NO_2 treatment of kraft pulp followed by oxygen bleaching

Influence of black liquor

Olof Samuelson and Urban Ojteg

Dept. of Engineering Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

ABSTRACT *Kraft pulp from softwood containing large amounts of black liquor was delignified by oxygen bleaching following pretreatment with nitrogen dioxide. The alkaline pulp was treated with NO_2 for a few minutes at 40–60° C and high or medium consistency. The consistency was decreased to 5–8% by dilution with an aqueous solution of $NaNO_3$ and HNO_3, simulating spent liquor from the pretreatment. After ripening under conditions which favor generation of NO_2 from HNO_3 (180 min at 90° C), the pulp was oxygen bleached.*

A kappa number of 3.5 was obtained at an intrinsic viscosity of 950 dm^3/kg even when the pulp contained 43 kg of solids from the black liquor per 1000 kg pulp. Nitric acid was added to compensate for NO_2 reactions with alkali, lignin, and sulfur compounds in the black liquor. A large consumption of HNO_3 is obtained unless the liquor is removed effectively before the pretreatment.

KEYWORDS
Black liquor
Bleaching
Kraft pulps
Nitrogen dioxide
Oxygen

Oxygen bleaching of kraft pulp following pretreatment with active nitrogen compounds (for simplicity denoted NO_2) permits mills to produce fully bleached kraft pulp without applying elementary chlorine (*1*). NO_2 is generated autocatalytically from produced and optionally added HNO_3 in reactions in which lignin is involved (*2*). The generation of NO_2 is a prerequisite for extensive delignification without serious attack on the cellulose. Results achieved in a pilot plant are inferior to those in laboratory experiments. It has been suggested that the carry-over of spent cooking liquor may explain the inferior results (*3*). It was therefore of interest to study the effect of black liquor and kraft lignin in laboratory experiments by the S3 process (*4*) based on pretreatment with NO_2 at medium or high consistency, dilution with acid liquor containing nitrate, heating, and ripening at high temperature. The reported experiments refer to ripening for 180 min; the standard ripening temperature was 90°C.

Results and discussion

The influence of the pretreatment conditions is illustrated by plots of intrinsic viscosity versus kappa number after the pretreatment and after oxygen bleaching for 20, 40, 70, and 120 min. The pulp with the highest kappa number in each series refers to the pretreated pulp (*5*). The selectivity is defined as intrinsic viscosity at a given kappa number.

The additions of free HNO_3, NO_2, lignin, and black liquor refer to 100 kg of dry unbleached pulp. The yields of acids are reported on the same basis.

Additions of kraft lignin

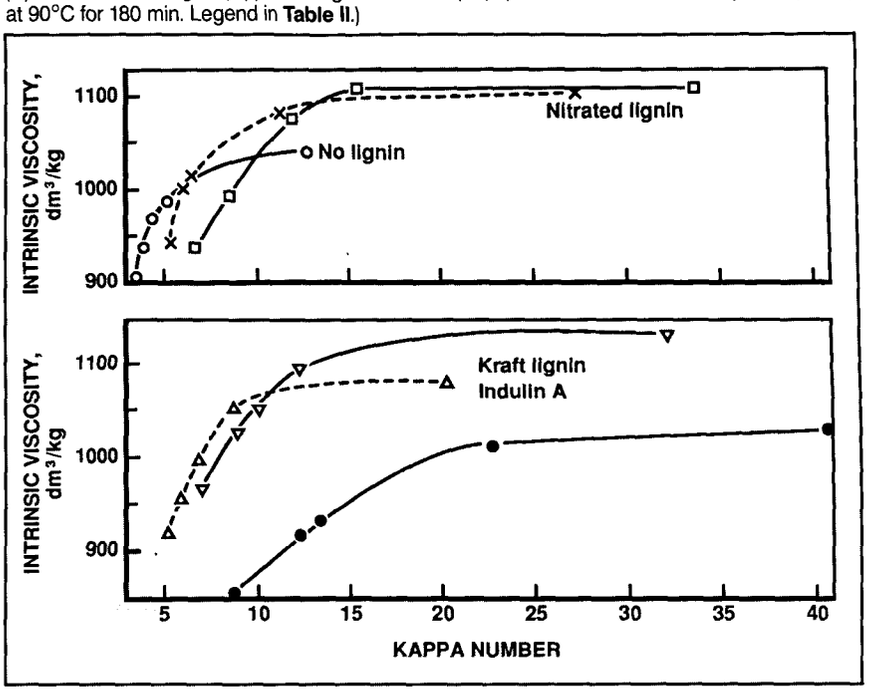
Kraft pulp impregnated with lignin dissolved in NaOH (1.47 mol/kg of lignin) was pretreated with NO_2 at 40°C. After 15 min, the diluent was added by suction, and the pulp suspension was heated and ripened at 5% consistency. The lignin (Indulin A) from the production of strong kraft pulp was precipitated more easily in acid medium than lignin from cooks of soft kraft pulps. The pretreatments in **Fig. 1** were carried out with 43.5 mol (2 kg) NO_2 per 100 kg of pulp. The ripening temperature was 90°C. The experiments show that after the oxygen bleaching, the delignification and selectivity were suppressed markedly by the added lignin. The pretreatment conditions had a deci-

