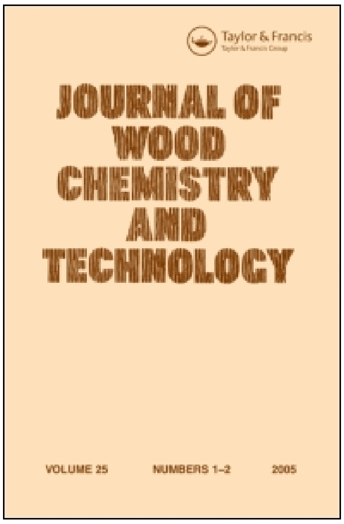

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Dissolution of Lignin in Kraft Pulp by Oxygen Bleaching

Per Larsson[a]; Olof Samuelson[a]
[a] Department of Engineering Chemistry, Chalmers University of Technology, Gothenburg, Sweden

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DISSOLUTION OF LIGNIN IN KRAFT PULP BY OXYGEN BLEACHING

Per Larsson and Olof Samuelson

Department of Engineering Chemistry

Chalmers University of Technology

S-412 96 Gothenburg, Sweden

ABSTRACT

Gel permeation chromatography of spent liquors from oxygen bleaching showed that cleavage of covalent linkages in the fiber was a prerequisite for the dissolution of the lignin. The reactions continued in the liquor phase. The cleavage was related to the oxidation of the lignin. With pulps pretreated with nitrogen dioxide an appreciable number of lignin linkages were cleaved also by the direct influence of the hydroxide ions on the nitrated lignin. In the alkaline medium the acidic sites in the fiber and in dissolved lignin fragments are ionized. Donnan-exclusion and an increased fiber swelling promote the transfer of the fragments into the liquor. Hydrophilic groups introduced into the lignin during oxygen bleaching promote the delignification.

INTRODUCTION

Previous reports show that fragments of nitrolignin produced during pretreatment of kraft pulps with nitrogen dioxide are not dissolved in the acid liquor unless their relative molecular mass is about 700 or less. In alkaline media the acidic groups in the fragments become ionized. This leads to an increased dissolution. Consecutive extractions with 0.1M NaOH under nitrogen showed that lignin fractions with a relative molecular mass of about 5000-10 000 were dissolved at 20° and 50°C. An improved delignification at 106°C is ascribed to an alkaline cleavage of covalent lignin bonds in the nitrated lignin [1,2].

We here report on the dissolution and properties of the lignin dissolved during oxygen bleaching of untreated and pretreated kraft pulps. Pretreatments were carried out both with the S3-method[3] which favored the generation of NO_2 from produced and added nitric acid, and with methods in which the generation was less important.

EXPERIMENTAL

The unbleached kraft pulps were produced industrially from softwood, mainly Pinus sylvestris. The S3-pretreatments were carried out with 43.5 mmol (2g) NO_2 per 100g pulp. The nitrogen dioxide was evaporated into the evacuated reactor at 40°C and 27% consistency. After 15 min, a diluent consisting of an aqueous solution of $NaNO_3$ (corresponding to 0.28 mol per kg water at 8% consistency) and optionally HNO_3 was mixed with the pulp so that a consistency of 8% was obtained. After heating to 90°C in 50 min the suspension was ripened at this temperature for 3 hours.The reactor volume was 3600 ml. The loading of the never-dried pulp corresponded to 195 g dry pulp.

The oxygen bleaching[4] was carried out at 106°C, 8% consistency and an oxygen pressure of 0.6 MPa determined at 22°C. The heating period was included in the reported duration of the bleaching. Magnesium sulfate was added as protector. The amount corresponded to 0.5% Mg calculated on dry pulp.

The absorbance at 280 nm of extracts and spent liquors determined at pH 6.6 (denoted A_{280}) was recalculated to 100 g pulp by multiplication with the volume of liquor (V dm^3) per 100 g pulp. These determinations and other analyses and treatments were, unless otherwise stated, carried out as described in our previous report[1]. Gel permeation chromatography (GPC) of the lignin samples was carried out on hydroxypropylated dextran gel in dimethylformamide (DMF) acidified with acetic acid[2]. The Mw(50)-values are defined as the relative molecular mass at the eluent volyme at which a perpendicular line divides the elution curve in two equal parts[1]. Any deviations from these standard methods for pretreatment, oxygen bleaching and analyses are reported in the discussion.

TABLE 1

Treatment at 106°C under nitrogen or oxygen of an alkaline extract obtained by extraction with 0.1 M NaOH for 5 min at 50°C and 4% consistency after S3-pretreatment[a] of kraft pulp B (kappa number 29.2, viscosity 1125 dm^3/kg, acid consumption 6.0 mmol per 100 g determined by titration to pH 4.5).

Treatment of extract min	gas	$A_{280}xV$ of extract Treated extract	After precipitation	Precip. lignin,% of pulps	Analysis of precipitated lignin %C	%H	%N	Sorption, H_2O mol per 100 g lignin	$Mw(50)x10^{-3}$ Alkaline extract	Precipitate
0	-	21.8	5.5	0.65	58.32	5.54	2.84	1.46	5.0	8.7
30	N_2	21.8	6.2	0.59	58.75	5.45	2.71	1.26	3.7	8.6
90	N_2	21.8	7.3	0.59	59.29	5.48	2.64	1.37	2.7	7.2
70[b]	O_2	20.1	10.1	0.28	59.25	6.25	2.57	3.12	1.3	4.5

a. No addition of nitric acid in the diluent. Kappa number 21.1 after pretreatment and 16.0 after NaOH-extraction. Viscosity 1080 dm^3/kg for both pulps.

b. Addition of $MgSO_4$ corresponding to 0.5 % Mg of the weight of the pulp from which the extract was prepared.

