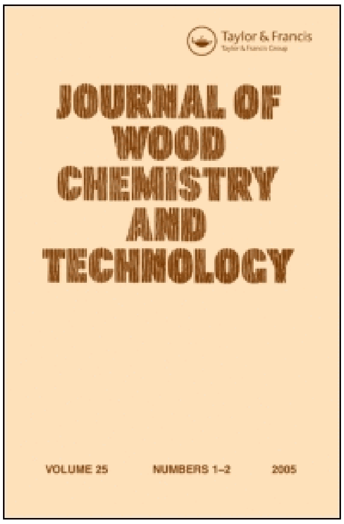

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RESIDUAL LIGNIN IN UNBLEACHED KRAFT PULP. Part I

-Alkali-Extraction of Residual Lignin from Unbleached Kraft Pulp Solution-

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ABSTRACT

Unbleached kraft pulp containing 4.7% Klason lignin has been found to dissolve completely in several nonaqueous cellulose solvents. Extraction of the residual lignin in the unbleached kraft pulp from these solutions was attempted using several kinds of solvents for kraft lignin and hemicelluloses.

When the solvents for only kraft lignin were used, a small amount of the residual lignin (<7% of the original residual lignin) was extracted. On the other hand, 24% sodium hydroxide solution extracted approximately one-half of the residual lignin together with polysaccharides. These results indicate that the residual lignin has some chemical linkages with some polysaccharides.

INTRODUCTION

Unbleached kraft pulp (UKP) has dark color derived mainly from the lignin in pulp. The residual lignin in UKP cannot be removed completely by further delignification procedures without severe losses in pulp yields and quality. This difficulty of removing the final part of lignin from UKP necessitates the use of multistage bleaching including chlorination. Such bleaching systems, however, are not favorable from the viewpoints of bleaching cost and environmental pollution. Therefore, it is very important to clarify the structure and properties of the residual lignin in UKP for the pulping and bleaching processes.

Yamazaki et al.[1] reported a comprehensive study on the residual lignin, namely its isolation by the procedure consisting of enzyme treatments of pulp and extraction of the lignin with organic solvents, and also its characterization by various analytical methods. They suggested that the stability of the lignin-hemicellulose linkage under kraft pulping conditions might be a main reason for its resistance to further delignification reactions.

Gellerstedt and Lindfors[2,3] reported the characterization of the residual lignin in UKP by an acidolysis-gas chromatography technique. Their results supported the idea that the chemical structure of the residual lignin causes its resistance to further delignification reactions.

Recently, Gierer and Wannstrom found the formation of alkali-stable carbon-carbon[4] and ether[5] linkages between lignin and polysaccharides during alkali and kraft cooks. Their results indicated that the formation of these linkages provides one explanation for the gradual inhibitation of the residual lignin dissolution during kraft pulping.

Other investigations have been reported[6,7], but little progress has been achieved in increasing our knowledge about the residual lignin in UKP.

In the last two decades, many kinds of nonaqueous cellulose solvents have been found. These have made it possible to develop new preparation methods for regenerated cellulose films or fibers and to prepare cellulose derivatives in nonaqueous and homogeneous systems. We have utilized nonaqueous cellulose solvents as media for the chemical modifications of cellulose[8-11].

In the present work, the solubility of UKP in nonaqueous cellulose solvents was examined and extraction of the residual lignin from nonaqueous sloutions of UKP was then attempted with several kraft lignin solvents or aqueous sodium hydroxide solutions. The extracts were analysed for sugar composition and lignin content. On the basis of these analytical results and the response of the residual lignin to these extractions, the characteristics of the residual lignin were discussed.

EXPERIMENTAL

Materials and reagents: Commercial UKP (a mixture of soft woods, Tokai Pulp Co. Ltd.) was used. Dimethylsulfoxide (DMSO) of pure grade was dried by using molecular sieve 3A. Other reagents and solvents of pure grade were used without further purification.