sive effect. The lower diagram shows that, in the experiment with the smaller amount of pulp (45 g), the kappa number after the pretreatment was much higher than that of the untreated pulp. This result shows that added lignin precipitated when the pulp became acidic. When 90 g of pulp was pretreated in the same reactor (2480 mL), the kappa number was close to that of the untreated pulp. Evidently, the increased reactor loading during the pretreatment led to an improved solubility of the lignin. Similarly, both the delignification after any given duration of oxygen bleaching and the selectivity were greatly improved.

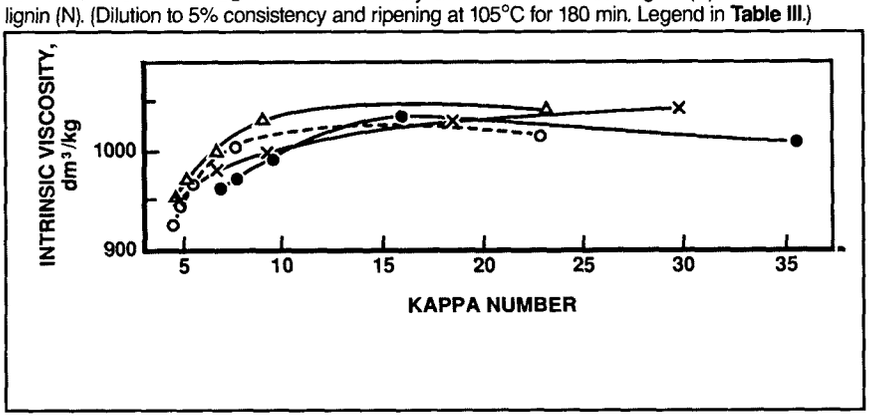
The pretreatment conditions were chosen so that the gas volume in the reactor during the ripening was small in the experiments with 90 g pulp, while in those with 45 g the gas phase occupied more than 50% of the reactor volume. The improvements observed with the increased reactor loading can be explained by a higher partial pressure of the active gas components that participated in the autocatalytic reaction. Under applied conditions, titrating the spent pretreatment liquor to pH 3.5 using NaOH gives a rough measure of the amount of nitric acid. The legend to Fig. 1 shows that in the experiment with the larger gas volume, the yield of acids titrated to pH 3.5 was equivalent to approximately 50% of the added NO_2. In the experiment with the small gas volume, the corresponding yield was only about 2%. Since the consumption of NO_2 is very rapid, the titrations confirm that an extensive generation of NO_2 from HNO_3 occurred during the pretreatment at the higher reactor loading (*4–6*). The high yield of acid found at the lower loading indicates that the generation of NO_2 was less important.

