

SUPPRESSION OF UNDESIRABLE CARBOHYDRATE REACTIONS DURING OXYGEN BLEACHING OF WOOD PULP

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Abstract - Free radicals produced in lignin reactions lead to a depolymerization of carbohydrates during oxygen bleaching. A loss of carbohydrates occurs in consecutive reactions which start at reducing sugar end groups. The fact that the depolymerization is suppressed by magnesium compounds, formaldehyde and phenylenediamines supports this scheme. A dramatic protection of the carbohydrates is obtained by pretreatment of the pulp with nitrogen dioxide and oxygen in acid medium. Lignin reactions during the pretreatment are responsible for the retarded depolymerization of carbohydrates during the subsequent oxygen bleaching.

INTRODUCTION

Cellulose and other polysaccharides present in wood are depolymerized and modified with regard to their structure during conventional pulping processes. When pulps are produced from softwood by kraft cooking followed by bleaching the cooking is usually interrupted when the pulp has a lignin content of 4-5%. The remainder is removed by bleaching. After bleaching with chlorine and chlorine dioxide the spent bleach liquor cannot be recovered and burned in conventional systems for recovery of chemicals and for energy production from the spent cooking liquor. The reason is that severe corrosion occurs unless very expensive materials are used. Toxic and mutagenic compounds are produced and the influence in aquatic systems of the major component, the chlorinated high molecular weight lignin, is still incompletely known.

Another disadvantage with conventional bleaching is the high consumption of electric energy for the production of the chemicals used for bleaching. Bleaching with oxygen combined with burning of the spent liquor from this stage is now used for the major part of the bleached kraft pulp, produced in Sweden from softwood. Bleach plants with oxygen in the first stage are also in operation in other countries. Oxygen bleaching is carried out in the presence of sodium hydroxide. To avoid excess alkali in a system with effective recovery of sodium compounds, oxidized white liquor containing sodium hydroxide and thiosulfate as main constituents is employed.

A serious problem is that the cellulose molecules suffer a severe depolymerization during the oxygen bleaching. An appreciable loss in paper strength appears when the cellulose is depolymerized so far that a critical viscosity is reached. For kraft pulps from softwood subjected to oxygen bleaching this limit is often taken as 950 dm³/kg determined according to SCAN (Ref. 1). In conventional practice this limit is crossed when the lignin content is decreased by more than 40-50%. The remaining lignin is removed by treatments with chlorine, alkali and chlorine dioxide. With regard to environment and energy conservation it would be of outmost importance to increase the proportion of lignin removed in the oxygen stage. Suppression of the depolymerization of the cellulose and hemicellulose and some undesirable consecutive reaction is therefore a challenging problem.

CARBOHYDRATE REACTIONS

The depolymerization of the cellulose and hemicellulose in wood pulp during oxygen bleaching follows a well established scheme. As shown in Fig. 1 the cleavage of the macromolecules is a β -elimination resulting in the formation of one reducing sugar end group and one unsaturated sugar end group which is destroyed so rapidly that its structure has never been established experimentally. The cleavage is preceded by the introduction of a keto group at C-2 in the sugar units in the macromolecule (Ref. 2 & 3). A few research workers have been interested in suppressing the cleavage reaction. From a practical point of view this seems to be a difficult task. We and many other research groups have instead tried to suppress the oxidation which results in the introduction of

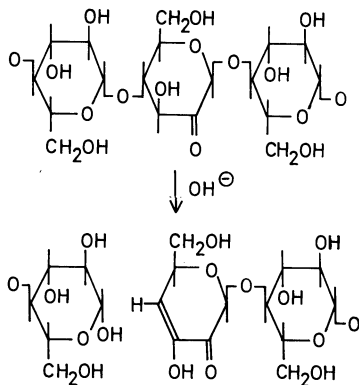


Fig. 1. Depolymerization of cellulose during oxygen bleaching.

the keto group. The main purpose of this paper is to elucidate various possibilities to suppress this oxidative depolymerization.

Since oxygen bleaching is carried out in alkaline medium the reducing sugar end groups are attacked by alkaline peeling. The aldose end group is isomerized to a ketose group. Subsequent β -elimination leads to the liberation of a new aldose end group and the formation of 4-deoxy-2,3-aldodiulose. The new reducing aldose group is isomerized and lost according to the same reaction route etc. Determinations of the number of molecules by osmotic measurements and end group methods show that the peeling can continue until the whole macromolecule has been brought into solution (Ref. 4).

