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Delignification of Wood Pulp by Hot Alkali Treatment Following NO_2/O_2 Pretreatment

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Summary

An effective delignification of kraft pulp without serious depolymerization of the cellulose was achieved by alkali treatment above 100°C, following pretreatment with NO_2/O_2 at approximately 50°C. Compared at the same degree of delignification the depolymerization of the carbohydrates and the yield were less than after oxygen bleaching of the pretreated pulp.

Introduction

The dissolution of lignin in a well washed kraft pulp during hot alkali treatment in the absence of oxygen is very small. CLARKE (1944) showed that the pulp can be partially delignified even by a mild alkali extraction at 50°-90° if the alkali stage is preceded by a treatment with nitrogen dioxide. At the high temperature in the pretreatment stage required for an appreciable delignification (approximately 90°C) at the low pulp consistency (3%) used by CLARKE the cellulose suffered a severe depolymerization. In agreement with information given in the patent literature, recent studies of peroxide bleaching (LACHENAL, CHOUDENS, MONZIE 1980) and oxygen bleaching (ENGSTRÖM, SAMUELSON 1981) following pretreatment with nitrogen dioxide showed that superior results were obtained if the pulp consistency during the pretreatment was increased to approximately 40%. We here report on the delignification and the depolymerization of the carbohydrates during pretreatment with nitrogen dioxide plus oxygen at varying temperatures and reaction times followed by hot alkali treatment with no oxygen present.

Experimental

A commercial kraft pulp from pine with a kappa number of 30.4 and an intrinsic viscosity of 1190 dm^3/kg was used in all experiments except those presented in Figure 4. The pulp was washed with water and subjected to NO_2/O_2-treatment under conditions described previously (ABRAHAMSSON, LÖWENDAHL, SAMUELSON in press), with the exception that residence time and temperature were varied. The alkaline treatments were made in eight 1500 ml autoclaves which were rotated in a preheated polyglycol bath.

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Results and discussion

The effect of the temperature and the duration of the NO_2/O_2-pretreatment was studied at a very low pulp consistency (0.5%) in the subsequent hot alkali treatment to avoid large changes in the sodium hydroxide concentration. In accordance with common practice in pulping chemistry the kappa number determined by treating the pulp with permanganate under standardized conditions was used as a measure of the lignin content in the pulp. The percentage of Klason lignin (acid insoluble lignin) is approximately equal to the kappa number multiplied by 0.15.

As shown in Figures 1 and 2 more than 60% of the lignin could be removed by NO_2/O_2-treatment for 10 min, followed by hot alkali treatment. Under otherwise unchanged conditions an addition of 4% NO_2 (calculated on dry pulp) resulted in lower lignin contents than did an addition of 2% NO_2. An increased temperature during the NO_2/O_2-treatment had a larger effect than an increased amount of NO_2. The improvement gained by increasing the temperature was larger in the experiments with 4% NO_2 than in those with 2% NO_2. Markedly lower lignin contents after the hot alkali treatment were obtained when the duration of the NO_2/O_2-pretreatment was extended from 10 to 60 min. An additional delignification was obtained when the time was increased to 120 min (Fig. 2).

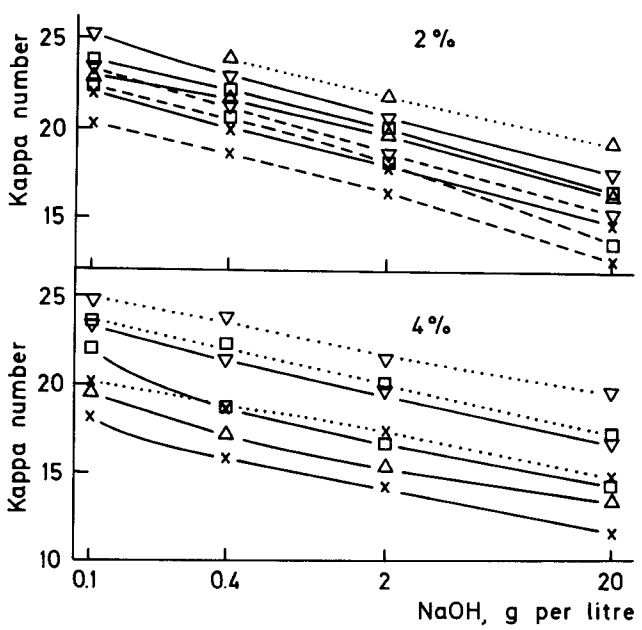

Fig. 1. Kappa number as a function of the concentration of sodium hydroxide (logarithmic scale) during the hot alkali treatment at 106°C for 15 min (dotted lines), 60 min (full lines) or 120 min (broken lines).
Pretreatment with 2% NO_2 (upper diagram) or 4% NO_2 (lower diagram for 10 min at
▽ 25°C; □ 40°C; △ 55°C; X 68°C

