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## Sulfuric acid bleaching of kraft pulp II: Behavior of lignin and carbohydrate during sulfuric acid bleaching

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**Abstract** The purpose of this study was to investigate the behavior of lignin and carbohydrates in kraft pulps during sulfuric acid bleaching. Beech kraft pulp and red pine kraft pulp were bleached with dilute sulfuric acid at pH 1.3 with addition of sodium nitrate and sodium nitrite at 100°C for 1 h. The pulps were then extracted with aqueous sodium hydroxide solution at 70°C for 1 h. Lignin and carbohydrates in the acid effluents and the alkali effluents were analyzed. The carbohydrate compositions of unbleached and bleached kraft pulps were also determined. The residual lignin in kraft pulp was degraded to a molecular size similar to that of milled wood lignin during sulfuric acid bleaching without additives, and it was further degraded to a much smaller molecular size during sulfuric acid bleaching with additives. It was found that the amount of carbohydrate dissolved in the bleach effluents were only about 1% of the dry weight of the kraft pulp under these bleaching conditions. The carbohydrates dissolved during bleaching were mostly of hemicellulose origin.

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

### Introduction

Environmental problems, including the discharge of organochloro compounds from kraft bleach plants, have

recently been one of the greatest concerns of the pulp and paper industry. Worldwide pulp manufacturers, accordingly, have been shifting the bleaching technologies from elemental chlorine-based ones to these with no chlorine or lower chlorine levels. As a consequence, the amount of elemental chlorine in use for pulp bleaching has been decreasing rapidly, chlorine dioxide being substituted for elemental chlorine to a great extent. Moreover, the amount of oxygen-based bleaching chemicals, such as oxygen, peroxides, and ozone, has been increasing gradually during the past decade.

In our preceding paper (part I of this series),<sup>1</sup> sulfuric acid bleaching of kraft pulp was proposed as one stage of the nonchlorine bleaching processes. Kraft pulp and oxygen predelignified kraft pulp were successfully bleached with dilute sulfuric acid, keeping the pulp viscosity within acceptable levels. The delignification selectivity was appreciably improved by the addition of sodium nitrate and sodium nitrite. The principal chemistry involved in this bleaching, as described previously,<sup>1</sup> is acidolytic fragmentation and solubilization of the residual lignin in kraft pulp. Because kraft pulp has been exposed only to alkaline conditions, the residual lignin in kraft pulp could have acid-labile bonds such as vinyl ether-type interunit linkage in lignin or benzylether-type lignin-carbohydrate linkages. In our earlier paper,<sup>2</sup> through characterization of the residual lignin, the resistance of the residual lignin in kraft pulp was explained by these lignin-carbohydrate linkages. The stability of the lignin-carbohydrate linkages during kraft cooking was also confirmed by model experiments in another earlier paper.<sup>3</sup> In addition to acidolytic reactions, some oxidative fragmentation reactions can be expected after adding sodium nitrate and sodium nitrite during sulfuric acid treatment.

In this paper the behavior of chemical components in kraft pulp, lignin, and carbohydrates during sulfuric acid bleaching is discussed. The discussions are mainly focused on the sulfuric acid bleaching with addition of sodium nitrate and sodium nitrite, although some reference samples were also obtained from bleaching without addition of sodium nitrate and sodium nitrite. The contribution of lignin

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removal and hexeneuronic acid removal<sup>4,5</sup> to the kappa number reduction during sulfuric acid bleaching, including some lignin model experiments, will be subsequently published.

## Experimental

### Kraft pulping

Species used were Japanese beech (*Fagus crenata Blume*) and Japanese red pine (*Pinus densiflora Sieb. et Zucc.*). Condition were as follows: 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 a TAPPI standard method.