Important stopping reactions which compete with the peeling reactions in the absence of oxygen are the formation of 3-deoxyaldonic (Ref. 5) and 2-C-methylglyceric (Ref. 6) acid end groups. The deoxyaldonic acid groups are formed by β -hydroxyelimination and benzilic acid rearrangement while the formation of 2-C-methylglyceric acid groups is initiated by Lobry de Bruyn - Alberda van Ekenstein rearrangement of the glucose end groups in cellulose which gives rise to terminal moieties having a keto group at C-3 (Fig. 2). A reverse aldol reaction results in a loss of C-6 and C-5 as glycolaldehyde. The ketose end group gives rise to elimination of the β -hydroxyl group at C-1 accompanied by the formation of an unstable dicarbonyl end group which is converted to a terminal 2-C-methylglyceric acid group by benzilic acid rearrangement.

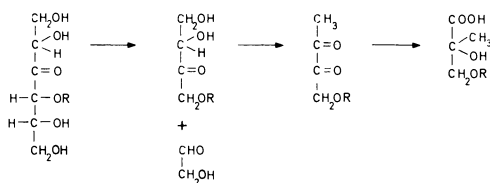


Fig. 2. Formation of 2-C-methylglyceric acid end groups in cellulose.

These desirable stopping reactions are suppressed by the presence of oxygen and are of limited importance during oxygen bleaching at high oxygen pressure. One important competing reaction is the oxidation of the reducing sugar end groups to aldonic acid end groups. This reaction is favored by a high oxygen pressure and seems to be the main explanation of the observation that, compared at any given viscosity of the pulp, the loss of carbohydrates decreases with an increased oxygen pressure. In strongly alkaline medium the reaction path via aldulosulose end groups predominates (Fig. 3). This dicarbonyl end group is subjected to benzilic acid rearrangement which gives rise to mannonic and gluconic acid end groups in the cellulose molecules. Fragmentation reactions which are favored by the presence of oxygen give rise to arabinonic and erythronic acid. In strongly alkaline medium arabinonic acid predominates (Ref. 7 & 8).

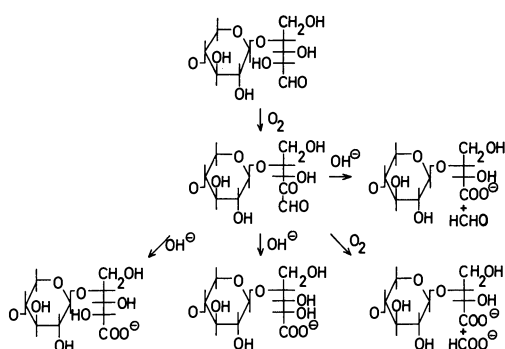


Fig. 3. Formation of lyxonic, xylonic and threonic acid end groups from a reducing xylose end group in xylan via pentosulose end groups.

Another peeling reaction leads to a loss of oxidized sugar end groups. The structure of the aldulosulose end groups in cellulose, glucomannan and xylan suggests that this end group or more correctly its 2,3-enediol, will give rise to a rapid β -elimination. Hence, a polysaccharide of DP = n will produce a reducing polysaccharide with a DP = n-1 and an intermediate containing three adjacent carbonyl groups. The reducing aldose end group in the polysaccharide can be oxidized to an aldulosulose end group, which is lost by the same reaction and gives rise to a polysaccharide of DP = n-2. Only one terminal sugar group can be lost according to this scheme unless oxygen is present. This type of repeated endwise degradation will therefore be called oxidative peeling (Ref. 9 & 10).

A reaction scheme illustrating the reactions of the tricarbonyl intermediate is shown in Fig. 4. It is based on alkali and oxygen-alkali treatments of O- β -D-glucopyranosyl-(1 \rightarrow 4)-D-arabino-hexosulose (Ref. 9) and oxygen-alkali treatments of 3-deoxy-erythro-pentose which is rapidly isomerized to 3-deoxypentulose. Analyses of spent liquors from oxygen-alkali treatments of hydrocellulose, cellulose, ivory nut mannan and xylan support this scheme (Ref. 10).