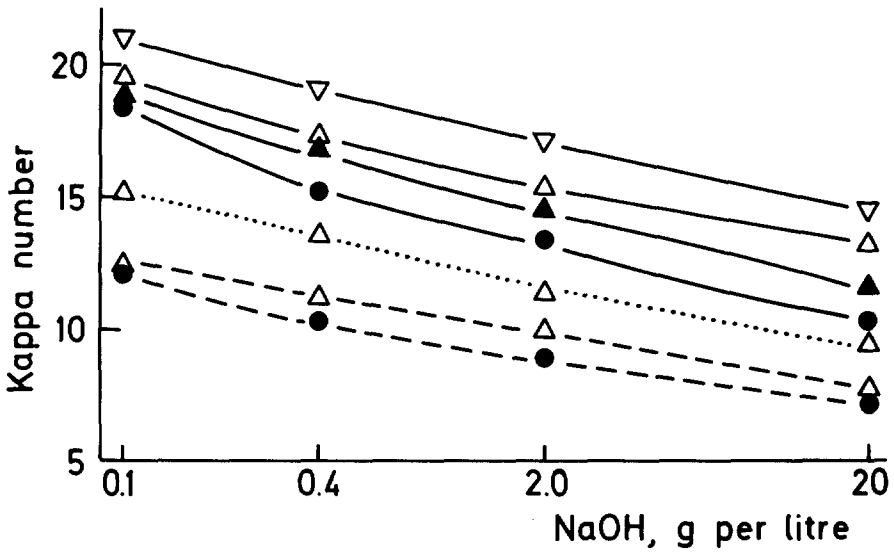

Fig. 2. Kappa number as a function of the concentration of sodium hydroxide (logarithmic scale) during hot alkali treatment of pulp subjected to NO_2/O_2 pretreatment at 55°C (4% NO_2) for 10 min (full lines), 60 min (dotted lines) or 120 min (broken lines).
Conditions during hot alkali treatment:
▽ 96°C, 60 min; △ 106°C, 60 min; ▲ 106°C, 120 min;
● 106°C, 60 min plus 116°C, 60 min

The experiments were restricted to the temperature interval 25-68°C. Separate experiments showed that in addition to an improved delignification a severe depolymerization of the cellulose occurred already after 10 minutes in the NO_2/O_2 stage when the temperature was increased to 80°C.

The intrinsic viscosities of the pulps pretreated with NO_2/O_2 for 10 min at or below 55°C and subsequently subjected to hot alkali treatment were equal to or slightly higher than that of the untreated pulp. The slight increase is explained by the dissolution of lignin and polysaccharides during the treatments. The pulps treated for 10 min at 68°C with 4% NO_2 exhibited viscosities within the range of 1110-1130 dm^3/kg compared with 1190 dm^3/kg for the unbleached pulp. Treatment at this temperature

with 2% NO_2 resulted in pulps with viscosities of between 1150 and 1180 dm^3/kg. A significant loss in viscosity occurred when the treatment with 4% NO_2 was extended from 10 to 60 or 120 min at 55°C. After 60 min the average viscosity was 1070 and after 120 min 1000 dm^3/kg. A small increase in viscosity was observed with increasing concentration of alkali during the hot alkali treatment.

The loss in viscosity at high temperature and after prolonged NO_2/O_2-pretreatment is explained by hydrolysis of glycosidic linkages in nitric acid which was a major product formed during the pretreatment. Heating of the pretreated pulp in hydrochloric acid showed that acid hydrolysis of lignin linkages cannot explain the large decrease in lignin content due to an increased residence time and temperature. It may be mentioned that already after pretreatment for 10 min at 25°C, less than 1 mole percent of the added NO_2 remained as NO_2 + NO in the gas phase. The results suggest that the increased delignification resulting from a prolonged pretreatment at high temperature was related to the decomposition of some unstable nitrogen compound formed by the reaction with lignin. The formation of unstable intermediates was confirmed by the observation that NO was formed when a pretreated pulp was heated with exclusion of oxygen.

