

Oxygen bleaching following NO₂ treatment by a new process

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ABSTRACT *Oxygen bleaching of conventional kraft pulp after pretreatment with 2% NO₂ decreased the kappa number by 88% while maintaining a viscosity higher than that of most oxygen-bleached pulps produced industrially. After NO₂ treatment at high consistency and after dilution with weakly acidic sodium nitrate solution, which simulates spent liquor from the process, the pulp is ripened at a high temperature of around 90°C for 2 h. Generation of NO₂ from HNO₃ is a key reaction during ripening.*

KEYWORDS

Kappa number
Kraft pulping
Oxygen bleaching
Stock preparation
Viscosity

A two-staged process for pretreatment of kraft pulp with nitrogen dioxide followed by oxygen bleaching permitted the removal of more than 85% of the lignin without serious depolymerization of the cellulose (1). In this process, denoted S3, the pulp was treated with 2% NO₂ in an initial stage at medium consistency and modest temperature. An acidified sodium nitrate solution, which simulated spent liquor from a closed recovery system, was then added to bring the consistency to about 5%. This suspension was ripened at high temperature.

Here, we will deal with the effect of the time and temperature in the initial stage at 12% consistency. A modified S3 process in which this stage is carried out at 26% consistency has also been studied.

General discussion

In all pretreatments reported here, the pulp and diluent added after the initial stage contained 0.3 mol NaNO₃ per kg of water. Unless otherwise stated, the molality of HNO₃ was 0.01 m in pulp and diluent. The addition of NO₂ was 2%, and the consistency during the ripening was 5%. No oxygen was added. The general technique was that described previously (1).

The effects of the pretreatment conditions are illustrated in Figs. 1-4 by plots of intrinsic viscosity vs. kappa number. In each series, the sample with the highest kappa number was withdrawn directly after the pretreatment and washed with 0.2 M NaHCO₃ solution at room temperature. The pulps with lower kappa numbers refer to oxygen bleaching for 20, 40, 70, and 120 min.

For comparison, control blanks without NO₂ treatment were subjected to oxygen bleaching under identical conditions and are shown in Fig. 1. Metal compounds that can affect the oxygen bleaching are dissolved during the pretreatment with nitrogen dioxide and are removed during the subsequent washing. In the blank, the kraft pulp was soaked with SO₂ and water before oxygen bleaching to remove these metal compounds.

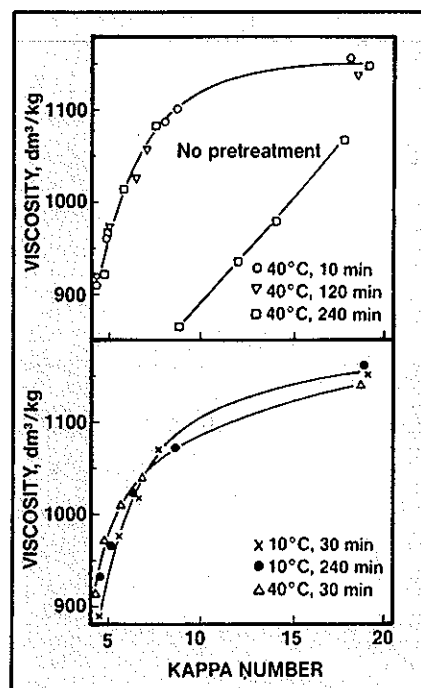
In the S3 process, a superior selectivity, defined as viscosity at a given kappa number, was obtained compared to the blank without NO₂ treatment before the oxygen bleaching. A lower kappa number after a given duration of the oxygen bleaching contributed markedly to this improvement. The soaked pulp exhibited a kappa number of 29.8 and an intrinsic viscosity of 1190 dm³/kg. Before soaking, the kappa number was 32.1,

and the viscosity was 1227 dm³/kg.