RESULTS AND DISCUSSION

Treatments of alkaline extracts

One complication, when it is desired to elucidate the reactions in the fiber phase by analysis of spent liquors and alkaline extracts, is that solutes produced in the fiber can react after dissolution in the liquor phase. This complication and the possibility to obtain information about the complex reactions without interference of morphological factors justified a study of lignin fragments in alkaline extracts and in spent liquor from oxygen bleaching of kraft pulp. Large amounts of nitrated lignin fragments can be extracted with alkaline solutions under very mild conditions from kraft pulp pretreated with nitrogen dioxide while the amount extracted from untreated pulp under the same conditions is negligible.

Table 1 shows the results by treatments of an alkaline extract from a pretreated and subsequently water-washed kraft pulp extracted with 0.1 M NaOH under mild conditions. Two portions of the alkaline extract separated from the pulp by centrifugation were treated at 106°C under nitrogen. A third portion was treated under oxygen (0.6 MPa) at the same temperature.

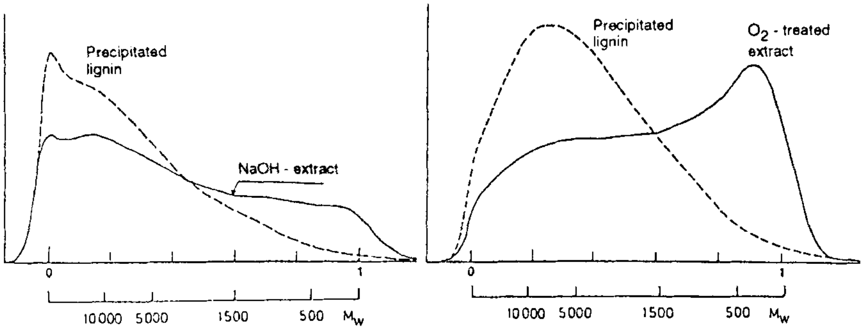

FIGURE 1. Absorbance at 280 nm versus eluent volume during GPC of NaOH-extract from pretreated pulp (left diagram), of the O_2-treated NaOH-extract (right diagram) and of lignin precipitated from these extracts. (Experimental details in Table 1).

The absorbance of the extract at 280 nm and the gravimetric determinations of lignin precipitated at pH 2 showed that the concentration of precipitable lignin and nitrogen contents of the precipitated lignin were slightly lower than in the lignin from the untreated extract. The relative molecular mass, Mw(50), determined in the extracts and which hence included all solutes recorded at 280 nm decreased markedly by the treatment under nitrogen while the values recorded for the precipitated lignin decreased less. Our results show that a fraction of the precipitable lignin was converted to fragments which were not precipitated at pH 2 and that these fragments had a much lower relative molecular mass than the precipitated lignin. The results are in agreement with those obtained by alkali treatments of pretreated kraft pulps[2] and nitrated lignin models[5]and show that linkages in nitrated lignin fragments can be cleaved by an attack of hydroxide ions in the liquor. This cleavage occurs at appreciable rate within the interval of temperature and alkali concentration suitable for oxygen bleaching of pretreated pulps.

As shown in the table the treatment under oxygen pressure led to a drastically increased fragmentation of the dissolved lignin. The precipitable amount was only about 40% of that in the untreated extract. The absorbance at 280 nm determined after precipitation and removal of the precipitated lignin increased by about 80% as a result of the oxygen-alkali treatment while the absorbance before precipitation decreased by less than 10%. The results indicate that more than 50% of the precipitable lignin was converted to lignin fragments which were not precipitated at pH 2. A comparison between the chromatograms recorded for the lignin precipitated from the O_2-treated extract and that from the untreated extract (Fig. 1) shows that the molecular size distribution of the precipitated lignin was changed markedly by the oxygen treatment. While the curve representing the lignin from the untreated extract exhibited a sharp maximum close to the interstitial volume (position 0), the lignin from the O_2-treated extract had a broad maximum at a position between the Mw(50)-values10000 and 5000. The O_2-treated extract exhibited a prominent peak ahead of position 1 (acetone) indicating the formation of a large proportion of fragments with a relative molecular mass below 1000.

The contents of carbon and nitrogen in the precipitated lignin were only slightly affected despite the extensive conversion of this lignin fraction to acid-soluble fragments during the O_2-treatment. This suggested that the lignin isolated from this extract had a rather uniform elemental composition throughout the precipitate. In contrast to lignin precipitated after the NaOH-treatments at 106°C under nitrogen the precipitate isolated after the O_2-treatment under conditions simulating oxygen bleaching showed a dramatically increased moisture sorption. Our results indicate that in addition to the decrease in molecular size of the lignin during oxygen bleaching, the formation of hydrophilic groups contributes to the improved delignification by oxygen bleaching compared to hot alkali treatment in the absence of oxygen (cf. ref 6).

Oxygen treatment of liquors from oxygen bleaching

Dissolved material present in the liquor can be wet-oxidized during oxygen bleaching[7]. To study the influence of oxygen-alkali treatment on the amount of dissolved lignin, spent liquor from oxygen bleaching of pulp B with 4% NaOH for 70 min was subjected to oxygen-alkali treatment in the absence of pulp. In addition the oxygen consumption, the Mw(50)-values of the solutes recorded at 280 nm and A_{280} were determined. Table 2 shows that lignin precipitated with hydrochloric acid at pH 2 constituted a major proportion of these solutes in the spent liquor and that this proportion decreased during the oxygen treatment. The

TABLE 2.

Influence of the duration of O_2/NaOH-treatment[a] of spent bleach liquor at 106° C on the oxygen consumption, the absorbance at 280 nm before and after precipitation of lignin, Mw(50) of solutes recorded at 280 nm and of precipitated lignin.