The results given in Figures 1 and 2 show that for all NO_2/O_2 treated pulps the conditions during the hot alkali treatment exerted a dramatic effect on the delignification. The lignin content decreased markedly with increasing alkali addition and temperature. A higher temperature than employed during conventional alkali extraction of chlorinated pulp was required for an effective delignification. An increased duration of the hot alkali treatment from 15 to 120 min led to a prominent decrease in lignin content.

Hot alkali treatments under conditions feasible in practice (Table 1) confirmed that the delignification was more effective when the pretreatment was carried out under severe than under mild conditions. The delignification was also improved by an increased alkali addition and an increased duration of the hot alkali treatment. A depolymerization of the cellulose was reflected in a severe loss in viscosity for the pulps pretreated for 60 min at 60°C. Again, the viscosities increased significantly with an increased addition of sodium hydroxide during the hot alkali treatment.

The influence of the conditions during the alkaline stage was studied further with the same pulp pretreated under conditions resulting in a modest depolymerization of the cellulose (Fig. 3). A sample washed with 0.2 M sodium bicarbonate solution and then with water at room temperature had a kappa number of 22.5 and an intrinsic viscosity of 1030 dm^3/kg. Again, the viscosity increased during the hot alkali treatment and amounted to 1070 dm^3/kg after 120 min treatment at 5% consistency with an initial alkali concentration of 21 g NaOH per 1000 g H_2O. The highest viscosities, 1110-1130 dm^3/kg, were obtained at 15% consistency with the largest addition of NaOH. Figure 3 confirmed that the lignin contents were lowered when the duration of the alkali treatment was increased. The pulp consistency had only

TABLE 1

Influence of the conditions during NO_2/O_2 pretreatment with 4% NO_2 and during subsequent hot alkali treatment at 106°C and 15% consistency on the kappa number and intrinsic viscosity

NO_2-treatment Time min	Temp. °C	Alkali treatment NaOH g per litre	Time min	Kappa number	Viscosity dm^3/kg
10	55	14[a]	30	16.5	1158
10	55	14[b]	120	14.6	1157
10	55	70	30	12.8	1208
10	55	70	120	9.6	1208
60	60	14	30	10.5	972
60	60	14	120	9.0	990
60	60	70	30	6.4	1053
60	60	70	120	5.3	1013

[a] 8% calculated on dry pulp; [b] 40% calculated on dry pulp.

a slight influence while the delignification was improved dramatically by an increased initial concentration of sodium hydroxide.

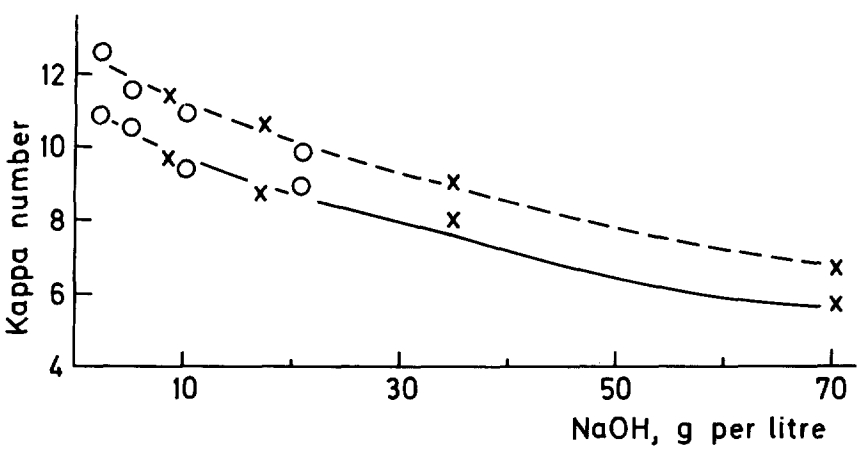

Fig. 3. Kappa number as a function of the concentration of sodium hydroxide during hot alkali treatment for 30 min (broken line) or 120 min (full line) at 106°C of pulp subjected to NO_2/O_2-pretreatment at 55°C (4% NO_2) for 60 min.
O 5% consistency; X 15% consistency