Under the most severe pretreatment conditions, the pulp suffered a loss in viscosity of more than 150 dm³/kg. The viscosities after oxygen bleaching for 120 min were, however, higher or virtually the same as that obtained in the blank without NO₂ treatment. The slower depolymerization of the cellulose during oxygen bleaching as a result of pretreatment (the "protection effect") is explained by a modification of the lignin which leads to a suppressed formation of aggressive intermediates, e.g., free radicals during the oxygen bleaching (2).

The modified S3 process, with 26% consistency in the initial stage followed by dilution and ripening, is compared in Fig. 3 with the S2 process (3) in which no dilution was made. As the figure shows, the S2 process at a consistency of 26% resulted in a lower selectivity after oxygen bleaching than that obtained by the modified S3 process. The high consistency during the whole pretreatment resulted in an increased yield of HNO₃, as shown in Table I. This higher yield indicates a less effective generation of NO₂ (including other active species) from nitric acid and explains in part the loss in selectivity (3-5).

1. The influence of temperature and time in the initial stage at 12% consistency on the relationship between intrinsic viscosity and kappa number (ripening at 90°C for 90 min)



In addition, the lower proportion of water during the period at the highest temperature contributed to a higher concentration of produced nitric acid. This higher concentration was reflected in a larger loss in viscosity during the pretreatment.

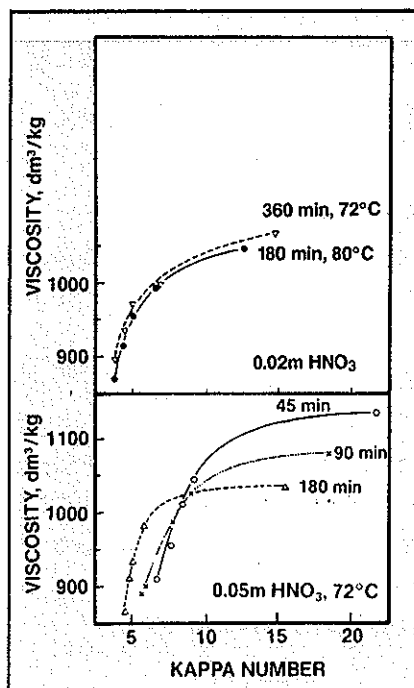
Initial stage

In the pretreatments at 12% consistency in the initial stage, the residence time in this stage was 15 min. A higher selectivity after oxygen bleaching was obtained at 40° and 10° in the initial stage than at 80°C (1). A consistency of 12% in the initial stage was used also in the pretreatments of Fig. 1. After dilution to 5% consistency, the suspension was ripened for 90 min at 90°C.

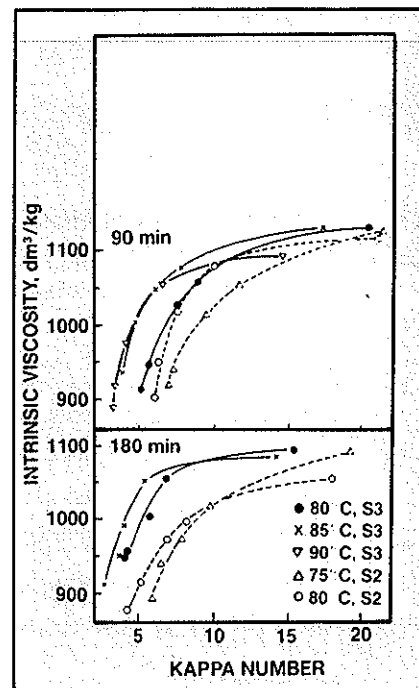
Figure 1 shows that under the applied conditions, wide changes in the length of the initial stage had no appreciable effect on delignification nor on selectivity after oxygen bleaching. Only small effects of a change in temperature from 40° to 10° were observed. A slightly higher selectivity than in the other experiments was observed after treatment at 40°C for 30 min in the initial stage.