Time min	Oxygen mmol per L	A_{280}xV of spent liquor Treated liquor	After precipitation	Mw(50)x10^{-3} Treated liquor	Precipitate
0	0	48.3	18.9	3.1	5.3
20	4.0	47.2	20.6	2.5	5.2
70	5.7	46.6	24.7	1.9	4.2
120	5.8	46.2	25.3	1.6	3.7

[a] Addition of 2.90 g NaOH to 500 ml spent bleach liquor, and treatment with oxygen (initial pressure 0.18 MPa determined at 20°C) in a rotating 1400-ml autoclave. Oxygen consumption reported per liter of spent liquor.

Mw(50)-values determined both directly in the liquor and those of the lignin precipitated at pH 2 decreased markedly by the wet oxidation. A large amount of oxygen was consumed during the first 20 min although a very low oxygen pressure was applied to obtain reliable manometric determinations of the consumption. The consumption continued at a low rate on prolonged treatment.

Wet oxidation under the same conditions was applied to a spent liquor from oxygen bleaching with 4% NaOH for 70 min of pretreated pulp B. In this series of experiments the pulp was pretreated with nitrogen dioxide under severe conditions before the oxygen bleaching. As shown in Table 3 the behavior of this liquor was very similar to that of the liquor from the untreated pulp.

Oxygen bleaching of untreated pulp

The Mw(50)-value of the lignin fragments in the spent liquor from oxygen bleaching of the untreated kraft pulp referred to in Table 2 was 3100.

The effect of the duration of the oxygen bleaching of unbleached kraft pulps from two pulp mills on the dissolution of lignin and the molecular size of lignin fragments in the spent liquors is shown in Table 4. Large amounts of

TABLE 3.

Influence of the duration of O_2/NaOH-treatment at 106° of spent liquor from oxygen bleaching of pretreated pulp on the absorbance at 280nm on Mw(50) of solutes recorded at 280 nm and the oxygen consumption.Ripening for 120 min after addition of 26 mmol total HNO_3 per 100g dry pulp.

Time min	Oxygen mmol per L	A_{280}xV Treated liquor	Mw(50)x10^{-3} Treated liquor
0	-	47.6	4.2
20	3.2	47.4	3.6
70	5.2	46.7	2.4
120	5.3	46.4	1.9

sodium hydroxide and oxygen were applied to avoid alkali and oxygen starvation. These experiments show that the molecular size of the fragments dissolved in alkaline medium was larger than that of the fragments soluble in the acid pretreatment liquors. As usual the delignification was more rapid during the first 20 min period than towards the end of the bleaching period. The results indicate that high chemical reactivity and accessibility of some parts of the lignin contributed to the comparatively large initial dissolution of lignin.

Despite the decrease in Mw(50) of the dissolved lignin by wet oxidation, the lignin fragments in the spent liquors from both pulps referred to in Table 4 exhibited higher Mw(50)-values after oxygen bleaching for 40 min than the fragments present after 20 min. On the other hand the lignin fragments in the liquor after 70 and 120 min exhibited lower values than those observed after 40 min. The results indicate that the dissolution of the lignin during the oxygen bleaching was preceded by an oxidative cleavage of covalent lignin bonds in the fibers. The low Mw(50) of the fragments dissolved during the initial 20-min-period confirms the presence of highly reactive lignin linkages in accessible parts of the fiber. These bonds are cleaved during an early period of the oxygen bleaching. The low Mw(50) after 120 min indicates that at the applied oxygen pressure the cleavage of lignin bonds by wet oxidation continued at an appreciable rate for a long period of

TABLE 4.

Oxygen bleaching of untreated kraft pulps with 6% NaOH (calculated on pulp)

Time	Oxygen bleached pulp		Spent bleach liqour		
min	Kappa number	Viscosity	pH	$A_{280}xV$	$Mw(50)x10^{-3}$
Pulp A[a]					
20	22.2	1101	12.8	22.0	3.3
40	17.6	1016	12.7	43.8	4.6
70	14.8	963	12.5	58.9	4.5
120	11.1	935	12.1	64.9	3.6
Pulp B[b]					
20	20.0	1026	12.6	29.5	3.3
40	15.2	932	12.5	49.3	4.4
70	13.3	923	12.3	59.2	3.5
120	10.0	855	11.7	65.5	3.1

a. Kappa number 30.5, viscosity 1266 dm^3/kg, acid consumption 2.3 mmol

b. Kappa number 29.2, viscosity 1125 dm^3/kg, acid consumption 6.0 mmol

time. It may be pointed out that the Mw(50)-values of the lignin fragments in the spent liquors after oxygen bleaching were lower than those recorded after alkaline extraction in the absence of oxygen of kraft pulps pretreated with nitrogen dioxide under such conditions that an extensive delignification occurred during the extractions (cf. Fig.5 and alkali extractions in ref.1 and ref.2). This confirms that lignin bonds both in the fiber and in dissolved lignin fragments were broken during the oxygen bleaching.

The spent bleach liquors after oxygen bleaching of pulp A with addition of 4% NaOH for 20, 70 and 120 min were studied by ultrafiltration. The retention on a coarse filter with the separation limit 10000 was 27, 37, and 34%, respectively. The proportions retained on the tight filter (separation limit 1000) were 93, 86 and 93%. The results confirm that a substantial proportion of lignin fragments dissolved during the oxygen bleaching exhibited much larger molecular dimensions than the fragments dissolved during pretreatments with nitrogen dioxide[1].

