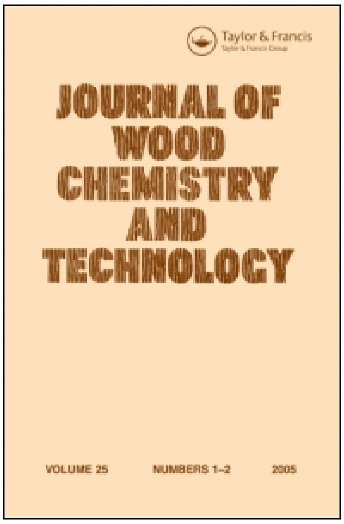

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Kalén, Gunnar , Samuelson, Olof and Svedmark, Gunnar(1987) 'Influence of Oxygen During Pretreatment of Kraft Pulp with NO_2', Journal of Wood Chemistry and Technology, 7: 2, 245 — 258
To link to this Article: DOI: 10.1080/02773818708085265
URL: http://dx.doi.org/10.1080/02773818708085265

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(2), 245-258 (1987)

INFLUENCE OF OXYGEN DURING PRETREATMENT OF KRAFT PULP WITH NO_2

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ABSTRACT

Large additions of O_2 during the pretreatment of modified or industrial kraft pulp with NO_2 under conditions which favored an autocatalytic generation of NO_2 from produced and added HNO_3 led to a decreased viscosity after a subsequent oxygen bleaching, if the comparison was made at high kappa numbers. The difference was less apparent when the oxygen bleaching was extended. The yield of pulp at a given kappa number was reduced by large O_2 additions. An increased yield of nitric acid contributed to these effects.

Hydrogen cyanide and ammonia were produced during the pretreatment in reactions between lignin and generated nitrogen oxides. Addition of O_2 led to decreased yields of these products.

INTRODUCTION

Pretreatment of wood pulp with NO_2 leads to a greatly improved delignification and to a protection of the carbohydrates during a subsequent oxygen bleaching [1]. For good process economy it is essential that the conditions can be adapted so that the NO_2 is efficiently regenerated during the pretreatment [2,3]. The addition of oxygen in the reactor during this pretreatment is advantageous both for the environment and for simplicity in the pretreatment. An improved selectivity, defined as intrinsic viscosity at a given kappa number, is obtained under mild conditions [1]. Under more severe pretreatment conditions of actual interest in an industrial application of the PRENOX [R] method, large additions of oxygen can, however, result in a loss in selectivity [4]. It was therefore of interest to study further the effect of oxygen on selectivity and to elucidate its influence on yield of pulp and formation of hydrogen cyanide, ammonia and nitric acid.

EXPERIMENTAL

The never-dried pulp was soaked at room temperature for 30 min with an aqueous solution containing 5 g SO_2 per liter to remove ash constituents and was then washed with deionized water. Acid nitrate solution was impregnated into the pulp so that the consistency was 26% and the pulp contained 0.08 moles of HNO_3 and 0.3 moles of $NaNO_3$ per kg water. No solution was removed. The impregnated pulp with a weight corresponding to 125 g dry pulp was introduced into the reactor which was then evacuated and heated. NO_2 (2% on dry pulp) was evaporated into the reactor when the temperature reached either 52° or 55°C, oxygen or nitrogen being used to displace the NO_2 quantitatively into the reactor. The temperature was then raised to the final level, and additional gas added according to the schemes given in the legends to the figures. The treatment was interrupted after 60 min and the pulp treated as described previously [5]. The reported time was determined from the moment when NO_2 was added.

Unless otherwise stated the reactor volume was 2 dm^3. The addition of O_2 and N_2 was adjusted so that atmospheric pressure was approached after the final addition. During pretreatment in the larger reactor (4 dm^3) an additional amount of N_2 was added to atmospheric pressure at 68°C. The gas volumes refer to room temperature and atmospheric pressure.

The oxygen bleaching was carried out at 106°C and either at 26% consistency for 45 min with additions of 0.5, 3.0, 4.5 or 6.0% NaOH [5] or at 8% consistency with 10% NaOH for 20, 40, 80 and 160 min [4].

Nitric acid was estimated by potentiometric titration [5], a correction being applied for ammonia including volatile amines [4] present in the spent pretreatment liquor. Hydrogen cyanide was stripped off from the liquor and absorbed in an aqueous solution of sodium hydroxide [6]. The final determination was carried out by potentiometric titration with silver nitrate.

