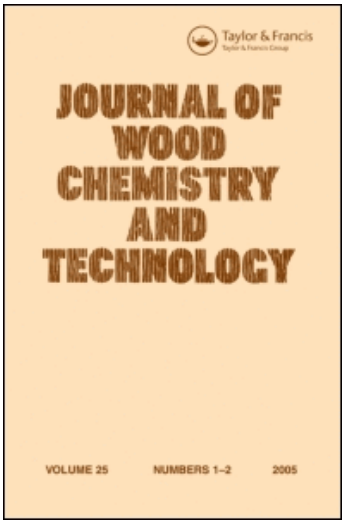


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# Soda Cooking of Wood Meal Pretreated with Nitrogen Dioxide

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# SODA COOKING OF WOOD MEAL PRETREATED WITH NITROGEN DIOXIDE

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## ABSTRACT

An increasing dry content during $NO_2/O_2$ pretreatment of wood meal led to an improved delignification during a subsequent soda cooking, both with and without addition of anthraquinone, and to an increased depolymerization of the carbohydrates during the pretreatment. The carbohydrates were stabilized towards alkaline peeling. The highest viscosity and yield compared at a given kappa number of the alkali-cooked pulp were obtained at an intermediate dry content. A pretreatment of birch meal gave rise to an enhanced yield compared at a given kappa number, while for aspen a loss was obtained. An alkaline extraction after the pretreatment led to a decreased yield of final pulp.

## INTRODUCTION

Treatment of wood by nitric acid followed by an alkali treatment has been described in numerous publications and applied industrially in the production of dissolving pulps.[1] In the patent literature and in preprints of conference papers,[2] nitrogen dioxide has been proposed instead of nitric acid.

A previous study showed that pretreatment of wood meal with a small proportion of nitrogen dioxide and oxygen leads to an improved delignification in a subsequent soda cook and to a stabilization of the carbohydrates towards alkaline peeling.[3] The stabilization is due to an oxidation of reducing sugar end groups

to aldonic acid end groups.[4] Several process parameters are of great importance, and the optimum conditions are different for hardwood and softwood. The most favorable results were obtained with hardwood. We here report on the effects of the dry content in the wood and of the conditions during an intermediate washing between the pretreatment and the soda cook.

## EXPERIMENTAL

Birch meal (Betula verrucosa, Ehrh. 0.13-0.35 mm) and Aspen meal (Populus tremula, L. 0.25-0.50 mm) prepared by grinding in a Wiley mill were conditioned with water in a polyethylene bag for 18 hours and then subjected to $NO_2/O_2$ pretreatment as described previously.[5] The $NO_2$ addition (3%) and the other additions were calculated on dry, untreated wood meal. The temperature was 55°C and the time 60 min. The pretreated wood meal was washed with either water at 10% consistency or 0.1 M sodium hydroxide at 6% consistency for 30 min. After drainage, the wood meal was subjected to NaOH ("soda") cooking at 170°C in autoclaves filled with nitrogen. The autoclaves were rotated in a polyglycol bath preheated to 170°C. The ratio of liquor to untreated wood was 7:1. In some experiments in which the washing was omitted, the sodium hydroxide addition was increased by one mole per mole of added $NO_2$. This additional alkali is not included in the reported additions.

After the cooking the autoclaves were cooled in tap water and the pulp was washed with water, 1% acetic acid, and finally with water before being dried at 35°C in circulating air for 24 h. The analyses were made according to SCAN. The viscosities were determined after delignification with chlorine dioxide and are reported as intrinsic viscosity ($dm^3/kg$).

A relationship between lignin content and kappa number was determined for pulps prepared by cooking birch meal which had been extracted with dichloromethane and ethanol. Kappa number and Klason lignin were determined without further extraction. For the pulps prepared from untreated wood the proportion of Klason lignin

(%) was equal to the kappa number multiplied by 0.18 while for those from pretreated wood the conversion factor was equal to 0.16.

## RESULTS AND DISCUSSION

### Yield after Pretreatment

The dry content in pretreated wood meal is difficult to determine unambigously since a decomposition of reaction products in the washed wood meal occurs during the drying. The yields of final pulp after the alkaline cook were therefore calculated from the weight and moisture content of the untreated wood meal. In some experiments a portion of the pretreated wood meal was, however, dried under standard conditions so that a rough estimate of the loss in yield during the pretreatment could be obtained.