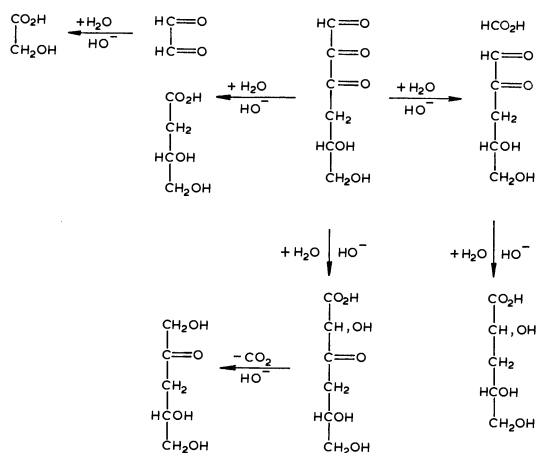


Fig. 4. Consecutive reactions of the tricarbonyl compound formed from arabino-hexosulose end groups in oxidized cellulose and glucomannan. Final products: 3,4-dihydroxybutanoic and glycolic acids; 3-deoxy-threo-pentonic, 3-deoxy-erythro-pentonic and formic acids. Isolated intermediate: 3-deoxypentulose.

CATALYSTS AND PROTECTORS

About 15 years ago we intended to study the formation of end groups in cellulose subjected to oxygen bleaching. To simplify the analyses the experiments were made with carefully purified cotton. Following Robert, Traynard and Martin-Borret (Ref. 11) magnesium carbonate was added to protect the cellulose. Although high consistency, high temperature and oxygen of superatmospheric pressure were used no formation of carboxylic acid groups was observed. Instead a lowered proportion of 4-O-methylglucuronic acid derived from traces of hemicellulose was observed. The change in viscosity was negligible. Hence, no significant depolymerization occurred by the direct reaction between oxygen molecules and pure cellulose. Since a kraft pulp suffered a severe depolymerization when subjected to the same treatment it was evident that the depolymerization of the cellulose was initiated by other compounds present in kraft pulp. Accordingly, addition of either kraft lignin or traces of iron, cobalt or copper compounds to the purified cotton led to a severe depolymerization (Ref. 12).

The results show that intermediates from reactions in which oxygen is involved are responsible for the oxidative depolymerization along the polysaccharide molecules. Expected intermediates are peroxides the presence of which has been well established (Ref. 12). The peroxide concentration in the solution is higher in experiments carried out in the presence of magnesium compounds than in their absence (Ref. 12). The increased peroxide level (Ref. 13) and the protective effect of magnesium compounds (Ref. 14 & 15) depend at least mainly on a coprecipitation with magnesium hydroxide of trace metals. When no magnesium compounds are present the trace metals decompose peroxide and give rise to free radicals. The results suggest that direct reactions between peroxides and the secondary hydroxyl groups along the polysaccharide chains cannot be mainly responsible for the formation of the keto groups which precedes the depolymerization.

The results are consistent with the reaction scheme suggested by Entwistle, Cole and Wooding (Ref. 16) for the aging of alkali cellulose which is an autooxidation by air of cellulose impregnated with approximately 5 M sodium hydroxide. According to this scheme the polysaccharides are attacked by free radicals produced by decomposition of peroxides in reactions catalyzed by transition metal compounds. Additional support for this scheme is obtained by the observation that addition of formaldehyde which leads to a decomposition of hydrogen peroxide under formation of hydrogen and formate anions results in a greatly suppressed depolymerization both in the absence and presence of magnesium compounds (Ref. 17).

Another more recent observation which supports this reaction scheme is that aromatic diamines, e.g. phenylenediamines protect the carbohydrates against depolymerization and that an appreciable protection is obtained even when magnesium compounds are added. The results indicate that the diamines serve as radical scavengers. Some results illustrating the influence of the three isomeric phenylenediamines (0.2 g per liter) is shown in Fig. 5. Magnesium sulfate corresponding to 0.05 g of magnesium per liter was added in all experiments.

The observation that lignin can initiate the depolymerization of the carbohydrates leads to the conclusion that the autooxidation of the carbohydrates and lignin during the oxygen bleaching are interrelated (Ref. 12 & 18) and that free radicals generated in lignin reactions attack the carbohydrates and *vice versa*. Additional evidence is the observation that not only the carbohydrate reactions but also the delignification is retarded markedly by additions of magnesium compounds, formaldehyde and phenylenediamines. Conflicting results have been reported regarding the effect of magnesium compounds. This can be explained by the presence of different proportions of transition metals in the pulps and to differences in pH during the treatment. According to our experience the delignification is retarded in all oxygen-alkali treatments of wood pulp in which an appreciable proportion of magnesium hydroxide has remained undissolved throughout the process. It is essential that a protector has a much larger effect on the depolymerization of the carbohydrates than on the delignification i.e. that an increased selectivity, defined as viscosity at a given lignin content, is obtained. In practice the lignin is conveniently determined by permanganate titration and reported as kappa number. For the pulps discussed in this paper the percentage of lignin in the pulp is approximately equal to the kappa number multiplied by 0.15.