Some results from pretreatment in the presence of nitrated lignin (45 g pulp) are shown in the upper diagram in Fig. 1. The nitrated lignin was prepared from the same sample of Indulin A by treatment with acid nitrate solution in a continuous reactor (*7*). The nitrogen content was 3.0%. As can be seen, markedly lower kappa numbers were observed after pretreatment and subsequent oxygen bleaching than those obtained with untreated Indulin A. The dramatic improvement in selectivity and the lower yield of acids titrated to pH 3.5

1. Pretreatment with NO_2 at 12% consistency after impregnation with 5.8 kg of either kraft lignin (A) or nitrated kraft lignin (N) per 100 kg unbleached pulp. (Dilution to 5% consistency and ripening at 90°C for 180 min. Legend in **Table II.**)



2. Pretreatment with NO_2 at 12% consistency after addition of kraft lignin (A) or nitrated kraft lignin (N). (Dilution to 5% consistency and ripening at 105°C for 180 min. Legend in **Table III.**)

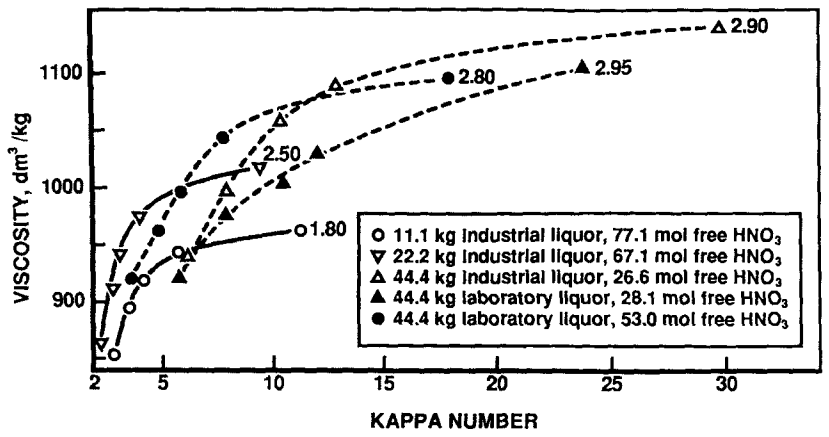


permit the conclusion that more NO_2 was generated when nitrated lignin was added instead of untreated lignin.

With both types of lignin, a modest increase in the amount of HNO_3 resulted in lowered kappa numbers, a markedly enhanced selectivity, and a negative yield of strong acids, reflecting a net consumption of added nitric acid. The results show that the increased addition of nitric acid led to markedly favored generation reactions.

All experiments in **Fig. 2** were carried out at a ripening temperature of 105°C with 45 g of pulp in a 1240-mL reactor—that is, with a small gas volume present during ripening. Irreproducible kappa numbers and viscosities were obtained when the addition of Indulin A was the same as in the pretreatments referred to in Fig. 1. Dark spots of precipitated lignin were present even in oxygen-bleached pulps. The results indicate a lignin condensation which was favored by the high temperature in acid medium. An increased charge of NO_2 decreased the number of spots. When the charge was increased from 43.5 mol NO_2 per 100 kg pulp to twice this value and the added amount of Indulin A was decreased by 50% at the same time, the kappa number after the oxygen bleaching decreased below 5 before the intrinsic viscosity dropped to 950 dm³/kg.

3. Pretreatment with 43.5 mol (2 kg) NO_2 per 100 kg pulp impregnated with varying amounts of black liquors. (NO_2 treatment at 40°C and 12% consistency for 15 min before dilution to 5% consistency.)



I. Analyses of black liquors

	Industrial liquor	*Laboratory liquor**
Total solids, g/kg	194	148
Sodium, g/kg	39.8	27.4
Total sulfur, g/kg	11.5	7.9
Sulfide (S^{2-}, g/kg	1.12	4.4
Titratable alkali, mmol/100 g	90	54

*Used only in pretreatments reported in Fig. 3.

II. Legend and experimental factors for Fig. 1

Symbol	*Lignin*	*Added free HNO_3*	*Yield of acids, mol* pH 3.5	*Yield of acids, mol* pH 7.0	*Spent liquor pH*
●	A	19.0	22.6	4.5	1.80
▽	A	19.0*	0.9	10.9	2.80
△	A	45.0*	-35.5	7.7	2.70
□	N	19.0	1.5	6.7	2.06
×	N	30.6	-6.1	12.3	2.48
○	...	19.0	2.0	8.6	2.10

*90 g pulp in a 2500-mL reactor. 45 g pulp in the other pretreatments.