### Sulfuric acid bleaching

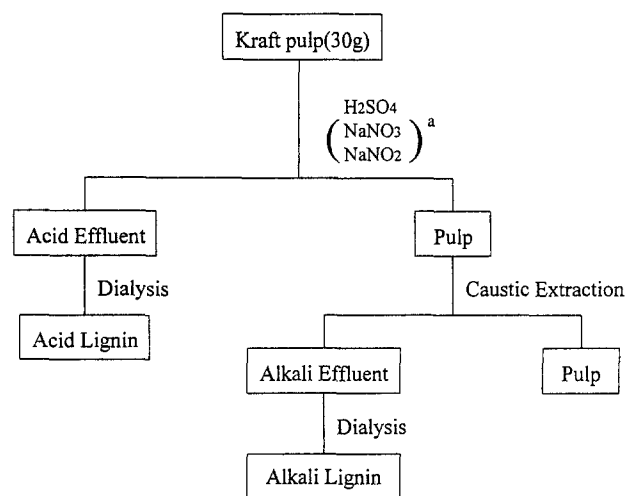
Kraft pulp was placed in a plastic bag (polyvinylidene chloride), and pH 1.3 aqueous sulfuric acid solution was added to make the pulp consistency 10%. Also added were sodium nitrate (4.5% on beech kraft pulp and 8.1% on red pine kraft pulp) and sodium nitrite (0.9% on each pulp). Then the plastic bag was placed in a boiling waterbath and kept for 1h. The same bleaching was also carried out separately without sodium nitrate and sodium nitrite. The pulp was then filtered, and the effluents were collected for lignin and carbohydrate analyses.

### Caustic extraction

The kraft pulp treated with sulfuric acid was then washed with water, placed in a plastic bag again, and extracted with aqueous sodium hydroxide solution at 70°C for 1h. The alkali charge was 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 caustic extraction liquor was collected for lignin and carbohydrate analyses.

### Lignin analysis

A sample preparation scheme is shown in Fig. 1. The effluents obtained from the sulfuric acid treatment and the caustic extraction were neutralized to pH 6.0, dialyzed (Spectra/Por Membrane MWCO:1000), and freeze-dried. Alkali lignins thus prepared were analyzed by gel permeation chromatography (GPC). The analytical conditions for GPC were as follows: apparatus, ISCO UA-5; column, Sephadex LH-20 (1.5 × 30.0cm); eluents, dioxane/water (8:2); detector, UV 280nm. Acid lignins and alkali lignins (Fig. 1) were hydrolyzed with 3% sulfuric acid solution in an autoclave at 120°C for 1h. The solutions were filtered by 1G4 filter, and the Klason lignin content was determined. Carbohydrates



**Fig. 1.** Sample preparation scheme for acid lignin and alkali lignin in sulfuric acid bleaching of kraft pulps. <sup>a</sup>Bleaching was done with and without additives separately

in filtrates were analyzed by high performance liquid chromatography (HPLC). HPLC conditions were as follows: column, Shimadzu Shim-pack ISA-07/S2504 (4.0mm × 25cm); column temperature, 65°C; eluents, H<sub>3</sub>BO<sub>3</sub>/KOH buffer gradient; flow rate, 0.6ml/min; detector, Shimadzu FLD-1 fluorescence detector. The total sugar contents of the lignin preparations were obtained from the sum of each sugar.

### Carbohydrate analysis of the pulp

Sulfuric acid (72%, 3ml) was added to kraft pulps before and after bleaching, and the preparation was hydrolyzed at 30°C for 1h. The sulfuric acid was then diluted to 3%, and it was heated in an autoclave at 120°C for 1h. The hydrolysate was neutralized to pH 6.0 and then analyzed by HPLC.

### Carbohydrate analysis of the bleach effluents

The bleach effluents from the sulfuric acid treatment and the following caustic extraction were neutralized to pH 6.0, and concentrated sulfuric acid was added to make the sulfuric acid concentration 3%. This preparation was kept in an autoclave at 120°C for 1h. The hydrolysates were neutralized to pH 6.0 and subjected to HPLC analysis.