In the experiments with a water wash at 5°C or 55°C after the pretreatment of birch meal with a dry content of 40%, the yield was approximately 100%, although acetic acid and saccharides were present in the liquor. Evidently, the losses were compensated for by the formation of nitrogen-containing compounds and oxidation products. A significant loss in yield amounting to 1.5-3% was obtained when the dry content of the birch meal was 55-75%. The results can at least in part be ascribed to an increased acid hydrolysis of the carbohydrates with decreasing water content in the wood meal. The influence of the temperature of the wash water was insignificant under the conditions studied.

When the washing was made with 0.1 M sodium hydroxide at 70°C, the loss in yield increased dramatically and amounted to 5% after pretreatment at a dry content of 55% and to 8-9% when the dry content was increased to 70-80%. A dissolution of lignin and low-molecular mass carbohydrates occurred during this alkali extraction.

With aspen the washing was in all experiments made with water at 55°C. The loss in yield was approximately 4% regardless of the dry content of the wood meal. Hence, the loss obtained with aspen was larger than that with birch, especially at low dry content.

## Delignification rate

In agreement with results reported previously, the plots of kappa number versus duration of the NaOH cook (Figs. 1 and 2) show that the time required to reach a desired kappa number of the final pulps was shortened dramatically as a result of the $NO_2/O_2$ pretreatment. In this respect birch and aspen exhibited a similar behaviour. Compared at the same duration of the cooking the proportion of remaining alkali (determined by potentiometric titration to pH 10.5) was lower than in the blanks without pretreatment. The difference corresponded to approximately 5% NaOH calculated on untreated wood. The improved delignification must therefore be ascribed to lignin reactions occurring during the pretreatment, e.g. demethylation[5] and other cleavages of

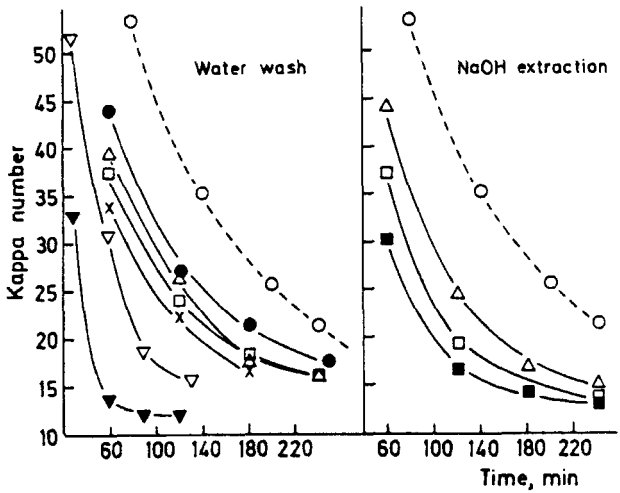


FIGURE 1. Kappa number versus duration of the alkali (21% NaOH) cooking of birch meal.

o Blank without pretreatment
Pretreatment at different dry contents:
● 40% Δ 55% □ 70% X 75% ■ 80%
Experiments with AQ addition during the cooking:
▽ No pretreatment ▼ Pretreatment at 70% dry content

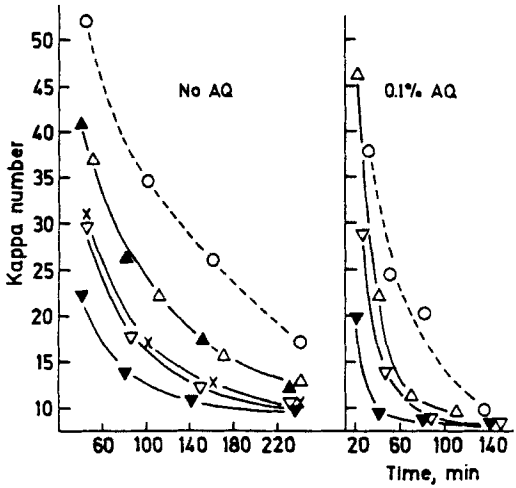


FIGURE 2. Kappa number versus duration of the alkali (20.5% NaOH) cooking of aspen meal.

o Blank without pretreatment
Pretreatment at different dry contents:
Δ 38% X 52% ▽ 67% ▼ 80% ▲ 38% (stored wood meal)



ether linkages, resulting in an improved dissolution in the alkaline stage.

A similar increase in delignification rate was obtained when the pretreatment was followed by an extraction with sodium hydroxide at 70°C. The dissolution of wood constituents during the extraction resulted in an increased sodium hydroxide concentration. The intermediate extraction stage had a small effect on the time required to reach a desired kappa number after the NaOH cook.