III. Legend and experimental factors for Fig. 2

Symbol	*Added per 100 kg pulp* Lignin, kg	HNO_3, free, mol	*Yield of acids, mol* pH 3.5	*Yield of acids, mol* pH 7.0	*Spent liquor, pH*
		43.5 mol NO_2 per 100 kg pulp			
●	5.8 N	19.0	3.7	13.1	2.55
×	5.8 N	45.0	-19.5	13.3	2.20
		87.0 mol NO_2 per 100 kg pulp			
△	2.9 N	19.0	11.2	15.1	2.20
○	2.9 A	19.0	11.1	10.7	2.10

Under the conditions which favored the generation reactions, a rather modest improvement in selectivity was obtained when nitrated lignin was added instead of Indulin A. Only a small loss in selectivity occurred when the addition of nitrated lignin was increased. When the addition of free HNO_3 was increased from 19.0 mol to 45.0 mol per 100 kg of pulp, the use of less NO_2, added to the levels employed in the experiments reflected in Fig. 1, had a small effect on the selectivity. An effective generation of NO_2 reflected in a large consumption of HNO_3 explains the comparatively high selectivity.

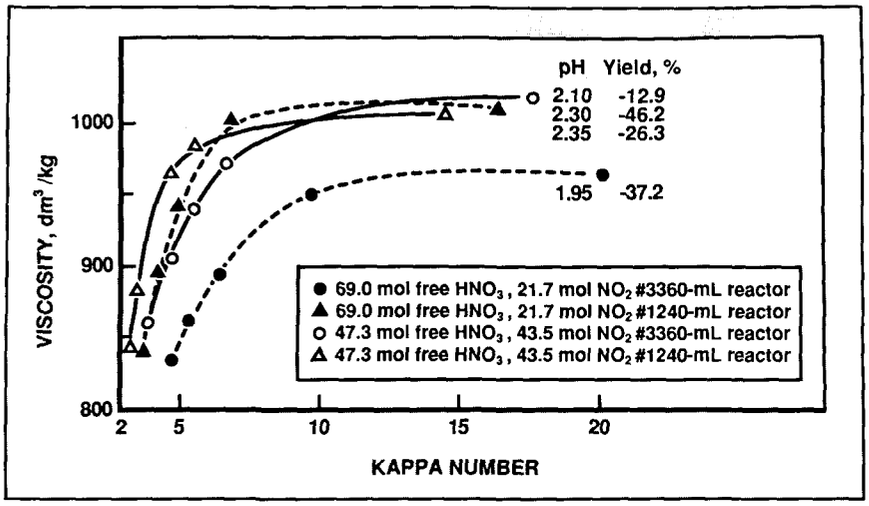
The yields of acids titrated to pH 7.0 (calculated from the NaOH consumption at pH 7.0 minus that at pH 3.5) show that substantial amounts of weak organic acids were produced. Produced acids were destroyed in an appreciable proportion under severe pretreatment conditions.

Impregnation with black liquors

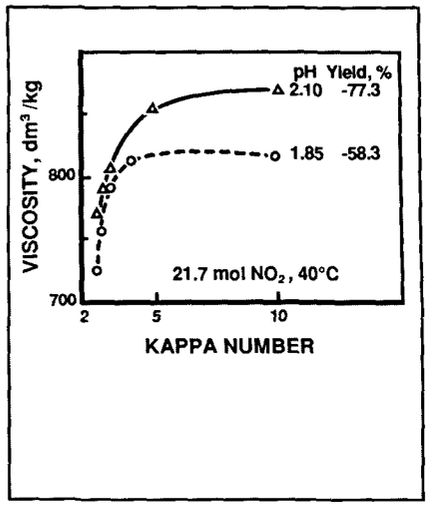
Pretreatments at medium or high consistency followed by dilution and ripening at 90°C were carried out with kraft pulp impregnated with an industrial black liquor from a mill producing bleached pulp from softwood, mainly *Pinus sylvestris*, or with liquor from a laboratory cook of chips from 100% of this kind of wood. The industrial liquor was from a mill performing oxygen bleaching of the unbleached kraft pulp with oxidized white liquor as active alkali, which explains the low proportion of sulfide (**Table I**). Reported amounts refer to undiluted liquors.