In contrast to kraft pulps pretreated with nitrogen dioxide, untreated kraft pulps are extremely resistant to alkaline attacks on lignin and polysaccharides

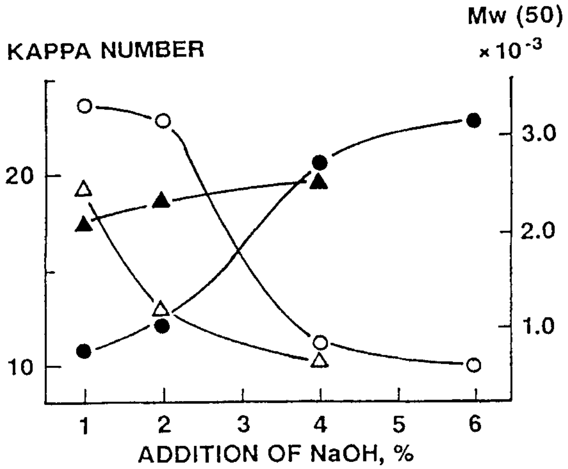

FIGURE 2. Influence of the alkali addition during oxygen bleaching for 120 min of untreated kraft pulp B on kappa number (open symbols) and Mw(50) of the lignin fragments in the in the spent bleach liquors (filled symbols). Bleaching with either 0.5% Mg (circles) or 0.1% Mg (triangles).

unless oxygen is present. Hence, alkali is consumed in consecutive reactions following an oxidative attack in the presence of oxygen while a direct cleavage of covalent bonds by, for instance, alkaline hydrolysis can be disregarded at the applied temperature.

The kraft pulp with the highest initial viscosity exhibited the highest viscosity after the oxygen bleaching. With few exceptions the same observation has been made in numerous other experiments with kraft pulps subjected to oxygen bleaching in the presence of magnesium protector.

The influence of the added amount of sodium hydroxide in the oxygen bleaching of an untreated kraft pulp is shown in Fig.2. One series of experiments was carried out with magnesium sulfate corresponding to 0.5% Mg. This means that during an early period of the bleaching with 1 and 2% NaOH the hydroxide ions were present virtually completely or mainly in precipitated magnesium hydroxide. As shown previously this leads to a retarded delignification but can also have advantages[8]. The slow delignification under these conditions is

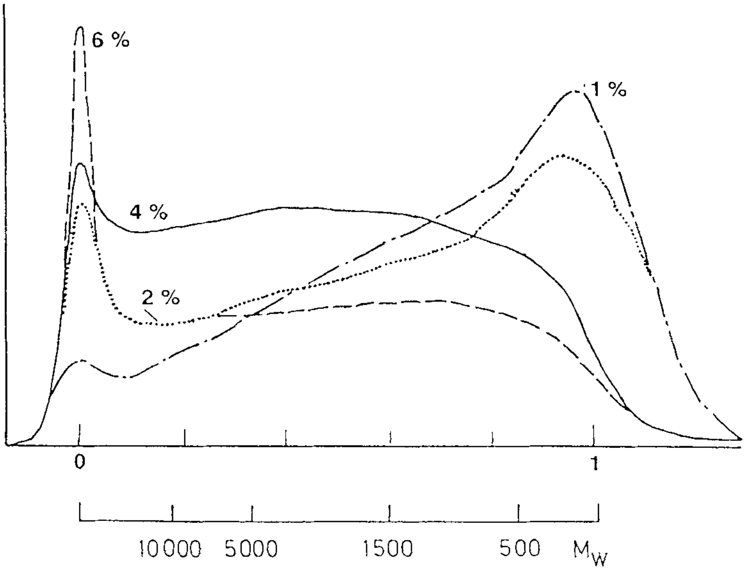

FIGURE 3. Absorbance of 280 nm versus eluent volume during GPC of spent liquors from oxygen bleaching of untreated kraft pulp (B) with varying additions of NaOH (% on pulp). Oxygen bleaches with 0.5 % Mg reported in Fig 2.

confirmed in Fig.2 which also shows that the dissolved lignin fragments exhibited a very low relative molecular mass in the oxygen bleaches with extremely large proportions of precipitated magnesium hydoxide. Since the mass transfer limits the dissolution rate of the magnesium hydroxide[9], the low Mw(50)-values can be ascribed to a prominent degradation of dissolved lignin fragments. The chromatograms recorded by GPC (Fig.3) for the liquors from the experiments with the largest addition of magnesium are in agreement with this conclusion.

It can be mentioned that with the larger addition of magnesium the final pH was 9.3 in the liquor from the bleaching with 1% NaOH compared to 11.8 when 6% NaOH was employed.

The observation that much larger lignin fragments can be removed from the fibers during the alkaline oxygen bleaching than during the acid pretreatment is related to an increased solubility of the fragments due to dissociation of acidic groups in the fragments.

In addition acidic groups in the fiber will be charged and converted to anions. This means that the fiber will become a dissociated cation exchanger and that Donnan-exclusion will promote the transfer of the anionic lignin fragments into the solution. In addition the presence of anions linked to the fiber will increase its swelling which will also facilitate the removal of the lignin fragments. Accessible acidic sites are dissociated almost instantaneously by an addition of alkali. Attempts were made to remove lignin from the oxygen bleached and carefully water-washed pulps by extraction for 10 min with 0.1M NaOH at 22°C and 4% consistency. This extraction resulted in a loss in kappa number of only 4-5%, indicating that within the applied range of hydroxide concentration the increased number of charges had less effect on the delignification than the size of the fragments and the linkages to the fibers which prevent the transfer of lignin to the liquor outside the fibers.

Extraction with 2.5 M sodium hydroxide at -10°C for 10 min which is known to give an extremely high swelling and dissolution of regenerated cellulose[10] led to an extract containing small amounts of solutes with an absorbance at 280 nm. The kappa number decreased by 10% or less. The results confirm that it is difficult to prepare kraft pulps with low lignin contents by oxygen bleaching even if a cold-alkali extraction is included.

Oxygen bleaching of pretreated pulp

A similar study on the influence of the amount of sodium hydroxide and a subsequent cold-alkali extraction was carried out after pretreatment by the S3-method of the water-impregnated kraft pulp referred to in Figs. 2 and 3. The pulp which was pretreated without nitric acid in the diluent exhibited kappa number 20.1 after this stage. As shown in Table 5 an increased amount of sodium hydroxide from 1 to 4% led to a decrease in kappa number from 9.3 to 5.0. The improved dissolution of lignin was confirmed by the determination of the absorbance at 280 nm in the spent bleach liquors.