Regardless of the washing method used between the pretreatment and the alkali cook, an increased dry content in the birch meal led to lowered kappa numbers after a given duration of the alkali cook. This holds true also for experiments with birch meal in which the washing was omitted (not reproduced) and for the experiments with aspen (Fig. 2).

Under the conditions studied, the influence of the pretreatment of birch meal on the delignification was less than that of an addition of 0.1% anthraquinone (AQ) calculated on dry wood. With aspen meal the pretreatment at high dry content had a larger effect on the final kappa number than 0.1% AQ. It is noteworthy that with both birch and aspen the pretreatment led to a dramatic decrease in the kappa number of the final pulp also when AQ was used as catalyst during the NaOH cook.

## Depolymerization of Carbohydrates

The depolymerization of the carbohydrates during the alkaline cook is reflected in decreased viscosities of the pulp. A comparison between Figs. 1 and 3 shows that after a short duration of the alkaline cook the viscosities of the pulps from birch meal pretreated at a dry content of 55-75% were lower than that obtained for the blank without $NO_2/O_2$ pretreatment. Compared at a constant cooking time, an increased dry content during the pretreatment led to a lowered viscosity. The results suggest that the carbohydrates suffered a depolymerization during the pretreatment, which increased with a decreasing proportion of



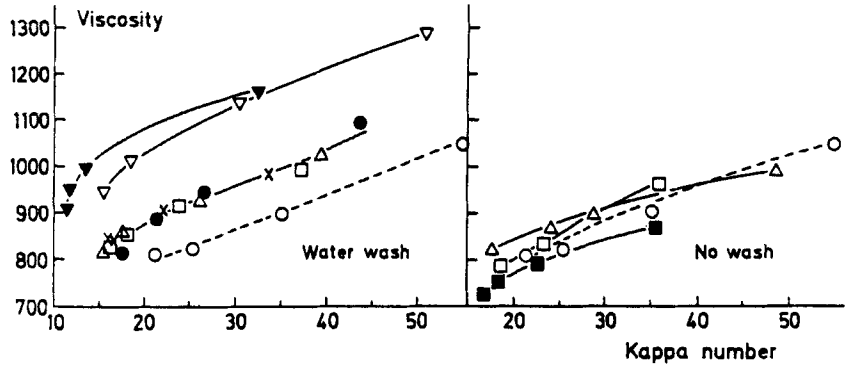


FIGURE 3. Intrinsic viscosity as a function of kappa number after alkali cooking of birch meal. Symbols: see Fig. 1.

water in the wood meal. The results are consistent with the observation that acid hydrolysis of glycosidic linkages occurred due to acids formed during the pretreatment.[6]

Fig. 3 shows the intrinsic viscosity of birch pulps after the alkali cooks as a function of kappa number. In the experiments with a water wash after the pretreatment, much higher viscosities were obtained for all pulps from $NO_2/O_2$ pretreated meal than for those from untreated wood meal. The variations in the dry content from 40 to 75% during the pretreatment had a slight influence only. As shown below, the pretreatment resulted in an increased proportion of hemicellulose in the pulp. It is therefore evident that the degree of polymerization of the cellulose in the pulps prepared from pretreated birch meal was much higher than in pulps of the same kappa number cooked without pretreatment. This shows that the depolymerization during the pretreatment had less effect than the shorter duration of the alkali cook.

The experiments with birch without any washing after the pretreatment showed that the viscosities at any given kappa number were lower than in those with a water wash (Fig. 3). When the pretreatment was done at a dry content of 80%, the viscosities were lower than in the blanks without pretreatment.

For the pulps produced from birch meal subjected to alkali extraction at 70°C, after pretreatment at 55% and 75% dry content, the viscosities after the alkali cook compared at a given kappa number (not reproduced) differed only slightly from those in the experiments with a water wash. As expected, somewhat lower viscosities were obtained for the pulps from the meal pretreated at 80% dry content, although a large proportion of hemicellulose was lost.

In the experiments with AQ addition lower viscosities were obtained after a given duration of the alkali cook when the birch meal had been subjected to $NO_2/O_2$ pretreatment (Fig. 3). The results confirmed that a depolymerization of the carbohydrates occurred during the pretreatment. Despite this loss in

viscosity, the highest viscosity of all birch pulps, compared at any given kappa number, was obtained after the AQ cook of pretreated wood meal. This is explained by the extremely rapid delignification under these conditions. As can be seen in the figure, AQ addition without pretreatment gave rise to a larger increase in viscosity at any given kappa number than $NO_2/O_2$ pretreatment without AQ addition in the alkali cook.

