

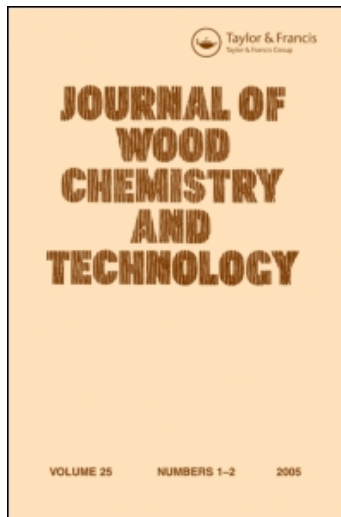
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PRETREATMENT OF BIRCH WITH
NITRIC OXIDE AND OXYGEN BEFORE SODA COOKING

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ABSTRACT

During treatment of birch meal with nitric oxide and oxygen methanol was produced at high rate even when only 2% of the added nitric oxide was present as nitrogen dioxide and nitric oxide. This confirms that nitrogen dioxide was regenerated in a reaction cycle. A high temperature and a large addition of nitric oxide favored the regeneration.

Soda cooking of pretreated birch chips showed that an increased regeneration led to an improved delignification reflected in an enhanced yield and pulp viscosity provided that a severe depolymerization of the carbohydrates during the pretreatment was avoided.

INTRODUCTION

Pretreatment of wood meal with nitrogen dioxide and an excess of oxygen leads to a greatly increased delignification rate during a subsequent soda (NaOH) cook^{1,2} and to a stabilization of the carbohydrates by converting reducing sugar end groups to aldonic acid groups.³ Under suitable conditions the nitrogen dioxide is regenerated effectively in a reaction cycle. The modified lignin, oxygen and nitric acid which is a major reaction product, participate in the regeneration cycle.^{4,5}

In this study the regeneration was elucidated by determination of the methanol formation. In addition we report on soda cooking of birch chips after pretreatment with small additions of nitric oxide and oxygen in excess. Nitric oxide is inert in the absence of oxygen.⁶ Its penetration into the chips before the addition of oxygen permits a more uniform reaction than that obtained with nitrogen dioxide.⁷

EXPERIMENTAL

Kraft cooks at 20% sulfidity of never-dried birch chips resulted in significantly higher yields at any given kappa number than cooks with dried chips, subsequently rewetted to the dry content of 60%. Under pretreatment conditions which for the never-dried chips led to an increase in yield by 1% compared to the blank without pretreatment, a loss by 1.5% was observed for the dried and rewetted chips.⁸ Inferior yields and pulp viscosities resulting from the drying of the chips were also found in preliminary cooks carried out in connection with the present study. In addition, the reproducibility was not satisfactory in these experiments.

For these reasons only results obtained with never-dried birch chips (Betula verrucosa Ehrh.) will be reported here. Freshly prepared chips were kindly supplied by Mo och Domsjö, Research and Development. High temperature was avoided during the transportation. The chips were stored at +3°C.

Chips with a moisture content of 55% corresponding to 800 g dry wood were introduced into a 10 liter reactor. The reactor was evacuated and then heated to the desired temperature under rotation. Nitric oxide was introduced into the reactor in five portions, each followed by a small proportion of oxygen so that vacuum

was maintained until the last portion of nitric oxide had been added. Finally, oxygen was introduced to obtain atmospheric pressure. The total time required for these additions was 10 min.

After the pretreatment the chips were washed with tap water and centrifuged. Portions of the chips corresponding to 200 g dry untreated wood were transferred into stainless steel autoclaves with a volume of 1500 ml. Sodium hydroxide solution was added so that the wood to liquor ratio was 1:5. The autoclaves were rotated in a polyglycol bath preheated to 80°C. The temperature was raised to the final temperature, 165°C, in 72 min. After cooking for different periods of time at this temperature the autoclaves were taken out from the bath and cooled rapidly under cold water. The pulp was disintegrated and washed with water, 1% acetic acid and finally with water before being dried at 35°C in circulating air.