Preparation of UKP solutions:

1) SO_2-diethylamine (DEA)-DMSO system - SO_2/DMSO solution was prepared by bubbling SO_2 gas into DMSO in a volumetric flask, and the concentration of SO_2 was determined by the weight increase (ca. 0.3 g/mL). One g of UKP dried at 105°C for 3 h was dispersed in 43 mL DMSO and heated at 60°C for 0.5 h. After cooling to room temperature, appropriate amounts of the SO_2/DMSO solution containing 1.19 g SO_2 and 1.91 mL DEA were added to the stirred mixture. The amounts of SO_2 and DEA added were adjusted to equal the moles of hydroxyl groups in 1 g of UKP, calculated as (wt. X 3)/162 (moles), although xylan and lignin are also present in UKP. After stirring for 3 h, a clear solution of UKP was obtained (usually 2%, wt.).

2) Other nonaqueous solvent systems - Dimethylformamide (DMF)-chloral-pyridine and DMOS-chloral-pyridine systems were prepared according to the procedures described in another paper[10]. In DMF-N_2O_4 and DMSO-N_2O_4 systems, the amounts of N_2O_4 added to the UKP suspensions were adjusted to equal the moles of hydroxyl groups in UKP.

Extractions from UKP solutions:

1) Kraft lignin - To the UKP solution (ca. 50 mL) containing 1 g of UKP, 300 mL of kraft lignin solvent was poured under vigorous stirring. Dioxane-water, methycellosolv-water, glacial acetic acid, and dichloromethane-ethanol were used as solvents for kraft lignin. Compositions of these solvents are shown in Table 1. After stirring for 2 days at room temperature, precipitates were centrifuged and washed several times with the same solvent used for extraction. The centrifuged solutions were combined and evaporated to remove volatile solvents. The extracts were isolated by dialysis followed by lyophilization.

2) Sodium hydroxide solutions - A typical extraction procedure is shown in Fig. 1. Sodium hydroxide solution (300 mL)

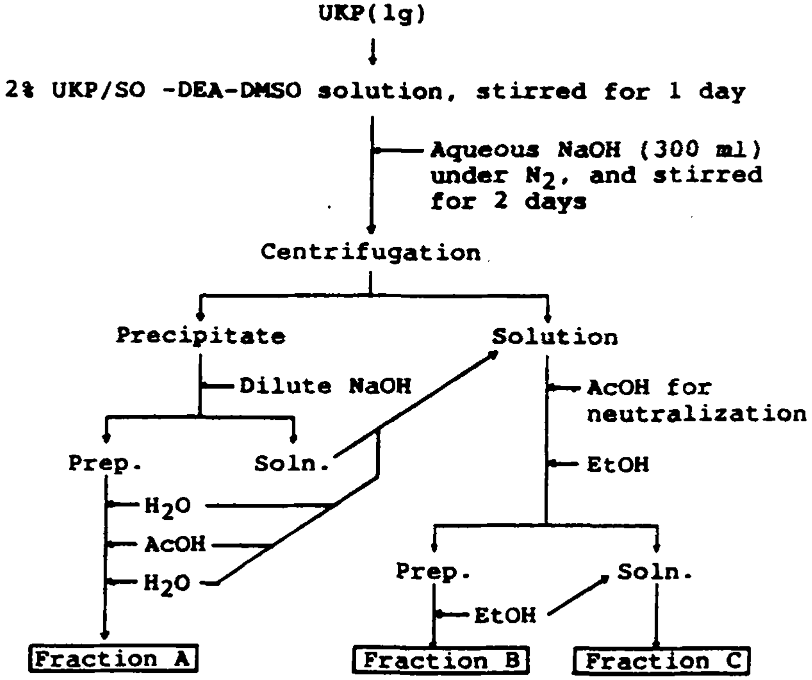

Figure 1 Fractionation of UKP using the SO_2-DEA-DMSO system and aqueous NaOH.

was poured into the UKP solution containing 1 g of UKP (2%, wt. %) under vigorous stirring in an N_2 atmosphere. After stirring for 2 days, the precipitates (Fraction A) were separated by centrifugation; washed with successively dilute alkali, water, dilute acetic acid and water; and dried by lyophilization. The supernatant and the washings were combined and neutralized with acetic acid. The solution was poured into a large volume of ethanol, and the ethanol-insoluble part (Fraction B) was separated from the ethanol-soluble part (Fraction C) by centrifugation.