In the experiments with aspen much higher viscosities were obtained than in those with birch, when compared at the same kappa number and after the same duration of the NaOH cook. Fig. 4 shows that in the experiments without AQ addition the viscosities after a given time in the NaOH cook were lower when the meal had been pretreated at 80% dry content than for the blanks without pretreatment. Within the whole time interval studied, the pulps obtained after pretreatment at low dry contents exhibited higher viscosities than the blanks, the highest viscosity being observed at the lowest dry content. Similar results were obtained in the experiments with an addition of 0.1% AQ.



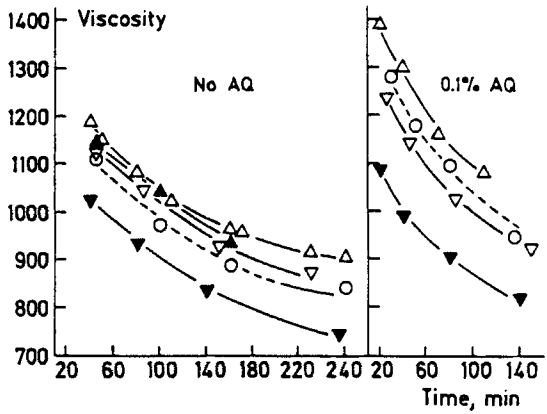


FIGURE 4. Viscosity versus time for the experiments with aspen meal referred to in Fig. 2.

Compared at a given kappa number, the pulps prepared from pretreated aspen meal exhibited much higher viscosities than those from untreated meal. At kappa number 20 the increase was approximately 200 $dm^3/kg$ after pretreatment at dry contents of 38% and 80%, while at dry contents of 52% and 67% the difference approached 300 $dm^3/kg$. This is approximately the same improvement in viscosity as that obtained by an addition of 0.1% AQ.

The shortened duration of the alkali cook when AQ was present led to an additional increase in viscosity by about 100 $dm^3/kg$ when the aspen meal was pretreated at a dry content of 67%, while the increase was twice as high at a dry content of 38%. At kappa number 20 the pulp produced after pretreatment at a dry content of 80% exhibited about the same viscosity as that after the AQ cook of untreated meal.

In summary, the results obtained with both birch and aspen show that a depolymerization of the carbohydrates occurred during the pretreatment and that the largest effect was obtained when a low proportion of water was present. The rapid delignification during the alkali cook explains the observation that an increased viscosity at any given kappa number of the final pulp was obtained also under pretreatment conditions which led to a dramatic depolymerization of the carbohydrates.



## Yield after Alkali Cooking

Plots of yield of the final birch pulp versus kappa number (Fig. 5) show that pretreatment under favorable conditions resulted in an increase of about 2%. The proportion of extractives (dichloromethane and ethanol) in the final pulps was the same (0.8-1.0%) for pulps from pretreated and untreated birch meal. As already mentioned, the relationship between kappa number and lignin content was only slightly affected by the pretreatment. The gain in yield compared at a given kappa number can therefore be ascribed to an increased carbohydrate yield, which is mainly

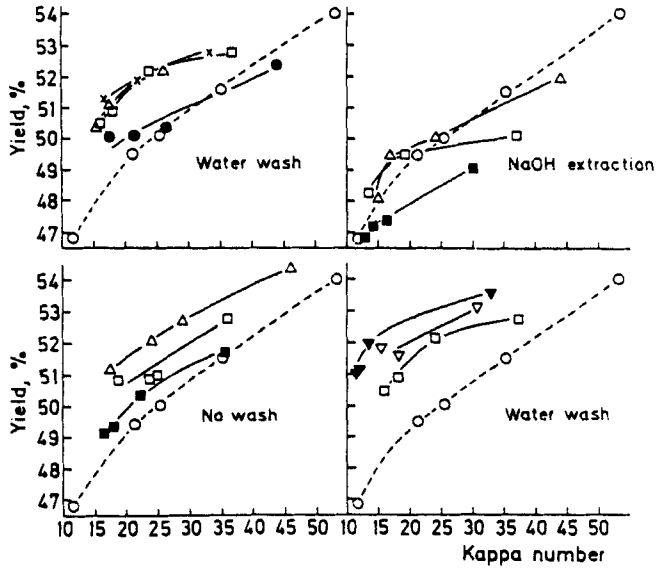


FIGURE 5. Relationship between yield (calculated on dry, untreated meal) and kappa number after alkali cooking of birch meal. Symbols: see Fig. 1.



due to an increased proportion of hemicellulose. This can in part be explained by the shortened time in the NaOH cook. There is, however, no simple relationship between the carbohydrate yield and the duration of the final NaOH cook even in experiments with the same working conditions after the pretreatment. The most striking exception was obtained at 80% dry content during the pretreatment, which resulted in lower yields at any given kappa number than comparable experiments with a lower dry content. The low yield can be related to the severe acid hydrolysis during the pretreatment mentioned above.