A comparison between the Mw(50)-values of the lignin fragments in the spent liquors shows that after bleaching with 1.0% NaOH the value was higher than that in the experiment with the untreated pulp (Fig.2.). The order was reversed when 4% NaOH was applied. During the subsequent cold-alkali

TABLE 5.

Influence of the alkali addition during oxygen bleaching for 120 min of S3-pretreated kraft pulp B and on a subsequent extraction with 2.5 M NaOH at -10°C. Magnesium sulfate corresponding to 0.1 % Mg in all bleaches.

NaOH % on pulp	Spent bleach liquor pH	Mw(50) x10^{-3}	A_{280}xV	Kappa number After O_2 bleaching	After NaOH extraction	A_{280}xV of NaOH extract	Mw(50) x10^{-3} of extract
1	8.3	3.2	42.8	9.3	7.8	25.8	7.3
2	9.8	3.1	50.0	7.4	4.8	20.5	15.3
4	11.5	1.9	55.6	5.0	3.5	21.3	15.4

extraction with 2.5 M NaOH the kappa number decreased by about 15% for the pulp with 1% NaOH-addition and 30-35% for the pulps with 2 and 4% NaOH in the oxygen bleaching. One portion of the extract was diluted with water and acetic acid to pH 6.6 and A_{280} determined immediately after the dilution. The formation of a yellow precipitate and a large loss in A_{280} at pH 6.6 after about one week indicated the presence of lignins linked to hemicellulose.

Another portion of the extract was chromatographed in O.1 M NaOH directly after dilution of the extract with water to a sodium hydroxide concentration of 0.5 mol per liter. A non-substituted dextran gel (Sephadex G75) was used as stationary phase. As usual, the Mw(50)-values reported in Table 5 refer to solutes recorded at 280 nm. As shown in the table the observed molecular size was much larger than that of the lignin fragments in the spent liquors from the oxygen bleaching. The results are in agreement with the conclusion that an extensive cleavage of covalent bonds in which the lignin is involved is a prerequisite for an extensive delignification during the oxygen bleaching.

The pretreatment of the same unbleached pulp with a total addition of 26 mmol nitric acid per 100 g pulp led to kappa number 11.4. With 1, 2 and 4% NaOH the kappa numbers after the oxygen bleaching were 4.5, 4.2 and 3.4, respectively (not shown). Small portions of these pulps were extracted with 0.1M NaOH for 10 min at 22°C. The decrease in kappa number was only 0.1-0.3 kappa

TABLE 6.

Amounts and analysis of dried precipitates from the cold-alkali extracts recorded in Table 5.

NaOH % on pulp	Precipitate g/100g pulp	A_{280}xV In filtrate	Analysis of precipitate % C	% H	% N
1	5.3	4.3	40.76	5.97	0.15
2	4.8	3.5	40.77	5.89	0.16
4	4.7	1.9	40.17	5.81	0.16

units. When the remaining portions were subjected to cold-alkali extraction with 2.5 M NaOH, the kappa numbers decreased to 3.2, 3.0 and 2.7, respectively.

Large amounts of organic material were precipitated and isolated from the cold-alkali extracts referred to in Table 5. Carbon dioxide was first introduced into the extracts for about 30 min under cooling. The precipitated sodium bicarbonate mixed with precipitated organic material was filtered off and A_{280} determined in the filtrate. As indicated by the determinations in Table 6, only minor proportions of the UV-absorbing solutes in the NaOH-extracts (Table 5) were present in the filtrates. The bicarbonate was then dissolved by stirring with water for 3 hours at room temperature. A voluminous precipitate remained suspended in the solution. After sedimentation for 2 days, the precipitate was separated from the the solution by filtration. The filtrate was virtually free from the solutes with UV-absorption at 280 nm. After washing with water, ethanol and finally diethyl ether the precipitate was air-dried. A lightly yellow powder was obtained.

As shown in Table 6 the weight of the precipitate was about 5% of the weight of the pulp. In contrast to the lignin fragments in the spent liquors studied in this and in previous papers[1,2], the powders isolated from the cold alkali extracts were virtually insoluble in the solvent (DMF + acetic acid) used during GPC of the lignin samples. Estimates of the lignin in the precipitates from the decrease in kappa number of the pulp and from the absorbance determinations indicated that the lignin content was less than 20 % of the weight of the precipitate. The elemental analysis showed that lignin was not a major constituent. Determination of the absorptivity coefficient of nitrated kraft lignin (softwood) gave the value 26.6 dm^3/g·cm while a somewhat lower value (25.0) was found for kraft lignin. Under the assumption that the coefficient is about the same for the lignin in the precipitates in Table 6,the lignin contents should be about 15%. Sugar analysis showed that the amount of anhydrosugar in the precipitates was about 90%. Xylose was the most abundant monosaccharide obtained by acid hydrolysis. The relative amounts of the sugars found in the precipitate from the pulp bleached with 1.0% NaOH were : 61.4% xylose, 8.7% glucose, 16.1% mannose, 6.5% arabinose and 7.3% galactose. These results confirm that the lignin in the pulp after the oxygen bleaching was at least in part linked to hemicellulose.

Influence of the pretreatment conditions

The influence of the sodium hydroxide addition during the oxygen bleaching was studied also with another kraft pulp (kappa number 28.5, viscosity 1202 dm^3/kg) pretreated by the S3-method under more severe conditions than those in Table 5. The pretreatment with 2% NO_2 was started in alkaline medium after impregnation with 22.2 g of an industrial black liquor[12] per 100 g pulp to simulate an extremely large carry-over in a closed recovery system. After ripening and removal of the spent pretreatment liquor, the pulp was washed with water and divided into 17 batches. One of these was used for analysis (kappa number 14.1, viscosity 1028 dm^3/kg). The other batches were subjected to oxygen bleaching for varying lengths of time.

