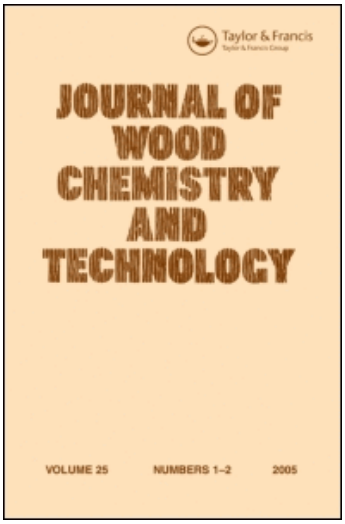

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Anna-Stiina Jääskeläinen[ab]; Tarja Tapanila[a]; Kristiina Poppius-Levlin[a]
[a] KCL, Espoo, Finland [b] Pulp and Paper Research Centre, McGill University, Montreal, Quebec, Canada

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CARBOHYDRATE REACTIONS IN PEROXYACETIC ACID BLEACHING

Anna-Stiina Jääskeläinen*, Tarja Tapanila and Kristiina Poppius-Levlin
KCL
P.O. Box 70, FIN-02151 Espoo, Finland

ABSTRACT

The process parameters affecting peroxyacetic acid delignification, i.e. temperature, pH and chemical charge, were studied in relation to their effect on carbohydrate depolymerization and dissolution for a softwood kraft pulp. Carbohydrate reactions were found to follow different paths in different pH regions. At low pH, acid hydrolysis was probably the main reason for carbohydrate depolymerization and dissolution. At neutral pH, however, carbohydrate depolymerization was probably caused by the decomposition products of peroxyacetic acid. Peroxyacetic acid may also react with dissolved monosaccharides to form aldonic acids with corresponding and shorter carbon chain lengths as well as aldoses with shorter carbon chains. These reactions were verified through model compound studies. Because of these reactions the amount of carbohydrates in spent liquor is not equal to that removed from pulp fibres during the treatment. These side reactions also consume a small amount of peroxyacetic acid during pulp bleaching.

*Present address: Pulp and Paper Research Centre, McGill University
3420 University Street, Montreal, Quebec, Canada H3A 2A7

INTRODUCTION

The bleaching agents most commonly used in totally chlorine-free (TCF) pulp bleaching are oxygen and peroxide. These chemicals cannot remove all lignin from pulp fibres, and hence a more effective bleaching agent is needed. This is why ozone is often included in TCF bleaching sequences as a delignification agent. Ozone may, however, break down to form other reactive species, such as hydroxyl radicals,[1] which can react with carbohydrates and cause their depolymerization.[2] Depolymerization, in turn, causes yield loss and loss of pulp strength.

Nowadays, one of the most promising alternatives to ozone is peroxyacetic acid, an agent capable of producing a high degree of delignification. Peroxyacetic acid is more selective towards lignin than ozone because it does not depolymerize carbohydrates to the same extent.[3,4] Transition metals, however, catalyse peroxyacetic acid degradation[5] and the reaction products may include cellulose-degrading radicals. Removing most of the transition metals is therefore important for successful peroxyacetic acid delignification. However, in spite of metal removal, some carbohydrate reactions may occur and cause depolymerization and dissolution of carbohydrates in the peroxyacetic acid stage.[4]

The process variables influencing the delignification rate of kraft pulp during peroxyacetic acid treatment are temperature, pH and peroxyacetic acid charge.[6] An increase in any of these parameters increases the delignification rate. In this work, the effect of these process variables on pulp carbohydrates was studied. Changes in the carbohydrate chain length and the content and composition of dissolved carbohydrates were investigated. The reaction of peroxyacetic acid with a carbohydrate monomer (glucose) was also studied in order to explain the reactions of dissolved carbohydrates with peroxyacetic acid.

EXPERIMENTAL

Materials

The pulp used in these experiments was a laboratory-cooked and oxygen-delignified SuperBatch pine (*Pinus sylvestris*) kraft pulp, provided by Western Laboratories Inc., Rauma, Finland. The same initial pulp has been used in some previous studies.[6, 7, 8] The pulp was chelated with Na_4-EDTA (charge 0.2% on pulp) at pH 4.5 and 90°C for 60 min and then carefully washed with distilled water, centrifuged to 35% consistency, homogenized and stored at 4°C until used. Distilled peroxyacetic acid (containing 350 g/L peroxyacetic acid and less than 10 g/L hydrogen peroxide) was kindly provided by Finnish Peroxides Inc., Voikkaa, Finland.

Peroxyacetic Acid Treatments

The conditions for the peroxyacetic acid delignifications followed the experimental design shown in Table 1. Peroxyacetic acid treatments were performed by preheating the pulp, water and acetic acid or NaOH solution (used to adjust pH) separately to the delignification temperature so that heat transfer could be neglected. Distilled peroxyacetic acid was added to the preheated water and then mixed into the pulp with acetic acid or NaOH solution. The pH was measured every 2 to 15 min during delignification and some NaOH solution was added if the pH had fallen. After delignification for 5, 10, 20, 45, 90 and 180 min the pulp was filtered in a Büchner funnel. The filtrate was retained and the pulp was washed twice with hot and twice with cold distilled water.

Analytical Procedures

Viscosities of all pulps were determined using the standard analytical procedure (SCAN-C 15:88).

TABLE 1.
Experimental Design for Peroxyacetic Acid (Paa) Treatments. Variations of ±1°C in Temperature and ±0.1 Units in pH Were Allowed.