RESULTS AND DISCUSSION

Selectivity

Figs. 1 and 2 show the results of experiments with a "modified" kraft pulp cooked by a process simulating counter-current cooking [7,8]. The kappa number was 34.8 and the intrinsic viscosity 1322 dm^3/kg. The other experiments were carried out with an industrial kraft pulp (kappa number 28.2; viscosity 1160 dm^3/kg).

In the plots of viscosity versus kappa number the highest value in each series refers to the preoxidized pulp. The other points refer to oxygen bleached pulps.

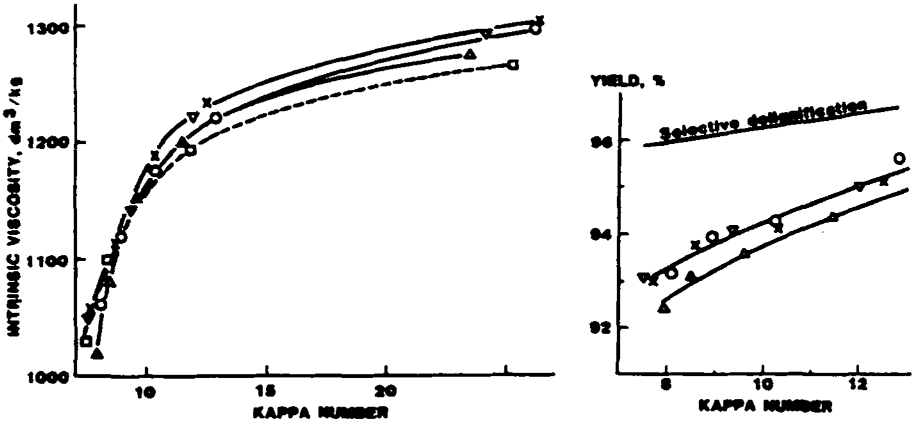

FIGURE 1. Intrinsic viscosity and yield of pulp versus kappa number after oxygen bleaching at 26% consistency of modified kraft pulp. Final pretreatment temperature 68°C.

Symbol	X	○	△	▽	□
Reactor, vol. dm^3	2	2	2	4	4
Gas (ml) after					
0 min (52°)	100 N_2	100 N_2	300 O_2	100 N_2	300 O_2
12 min (60°)	300 Air	300 Air	300 O_2	300 Air	300 O_2
20 min (68°)	300 Air	300 Air	300 O_2	300 Air	300 O_2
30 min (68°)	150 Air	100 O_2	275 O_2	150 Air	275 O_2
Added O_2, mol	5.2	7.4	38.7	5.2	38.7
Yield CH_3OH, mol^a	-^{b}	8.3	10.4	8.3	9.7
Yield HNO_3, mol^a	14.1	16.5	29.1	16.4	25.9
Yield HCN, mol^a	-^{b}	0.63	0.44	0.63	0.56

a. Per 100 kg pulp, b. Losses due to high pressure

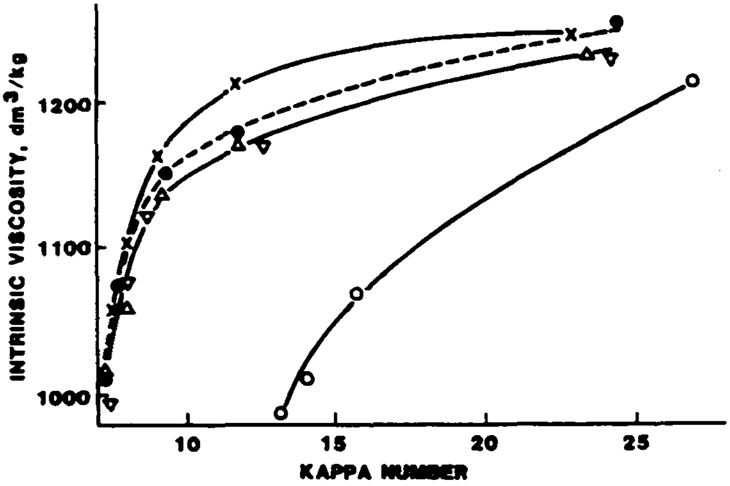

FIGURE 2. Intrinsic viscosity versus kappa number after oxygen bleaching at 26% consistency of modified kraft pulp. Final pretreatment temperature 72°C.