Table 7 shows that the kappa number decreased rapidly during an initial period and that the delignification continued at a low rate after a kappa number of about 5 had been reached. In agreement with the results with untreated kraft pulp, the delignification and the depolymerization of the cellulose after a given duration of the bleaching increased markedly with increasing addition of alkali. The lowest selectivity (defined as viscosity at a given kappa number) was obtained with the largest addition. When it is desired to produce pulps of low kappa numbers after the oxygen bleaching, an alkali charge within the range 3.3-6.5% can be applied.Gel permeation chromatography of the spent liquors from the oxygen bleaching showed that the relative molecular mass of the material recorded at 280

TABLE 7.

Influence of the alkali charge and the residence time during oxygen bleaching of kraft pulp subjected to S3-pretreatment after impregnation with black liquor. Addition of nitric acid corresponding to 59.4 mmol free HNO_3 per 100 g pulp[11].

Oxygen bleaching		Oxygen bleached pulp		Spent bleach liquor	
NaOH %	Time min	Kappa number	Viscosity dm^3/kg	pH	Mw(50) $x10^{-3}$
3.3	20	7.0	1016	11.2	6.5
3.3	40	5.4	1012	10.8	5.9
3.3	70	4.9	996	10.5	5.7
3.3	120	3.9	932	10.4	5.0
6.5	20	6.0	976	12.5	4.7
6.5	40	4.6	961	12.4	4.1
6.5	70	4.1	952	12.3	4.0
6.5	120	3.8	927	11.9	3.0
10.0	20	5.7	971	12.6	4.7
10.0	40	4.3	933	12.6	4.2
10.0	70	3.8	875	12.6	2.9
10.0	120	3.1	853	12.5	2.7
20.0	20	4.4	916	12.7	2.2
20.0	40	3.8	890	12.7	1.9
20.0	70	3.3	846	12.6	1.7
20.0	120	2.9	786	12.6	1.2

nm was lower than that in the liquors from the alkaline extractions in the absence of oxygen (cf. ref. 1 and 2). In agreement with the results in Table 5, Mw(50)-values decreased markedly with increasing NaOH-addition. An increased duration of the oxygen bleaching, exerted the same effect. No generally valid relationship between Mw(50) and the kappa number of the oxygen bleached pulp was obtained. Compared at the same NaOH-addition or the same duration of the oxygen bleaching the decrease in kappa number parallelled that in the molecular size of the dissolved lignin fragments. It is noteworthy that a drastic decrease in the molecular size occurred during the oxygen bleaching with the largest

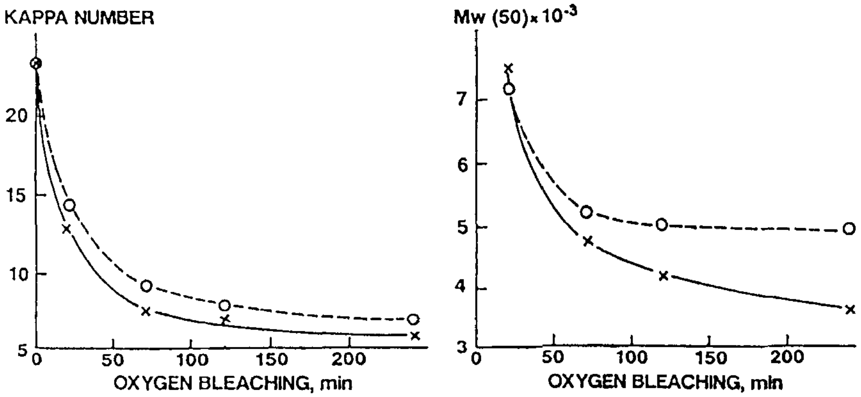

FIGURE 4. Influence of the duration of the oxygen bleaching on the kappa number of the kraft pulp pretreated by the S3-method and on the relative molecular mass, Mw(50), of solutes recorded at 280 nm in the spent liquors from the oxygen bleaching. Alkali addition during the bleaching:
O 4 % NaOH; × 6 % NaOH.

NaOH-addition. A severe attack on the cellulose was reflected in extremely low viscosities. The results are in agreement with our experience that it is difficult to reach kappa numbers below 3 by oxygen bleaching even if the conditions in the pretreatment are so severe that the strength properties of the pulp are drastically impaired.

The influence of the NaOH-addition and the duration of the oxygen bleaching was also studied after pretreatment under much milder conditions. Another kraft pulp from the same pulp mill (kappa number 30.3, viscosity 1244) was impregnated with 11.1 g black liquor per 100 g pulp. NO_2 was added at 60°C and after dilution the suspension was heated to 90°C in 30 min and ripened at this temperature. To avoid severe depolymerization of the cellulose under the acid conditions prevailing during the major part of the pretreatment, the addition of nitric acid was decreased to 24 mmol per 100 g pulp which corresponds to 10 mmol free nitric acid per 100 g pulp. The addition of sodium nitrate was 0.2 mol per kg water at 8% consistency. The pretreated pulp exhibited kappa number 23.6 and viscosity 1150 dm^3/kg. As can be seen in Fig. 4 both the kappa numbers and Mw(50)-values decreased rapidly during the first 70 min-period of the oxygen