In the experiments given in **Fig. 3**, the reactor loading corresponded to 90 g of dry pulp. The volume was 2480 mL, which means that the gas volume was small during the ripening. As shown, excellent results were obtained after oxygen bleaching following NO_2 treatment at 12% consistency and ripening at 5% consistency. Both delignification and selectivity were greatly dependent on the amounts of

4. The influence of the volume of the pretreatment reactor and the amount of NO_2 at constant molar addition of NO_2 plus HNO_3. (Treatment with NO_2 at 40°C and 27% consistency for 15 min before dilution to 8% consistency.)



5. The influence of the volume of the pretreatment reactor during NO_2 treatment at 27% consistency for 15 min before dilution to 8% consistency (109.5 mol of free HNO_3). Δ 1240-mL reactor; O 3360-mL reactor.



black liquors in the pulp and on the amount of nitric acid introduced with the diluent. Under favorable conditions, a kappa number of 3.5 was obtained at an intrinsic viscosity of 950 dm^3/kg, even when the pulp contained 22.2 kg of industrial black liquor (4.3 kg of black liquor solids) per 100 kg of pulp.

The observed selectivity was close to the most favorable results in parallel runs performed without the addition of black liquor. A prerequisite for a high selectivity was that a proper and fairly large amount of nitric acid should be introduced with the diluent. A large proportion of this acid was consumed for neutralization of the alkaline liquor and in various other reactions, such as in the autocatalytic lignin reactions which give rise to the generation of active nitrogen oxides. This means that with regard to the process economy, it can be highly desirable to remove the major part of the black liquor from the pulp before it enters the pretreatment.

Reactor volume

With regard to heat economy, pressing is an attractive method for removing black liquor. In all pretreatments described below, the initial consistency was 27%. The pulp was impregnated with the diluted industrial liquor in an amount corresponding to 22.4 kg of undiluted liquor per 100 kg pulp. After the NO_2 treatment, diluent was added to a consistency of 8%. The pH values given in the diagrams refer to the spent pretreatment liquors. The yields are those of acids titrated to pH 3.5.

Figure 4 shows that, under applied conditions, an addition of NO_2 decreased by 50% led to suppressed delignification and a loss in selectivity, although the total molar addition of $NO_2 + HNO_3$ was kept constant. The effects were serious after pretreatment in the large reactor. In comparable experiments, the effects were significant also in the small reactor. In this reactor, 1% NO_2 gave rise to a slightly higher selectivity than that obtained with 2% in the large reactor.

The beneficial effects of the low reactor volume are consistent with the observation that gaseous products have a decisive influence on the generation process (*6*). The yields of acids titrated at pH 3.5 confirm this conclusion.

At extremely high concentration of added nitric acid (**Fig. 5**), the effect of the reactor volume on delignification was hardly detectable. On the other hand, the viscosity after pretreatment was much higher when the small reactor was used. A lower concentration of nitric acid arising from a more extensive generation of NO_2 from HNO_3 explains the lower depolymerization rate of the cellulose. Large differences in viscosity remained after the oxygen bleaching. Hence, the selectivity was greatly improved when the gas volume was small during the pretreatment.

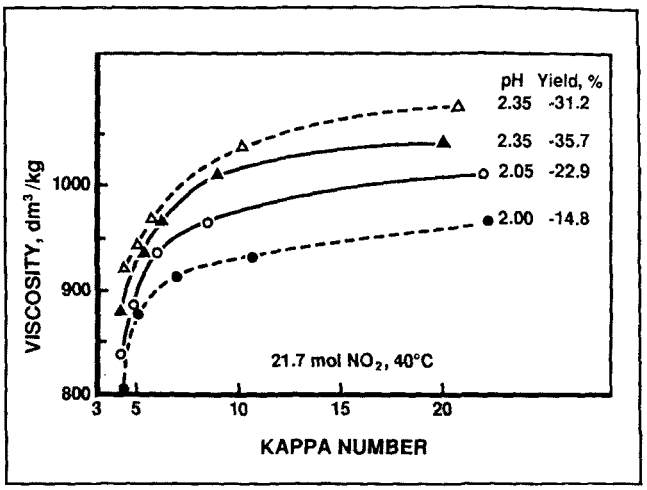
The greatly enhanced selectivity gained by using a small reactor volume in pretreatments with larger amounts of $NO_2 + HNO_3$ are illustrated also in **Figs. 6 and 7**. Again, the improved selectivity was obtained at the expense of an increased consumption of nitric acid reflected in decreased yields of acid titrated to pH 3.5.