Symbol				
Gas (ml) after				
0 min (52°)	100 N_2	200 N_2	200 O_2	300 O_2
12 min (60°)	300 Air	100 O_2	200 O_2	300 O_2
20 min (68°)	300 Air	100 O_2	200 O_2	300 O_2
30 min (72°)	25 Air	400 N_2	700 N_2	-
Added O_2, mol[b]	4.3	6.6	19.8	29.7
Yield NH_3, mol[b]	2.1	1.4	1.4	1.2
Yield HNO_3, mol[b]	12.6	17.4	25.6	26.4
Yield HCN, mol[b]	-[c]	0.80	0.64	0.56
Yield pulp (%) at				
kappa number 7.5	92.6	93.2	92.5	92.2
kappa number 9.0	93.8	94.5	93.8	93.3

a. Open circles refer to oxygen bleaching without pretreatment.
b. Per 100 kg pulp. c. Losses due to high pressure.

It can be seen that the depolymerization of the polysaccharides during the pretreatment was more extensive when large amounts of oxygen were added. The increased depolymerization is ascribed to a larger production of nitric acid leading to an increased acid hydrolysis. When the largest amounts of oxygen were added an appreciable proportion remained in the gas phase at the end of the pretreatment while the proportion of nitric oxide was negligible compared with the added nitrogen dioxide [9]. During treatment with small additions, the oxygen was consumed virtually completely while nitric oxide was present in large amounts. After oxygen bleaching to a comparatively high kappa number the selectivity for pulp pretreated with a very large addition of oxygen was inferior to that of pulp pretreated with a small or no addition of oxygen.

With the modified kraft pulp the difference decreased with increasing delignification during the oxygen bleaching and the detrimental effect of oxygen addition during the pretreatment was insignificant at low kappa numbers. An increase by 100% in the reactor volume had no appreciable effect on selectivity and reaction rates. This is noteworthy since the transfer of NO_2 (including N_2O_4) from the gas phase to an aqueous phase depends strongly on the equilibrium between NO_2 and N_2O_4.

An increase from 68° (Fig. 1) to 72° (Fig. 2) in the final temperature led to a decrease in viscosity after the pretreatment and for oxygen-bleached pulps of rather high kappa number (e.g. 12). For pulps with low kappa numbers after the oxygen bleaching, the change in the temperature program during the pretreatment had no significant effect on selectivity. When the pretreat-

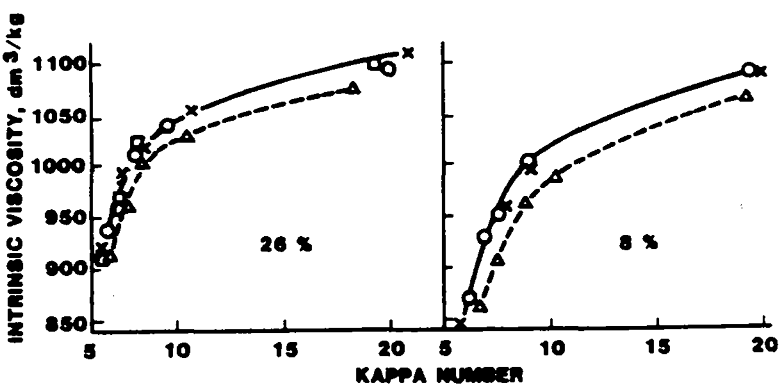

FIGURE 3. Intrinsic viscosity versus kappa number after oxygen bleaching at 26 and 8% consistency of industrial kraft pulp. Final pretreatment temperature 68°C.

	O_2-bleaching, 26% consistency				O_2-bleaching, 8% consistency		
Symbol	×	○	□	△	×	○	△
Gas (ml) after							
0 min (55°)	200 N_2	200 N_2	200 N_2	200 N_2	200 N_2	100 O_2	1200 O_2
10 min (60°)	500 N_2	200 O_2	-	500 O_2	500 N_2	500 O_2	200 O_2
20 min (68°)	-	-	200 O_2	-	-	-	-
25 min (68°)	0 N_2	500 N_2	575 N_2	550 O_2	-	80 O_2	25 O_2
Added O_2, mol[a]	0	6.6	6.6	34.6	0	3.3	47.0
Yield NH_3, mol[a]	1.3	1.2	1.2	1.0	1.3	1.1	1.0
Yield HNO_3, mol[a]	16.6	20.0	21.5	28.1	16.4	17.4	30.5
Yield HCN, mol[a]	>0.68	0.65	0.64	0.59	0.68	0.69	0.51

a. Per 100 kg pulp.

ment was adopted, a viscosity of 1050 dm^3/kg was obtained when the modified kraft pulp was delignified to a Kappa number of 7.5, but when the pretreatment was omitted, the viscosity dropped to this level at kappa number 15. Hence, the modified pulp was well suited for oxygen bleaching following pretreatment with NO_2. The selectivity after oxygen bleaching without pretreatment was higher than that obtained with most industrial kraft pulps.