The kappa number was determined according to SCAN-C7:77. The pulps were delignified with chlorine dioxide at room temperature before the determination of the intrinsic viscosity according to SCAN-C15:62.

The sugars were determined in spent liquors from pretreatment of wood meal prepared from the same birch chips. The meal, corresponding to 40 g dry wood, was treated with nitric oxide and oxygen in a 2 liter reactor. After the treatment 300 ml water was added. Nitrate formed during the pretreatment was removed by passing the spent liquor through a column filled with an anion exchanger in hydrogen-carbonate form. The effluent was concentrated by evaporation and the sugars were determined by partition chromatography on an anion exchange resin.⁹ The same chromatographic technique was applied for determination of xylose in hydrolyzates from pulp.

The methanol formation was studied with wood meal to simplify the sampling. In these and all other treatments with nitric oxide and oxygen the reaction time was calculated from the moment when the first portion of oxygen was introduced into the reactor.

RESULTS AND DISCUSSION

Formation of Methanol

Appreciable amounts of methanol are produced during the pretreatment of lignin with nitrogen dioxide.¹⁰ Previous investigations with kraft pulp from softwood showed that the delignification after oxygen bleaching following pretreatment with nitrogen dioxide and oxygen parallels the formation of methanol during the pretreatment.¹¹ It was therefore of interest to study the influence of the conditions during the pretreatment of birch on the formation of methanol and to compare the results with the delignification rate during a subsequent alkali cook.

No appreciable formation of methanol occurred from 4-0-methylglucuronoxylan under conditions applied previously.¹¹ More severe conditions were used in the present investigation. Birch xylan with a dry content of 55% was treated with 6% nitrogen dioxide and oxygen at 60°C for one hour. The formation of methanol was negligible (<4 mg per 100 g xylan).

These results permit the conclusion that the methanol formed during pretreatment of birch meal (Fig. 1) is produced by demethylation of the lignin. In agreement with the results obtained with kraft pulp, methanol was produced in a rapid initial reaction followed by a reaction at lower rate.

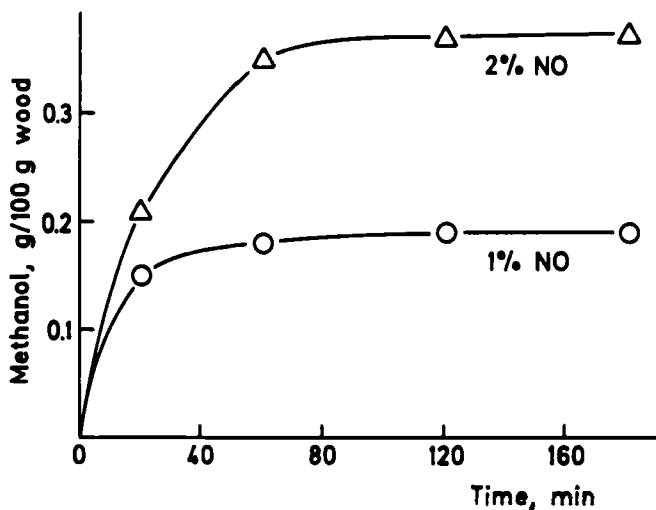


FIGURE 1. Formation of methanol during pretreatment at 50°C.

Determinations of nitric oxide and nitrogen dioxide in the gas phase showed that after pretreatment for 20 min at 50°C with an addition of 2% nitric oxide on dry wood, 97.9% of the added amount (calculated as nitrogen) was present in other compounds, mainly as nitric acid and as nitro groups in the lignin. This proportion increased to 99% when the added amount of nitric oxide was 1%. Upon prolonged pretreatment the concentrations of these nitrogen oxides dropped very slowly. Hence, the conversion to other nitrogen compounds in the experiment with 2% nitric oxide corresponded to 98.6% after 60 min. A calculation of the methanol formation within the interval 20-60 min, based on these analyses and the results given in Fig. 1 shows that at 50°C approximately 9 moles of methanol were produced per mole of consumed nitric oxide. For the period 0-20 min the corresponding

figure was 0.1. The results show that the enhanced formation of methanol on prolonged pretreatment is related to the regeneration of nitrogen dioxide.