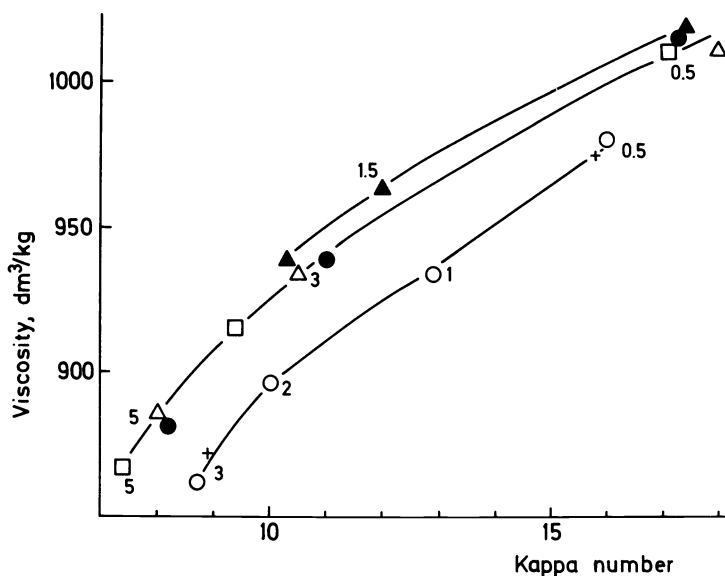


Fig. 5. Influence of phenylenediamines on the relationship between intrinsic viscosity and kappa number after oxygen bleaching in 0.05 M NaOH at 0.7 MPa, 106°C and 1% consistency of a kraft pulp (kappa number 34.3; intrinsic viscosity 1233 dm³/kg). Values given in the diagram refer to bleaching time (hr).

○ No addition
 □ m-Phenylenediamine
 ▲ Spent liquor after bleaching at 2% consistency with 0.4 g o-phenylenediamine per litre
 + Nitrobenzene, 2 g/l
 ● o-Phenylenediamine
 △ p-Phenylenediamine

(K. Abrahamsson and O. Samuelson, unpublished work.)

TRANSITION METAL COMPOUNDS

Although transition metal compounds present during oxygen-alkali delignification exert dramatic effects both on the delignification rate and on the reaction rates of the carbohydrates our knowledge about their action is still very limited. One reason is that conventional oxygen bleaching at high consistency is started at a pH of approximately 13 and that the pH decreases to approximately 9 during the treatment. Complexing agents such as various hydroxy acids are formed during the treatment. For these reasons different metal compounds can be present during different stages of the oxygen bleaching. Another difficulty is that the influence of one metal depends on the presence of other metals. Moreover, the effect can change from catalysis to retardation dependent on the concentration of a metal compound. It is therefore difficult to draw any general conclusions about the effect of the catalytic and retarding effects of the transition metals of interest.

As an example it can be mentioned that manganese salts catalyze the delignification of wood by oxygen-alkali treatment in hydrogencarbonate medium at a pH of 7.5-8. Another beneficial effect of manganese in this process is that the depolymerization of the carbohydrates is retarded (Ref. 19). This is an exceptional behavior since in general additions which protect the carbohydrates lead to a retarded delignification. During aging of alkali cellulose a small addition of manganese increases the depolymerization rate of the cellulose, an effect which has been utilized industrially, while a large addition has a retarding effect (Ref. 16). During oxygen bleaching in sodium hydroxide with magnesium sulfate as protector a kraft pulp soaked with sulfurous acid and complexing agents suffered a severe loss in selectivity by 130 ppm of manganese added as manganese sulfate. The soaked pulp contained 3 ppm of manganese. On the other hand the same addition gave rise to a slightly improved selectivity in a parallel experiment with the unsoaked pulp which contained 137 ppm of manganese (Ref. 20). With other unsoaked pulps a loss in viscosity has been observed as a result of the addition of manganese.

NO₂/O₂ PRETREATMENT

Theoretically it should be possible to suppress the depolymerization of the carbohydrates by a pretreatment which modifies the carbohydrates or the lignin before the oxygen-alkali stage. Several types of treatments are possible but our research has been restricted to treatments resulting in spent liquors which can be evaporated and burned together with the black liquor in conventional mills for production of kraft pulp. The most successful results were obtained by pretreatment with nitrogen dioxide together with pure oxygen.