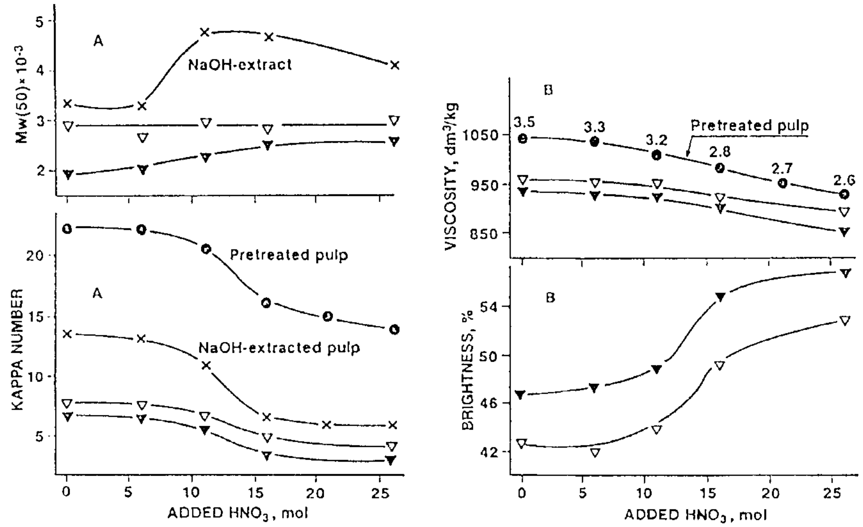

FIGURE 5. Influence of the addition of total nitric acid (mol per 100 kg pulp) during S3-pretreatment on pulps and liquors after subsequent oxygen bleaching for 120 min with 4% NaOH and 0.5% (open triangles) and 0.1% (filled triangles) Mg. For comparison kappa number and intrinsic viscosity of the pretreated pulps are included.

A. Kappa number of pulps and relative molecular mass, Mw(50) x 10^{-3}, of the lignin fragments in the spent bleach liquors. For comparison extraction of pretreated pulps under nitrogen in 0.1 M NaOH for 30 min at 106°C and 4% consistency are shown.

B Brightness according to ISO and intrinsic viscosity according to SCAN. Values given in the upper diagram are the pH-values in the spent pretreatment liquors.

bleaching and then more slowly when the time was increased to 120 and 240 min. During the later part of the bleaching the Mw(50)-values decreased more slowly in the experiment with 4% NaOH than in that with 6%.The results indicate that the lower kappa numbers reached with the larger addition of NaOH were related to a more effective cleavage of covalent lignin bonds.

Fig. 5 shows various effects of the amount of nitric acid added during S3-pretreatment on the pulps subjected to oxygen bleaching and on Mw(50) of the lignin fragments in the spent liquors from the oxygen bleaching. Water-impregnated kraft pulp B was used in two series of oxygen bleaches with different additions of magnesium sulfate. An increased addition of nitric acid resulted in decreased kappa numbers both after the pretreatment and after the subsequent oxygen bleaching. After the bleaches with an addition of magnesium sulfate corresponding to 0.1 % Mg, the kappa number, the Mw(50)-values and the viscosities were significantly lower than after the bleaches with 0.5% Mg. The effects were similar to those discussed for the untreated kraft pulp (Fig.2).

Extraction with 0.1M NaOH at 106°C instead of oxygen bleaching at the same temperature removed approximately 50% of the lignin in the pretreated pulps. As expected the delignification was less effective than after the oxygen bleaching. The markedly higher Mw(50)-values of the dissolved lignin fragments after the extraction under nitrogen than after oxygen bleaching confirmed that an oxidative degradation of the lignin contributed markedly to the improved delignification in the presence of oxygen. Evidently parts of the lignin in the fibers which were dissolved after oxidative fragmentation remained in the pulp when alkali extraction under nitrogen was employed instead of oxygen bleaching.

For comparison oxygen bleaching was carried out with pulps pretreated under conditions which gave very modest generation reactions compared to S3-treatments. The pulp was first treated at 25°C and 27% consistency with either 3x2% or 9x2% NO_2 for 10 min and a water-wash after each treatment. An appreciable number of nitrogen groups was introduced into the lignin[2]. These pulps were subjected to a treatment denoted HA carried out with 2% NO_2 under the same conditions as used in the S3-method with the exception that NaCl and HCl were added instead of $NaNO_3$ and HNO_3.

Oxygen bleaching of these pulps (Table 8) showed that the kappa number decreased with an increasing addition of NaOH while the effect of an increased number of NO_2-treatments at 25°C from 3 to 9 was hardly significant. For the pulp pretreated with 3x2 % NO_2 before the HA-treatment, the oxygen bleaching decreased the kappa number to a much lower value than that (8.1) obtained by consecutive alkali extraction with a final extraction with 0.1M NaOH under nitrogen for 30 min at 106°C (see Table 4 ref. 2). Evidently, pretreatments which give rise to a massive generation of nitrogen dioxide are even more important for the delignification when the subsequent alkaline treatment is carried out in the absence of oxygen than when oxygen bleaching is employed.

TABLE 8.

Oxygen bleaching with varying additions of NaOH for 30 min of pulp treated with 3x2 and 9x2 % NO_2 followed by HA-treatment[a] with ripening at 90°C for 2h.

Pulp	NaOH %	Kappa number	Viscosity dm^3/kg	Spent liquor $A_{280}xV$	$Mw(50)x10^{-3}$
3x2	0	15.4	840	-	-
	3.3	5.8	808	54.7	7.7
	6.5	5.0	805	56.4	6.1
	10.0	4.7	795	56.5	5.2
9x2	0	14.8	840	-	-
	3.3	5.9	792	46.1	7.2
	6.5	4.6	782	45.5	5.2
	10.0	4.5	762	46.5	4.5

a. Addition of NaCl corresponding to 0.12 mol per kg water at 8% consistency and of 40 mmol HCl per 100 g pulp.

In agreement with the other oxygen bleaches an increased NaOH-addition gave rise to decreasing Mw(50)-values. The values were lower than that (9600) obtained by the final alkali extraction under nitrogen[2]. The increased number of treatments at 25°C from 3 to 9 was, in comparable bleaches, reflected in a modest decrease in molecular mass of the lignin fragments in the spent bleach liquors.