Within the time interval from 60-180 min the produced amount of methanol increased by 100% when the addition of nitric oxide was increased from 1% to 2%. On the other hand, the yield of methanol after 20 min increased by only 40% as a result of the doubled addition. The dramatic increase in the methanol formation within the time interval from 20-60 min obtained by the increased addition of nitric oxide is explained by an improved regeneration due to an increased formation of nitric acid.

As shown in Table 1 the yield of methanol increased with increasing pretreatment temperature within the range 30-75°C. Independent of the temperature, an increased addition of nitric oxide led to an improved demethylation. At 50°C the yield of methanol was doubled when the addition of nitric oxide was increased from 1% to 2% while the effect was smaller at 30°C. At 60°C the yield increased by a factor of 3.1 while at 75°C the corresponding value

TABLE 1

Methanol g/100 g wood in spent liquor after pretreatment of wood with 1% and 2% NO for 120 min at 55% dry content.

Pretreatment temp. °C	Methanol formation	
	g/100 g wood 1%	g/100 g wood 2%
30	0.12	0.21
50	0.19	0.37
60	0.24	0.75
75	0.27	1.03

was 3.8. The results are in agreement with the observation that the regeneration is strongly favored at higher temperature and by the presence of nitric acid.

Alkali Cooking of Pretreated Wood

Fig. 2 shows that pretreatment of the chips with 2% nitric oxide and oxygen increased the delignification rate during the subsequent cooking with sodium hydroxide. Appreciable effects were obtained in cooks with additions of either 24 or 26% sodium hydroxide calculated on dry wood.

In agreement with the results obtained with wood meal the pretreatment resulted in a substantial increase in yield of alkali cooked pulp compared at any given kappa number (Fig. 3). Both for the pulps from pretreated and untreated wood the highest yields

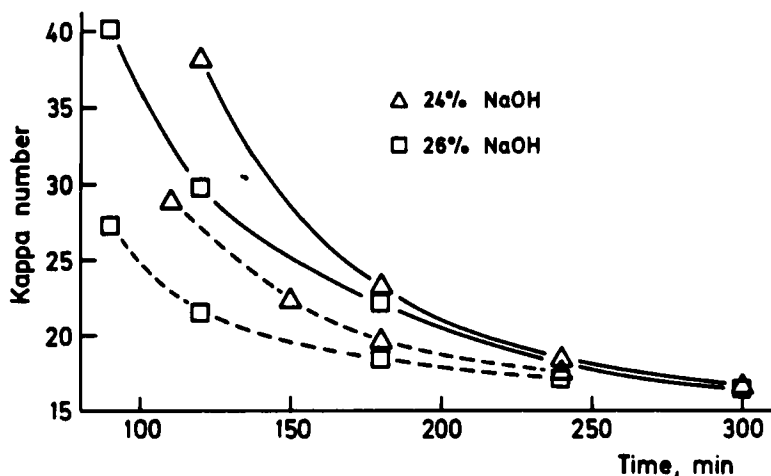


FIGURE 2. Kappa number versus duration of the alkali cooking of chips A at 165°C after pretreatment with 2% NO at 50°C for 120 min (dashed lines). Full lines refer to blanks without pretreatment.

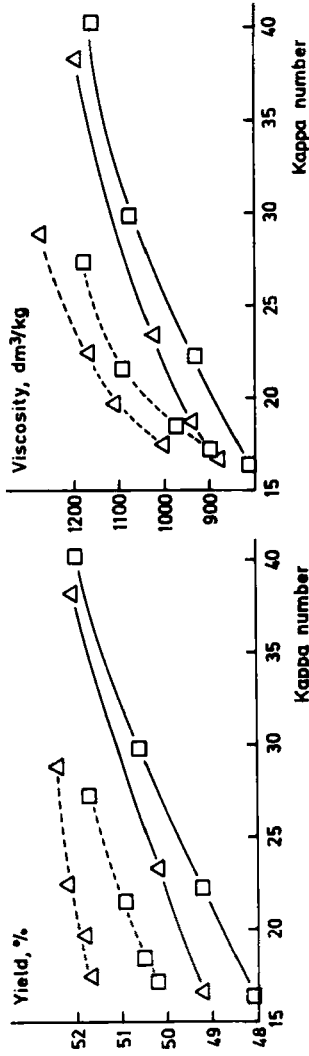


FIGURE 3. Yield and intrinsic viscosity versus kappa number of pulps referred to in Fig. 2.