Pretreatment of wood pulp with nitrogen dioxide or with a mixture of nitric oxide and nitrogen dioxide before oxygen bleaching has been described in patents by Yethon (Ref. 21). A large quantity of nitrogen oxides was present in the reactor at the end of the treatment. Our investigations showed that nitric oxide which is formed in large proportion as an intermediate is virtually inert (Ref. 22) and that oxygen, when introduced in excess, leads to larger improvements than those expected from the reoxidation of nitric oxide to nitrogen dioxide. An increased delignification is obtained by this pretreatment with nitrogen dioxide and oxygen under conditions of interest for practical application. The most striking effect is, however, the protection of the carbohydrates during the subsequent oxygen bleaching reflected in a suppressed rate of depolymerization of the carbohydrates in this stage. Both factors together contribute to a dramatic increase in selectivity provided that proper conditions are chosen (Ref. 22-24).

The protector effect can be illustrated by plots of intrinsic viscosity versus duration of the oxygen-alkali treatment. In the example shown in Fig. 6 a kraft pulp from softwood, mainly Scots pine was pretreated under so severe conditions that the intrinsic viscosity dropped by 12% in this stage. As shown in the figure the curves representing the pretreated pulp and the blank without pretreatment intersected after 80 min. On prolonged treatment the highest viscosity was observed for the pretreated pulp. In addition the lignin contents were lower for the pretreated pulp than for the untreated compared at the same duration of the oxygen-alkali treatment. After four hours in this stage the degree of delignification was 80% for the pretreated pulp compared to 55% in the blank without pretreatment.

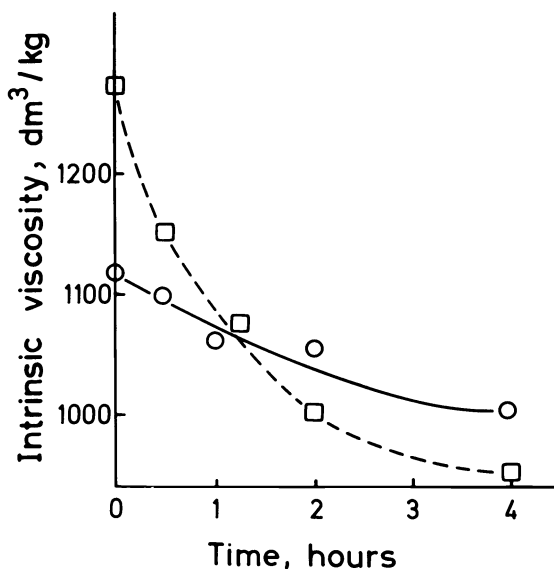


Fig. 6. Intrinsic viscosity (dm³/kg) versus duration of the oxygen bleaching at a partial pressure of oxygen of 0.23 MPa, 116°C and 10% consistency in the presence of 4% NaOH and 0.5% Mg. Initial kappa number of the kraft pulp:36.

□ No pretreatment

○ NO₂/O₂ pretreatment at 51°C and 37% consistency with 4% NO₂ for 60 min

(O. Samuelson and L.-A. Sjöberg, unpublished work.)

POLYMER REACTIONS

Glucomannan, which is the predominant type of hemicellulose in softwood, contains reducing mannose and glucose end groups. Approximately 30% of these groups were oxidized to mannonic, gluconic, arabinonic and erythronic acid end groups when spruce meal was pretreated with nitrogen dioxide and oxygen. On the other hand no cellobionic acid was found in model experiments, with cellobiose nor was there any appreciable formation of aldonic acid end groups when hydrocellulose was subjected to the same treatment. These results suggest that nitrogen dioxide cannot oxidize reducing sugar end groups to terminal aldonic acid end groups while active intermediates with this ability are formed during the pretreatment by reactions with the lignin in wood (Ref. 25).

In kraft pulps from softwood which have been used most extensively in our studies of oxygen bleaching of pretreated pulp, only a small proportion of the polysaccharide molecules contains reducing end groups which can be determined after hydridoborate reduction to the corresponding alditols. The unbleached pulp referred to in Table 1 contained a fairly large number of aldonic acid end groups due to the fact that it was prepared without steaming of the wood or other precautions to exclude air. Pretreatment at 55°C for 15 min led to an appreciable depolymerization of the carbohydrates reflected in a loss in viscosity and an increased number of aldonic acid end groups. The proportions of individual aldonic acids indicated that the reaction mechanism was related to that responsible for the oxidation of reducing end groups in wood.