An increase in the duration of the

2. The influence of nitric acid concentration, temperature, and time during ripening on the relationship between intrinsic viscosity and kappa number. (40°C for 15 min; 26% consistency in the initial stage)



3. The influence of temperature during ripening on the relationship between intrinsic viscosity and kappa number. (40°C for 15 min; 26% consistency in the initial stage)



1. Yield of HNO₃ for the experiments of Fig. 3

Symbol	Ripening, °C	Process	Yield of HNO ₃ moles/100 kg of pulp	
			90 min.	180 min.
●	80	S3	11.5	8.1
×	85	S3	9.0	6.1
▽	90	S3	6.2	...
△	75	S2	23.9	21.7
○	80	S2	22.1	19.6

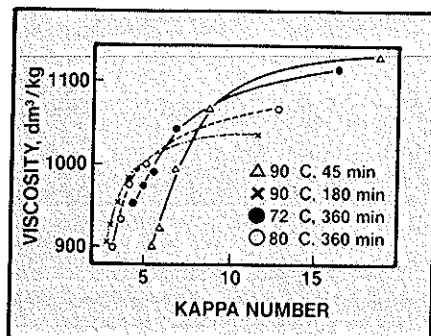
initial stage from 10 min to 240 min at 40°C had no significant effect on the selectivity after oxygen bleaching. Experiments were therefore carried out to study whether any lignin reactions occurred after a short initial period. Figure 5 shows that the production of N₂O and CO₂ continued at an appreciable rate even at the end of the studied period. In accord with previous observations, the rate of formation of N₂O was low during a short incubation period, and it increased on prolonged treatment (6). Since both compounds are produced in lignin reactions, these reactions evidently continued during a long period of time at 40°C, although this was not reflected in an improved selectivity.

Under the most favorable condi-

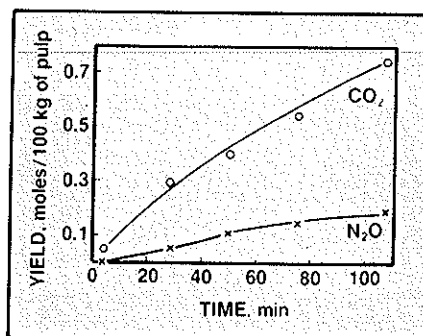
tions used in the experiments of Fig. 1, a kappa number of 4.5 after oxygen bleaching was obtained before the intrinsic viscosity dropped to 950 dm³/kg. In the previous study of the S3 process, the corresponding kappa number was 4.1 under the same conditions. In the study presented here, the kraft pulp was washed with water before pretreatment, while in the previous study the pulp was soaked with SO₂ and water.

We carried out potentiometric titrations of the unsoaked pulp with 0.1M HCl. The pulp sample was taken from a sample made up of 3 g of o.d. pulp slurried in 250 mL of an aqueous solution containing 1 g of NaCl. These titrations showed that 6.4 mmol of acid (calculated per 100 g of dry pulp) were consumed before pH 4.5 was

4. The influence of temperature and time during ripening on the relationship between intrinsic viscosity and kappa number. (40°C for 15 min; 26% consistency in the initial stage)



5. Formation of CO₂ and N₂O in an initial stage at 12% consistency and 40°C



II. Yield of HNO₃ for the experiments of Fig. 4

Sym- bol	Ripen- ing, °C	Time, min.	HNO ₃ , moles/ 100 kg
Δ	90	45	12.1
x	90	180	-0.7
●	72	360	13.9
○	80	360	6.4

obtained. Hence, the acid impregnated the pulp before the pretreatment was neutralized almost completely by the ash constituents. This reaction can explain the observed loss in selectivity (7).

Ripening conditions

Figures 2-4 show that in contrast to the initial stage, the ripening was strongly affected by the residence time. In all comparable experiments, the degree of delignification both during the pretreatment and after the oxygen bleaching increased markedly with increasing ripening time. Similarly, an increased temperature (Figs. 3 and 4) resulted in an improved delignification. A comparison between Figs. 2 and 4 shows that an increased concentration of nitric acid during the ripening exerted effects in the same direction.