were obtained at the lower sodium hydroxide concentration. Similar results were obtained with birch meal pretreated with 3% nitrogen dioxide.¹

The contents of extractives in the final pulps were not affected by the pretreatment. Hence, the improved yield as a result of the pretreatment must be ascribed to an increased yield of carbohydrates, mainly xylan. This was confirmed by determination of the sugar constituents in the pulp after acid hydrolysis.¹² Compared at the same kappa number the proportion of anhydroxylose was at least 1% higher in pulps from pretreated wood than in those from untreated wood.

The improved yield is explained as a combined effect of a shorter duration of the alkali cook and a stabilization of carbohydrates towards end-wise alkaline degradation (peeling) by oxidation of reducing sugar end groups to aldonic acid groups.³ Accordingly, plots of yield versus the duration of the cook showed that even when compared on this basis the highest yields were obtained from pretreated chips.

The shorter cooking time needed to obtain a desired kappa number was reflected in an enhanced viscosity of the pulp at any given kappa number (Fig. 3). The highest viscosity compared on this basis was observed after cooking with an addition of 24% sodium hydroxide. This is true for both pretreated and untreated chips.

The viscosity of the hemicellulose is low compared to that of the cellulose. The enhanced viscosity obtained as a result of the pretreatment can therefore be ascribed to a higher degree of polymerization of the cellulose.

The influence of the temperature during pretreatment before alkali cooking with 24% NaOH on the

delignification is shown in Fig. 4. Within the studied range an increased pretreatment temperature led to an improved delignification after a given duration of the cook. The results can be mainly ascribed to an increased regeneration of nitrogen dioxide reflected also in an increased formation of methanol with increasing temperature.

A comparison between Figs. 5 and 3 shows that a higher yield of alkali cooked pulp compared at any given kappa number was obtained after pretreatment at 50°C than at either 60°C or 30°C. Sugar determinations in spent pretreatment liquors (Table 2) showed that xylose and arabinose were the most abundant sugars. The major proportion of the sugars was derived from hemicellulose and pectic materials. The produced amounts increased with increasing temperature. At 60°C the total amount of sugars amounted to 0.13% of the weight of dry wood. Evidently, variations in the proportion of produced sugars during the pretreatment as a result of the

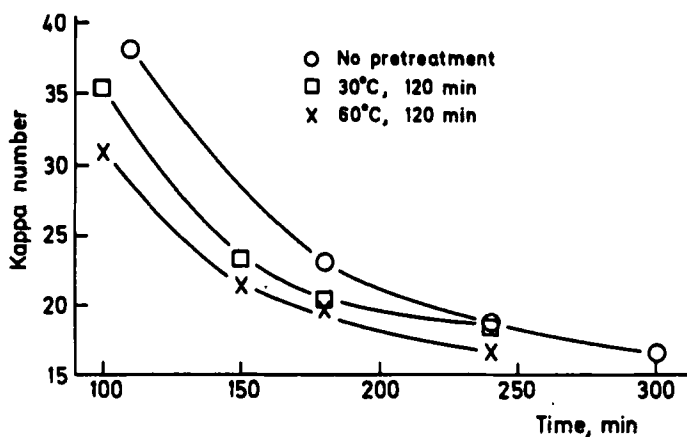


FIGURE 4. Kappa number versus duration of the alkali (24% NaOH) cooking of chips A at 165°C after pretreatment with 2% NO.