The decrease in kappa number by an increased alkali addition during the bleaching parallelled the decrease in the molecular size of the lignin fragments in the spent bleach liquor. The limited generation, indicated also by an extremely low pH in the spent pretreatment liquor, was reflected in a severe loss in viscosity (to 840 dm^3/kg) during the pretreatment and in low viscosities after the oxygen bleaching. On the other hand condensation of the nitrated lignin during the treatment in hydrochloric acid at 90°C had no decisive effect on the behavior of the lignin during the oxygen bleaching.

Two-stage oxygen bleaching

The influence of oxygen bleaching in two stages[13] of a water-washed pulp pretreated by the S3-method under comparatively mild conditions (no addition of

TABLE 9.

Oxygen bleaching of NO_2-treated[a] kraft pulp B in two stages each with 4% NaOH. No nitric acid in the diluent.

Duration of oxygen bleaching, min		Final spent liquor			Oxygen bleached pulp	
First	Second	A_{280} xV	pH	Mw(50) $\times10^{-3}$	Kappa number	Viscosity dm^3/kg
20	-	43.4	12.0	5.2	10.5	1033
20	20	6.1	12.3	3.3	9.0	992
20	40	10.5	12.2	3.1	7.9	960
20	70	13.5	12.0	2.9	6.8	946
20	120	15.5	11.8	2.6	5.4	913
20	240	16.2	10.6	2.3	4.7	901

a. Kappa number 20.1 and viscosity 1043 dm^3/kg after S3-pretreatment.

nitric acid) is shown in Table 9. After bleaching for 20 min the liquor was filtered off and the pulp was washed with distilled water. One portion of pulp was used for analyses and the remainder divided into five batches which were subjected to a second oxygen bleaching for varying periods of time under otherwise unchanged conditions. As can be seen the kappa number decreased by about 50% in the first oxygen stage. As shown both by the kappa number and the UV-absorbance, the removal of the lignin was much slower in the second stage. A significant dissolution of lignin occurred, however, even when the residence time in the second stage was increased from 120 to 240 min.

Table 10 shows additional results with two-stage bleaching of the same unbleached kraft pulp. In the first series S3-pretreatment was carried out with nitric acid addition while the other conditions were unchanged. The kappa number of the pretreated pulp was 11.4 and the viscosity 938 dm^3/kg. The low kappa number shows that a large proportion of the nitrated lignin was dissolved already during the pretreatment. After the first oxygen bleaching for 20 min the kappa number decreased to 4.5 while the viscosity was virtually unchanged. The small decrease in kappa number and the low A_{280} in the liquors obtained in the second oxygen bleaching for 20 and 40 min showed that only small amounts of lignin were dissolved. In the second series the untreated pulp was directly subjected to oxygen

TABLE 10.

Oxygen bleaching of NO_2-treated and untreated kraft pulp B in two stages each with 4% NaOH. NO_2-treatment with ripening with total addition of 26 mmol nitric acid per 100g pulp.

Pulp	Duration of oxygen bleaching, min First	Duration of oxygen bleaching, min Second	Final spent liquor A_{280} xV	Final spent liquor Mw(50) $x10^{-3}$	Final Kappa number
NO_2-treated	20	-	35.7	4.4	4.5
	20	20	1.7	2.3	4.2
	20	40	3.9	2.0	4.0
Untreated	20	-	25.2	2.8	21.2
	20	20	10.5	3.1	18.1
	20	40	23.7	2.9	14.3

bleaching under identical conditions. Only about 30 % of the lignin was removed in the first oxygen bleaching of this pulp while appreciable amounts were dissolved in the second stage.

The Mw(50)-values determined in the spent bleach liquors showed that for the pretreated pulps the dissolved lignin fragments from the second oxygen bleaching were much smaller than those from the first stage. The result support the conclusion that cleavage of covalent lignin bonds in the nitrated lignin in the fiber phase during the oxygen bleaching has a decisive effect on the delignification. An increased time in the second stage to 40 min led to a small decrease in Mw(50) although a fragmentation of lignin occurred also after the dissolution in the bleach liquor. In the liquor from the oxygen bleaching following pretreatment with nitric acid addition (Table 10), the lignin fragments were smaller than in the bleach liquor from the pulps pretreated without acid addition (Table 9).

As expected from the results in Table 4 the Mw(50)-value of the lignin fragments in the spent liquor from the oxygen bleaching of the untreated kraft pulp for 20 min was lower than the values observed for the corresponding liquors from pretreated pulps.

Concluding remarks

Our previous reports show that covalent lignin bonds are cleaved already during the pretreatment of kraft pulp with nitrogen dioxide[1,2]. Due to the low number of hydrophilic groups in the nitrated lignin, the produced fragments are sparingly soluble in the acid pretreatment liquor. This limits the delignification during the NO_2-treatment. During subsequent alkaline treatment, with or without the presence of oxygen, lignin fragments become ionized and are dissolved in the liquor. At high temperature some linkages are cleaved in the nitrated lignin even in the absence of oxygen.

Our results show that for both pretreated and untreated pulps a degradation of the lignin to fragments of small molecular size is necessary for an extensive delignification during the oxygen bleaching. Fragments of high molecular mass and lignin linkages to the carbohydrates in the fiber are a hindrance for a complete transfer of the lignin into the liquor. An increased number of hydrophilic groups can contribute to the improved dissolution of the lignin but under conditions (fairly high pH) mostly applied in actual practice the cleavage of lignin linkages seems to be the preponderant effect.

Under proper pretreatment conditions massive lignin reactions occur without severe attack on the cellulose. A prerequisite for obtaining favorable results is that the pretreatment conditions are chosen so that nitrogen dioxide and other active compounds are generated from produced and optionally added nitric acid. Oxygen bleaching after pretreatment can be easily carried out to kappa number 5 for kraft pulps from softwood of for instance kappa number 30-35. Lower kappa number e.g. 3 can be obtained but this target has not been reached without an attack on the polysaccharides which has detrimental effects on the properties of many types of paper pulps.

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