The intermediate NaOH extraction between the stages led to a severe loss in yield of final pulp compared at any given kappa number. For all pulps cooked to high kappa numbers, the yields were lower than those obtained in the blank without any pretreatment. The loss in yield compared to the losses in the experiments

with a water wash was larger the higher the dry content during the pretreatment. At 80% dry content the pretreatment followed by alkali extraction led to lower yields also for pulps of low kappa number compared to those obtained in the blanks without pretreatment. An intermediate alkali extraction should therefore be avoided when the production of pulps in high yield is desired.

The increase in yield of birch pulp compared at any given kappa number, resulting from an addition of 0.1% AQ, was slightly larger than that obtained due to the $NO_2/O_2$ pretreatment under the applied conditions, followed by a water wash (Fig. 5). The pretreatment of the wood led to an improved yield also when AQ was added to the subsequent NaOH cook. As expected, the effect of AQ was less for the pretreated than for the untreated birch meal.

In the experiments with aspen the extractive contents in the final pulps of kappa number 17 were 1.4% after cooking of pretreated wood meals compared to 1.3% in the blank. The ash content in the final pulps was lowered by about 0.1% as a result of the pretreatment. The influence of these changes are within the limits of experimental errors in the determination of the total yield of the pulp.

Fig. 6 shows that the yields of the final aspen pulp compared at any given kappa number were much higher than those obtained from birch. This can be ascribed to the larger proportion of cellulose in aspen. In contrast to the results obtained with birch, the pretreatment of aspen gave no improvement in yield. Significantly lowered yields of the final pulp were obtained after pretreatment at the highest (80%) and lowest (38%) dry contents, although the time in the NaOH cook required to reach a desired kappa number was reduced dramatically as a result of the pretreatment.

The large loss at the lowest dry content was puzzling, and the experiments were therefore repeated four months after the first series of cooks had been carried out. As shown in the plot

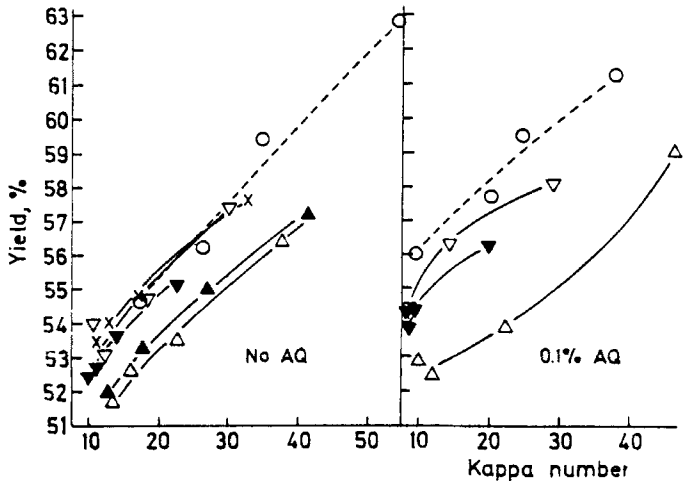


FIGURE 6. Relationship between yield (calculated on dry, untreated meal) and kappa number for aspen meal referred to in Fig. 2.



of kappa number versus time (Fig. 2), the delignification rate was virtually the same in these two series of experiments. Fig. 6 shows that an increase in yield of approximately 0.5% was obtained compared to the yield of the series with the fresh wood meal but that the yields in the later series were still about 2% lower than those in the blank without pretreatment. The increase can be ascribed to the fact that the wood meal had been stored for a period of time. The wood meal was prepared a few days after the tree had been cut and was subjected to pulping after one to five weeks in the first series of experiments.

In agreement with the results obtained with birch, the AQ addition led to a larger increase in yield for the aspen meal which had not been subjected to any pretreatment than for the pretreated meals (Fig. 6). For the experiments with AQ addition the highest yield was obtained with wood which had not been subjected to any pretreatment. The largest loss in yield resulting from the pretreatment was again observed at the lowest dry content.

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