleaching of NKP

Exp. no.	pH	NaNO <sub>3</sub> (%)	NaNO <sub>2</sub> (%)	Kappa number <sup>a</sup>	Viscosity <sup>b</sup> (cP)
30	1.0	0	0	16.7	12.3
31	1.0	2.7	0.9	6.5	12.4
32	1.0	4.5	0.9	4.3	11.3
33	1.0	6.3	0.9	3.9	12.3
34	1.2	0	0	17.9	15.8
35	1.2	2.7	0.9	11.4	16.0
36	1.2	4.5	0.9	8.4	14.6
37	1.2	6.3	0.9	5.7	16.0
38	1.4	0	0	19.2	20.6
39	1.4	2.7	0.9	15.0	19.3
40	1.4	4.5	0.9	12.2	19.2
41	1.4	6.3	0.9	9.2	19.5
42	1.6	0	0	19.1	22.7
43	1.6	2.7	0.9	15.8	21.3
44	1.6	4.5	0.9	15.6	23.6
45	1.6	6.3	0.9	12.5	20.5

Acid treatment conditions: 100°C, 60 min. Alkali extraction conditions: 70°C, 60 min, 4% NaOH on pulp

NKP, softwood kraft pulp

<sup>a</sup>Original kappa number: 23.0

<sup>b</sup>Original viscosity: 31.7

it is followed by sulfuric acid bleaching (compare Tables 1 and 2).

Sulfuric acid bleaching of softwood kraft pulp and oxygen-bleached softwood kraft pulp

(higher pH and less additives) than those for LKP bleaching were applied to LKOP. The bleaching results are summarized in Table 2. It was shown that sulfuric acid bleaching was also effective for LKOP. Compared with the results of LKP bleaching shown in Table 1, however, somewhat lower pulp viscosities were obtained at a similar kappa number (compare exp. 12 with exp. 2, and exp. 16 or exp. 24 with exp. 5). As was also observed with LKP bleaching, the increasing addition of sodium nitrate did not satisfactorily reduce the kappa number, although a kappa number was obtained that was 1–2 points lower. This observation was even more apparent in the case of LKOP bleaching. As far as kappa number reduction is concerned, it can be said that the oxygen-alkali predelignification stage is not necessary if

It was found that sulfuric acid bleaching was less effective for softwood kraft pulp (NKP) (Table 3) than for LKP (Table 1). Without the addition of sodium nitrate and sodium nitrite (Table 3: exps. 30, 34, 38, 42), even the strongest acidic treatment (pH 1.0, exp. 30) resulted in only 35% delignification. It was 58% for LKP under the same bleaching conditions except there was less alkali charge in caustic extraction for LKP (Table 1, exp. 1). The delignification selectivity in the sulfuric acid bleaching of NKP was also inferior to that of LKP bleaching. These differences in

**Table 4.** Sulfuric acid bleaching of NKOP

Exp. no.	pH	NaNO <sub>3</sub> (%)	NaNO <sub>2</sub> (%)	Kappa number <sup>a</sup>	Viscosity <sup>b</sup> (cP)
46	1.2	0	0	10.2	10.9
47	1.2	2.0	1.0	6.2	11.4
48	1.2	4.0	1.0	4.5	11.3
49	1.2	6.0	1.0	4.2	11.7
50	1.4	0	0	10.5	14.7
51	1.4	2.0	1.0	7.1	14.3
52	1.4	4.0	1.0	5.9	14.6
53	1.4	6.0	1.0	5.4	14.6

Acid treatment conditions: 100°C, 60 min. Alkali extraction conditions: 70°C, 60 min, 4% NaOH on pulp

NKOP, oxygen-alkali bleached softwood kraft pulp

<sup>a</sup>Original kappa number: 13.8

<sup>b</sup>Original viscosity: 22.4

bleachability between LKP and NKP could be explained partly by the different number of hexeneuronic acid groups in those two pulps. (The contribution of hexeneuronic acid removal to the kappa number reduction during sulfuric acid bleaching will be reported as part III of this series.) On the other hand, the effectiveness of the additives was found to be better for NKP bleaching than for LKP bleaching. The kappa number was halved by increasing the sodium nitrate from 2.7% to 6.3% (exps. 35, 37), whereas only a small additional decrease in kappa number was observed by increasing the amount of sodium nitrate in the case of LKP bleaching (Table 1). The same tendency was observed between the sulfuric acid bleaching of oxygen-bleached hardwood kraft pulp (LKOP) (Table 2) and the corresponding softwood pulp (NKOP) (Table 4). Because the viscosity of NKOP was already comparatively low, the pH of the sulfuric acid could not be too low. Accordingly, sulfuric acid bleaching without additives was not effective for delignification of NKOP (exps 46, 50). The delignification was again greatly enhanced by the addition of sodium nitrate and sodium nitrite (Table 4). More enhanced effectiveness of the additives during bleaching of softwood kraft pulps (NKP and NKOP) than that when bleaching hardwood kraft pulps (LKP and LKOP) could probably be explained by the differences in the structures of the residual lignin in the kraft pulps. Because softwood lignin consists of guaiacyl units and hardwood lignin consists of both guaiacyl units and syringyl units, it is conceivable that the residual lignin in NKP and NKOP is more condensed than that in LKP and LKOP. Oxidative reactions rather than acidolytic reactions should be more effective with these condensed structures. This is probably the reason for more enhanced

effectiveness of the oxidative additives when bleaching softwood kraft pulps. The superior bleachability of kraft pulps (LKP and NKP) compared to oxygen-predelignified kraft pulps (LKOP and NKOP) during sulfuric acid bleaching can be explained partly by the absence of a vinyl ether-type structure (Fig. 1B) in oxygen-bleached pulps, as these structural units are highly reactive to oxygen-alkali bleaching.

## Conclusions

Dilute sulfuric acid with the pH ranging from 1.0 to 1.8 can successfully delignify hardwood kraft pulp. Lower pH results in a higher degree of delignification but more viscosity loss. The delignification selectivity is similar to oxygen-alkali bleaching, but it is greatly enhanced by the addition of sodium nitrate and sodium nitrite. This bleaching is also effective when it is employed after oxygen-alkali predelignification. It is less effective for softwood kraft pulp and oxygen-alkali predelignified softwood kraft pulp than for hardwood kraft pulp.

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