Analyses: The sugar compostions of each fraction was determined by the usual method[13]. The lignin content of fractions B and C was determined by UV absorption at 280 nm (E_{280}=22.6 l/g·cm) of their aqueous solutions. These were prepared by neutralizing their alkaline solutions with sulfuric acid.

RESULTS

1. Solubility of UKP in nonaqueous cellulose solvents and extraction of residual lignin in UKP with solvents for kraft lignin

Solubilities of various cellulosic samples and pulps in nonaqueous cellulose solvents were thought to depend on the contents and properties of the residual lignin and hemicellulose in the samples. The UKP sample used in this work had 4.7% Klason lignin and approximately 14% neutral sugars other than glucose. As shown in Table 1, the UKP sample dissolved in all but two of the nonaqueous cellulose solvent systems under the conditions used for dissolution of cellulose.

Extraction of the residual lignin from the nonaqueous UKP solutions was attempted by addition of solvents for kraft lignin to the UKP solutions. Extracts less than 1.5% of the original UKP were obtained, and their lignin contents were less than 20%, indicating that at most only 6.4% of the residual lignin in UKP was extracted in the four cases examined (Table 1). There was little difference in the extractability among the lignin solvents used.

2. Extraction with sodium hydroxide solution

It is known that aqueous NaOH solution can extract polysaccharides from delignified plant cells, and the kinds and yields of polysaccharides depend on the concentration. The UKP used in this work contains approximately 14% of neutral sugars other than glucose. We examined the behavior of the residual lignin and hemicellulose in the SO_2-DEA-DMSO system towards aqueous NaOH solutions of various concentrations. In this experiment, the solvent systems containing DMF were omitted, because DMF is hydrolyzed to produce diethylamine and formate in basic media. The solvent systems containing chloral or N_2O_4 were also omitted, because they cause some side-reactions under basic conditions [8,12].

TABLE 1

Solubility of UKP in Nonaqueous Cellulose Solvents and Extraction of Lignin from UKP Solution with Solvents for Kraft Lignin

Nonaqueous cellulose solvent system	Solubility of UKP[*1]	Extractability of the residual lignin[*2]
Chloral-Pyridine-DMF	○	<3%
Chloral-Pyridine-DMSO	△	
N_2O_4-DMF	○	<7%
N_2O_4-DMSO	△	
SO_2-DEA-DMF	○	<5%
SO_2-DEA-DMSO	○	<5%

*1: ○; completely soluble, △; partly soluble.

*2: Based on the amount of the residual lignin. Dioxane-water (9:1, 8:2 and 1:1), methycellosolv-water (1:0, 7:3 and 1:1), glacial acetic acid, and dichloromethane-ethanol (2:1) were used as solvents for kraft lignin.

The dissolution mechanism and the dissolution state of cellulose in the SO_2-DEA-DMSO system have been clarified and no reactions other than complex formation between a hydroxyl group, a SO_2 molecule and a DEA molecule were found to occur in this solvent[14]. By addition of aqueous NaOH to the UKP/SO_2-DEA-DMSO solution, the SO_2 and DEA molecules in the complex were detached from the hydroxyl group to produce free DEA and Na_2SO_3. The Na_2SO_3 produced is thought to have little influence on the chemical structure of polysaccharides and lignin in UKP under the conditions used in this work, because IR spectra and sulfur contents of alkali-treated UKP isolated from the nonaqueous solutions were equal to those of the original UKP.

The influence of various dissolution and/or extraction conditions on yields of extracts was examined, and based on the