## Results and discussion

### Sulfuric acid bleaching of kraft pulp

The kappa number and viscosity of beech kraft pulp and red pine kraft pulp before and after sulfuric acid bleaching are shown in Table 1. Satisfactory bleaching results were obtained for both beech kraft pulp and red pine kraft pulp. Judging from the kappa number reduction versus viscosity

**Table 1.** Results of sulfuric acid bleaching of kraft pulps

Parameter	Beech kraft pulp		Red pine kraft pulp	
	Before bleaching	After bleaching	Before bleaching	After bleaching
Kappa no.	19.8	4.9 (9.2)	23.0	7.9
Viscosity (cP)	47.4	26.9 (27.0)	31.7	21.0

Data in parentheses are results of bleaching without additives

Bleaching conditions (beech): acid treatment (pH 1.3), 100°C, 60 min, 4.5% NaNO<sub>3</sub>, and 0.9% NaNO<sub>2</sub> on pulp. Alkali extraction: 70°C, 60 min, 3% NaOH on pulp

Bleaching conditions (red pine): acid treatment (pH 1.3), 100°C, 60 min, 8.1% NaNO<sub>3</sub>, and 0.9% NaNO<sub>2</sub> on pulp. Alkali extraction: 70°C, 60 min, 4% NaOH on pulp

loss, the delignification selectivity was better than oxygen-alkali bleaching. Because the objective of this report is to investigate the behavior of lignin and carbohydrate during sulfuric acid bleaching, bleaching conditions were not varied. The viscosities of bleached pulps were rather high during these bleaching runs, so the kappa numbers can be further decreased with possible sacrifice of pulp viscosity by applying a lower pH for the acidic treatment. The effect of pH and the amount of additives on kappa number reduction and viscosity loss were reported elsewhere.<sup>1</sup>

#### Isolation of lignin in bleach effluents derived from bleaching without additives

Lignin samples from the bleach effluents were prepared according to the scheme in Fig. 1. In the case of bleaching without additives, the amount of acid lignin was negligible for both beech kraft pulp and red pine kraft pulp. The yield of alkali lignin from beech kraft pulp was 0.72% (0.22 g) on pulp, and the Klason lignin content was 52.1%. The yield of alkali lignin from red pine kraft pulp bleaching was 0.72% (0.22 g) on pulp, and the Klason lignin content was 73.6%. These alkali lignins were subjected to ultraviolet (UV), infrared, (IR), and GPC analysis (described later) and compared with alkali lignins derived from the bleaching with additives (NaNO<sub>3</sub> and NaNO<sub>2</sub>).

#### Isolation and characterization of lignin in bleach effluents derived from bleaching with additives

Lignin samples from the bleach effluents were prepared according to the scheme in Fig. 1. Two lignin samples were prepared from the effluents gained after both beech kraft pulp bleaching and red pine kraft pulp bleaching: One is acid lignin, which was prepared via dialysis of the acid effluent; the other is alkali lignin, prepared via dialysis of the alkali effluent. The yields of lignin preparations are shown in Table 2. Klason lignin content and the sugar compositions of lignin preparations are shown in Table 3.

The yields of acid lignins were comparatively low (Table 2) because lignin is scarcely soluble in acidic water unless it is highly oxidized. Furthermore, the Klason lignin content of the acid lignins was less than 10% (Table 3) for both beech kraft pulp and red pine kraft pulp. The total sugars in

**Table 2.** Yields of alkali lignin and acid lignin by sulfuric acid bleaching of kraft pulps

Kraft pulp	Alkali lignin (g)	Acid Lignin (g)
Beech	0.341 (1.13%)	0.170 (0.57%)
Red pine	0.352 (1.17%)	0.069 (0.23%)

Data in parentheses are the yield based on 30 g kraft pulp  
See Table 1 for bleaching conditions

the hydrolysates of acid lignins were approximately 30% (Table 3). The rest of the samples were considered to be degradation products from lignin. These results indicated that acid lignins were highly oxidized by sodium nitrate and sodium nitrite, and most of these lignin fractions were not detectable as Klason lignin because of their high solubility in acidic water. This is why only the negligible amount of acid lignin was obtained from bleaching without additives as described above.

The sugar compositions of acid lignin fractions showed that most of the sugars were of hemicellulose origin. In the case of red pine, however, the yield of glucose was too high to believe that it came from glucomannan, suggesting that small cellulose fragments were included in this fraction. It should be noted here that the carbohydrate moiety in acid lignin fractions (also in alkali lignin fractions) are not necessarily chemically bonded to lignin. Because the lignin fractions were obtained through dialysis of the bleach effluents, some carbohydrate oligomers could possibly be included in these fractions, provided that those carbohydrate oligomers were soluble and were retained after dialysis.