TABLE 1. Influence of the duration of pretreatment with 4% NO₂ at 55°C on the number of reducing sugar end groups and aldonic acid end groups

	Untreated	15 min	130 min
Intrinsic viscosity, dm ³ /kg	1246	1140	1016
Loss in yield, % by weight	-	1	2
Glucose, mmol/kg pulp	0.3	0.23	0.52
Mannose, mmol/kg pulp	0.1	0.15	0.42
Xylose, mmol/kg pulp	0.3	0.44	0.90
Aldonic acids, mmol/kg pulp	4.2	8.7	5.7

(S.-I. Andersson and O. Samuelson, unpublished work)

When the pretreatment was extended to 130 min the pulp suffered a severe depolymerization reflected in a large loss in viscosity and in the formation of reducing sugar end groups. The increased number of these groups indicates that the depolymerization was due to acid hydrolysis. This was confirmed by determination of the nitric acid formed during the pretreatment and acid hydrolysis of the untreated pulp under comparable conditions after impregnation with hydrochloric acid of the same concentration. The number of aldonic acid end groups decreased on prolonged pretreatment which is explained by a loss of hemicellulose and of aldonic acid end groups by acid hydrolysis. Arabinonic, erythronic and glyceric acids were the major aldonic acids present both as end groups and in the spent liquor from the pretreatments indicating that C-1 and C-2 were lost in a large proportion of the terminal sugar moieties. Arabinose was the predominant monosaccharide in the liquor. The amount corresponded to 0.2% of the weight of the untreated pulp after treatment for 130 min at 55°C which is a more severe treatment than that which gives an optimum selectivity.

A well-known cellulose reaction during the treatment of dry cellulose with nitrogen dioxide is the introduction of uronic acid groups (at C-6). During pretreatment conditions of actual interest with pulps containing 50% or more of water, no formation of uronic acids was obtained. Our studies indicate that only slight amounts of nitrogen dioxide and oxygen were consumed in the carbohydrate reactions.

Reducing sugar end groups in wood pulp are known to promote the depolymerization during the aging of alkali cellulose. Treatments of the pulp which decrease their number can be used to suppress the depolymerization (Ref. 16). Similarly, a small amount of glucose serves as an effective initiator during oxygen-alkali treatment of cellobiitol (Ref. 26). A prolonged pretreatment of kraft pulp at high temperature which gives rise to a dramatic increase in the number of reducing sugar end groups, results in a very slow depolymerization of the carbohydrates during the subsequent oxygen-alkali treatment, i.e. to an effective

protection of the carbohydrates. It is therefore evident that the carbohydrate reactions during the pretreatment cannot be responsible for this protection.

Evidently, the acid hydrolysis of the carbohydrates which occurs during the pretreatment is an undesirable side reaction which limits the possibilities to utilize severe conditions during the pretreatment. A study of the reaction parameters during the pretreatment showed that the protection effect increased with an increased addition of nitrogen dioxide, temperature, duration and pulp consistency during the pretreatment (Ref. 22-24 & 27). All these changes promote the acid hydrolysis. A compromise must therefore be made so that the viscosity is not decreased so far before the oxygen-alkali stage that the losses in strength properties are too large and that the peeling reactions will lead to a severe loss in yield. It can also be mentioned that the same factors lead to an improved delignification after the oxygen bleaching. The only exception observed is that an extremely high consistency (50%) led to a suppressed delignification in experiments with low addition of nitrogen dioxide (1%). Both the delignification and the protection are improved when the pulp is impregnated with dilute nitric acid before the pretreatment. The nitric acid is kept at such a low concentration that virtually no effect is obtained unless nitrogen dioxide was added (Ref. 24 & 28).

Metal compounds present in the pulp were dissolved in the nitric acid formed during the pretreatment. A large proportion was removed during the subsequent washing with water. This led to a large decrease in the depolymerization rate during the oxygen bleaching for pulps containing a large proportion of copper. Experiments in which the pretreatment was replaced by soaking with nitric acid showed that with most industrial pulps the influence on reaction rates and selectivity was small compared to that obtained when the oxygen bleaching (carried out in the presence of magnesium protector) was preceded by a pretreatment with nitrogen dioxide and oxygen.