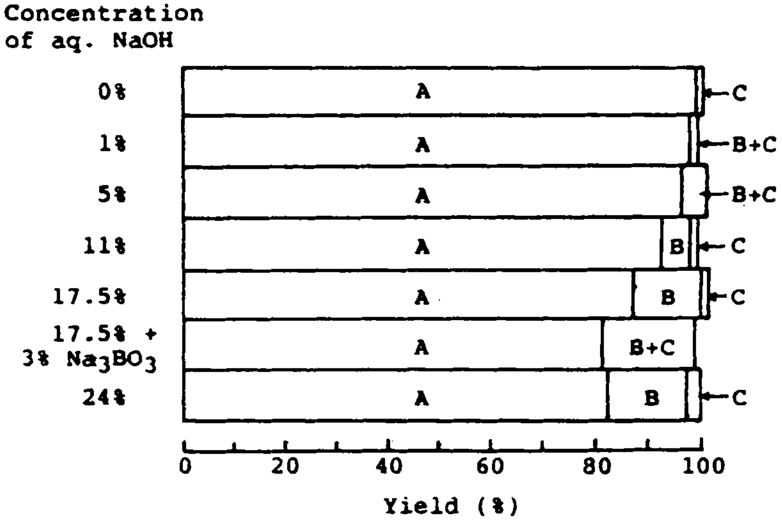

Figure 2 Yield of each fraction separated according to the scheme in Fig. 1.

results of those preliminary experiments the conditions shown in Fig. 1 were selected for preparation of UKP solutions and alkali-extractions of the residual lignin.

Fig. 2 shows the yield of each fraction obtained by extraction with various alkali concentrations. In this figure, B+C means total yields of fractions B and C. As expected, the yield of alkali-extracts increased with increasing alkali concentration. Extraction with 17.5% NaOH containing 3% Na_3BO_3 gave the maximum yield. This liquor is known to effectively extract glucomannan. By addition of water instead of an alkali solution to an UKP solution, 1.2% of UKP was extracted. This fraction, actually extracted by water-DMSO (6:1), consists of approximately 15% lignin and 85% polysaccharides.

Fig. 3 indicates the sugar compositions of fractions shown in Fig. 2. The UKP sample consisted of 85% glucose, 7% mannose, 7% xylose, and small amounts of arabinose and rhamnose. Galactose was also detected, but only a trace amount. As shown in the

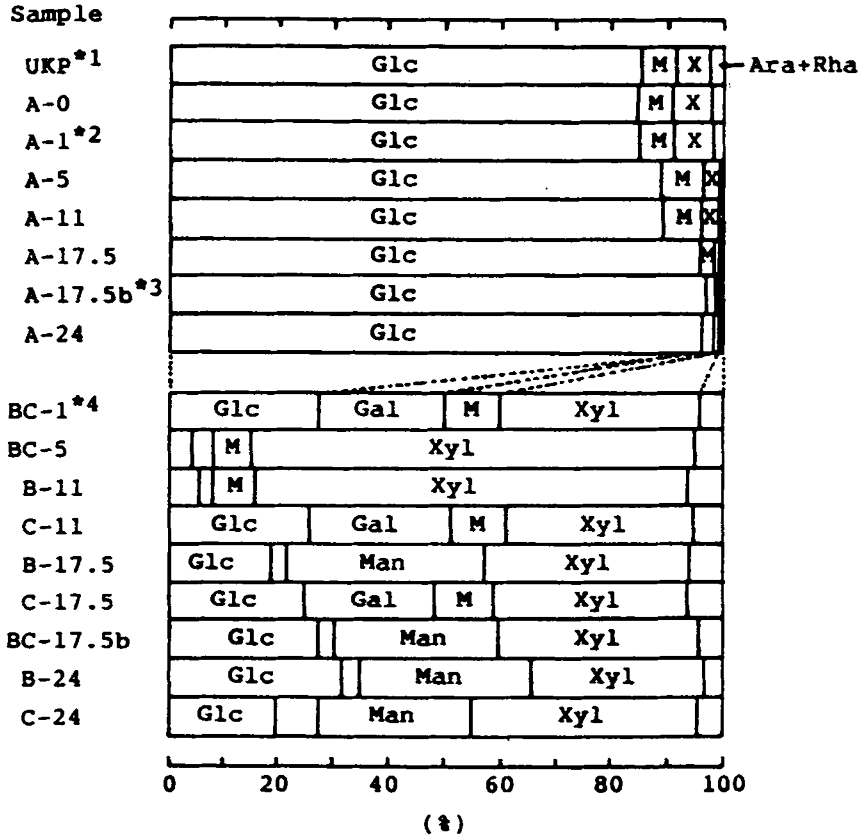

Figure 3 Sugar compositions of fractions in Fig. 2.
*1: Unbleached kraft pulp. *2: For example, fraction A obtained after extraction with 1% NaOH.
*3: Fraction A extracted with 17.5% NaOH + 3% Na_3BO_3.
*4: The same as Fraction B+C in Fig. 2.