Finally, the yields of pulp after hot alkali treatment under nitrogen of a NO_2/O_2-pretreated pulp will be compared with those obtained from the same batch of pretreated pulp after oxygen-alkali treatment. The pretreatment was made in a 10 litre reactor for 120 min with an addition of 4% NO_2. The initial temperature was 52°C, but the temperature increased to a maximum of 56°C after about 10 min and then returned to the initial temperature after approximately 15 min. Analyses of a bicarbonate washed sample showed that the kappa number had decreased from 34.1 to 25.7 and the intrinsic viscosity from 1157 to 985 dm^3/kg.

The alkaline treatments were made at 10% consistency with batches corresponding to 15 g of pulp. The autoclaves were filled with either nitrogen, oxygen of 0.1 MPa or oxygen of 0.8 MPa at room temperature. In the experiments under nitrogen the treatment was made for 60 min with 5, 10, 20 and 40% NaOH calculated on dry pulp. In the experiments under oxygen aqueous solutions of magnesium sulphate corresponding to 0.1% Mg and 4% NaOH were added in that order. The treatment was made for 13 to 180 min.

The plot of yield versus kappa number (Fig. 4) shows that the loss in yield was much larger than the dissolution of lignin calculated on the assumption that the lignin content was equal to the kappa number multiplied by 0.15. The difference between the idealized yield curve and the observed yields can almost exclusively be ascribed to the loss of carbohydrates. This loss was much larger under nitrogen than in comparable experiments under oxygen. The highest yield compared at any given kappa number was obtained at the highest oxygen pressure. This is noteworthy since lower viscosities were obtained in these experiments (879 dm^3/kg after 180 min) than after the same time at the lower oxygen pressure (959 dm^3/kg). For the treatment under nitrogen the viscosity increased to approximately 1020 dm^3/kg in the experiments with additions of 10-40% NaOH. The results show that the NO_2/O_2-pretreatment rendered the carbohydrates susceptible to alkaline degradation and that the reactions which gave rise to a loss of carbohydrates were suppressed by oxygen.

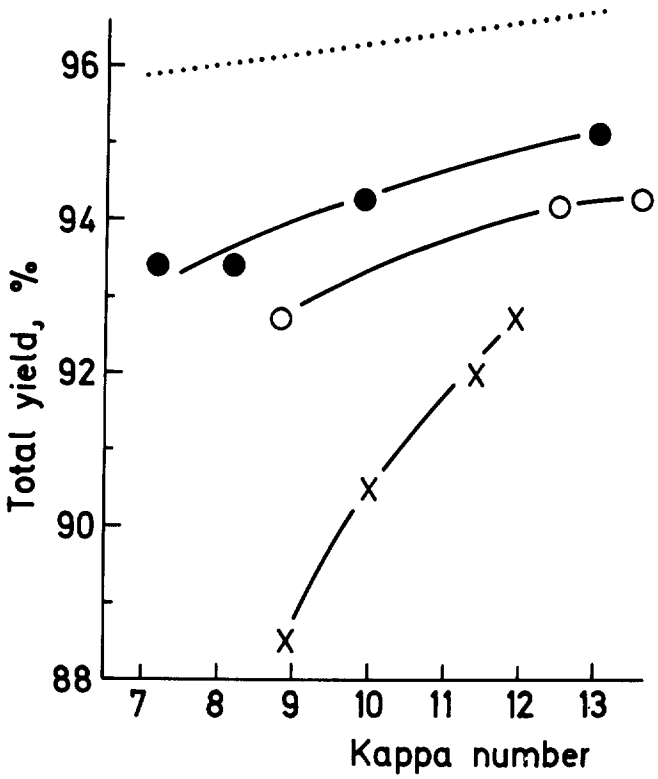

Fig. 4. Yield of pulp after alkali treatments at 106°C following NO_2/O_2 pretreatment with 4% NO_2.
X nitrogen; O oxygen 0.1 MPa; ● oxygen 0.8 MPa
The dotted line represents the yield calculated under the assumption that only lignin was removed from the pulp.

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