Duration of the NO_2 treatment before dilution

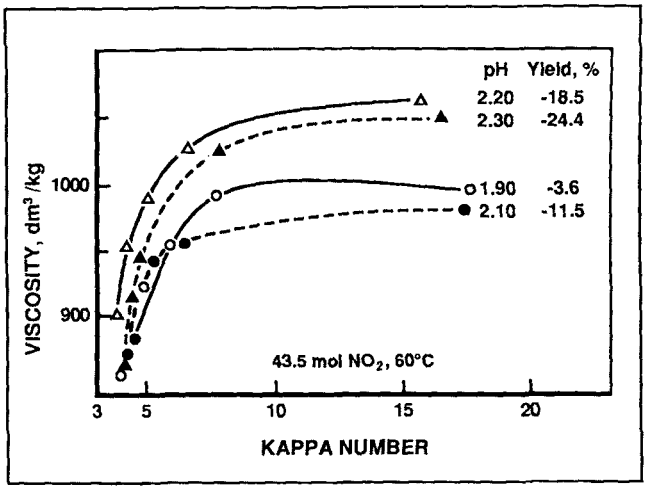
In all pretreatments reported so far, the diluent was introduced 15 min after the addition of NO_2. Parallel treatments in which this initial period was shortened to 3 min showed that the shortened time led to a loss in viscosity after pretreatment (Figs. 6–7). This result holds true both for pretreatment in the 1240-mL and in the 3360-mL reactor with additions of either 21.7 mol or 43.5 mol NO_2. The loss in viscosity can be ascribed at least in part to an increased acid hydrolysis of the cellulose as a result of higher acidity during pretreatment.

The highest selectivity was obtained after oxygen bleaching following pretreatment with 43.5 mol NO_2 for 15 min at 60°C in the small reactor before dilution from 27% to 8% consistency. In this experiment, a kappa number of 4.2 was obtained at an intrinsic viscosity of 950 dm^3/kg. In the experiments with the larger reactor given in Fig. 7, the curves representing viscosity vs. kappa number intersected.

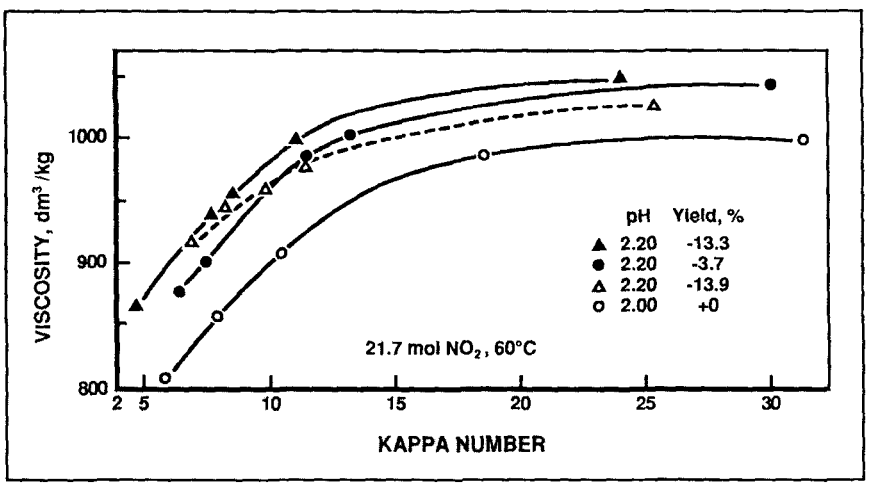
6. The influence of the volume of the pretreatment reactor and the duration of NO_2 treatment at 27% consistency [53.1 mol of free HNO_3; dilution to 8% consistency after 3 min (filled symbols) or after 15 min (open symbols).] Δ ▲ 1240-mL reactor; O ● 3360-mL reactor.