Figure 3 shows that oxygen bleaching at 26% consistency of the industrial kraft pulp to kappa number 7.5 following pretreatment without or with a low oxygen addition gave a viscosity of 970 dm^3/kg. When the pretreatment was carried out with a large amount of oxygen present during the whole pretreatment, the corresponding value was 930 dm^3/kg. Hence, the detrimental effect of oxygen during the pretreatment remained even after an extensive oxygen bleaching of this pulp. The selectivity after oxygen bleaching at 8% consistency differed only slightly from that observed at 26% consistency. The results show that, by the application of suitably programmed temperatures and the addition of oxygen during the pretreatment, pulps of low kappa number and comparatively high viscosity can be produced by oxygen bleaching even if the viscosity of the unbleached pulp is rather modest.

In all the pretreatments referred to in Figs. 1-3, the added HNO_3 and $NaNO_3$ in combination with a high pretreatment temperature gave rise to a massive autocatalytic generation of NO_2 from the nitric acid in contact with the lignin in the pulp. It should be emphasized that the presence of oxygen is not a prerequisite for this generation.[10] This explains why the oxygen had a small effect on selectivity although the composition of the gas phase was affected drastically. These results together with those referred to in the introduction show that oxygen promotes not only reactions which lead to a decreased selectivity but also reactions which have the opposite effect.

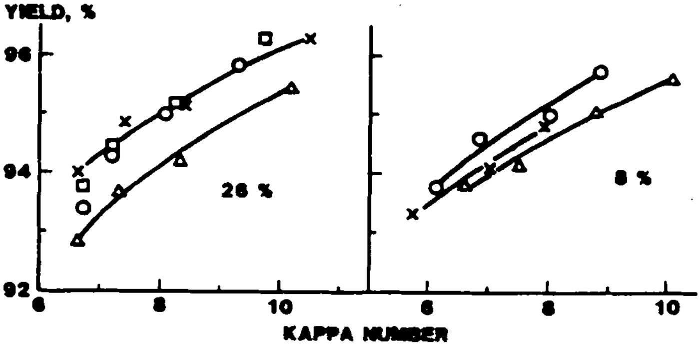

FIGURE 4. Yield of pulp versus kappa number after oxygen bleaching of pulps referred to in Fig. 3.

Yield after oxygen bleaching

The yield of pulp after oxygen bleaching following pretreatment of the modified kraft pulp with various additions of oxygen is shown in Fig. 1. The line denoted selective delignification was calculated from the decrease in kappa number on the assumption that the lignin content in the pulp was equal to the kappa number multiplied by 0.15. The results indicate that the loss of pulp constituents other than lignin was modest after delignification to a kappa number of 13 or higher. As shown in Figs. 1 and 4 an extended delignification during the oxygen bleaching at either 26 or 8% consistency resulted in a less selective dissolution of the lignin. At 26% consistency the delignification was extended by increasing the addition of sodium hydroxide from 1.5 to 6.0%, while at the lower consistency the duration of bleaching was increased from 20 to 160 min (Fig. 4). Evidently, these changes exerted a smaller effect on the delignification than on the reactions responsible for the loss of carbohydrates. The yields were, however, higher than those obtained after oxygen bleaching without pretreatment (94.6% at kappa number 12.7 and 95.3% at kappa number 13.5 in the case of the modified pulps).

The addition of oxygen and the time for its introduction into the pretreatment reactor had only a small influence on the yield of oxygen-bleached pulp at a given kappa number. The only significant effect (Figs. 1 and 4 and legend to Fig. 2) was a somewhat lower yield when oxygen of high concentration was present during the whole pretreatment than in experiments in which oxygen was absent during the whole or part of the pretreatment. The detrimental effect of oxygen can at least in part be ascribed to an increased number of alkali-labile, reducing sugar groups produced by acid hydrolysis. The loss in yield was observed with both types of pulp, independent of the temperature program and of the technique used during the subsequent oxygen bleaching.