The yields of alkali lignins from beech kraft pulp bleaching and red pine kraft pulp bleaching were higher than the corresponding yields of acid lignins (Table 2). The Klason lignin content of alkali lignins was also much higher than that in the corresponding acid lignins (Table 3). The results showed that the alkali lignins were less degraded than acid lignins, which is why those fractions were not dissolved in dilute sulfuric acid and were extracted later with aqueous alkali.

Molecular weight distributions of alkali lignins were compared with (milled wood lignins) (MWLs) prepared from beech wood meal and red pine wood meal (Fig. 2 for beech kraft pulp bleaching and Fig. 3 for red pine kraft pulp

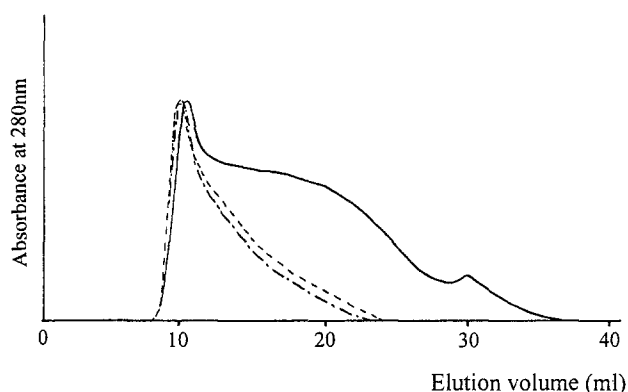
**Table 3.** Sugar compositions, yield of total sugars, and hydrolysis residues of alkali and acid lignins by sulfuric acid bleaching of kraft pulps

Parameter	Beech		Red pine	
	Alkali lignin	Acid lignin	Alkali lignin	Acid lignin
Hydrolysis residue (%) <sup>a</sup>	52.5	7.1	75.1	8.8
Total sugar (%) <sup>a</sup>	17.2	31.0	4.9	29.3
Sugar composition (%)				
Glc	4.0	8.9	39.7	48.9
Xyl	95.1	71.9	40.9	20.8
Man	–	2.0	9.7	6.6
Ara	–	0.5	1.2	0.7
Gal	0.9	16.7	8.5	23.0