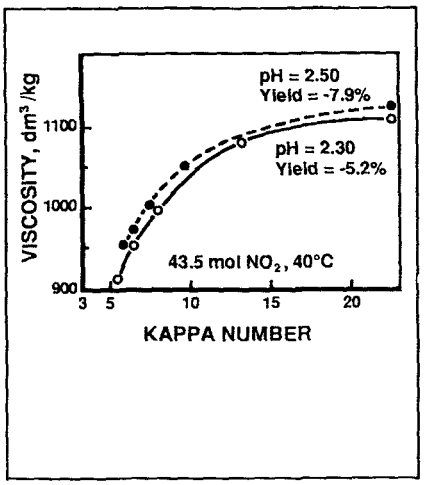
7. The influence of the volume of the pretreatment reactor and the duration of NO_2 treatment at 27% consistency [47.3 mol of free HNO_3; dilution to 8% consistency after 3 min (filled symbols) or after 15 min (open symbols).] Δ ▲ 1240-mL reactor; O ● 3360-mL reactor.



9. The influence of the duration of NO_2-treatment at 27% consistency in a 1240-mL reactor [Dilution to 8% consistency after 3 min (filled symbols) or after 30 min (open symbols).] O ● 22.0 mol free HNO_3; Δ ▲ 33.0 mol free HNO_3.



8. The influence of the duration of NO_2-treatment at 27% consistency in a 1240-mL reactor [Free HNO_3: 22.1 mol. Dilution to 8% consistency after 3 min (filled symbol) or after 15 min (open symbol).]



Comparable experiments in **Fig. 8** and Fig. 5 confirm that adding less nitric acid resulted in a less extensive delignification, a loss in selectivity, and a decreased consumption of acids titrated to pH 3.5. Interestingly, the effects of the duration of the treatment at high consistency on selectivity and acid consumption were reversed compared to those obtained after ripening with a larger addition of HNO_3 in the diluent (Figs. 6-7). With the low addition, a slightly higher selectivity and consumption of strong acid was obtained when the diluent was added already after 3 min instead of 15 min. The results indicate that the higher concentration of NO_2 in the gas phase after 3 min than after 15 min (*8*) promoted the generation process significantly during the ripening in the liquor with the lowest initial concentration of nitric acid.

Experiments with another batch of kraft pulp (kappa number 26.1 and intrinsic viscosity 11.93 dm^3/kg) confirmed that when less free HNO_3 was added in the diluent before ripening, an increased duration of the preceding NO_2 treatment at 27% consistency resulted in a loss in selectivity (**Fig. 9**). As can be seen, the kappa numbers after the pretreatments with the addition of 22.1 mol of free HNO_3 were much higher than that of the unbleached pulp. Evidently, lignin precipitated from the black liquor was not dissolved during the washing with water and with 0.2*M* $NaHCO_3$ carried out before the analysis of the pretreated pulp (*5*).

An increased addition of free HNO_3 to 33.0 mol gave rise to lower kappa numbers after pretreatment and a significantly improved selectivity, explained by an enhanced generation of active nitrogen oxides and reflected in markedly lowered yields of acids

titrated to pH 3.5. As expected from the results with the other kraft pulp, the influence of the duration of the initial treatment at 27% consistency was small at this acidity.

Concluding remarks

An extensive delignification of kraft pulp without severe depolymerization of the cellulose was achieved by the S3 process when the pulp entering the NO_2 treatment contained large amounts of dissolved lignin and black liquor. The additions retarded the delignification of the pulp. Nitrated lignin had less effect than kraft lignin. The consumption of NO_2 by added lignin, alkali, and sulfur compounds was compensated for by adding nitric acid in the diluent. Added acid also was consumed in autocatalytic lignin reactions giving rise to the generation of active nitrogen oxides. Extensive delignification was not obtained unless their partial pressures exceeded a threshold value necessary for a massive generation during ripening. This explains why delignification by treatments in reactors with a small gas volume is superior to delignification carried out in excessively large reactors. Moreover, a small gas volume during pretreatment led to suppressed losses in viscosity both during the pretreatment and after the subsequent oxygen bleaching.