The most likely explanation of the protection effect is therefore that the lignin is modified during the pretreatment with nitrogen dioxide and oxygen so that the proportion of active intermediates which attack the carbohydrates during the subsequent oxygen-alkali stage is lowered. Studies of the consumption of nitrogen dioxide and nitric oxide (Fig. 7) show that the consumption during an initial period is very rapid both with cotton and with unbleached pulp. The last few percent of the added amount were, however, consumed much more slowly by the unbleached pulp than by the cotton or bleached pulp. With lignin-free fibers nitric acid was the predominant reaction product. The reaction rates decreased

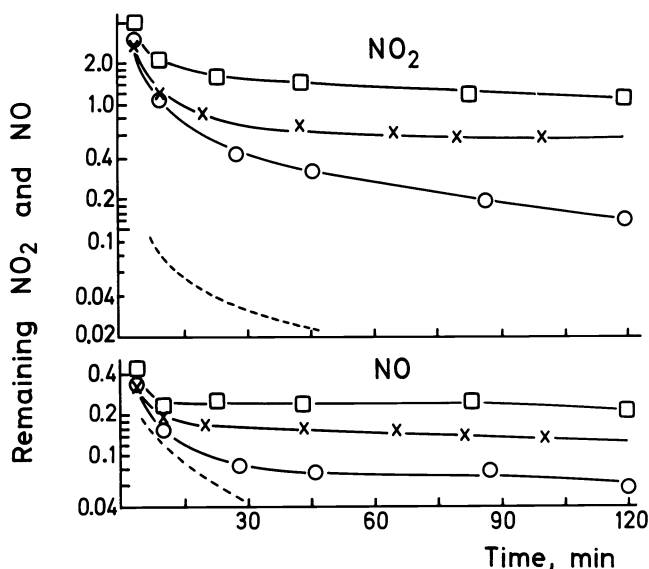


Fig. 7. Nitrogen dioxide and nitric oxide in the gas phase calculated as a percentage (by mole) of the added nitrogen dioxide (4% on dry pulp) after pretreatment of kraft pulp (50 g dry weight) at a consistency of 41% in a 2 liter reactor.

○ 25°C; × 54°C; □ 68°C

The dashed line refers to an experiment with purified cotton at 54°C.

(T. Engström and O. Samuelson, unpublished work.)

with an increasing temperature. For cotton and bleached pulp this is explained by the negative temperature coefficient for the reaction between nitric oxide and oxygen. The extremely slow consumption of the nitrogen oxides during prolonged pretreatment of unbleached pulp is due to lignin reactions. In the absence of oxygen prolonged treatment gave rise to a small proportion of nitric oxide whereas during NO_2/O_2 pretreatment oxygen was consumed for oxidation of lignin even after 98% or more of the added nitrogen dioxide had been converted to products other than nitric oxide. The prolonged pretreatment results in a slower depolymerization of the carbohydrates during a subsequent oxygen bleaching.

This protective effect of the modification of the lignin was most clearly demonstrated by experiments in which the unbleached pulp was first pretreated at ambient temperature for 15 min so that the nitrogen dioxide and nitric oxide were consumed virtually completely. A subsequent treatment at 50°C for 30-60 min led both to a large consumption of oxygen and to a greatly improved protection of the carbohydrates. Both effects decreased dramatically, if the nitric acid formed during the first treatment period was washed out before heating the pulp.

The improvement gained by the presence of nitric acid can be related to the observation that the concentration of nitrogen dioxide in the gas phase decreased more slowly when the pulp was impregnated with nitric acid before the pretreatment than for pulps which contained only the nitric acid formed in this stage (Fig. 8). Recent investigations show that nitric acid was consumed during the pretreatment. The improved delignification obtained after pretreatment with addition of nitric acid and an increased formation of methanol during this stage indicate that the nitric acid has a great influence on the lignin reactions during NO_2/O_2 pretreatment. The results support the conclusion that the modification of the lignin has a decisive effect on the depolymerization of the carbohydrates. From a practical point of view the recirculation of the nitric acid and nitrate produced in the process can be applied to suppress the consumption of nitrogen dioxide required for the pretreatment.