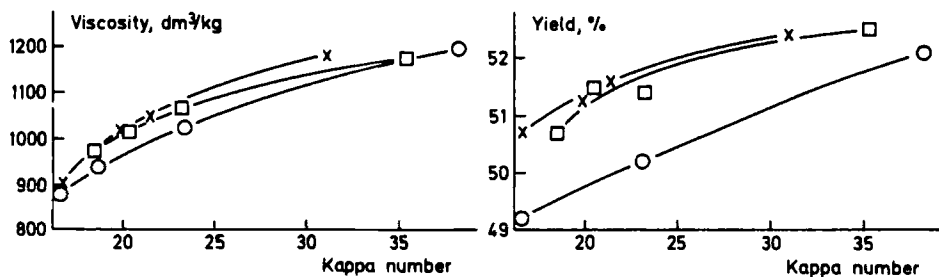


FIGURE 5. Yield and intrinsic viscosity versus kappa number of pulps referred to in Fig. 4.

TABLE 2

Monosaccharides (mg per 100 g dry wood) in spent liquors after pretreatment of birch meal (55% dry content) with 2% NO and oxygen or 0.53 M HNO₃ for 120 min.

	Pretreatment with NO/O ₂			0.53 M HNO ₃
	30°C	50°C	60°C	60°C
Xylose ^x	13.5	29.2	40.9	29.7
Arabinose	4.5	28.7	50.5	57.2
Mannose	1.3	6.8	13.5	13.0
Glucose	3.7	7.8	6.9	5.2
Galactose	trace	4.6	20.0	28.9

x Including a minor proportion of lyxose

altered conditions in this stage had little effect on the yield of alkali cooked pulp.

For comparison the dissolution of sugars was determined in an experiment with nitric acid so that the concentration was 0.53 moles per kg water. This is the concentration observed in a previous study of the formation of nitric acid under comparable conditions.⁶ Treatment with nitric acid at 55% consistency was carried out in the presence of oxygen. No nitric oxide was added. As shown in the table the formation of sugars in this experiment was similar to that obtained by pretreatment with nitric oxide and oxygen at the same temperature. Since, virtually no oxidation of the wood meal occurs during treatment with nitric acid under applied conditions, the results suggest that the dissolution of sugars during the pretreatment was mainly due to acid hydrolysis of the hemicellulose.

The higher yield of the final pulp obtained after pretreatment at 50°C compared to 30°C can be explained by the shorter duration of the alkali cook required to obtain a desired kappa number. Probably, an increased oxidation of reducing end groups was also achieved at the higher temperature.

Similarly, the more rapid delignification during the alkali cook following pretreatment at 50°C than at 30°C explains the significantly higher viscosity compared at any given kappa number found for pulps from chips pretreated at the higher temperature. Although the highest delignification rate was obtained after pretreatment at 60°C both the yield and the viscosity at any given kappa number were lower than those observed after pretreatment at 50°C. This can be attributed to a more extensive depolymerization of

the carbohydrates in the wood during the pretreatment at 60°C than at 50°C. Evidently, the difference was not levelled out during the alkaline cook. As already mentioned acid hydrolysis occurs during the pretreatment. The produced reducing sugar end groups will therefore be attacked by endwise alkaline degradation. This explains the lower yield after pretreatment at 60°C compared to 50°C.

Pretreatment gave rise to an improved delignification after the alkali cook also when the addition of nitric oxide was decreased to 1%. During alkali cooking with an addition of 24% sodium hydroxide the time required to reach kappa number 20 decreased from 220 to 180 min at 165°C when the chips were pretreated for 2 hours at 75°C. The corresponding figure for chips pretreated at either 50 or 60°C was 190 min. With this low addition of nitric oxide the increase in the methanol yield with increasing temperature was much less than that obtained with 2% nitric oxide. The results indicate that the nitrogen dioxide was regenerated much more effectively when a larger addition of nitric oxide was applied. This can at least in part be ascribed to the higher concentration of nitric acid obtained in the wood.⁶

In a cook with 22% sodium hydroxide, 280 min were needed to reach kappa number 20 when no pretreatment was made. For the chips pretreated at 50°C for 120 min the same kappa number was obtained after cooking for 235 min.