On the other hand, these changes resulted in an increase in depolymerization of the cellulose during the pretreatment, reflected in a loss in viscosity in this stage. Compromises must therefore be made in the choice of parameters during the ripening stage. The results are consistent with the observation that acid hydrolysis of

the cellulose is mainly responsible for its depolymerization during the pretreatment (8).

Figure 2 shows that a decrease in the nitric acid concentration from 0.05 to 0.02 moles/kg of water, combined with an increased temperature from 72° to 80°C, resulted in an improved delignification and an enhanced selectivity for pulps of low kappa numbers. Additional improvements in delignification and selectivity were obtained when the molality of the nitric acid was decreased to 0.01 moles/kg while the temperature was increased to 85° or 90°C (Figs. 3 and 4, respectively).

The highest selectivity after oxygen bleaching to low kappa numbers was obtained after ripening for 180 min at 90°C. During pretreatment, however, the viscosity decreased from 1190 to 1030 dm³/kg. When the duration of ripening was decreased to 90 min, we obtained a somewhat lower selectivity at low kappa numbers, although the loss in viscosity during pretreatment decreased markedly. This loss in selectivity with the decreased ripening time is explained by a slower delignification and a lower protection effect.

The effects of the increased time, temperature, and nitric acid concentration on the lignin reactions are explained by an increased generation of NO₂ from produced and added nitric acid. Accordingly, Table I and Table II show that the yield of HNO₃ decreased with an increasing temperature and duration of ripening. These results and the comparison with the S2 process show that the regeneration of NO₂ is a key reaction during the ripening stage.

The experiments referred to in Figs. 2-4 were carried out with the

same SO₂-soaked pulp as that used in our previous study of the S3 process (1). A comparison between the results shows that both at 12% and 26% consistency in the initial stage, the highest selectivity was obtained after ripening for 180 min at 90°C. Independent of the initial consistency, a kappa number of 3.5 was reached before the intrinsic viscosity was decreased to 950 dm³/kg. At 26% consistency, the pulp was fluffy, and the color indicated a uniform reaction after the initial stage, while at 12% consistency the pulp adhered to the reactor wall. The color indicated a nonuniform treatment. Evidently, the positive effect of the more uniform reaction was counterbalanced by some detrimental effect of the higher consistency. A decrease in the amount of nitrous acid in contact with lignin can probably suppress some beneficial reaction.

From a practical point of view, pulp of either medium or high consistency can be used in the initial stage, with excellent results. In our experiments with an industrial kraft pulp from softwood, oxygen bleaching after pretreatment with 2% NO₂ resulted in a decrease in kappa number by 88%. The pulp still maintained a degree of polymerization of the cellulose higher than that of most oxygen-bleached pulps currently produced in practice.

Literature cited

1. Samuelson, O. and Ojteg U., 1987 CPPA Annual Meeting Proceedings, CPPA, Montreal, p. A 81.
2. Samuelson, O., Pure Appl. Chem. 55(4): 695(1983).
3. Samuelson, O., 1987 International Oxygen Bleaching Conference Proceedings, TAPPI PRESS, Atlanta, p. 45.
4. Samuelson O., Proceedings of the 1983 Intl. Symposium on Wood and Pulp Chemistry, Japanese TAPPI, Tsukuba Science City, p. 39.
5. Engstrom T. and Samuelson, O., Svensk Papperstid. 86(15): R173(1983).
6. Rasmusson, D. and Samuelson, O., Holzforschung 40(suppl.): 147(1986).
7. Samuelson, O., Svensk Papperstid. 89(9): R96(1985).
8. Andersson, S. -I. and Samuelson, O., Tappi 66(7): 87(1983).

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