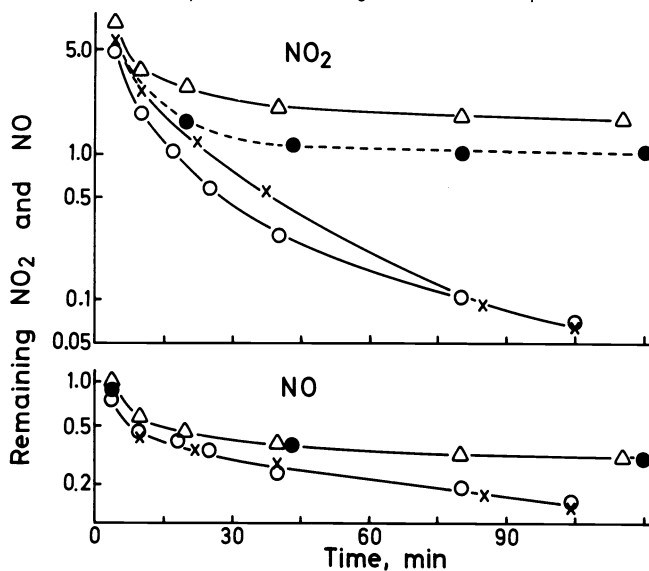


Fig. 8. Nitrogen dioxide and nitric oxide in the gas phase calculated as a percentage (by mole) of added nitrogen dioxide (2% on dry pulp) after pretreatment of kraft pulp (50 g dry weight) at 54°C and a consistency of 34% in a 2 liter reactor.

○ No addition; △ 0.4 M HNO_3 ; ● 1.2 M NaNO_3 ; × 0.4 M HCl
(T. Engström and O. Samuelson, unpublished work.)

OXYGEN BLEACHING AFTER PRETREATMENT

More than 80% of the lignin present in a kraft pulp can be removed without serious loss in viscosity by a pretreatment with nitrogen dioxide and oxygen under severe conditions followed by a hot alkali treatment in the absence of oxygen. Due to the loss of polysaccharides of low molecular mass by alkaline peeling an increased viscosity is often obtained in the hot alkali stage (Ref. 24 & 29). No economically feasible method is available which permits an effective stabilization of the carbohydrates before or during a hot alkali treatment. As already mentioned oxygen-alkali treatment leads to an oxidation of reducing end groups to aldonic acid end groups. These stabilize the carbohydrates

against endwise degradation. A main reason why oxygen bleaching is preferred to hot alkali treatment is that a higher yield of carbohydrates is obtained when oxygen is present.

During oxygen bleaching of pretreated pulp both the delignification rate and the rate of depolymerization of the carbohydrates increase markedly with an increased oxygen pressure. Interestingly, an improved selectivity is obtained when a lower oxygen pressure is applied than that used during conventional oxygen bleaching (Ref. 23). The largest effect on the selectivity of a decreased pressure is obtained when the concentration of sodium hydroxide is high i.e. under conditions which give rise to a very rapid delignification. On the other hand a lowered oxygen pressure leads to decreasing yields of carbohydrates (Ref. 29). This can be ascribed mainly to a slower oxidation of the reducing sugar end groups to terminal aldulose groups which are rapidly converted to aldonic acid groups. In fact the loss in viscosity can, when pretreatment followed by oxygen bleaching is applied, be a less intricate problem than the loss of carbohydrates. A compromise has to be made in practice so that a high yield is obtained without serious depolymerization of the carbohydrates. One method is a pretreatment followed by an alkali treatment, which starts at low oxygen pressure or as a hot alkali treatment and is continued at a higher oxygen pressure in the presence of the same sodium hydroxide solution (Ref. 24).

Determinations of the oxygen consumption during the oxygen-alkali stage showed that the proportion required for a decrease in kappa number from 36 to 16 was 20 kg per 1000 kg of an untreated kraft pulp compared to 5 kg for the same pulp pretreated with 4% nitrogen dioxide and oxygen. The saving is larger than the consumption of oxygen during the pretreatment. An additional decrease in oxygen consumption was obtained when the pulp was first treated with alkali in the absence of oxygen for 1 hour before oxygen was brought into contact with the pulp (Ref. 24). The observations that both the nitrogen dioxide-oxygen pretreatment and the intermediate hot alkali treatment led to an improved selectivity suggest that the proportion of aggressive intermediates which are produced during the oxygen-alkali stage and attack the carbohydrates, decreases with a suppressed oxygen consumption in this stage. The results support the theory that free radicals formed during the autoxidation of both lignin and carbohydrates are responsible for the depolymerization of the cellulose and hemicellulose during oxygen bleaching. When proper conditions are chosen during the NO_2/O_2 pretreatment and the subsequent oxygen-alkali stage about 80% of the lignin can be removed from conventional kraft pulps without serious depolymerization and losses of carbohydrates.

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