figure, xylose was extracted preferentially by alkali solutions with concentrations lower than 11.5%, and mannose was extracted by alkali solutions with concentrations higher than 17.5%. However, approximately 3.5% of sugars other than glucose still remained in the fraction A even after extraction with 24% NaOH solution. That is, about 20% of sugars other than glucose in the UKP samples were not extracted. It is noteworthy that galactose present in trace amounts in the original UKP is concentrated in fraction C. Glucose present in fractions B and C extracted with 17.5% and 24% alkali is derived from low molecular weight cellulose and glucomannan.

Table 2 shows the lignin content of the extracted fractions and the yield of lignin extracted. Every fraction in Table 2 has a higher lignin content than the original UKP (4.7%). As shown in the second column, the yield of extracted lignin increased with the alkali concentration used for extractions. This relation was similar to that between the alkali concentration and the yield of polysaccharides extracted.

By alkali extraction of UKP solutions, at most one-half of the residual lignin was extracted together with polysaccharides derived from hemicellulose and low molecular cellulose. In other words, one-half of the residual lignin still remained in fraction A, even after the most concentrated NaOH solution was used for extraction.

DISCUSSION

At most, only 6.4% of the residual lignin in UKP was extracted from its nonaqueous solutions with kraft lignin solvent. This low extractability of the residual lignin could possibly be explained in two ways. The residual lignin may have a different chemcial structure and/or molecular weight from that of kraft lignin. Namely, the residual lignin has a higher degree of condensation and/or higher molecular weight than kraft lignin. Alternatively, although the chemical structure and/or molecular weight of the residual lignin is not much different from that of kraft lignin it is not soluble in the solvents for kraft lignin, because of the existence of some chemical linkages between the residual lignin and polysaccharides.

TABLE 2

Lignin Content of Each Fraction Obtained After Extraction with Sodium Hydroxide Solution and Yield of Lignin Extracted

Fraction	Lignin content (%) in fraction	Yield of lignin extracted (%)[*1]
C-0[*2]	14.6	3.7
BC-1	27.6	10.0
BC-5	18.2	18.2
B-11	18.1	22.1
C-11	10.4	2.7
(B+C-11)[*3]		(24.8)
B-17.5	14.3	43.8
C-17.5	7.7	2.8
(B+C-17.5)		(46.6)
BC-17.5b	13.1	47.7
B-24	17.0	47.7
C-24	6.0	4.3
(B+C-24)		(52.0)

*1: Based on the weight of the original residual lignin in the UKP sample.
*2: Fraction C extracted with 0% NaOH.
*3: Sum of B-11 and C-11.

As to the solubility of the residual lignin in solvents for kraft lignin, Yamazaki et al.[1] reported that enzymatically isolated residual lignin is soluble in the usual solvents for kraft lignin such as a dioxane-water, DMF, DMSO, and others. Also, in the present work the UKP sample with 4.7% Klason lignin was soluble completely in the SO_2-DEA-DMSO system, which has DMSO as the main component (ca. 95%).

Thus, the solubility of the residual lignin must be similar to that of kraft lignin. Therefore, the unextractability of the residual lignin from homogeneous UKP solutions with solvents for kraft lignin should be explained by the existence of some chemical linkages between the residual lignin and polysaccharides, as Yamazaki et al.[1] pointed out.

In order to prove the presence of lignin-polysaccharides linkages, alkali extraction of UKP/SO_2-DEA-DMSO solutions was investigated. Yamazaki et al.[1] reported also that enzymatically isolated residual lignin in UKP is soluble in 0.1M NaOH solution. Nevertheless, only 10% of the residual lignin was extracted wtih 1% NaOH solution (0.25M) from the homogeneous UKP solution. However, yields of extracted lignin and polysaccharides increased remarkably with increasing alkali concentration. By using a 24% NaOH solution, approximately one-half of the residual lignin in UKP was extracted together with polysaccharides from the UKP solution. These results indicate that the extracted portions of the residual lignin in UKP have some chemcial linkages with alkali-extractable polysaccharides since extractions were performed from completely homogeneous UKP solutions, in which any physical absorptions among the residual lignin, hemicelluloses and cellulose were excluded.