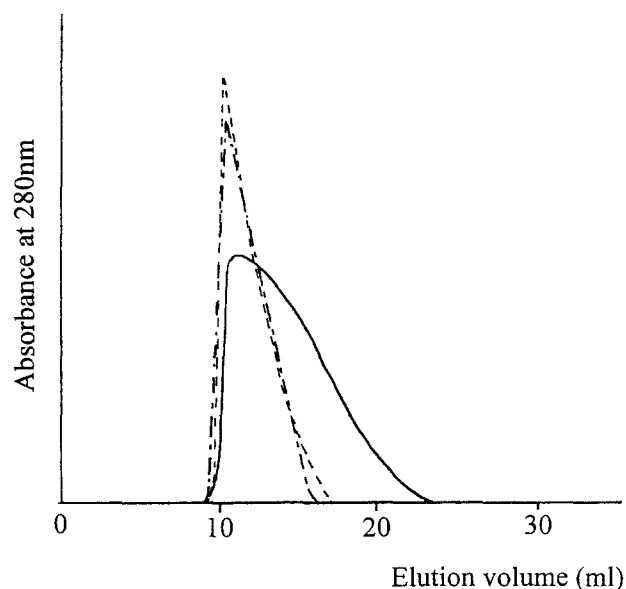
See Table 1 for bleaching conditions

Glc, glucose; Xyl, xylose; Man, mannose; Ara, arabinose; Gal, galactose

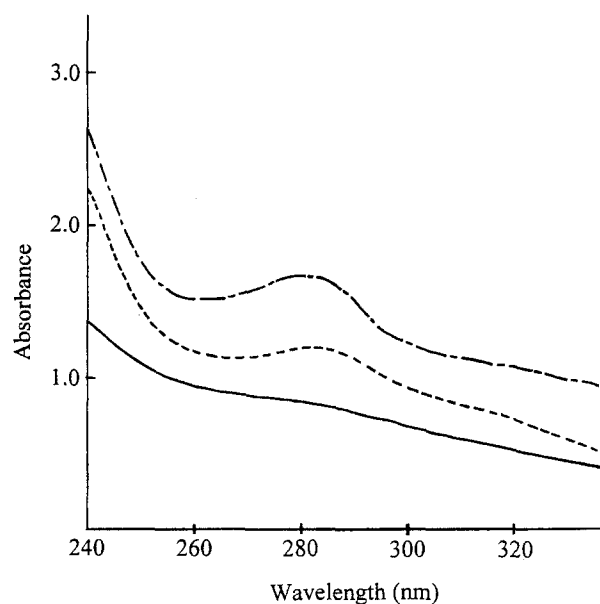
<sup>a</sup>The yields are based on the lignin preparations



**Fig. 2.** Gel permeation chromatography (GPC) of alkali lignin from beech kraft pulp bleaching and beech milled wood lignin (MWL). *Broken line*, MWL; *dotted line*, alkali lignin (without additives); *solid line*, alkali lignin (with additives)



**Fig. 3.** GPC of alkali lignin from red pine kraft pulp bleaching and red pine MWL. *Broken line*, MWL; *dotted line*, alkali lignin (without additives); *solid line*, alkali lignin (with additives)



**Fig. 4.** Ultraviolet (UV) spectra of alkali lignin from red pine kraft pulp bleaching and red pine MWL. *Broken line*, MWL; *dotted line*, alkali lignin (without additives); *solid line*, alkali lignin (with additives)

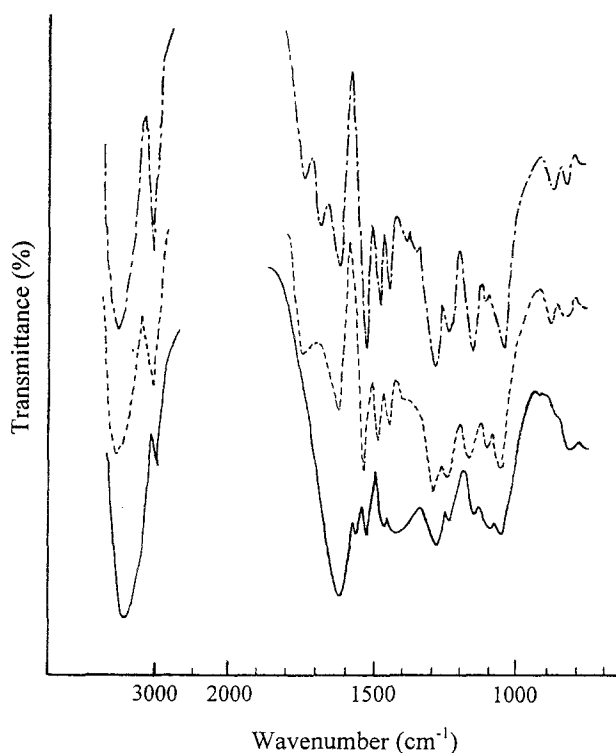
bleaching). When the additives sodium nitrate and sodium nitrite were not applied during sulfuric acid bleaching, the molecular weight distributions of alkali lignins were similar to those of the MWLs for both beech kraft pulp bleaching (Fig. 2) and red pine kraft pulp bleaching (Fig. 3). However, alkali lignins obtained from the bleaching with additives showed quite different molecular weight distribution patterns from the MWL region to the much lower-molecular-weight region (Figs. 2, 3), indicating severe degradation of the residual lignin in kraft pulps by sodium nitrate and sodium nitrite.