Again, the pretreatment resulted in an increased yield of pulp compared at any given kappa number. Fig. 6 shows that under favorable conditions the increase approached 1.5%. Hence, the improvement was significantly lower than that obtained by pretreatment with 2% nitric

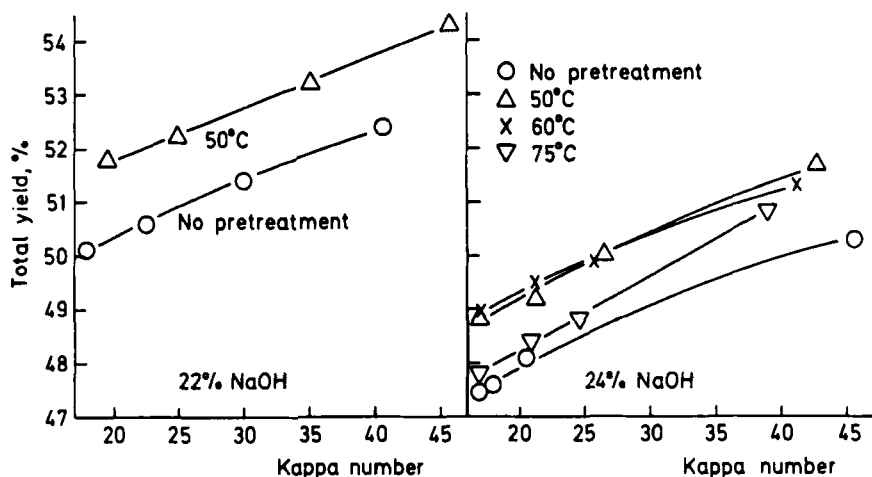


FIGURE 6. Yield versus kappa number after alkali cooking at 165°C of chips pretreated with 1% NO. Left diagram: chips A, 22% NaOH. Right diagram: chips B, 24% NaOH.

oxide. The influence of the temperature during the pretreatment was studied in the experiments with 24% sodium hydroxide in the alkali cook. As can be seen in the figure the yields were significantly higher after pretreatment at 50 and 60 than at 75°C .

Under comparable conditions a higher yield at any given kappa number was again observed during cooking with 22% sodium hydroxide instead of 24%. This can be ascribed to a higher yield of hemicellulose reflected also in a lower viscosity compared at a given kappa number (Fig. 7).

The viscosity of the pulps produced from pretreated chips was higher than that of pulp of the same kappa number produced from untreated chips. The enhancement was less than that obtained with 2% nitric oxide. Since, the carbohydrate yields were increased by the

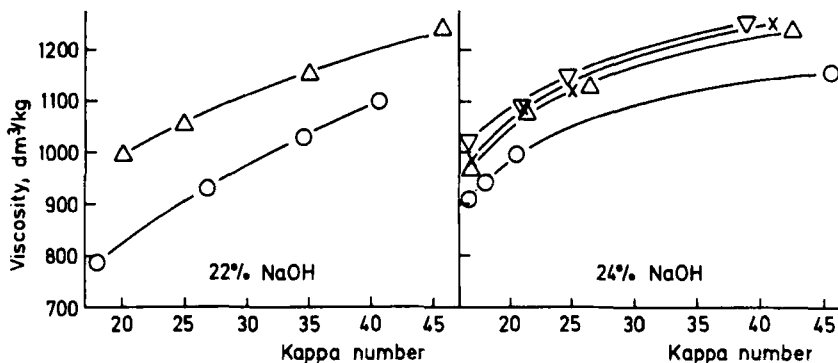


FIGURE 7. Intrinsic viscosity versus kappa number of pulps referred to in Fig. 6. Left diagram: chips A. Right diagram: chips B.

pretreatment the enhanced viscosity can also in these experiments be mainly ascribed to a suppressed depolymerization of the cellulose due to the shorter time in the cook required to obtain a desired kappa number. A higher viscosity of the final pulp was obtained after pretreatment at 75°C than at lower temperature. This indicates that at the low addition of nitric oxide the depolymerization of the cellulose during the pretreatment was slight even at this temperature.

ACKNOWLEDGMENTS

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