Concerning the kinds of polysaccharides linked chemically to the residual lignin, Yamazaki et al.[1] pointed out that galactose residues in galactoglucomannan might possibly be chemcially linked to the residual lignin. On the other hand, as shown in Fig. 3, fractions C contain galactose in relatively high ratios, whereas the original UKP sample contains it in trace. As shown in Table 2, yields of lignin extracted in fractions C were less than 4.3% of the residual lignin in UKP. By using 5-11% aqueous NaOH, 18-25% of the residual lignin was extracted in the fractions B and BC together with polysaccharides, 80% of which consist of xylose residues. Thus, some parts of the residual lignin extracted is probably linked chemically to xylan. By using NaOH solutions with higher concentrations (17.5-24%), yields of the extracts from UKP increased remarkably and the extracts consisted of comparable amounts of glucose, mannose and xylose residues, which are derived from low molecular cellulose, glucomannan and xylan, respectively. The yield of the residual lignin extracted from UKP solutions also increased to approximately 50%. The portion of residual lignin extracted additionally by the increment of alkali concentration from 5-11% to 17.5-24% should be linked to glucomannan and/or alkali-extractable cellulose molecules, and thus they are extracted together.

As discussed in the previous paragraphs, almost all the extracted residual lignin is most likely linked chemically to polysaccharides. Since polysaccharides remaining after kraft cooking are insoluble in such dilute alkaline solutions as used in kraft cooking (ca. 4%), it may be reasonable that lignin linked to polysaccharides resists delignification during kraft pulping. However, 18% of the residual lignin was extracted with 5% NaOH at room temperature from the homogeneous UKP solution. This suggests that a part of the lignin-polysaccharides complexes in UKP are soluble in dilute alkaline solutions but are retained in cell wall matrices by some physical factors such as adsorption.

Even after extraction with a 24% NaOH solution from the UKP solution, approximately one-half of the residual lignin still remained in fraction A together with a small amount of sugar residues originated from hemicelluloses. Possibly these components link each other and/or link to cellulose. However, the following two physical factors are also possible for explaining the presence of these components in fraction A; (1) these components were included in the cellulose matrix when fraction A was precipitated by adding NaOH solution into the UKP solution or (2) the residual lignin-polysaccharide complexes were adsorbed to cellulose when a fraction A was precipitated. The fact that glucamannan and xylan are apt to be strongly adsorbed to cellulose under alkaline conditions supports this possibility[15].

If the final part of the residual lignin and hemicelluloses are retained in fraction A by physical factors, they should be extracted completely. However, fraction A, a regenerated cellulose, was no longer soluble in the SO_2-DEA-DMSO system[14]. The relationships among the three components in fraction A, therefore, could not be clarified by the approach used in this work. This problem will be answered in the following paper.

CONCLUSIONS

A commercial unbleached kraft pulp containing 4.7% Klason lignin and 15% neutral sugars other than glucose was found to dissolve in four non-aqueous cellulose solvents (Table 1).

From one of these solutions, UKP/SO_2-DEA-DMSO, extraction of the residual lignin by adding organic solvents for kraft lignin yielded, at most, 6.4% of the residual lignin.

By using 5 and 11% aqueous NaOH instead of the organic solvents, 18 and 25% of the residual lignin respectively was extracted together with polysaccharides consisting mainly of xylan.

By using 24% aqueous NaOH, about one-half of the residual lignin was extracted together with polysaccharides consisting of cellulose, glucomannan and xylan. The extracted residual lignin is most likely linked chemically to xylan, glucomannan and cellulose.

Even after extraction with 24% NaOH solution, about one-half of the residual lignin and 20% of hemicellulose remained unextracted. This unextractable lignin and hemicellulose are probably linked chemcially to each other and also to cellulose. Physical factors were also suggested for the presence of these unextractable components. However, these possibilities could not be examined because of the insolubility of fractions A, a kind of regenerated cellulose, in the SO_2-DEA-DMSO system.

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