Alkali lignin obtained from the bleaching of red pine kraft pulp was subjected to ultraviolet (UV) (Fig. 4) and infrared (IR) (Fig. 5) spectroscopic analyses. When the additives ( $\text{NaNO}_3$  and  $\text{NaNO}_2$ ) were employed, there was no distinct UV absorption maximum, suggesting that the

**Table 4.** Sugar compositions and total amounts of sugars in bleach effluents from sulfuric acid bleaching of kraft pulps

Sugar	Beech (%)		Red pine (%)	
	Alkali effluent	Acid effluent	Alkali effluent	Acid effluent
Glc	3.6	1.5	16.8	5.5
Xyl	94.5	94.6	46.6	10.4
Man	—	—	6.2	1.7
Ara	0.3	1.6	7.2	74.5
Gal	1.6	2.3	23.2	7.9
Total (g)	0.07	0.13	0.14	0.20

See Table 1 for bleaching conditions  
Total sugars are based on 30g kraft pulp

**Fig. 5.** Infrared spectra of alkali lignin from red pine kraft pulp bleaching and red pine MWL. *Broken line*, MWL; *dotted line*, alkali lignin (without additives); *solid line*, alkali lignin (with additives)

lignin was extensively degraded by the additives. Without additives, alkali lignin had a UV absorption maximum at somewhat longer wavelength than MWL. This is probably because of the formation of ring conjugated side-chain structures (C=C or C=O) during acidolysis.<sup>6</sup> The IR spectrum of alkali lignin obtained from the bleaching with additives was quite different from that of MWL or alkali lignin obtained without additives. The presence of a nitro group was indicated by the strong bond at around  $1560\text{cm}^{-1}$ . The introduction of nitro groups under similar reaction conditions were reported previously by Ohi and Kishino in the reactions of lignin model compounds with nitrous acid.<sup>7</sup> These results indicated that the lignin in

**Table 5.** Changes in sugar composition of kraft pulps during sulfuric acid bleaching

Sugar	Before bleaching		After bleaching	
	Beech (%)	Red pine (%)	Beech (%)	Red pine (%)
Glc	74.6	86.3	75.6	85.3
Xyl	24.8	6.3	23.8	7.8
Man	0.4	6.4	0.4	6.9
Ara	0.1	0.6	0.1	—
Gal	0.1	0.4	0.1	—

See Table 1 for bleaching conditions

kraft pulp was extensively degraded to low-molecular-weight fragments by sodium nitrate and sodium nitrite during sulfuric acid bleaching, which contributed to a reduction of the kappa number. The effect of additives on the kappa number reduction was reported in part I of this series.<sup>1</sup>

Alkali lignins also contained a small amount of carbohydrates but not as much as did the acid lignins (Table 3). Sugar compositions of acid hydrolysates of alkali lignin showed that the sugars were mostly of hemicellulose origin in the case of beech kraft pulp bleaching. Alkali lignin from red pine kraft pulp bleaching, however, seemed to contain some cellulose fragments, as was observed for acid lignin described above.

#### Dissolution of carbohydrates during sulfuric acid bleaching with additives ( $\text{NaNO}_3$ and $\text{NaNO}_2$ )

To investigate the carbohydrate dissolution during sulfuric acid bleaching, sugar compositions of the kraft pulps were determined before and after sulfuric acid bleaching. Also analyzed were carbohydrates dissolved into acid effluents and alkali effluents during beech kraft pulp bleaching and red pine kraft pulp bleaching (Table 4). The total amounts of sugars found in the acid effluents and alkali effluents were only about 1% for both beech kraft pulp and red pine kraft pulp (Table 4). Accordingly, there was little difference in the sugar composition between the kraft pulps before and after bleaching (Table 5) except the disappearance of arabinose from red pine kraft pulp after bleaching. Most of

the arabinose in red pine kraft pulp was dissolved into the acid effluent (Table 4), which could reasonably be explained by the instability of the arabinose side chain on arabinoglucuronoxylan. Based on the carbohydrate analyses of kraft pulps and bleach effluents, it can be said that no serious degradation of carbohydrates took place during sulfuric acid bleaching of kraft pulp at pH 1.3.

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## Conclusions

Residual lignin in kraft pulp is degraded to a molecular size similar to that of MWL during sulfuric acid bleaching (pH 1.3) without additives. In the presence of the additives (sodium nitrate and sodium nitrite), the molecular size of the degraded lignin is much smaller; thus the additives contribute to a further decrease in the kappa number of the bleached pulp. Even though acidolytic reactions are involved in the reaction mechanisms of sulfuric acid bleaching, the dissolution of carbohydrates during bleaching is limited (only about 1%). The carbohydrates dissolved during bleaching are mostly of hemicellulose origin.

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