Cyanide, nitric acid, ammonia

As shown in the legends to Figs. 1-3, small amounts of hydrogen cyanide were present in the spent liquors from the pretreatment. This was not unexpected in view of previous observations of the formation of cyanide during nitric acid cooking of wood [11]. The amounts corresponded to a conversion to HCN of 1.0-1.8 mole percent of the added NO_2. Calculated per 1000 kg of dry pulp, the production was 0.12-0.22 kg HCN. A large addition of oxygen which favored the production of nitric acid led to a lower formation of hydrogen cyanide.

In blanks without the addition of NO_2, the unbleached industrial kraft pulp was impregnated with acid nitrate solution so that the composition was the same as in the other experiments. No cyanide was detected by the applied technique (< 0.02 mol per 100 kg pulp) after treatment for 60 min at either 65 or 80°C. This shows that addition of NO_2 is necessary for the formation of hydrogen cyanide under applied conditions. No cyanide could be detected when a bleached kraft pulp was heated with NO_2 under the same conditions as those used for the unbleached pulp. Evidently, hydrogen cyanide is produced in lignin reactions in which NO_2 is involved.

Tests were also carried out in which the unbleached industrial kraft pulp was pretreated in the absence of oxygen at constant temperature during the whole reaction period. Fig. 5A shows that at 65°C the production of HCN started during an early period of the treatment and continued for a long time with a very modest decrease in the reaction rate. The added NO_2 was virtually completely consumed after a few minutes. Instead, NO_2 was generated from produced and added nitric acid. Since no oxygen was added in these experiments nitric oxide accumulated in the gas phase [1]. Evidently, nitrogen oxides generated from the nitric acid were responsible for the formation of the major part of the hydrogen cyanide. The observed large decrease in the yield of nitric acid after a short initial period confirms the great importance of the generation process.

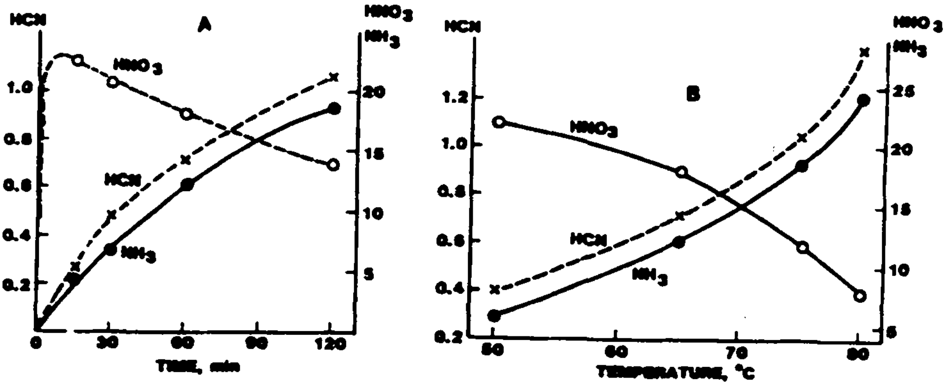

FIGURE 5. Yield of hydrogen cyanide (mol per 100 kg pulp, nitric acid (mol per 100 kg pulp) and ammonia (mol per 1000 kg pulp).

During pretreatment for 60 min without addition of oxygen the yield of HCN increased while that of HNO_3 decreased strikingly with increasing temperature (Fig. 5B). The shape of the curves confirms that, during a major part of the pretreatment, nitric acid is the main source of hydrogen cyanide.

Ammonia, including volatile amines, is produced during pretreatment of unbleached pulp with NO_2[4]. As in the case of hydrogen cyanide the yield of ammonia increased markedly with increasing temperature and duration of the pretreatment. Calculated on a molar basis, the production was 50-80% higher than that of hydrogen cyanide. Evidently, the major proportion was produced from nitrogen oxides generated from the nitric acid.

In practice, most of the hydrogen cyanide will be present in the gases leaving the pretreatment reactor. This compound can be destroyed in the recovery boiler. Ammonia and volatile amines will be present in the acid spent liquor. Carry-over to alkaline stages results in a liberation of the volatile bases. Possible air pollution must be taken into consideration.

ACKNOWLEDGEMENTS

We thank Rolf Brännland and Greta Fossum for permission to publish this report.

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