As shown previously (*8*), the partial pressure of NO_2 (including N_2O_4 and N_2O_3) decreases rapidly to a low level during NO_2 treatment of kraft pulp unless the conditions favor its generation from produced or optionally added nitric acid. A lower partial pressure explains the inferior selectivity after an initial treatment for 15 min or 30 min before the addition of a diluent containing a low amount of nitric acid, as compared to the selectivity obtained when the initial treatment was terminated by adding the diluent already after 3 min.

When a large amount of nitric acid was added to the diluent, the influence of the duration of the initial treatment at high consistency was reversed. This indicates that the threshold value decreased with increasing concentration of hydrogen and nitrate ions during the ripening. Working conditions that favor the generation of NO_2 from produced and added HNO_3 are strongly recommended during NO_2 treatments of pulps contaminated with spent cooking liquors.

Experimental procedures

Never-dried kraft pulps from softwood (mainly *Pinus sylvesteris*) produced in a Swedish pulp mill were washed with water. The pulps used in the pretreatments with lignin addition had a kappa number of 32.2 and an intrinsic viscosity of 1220 dm^3/kg.

For the pulp used in the black liquor experiments, the corresponding values were 28.5 and 1202. Black liquor or lignin dissolved in NaOH (1.47 mol/kg lignin) was impregnated into the pulp so that the desired consistency was obtained. If not stated otherwise, the reactor loading corresponded to 45 g of dry unbleached pulp.

The NO_2 treatments with added lignin were carried out as described in a previous study on the effect of spent bleach liquor (*5*).

In the pretreatments with black liquor present, the cooling before the introduction of the diluent was omitted. The temperature of the diluent was the same as that prevailing during the initial period.

The heating time from the initial to the final temperature was 45 min. If not stated otherwise, the amount of $NaNO_3$ in the diluent was chosen so that 0.28 mol/kg of water was present in the final pulp suspension.

Both types of experiments were terminated by cooling with ice-water and introducing oxygen to atmospheric pressure. After shaking to dissolve water-soluble compounds, the pulp was separated from the spent liquor, washed with water, and subjected to oxygen bleaching as described previously (*5*). Kappa number and intrinsic viscosity were determined according to SCAN.

The addition of free nitric acid is defined in the lignin experiments as the total addition minus the amount neutralized by the ash constituents in the pulp and by the added NaOH. In the pretreatments with added black liquor, the titratable alkali was used instead of added NaOH. The amount was determined by acidifying the liquor and boiling to remove H_2S, CO_2, and other volatile compounds. The solution was titrated with 0.1 *M* HCl to pH 7 until no appreciable consumption occurred when the boiling was continued for another 5 min. The reported yield of acids at pH 3.5 is equal to the consumption of NaOH found by titrating the spent pretreatment liquor to pH 3.5, minus the addition of free nitric acid.□

Literature cited

1. Samuelson, O., Research Disclosure, March 1988, p. 165.
2. Samuelson, O., Proceedings 1983 Intern. Symp. on Wood and Pulping Chemistry, Japanese Tappi, Tsukuba Science City.
3. MacLeod, M., Tappi J. 71(7): 216(1988).
4. Samuelson, O. and Ojteg, U., J. Pulp Paper Sci. 13(5): J150 (1987).
5. Samuelson, O. and Ojteg, U., Nordic Pulp Paper Res. J. 3(4): 203(1988).
6. Samuelson, O. and Ojteg, U., Nordic Pulp Paper Res. J. 1(3): 26(1986).
7. Samuelson, O., proceedings of the 1985 Intl. Symposium on Wood and Pulping Chemistry, CPPA, Montreal, 1985, p. 127.
8. Engstrom, T. and Samuelson, O., Svensk Papperstid. 86(15): R173(1983).

Sponsored by the Cellulosaindustriens Forskningsstiftelse, The National Swedish Board of Technical Development and Mo and Domsjo AB.

Received for review May 15, 1989.

Accepted June 6, 1989.

Presented at the TAPPI 1989 International Wood Pulping Conference.