Exp. no.	Temperature, °C	pH	Paa charge, % on pulp
301	56	3.5	1.0
302	56	6.0	1.0
303	56	3.5	2.5
304	56	6.0	2.5
305	78	3.5	1.0
306	78	6.0	1.0
307	78	3.5	2.5
308	78	6.0	2.5
309	68	3.0	1.75
310	68	7.0	1.75
311	68	5.0	0.5
312	68	5.0	3.0
313	50	5.0	1.75
314	83	5.0	1.75
315 & 316	68	5.0	1.75

The carbohydrate contents of the pulps were determined after total acid hydrolysis by determining the monosaccharide composition of the hydrolysate using a HPLC method described elsewhere.[9] Aliquots of the peroxyacetic acid effluents from treatments of 45 and 180 min from each experiment (301-316) were freeze dried for carbohydrate analysis (Appendix I). A small amount of dry residue was dissolved in 0.4 M H_2SO_4 solution and subjected to gentle acid hydrolysis at 100°C for 1 h. Monosaccharides were then determined as described elsewhere.[9]

Identification of Oxidation Products of Carbohydrates

Oxidation of D(+)-glucose (for biochemistry, Merck, Germany) was performed at pH 3.5 and 6.0 for 45 minutes at 80°C. The initial glucose

concentration was 3.0 g/L and the peroxyacetic acid concentration was 12.6 g/L (molar ratio 1:10). After oxidation the reaction mixture was ion-exchanged, vacuum-dried at 35°C and silylated as explained in detail elsewhere.[10] The oxidation products were separated and identified using GC-MS (HP6890 GC and HP5973 mass selective detector): 1 μL of silylated sample was injected via a split injector (260°C, split ratio 1:15) into a 30 m / 0.32 mm i.d. column coated with a 0.25 μm thick phenyl-methylpolysiloxane film (DB-1701, J&B Scientific). The column temperature programme was 100°C (2 min) - 10°C/min - 200°C (5 min) - 15°C/min - 280°C. Helium was used as carrier gas (2 mL/min, constant flow). Mass spectra were recorded at 70 eV electron energy and a commercial mass spectrum library (Wiley275) was used in identification.

Formic acid content was determined from ion-exchanged samples. pH was adjusted to 8 (with tetrabutylammonium hydroxide) and the solution was evaporated to dryness. The dry residue was dissolved in acetone and formic acid was determined as its benzyl ester by GC/FID. The method is described in detail in KCL method no 230:91.

Calculations

The polysaccharide composition of the pulp was calculated from the monosaccharide compositions using the method described by Janson.[11] Statistical analyses were performed using a commercially available computer program (Modde 4.0 by Umetri AB, Sweden).

RESULTS AND DISCUSSION

Carbohydrate Depolymerization

Prior to peroxyacetic acid treatments, the initial pulp was chelated in order to minimize the transition metal-catalysed peroxyacetic acid decomposition.[6]

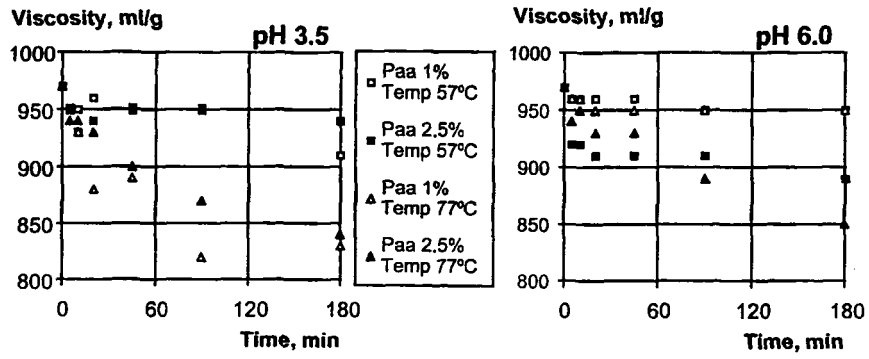

FIGURE 1. Effect of pH, Temperature and Peroxyacetic Acid (Paa) Charge on Pulp Viscosity as Function of Delignification Time.

Peroxyacetic acid treatments were performed under the conditions shown in Table 1 using delignification times of 5, 10, 20, 45, 90 and 180 min. After the peroxyacetic acid treatments, the extent of cellulose chain depolymerization was measured by determining pulp viscosity.

The viscosities of the peroxyacetic acid treated pulps from experiments 301-308 in Figure 1 show that at pH 3.5, increasing the temperature caused cellulose chain depolymerization, whereas at pH 6 temperature had no effect on viscosity. On the other hand, peroxyacetic acid charge had no effect on viscosity at pH 3.5, whereas at pH 6 increasing the peroxyacetic acid charge increased the extent of depolymerization, as reflected by the fall in viscosity.

The viscosity results indicate that there are at least two different reactions contributing to carbohydrate depolymerization during peroxyacetic acid delignification. The first reaction, possibly acid hydrolysis, i.e. acidic cleavage of glycosidic bonds, is dominant at low pH. Acid hydrolysis is not dependent on the concentration of oxidizing agent and therefore is not affected by peroxyacetic acid charge. Increasing temperature, however, significantly increased the rate of acid hydrolysis and caused viscosity reduction.

At low pH, the selectivity of delignification with peroxyacetic acid, i.e. reactions of peroxyacetic acid with lignin over those with carbohydrates, can be increased by increasing the peroxyacetic acid charge, because a high peroxyacetic acid concentration significantly increases the rate of delignification[12] but does not affect cellulose depolymerization. On the other hand, increasing temperature does not lead to increased selectivity. Although increasing temperature increases the rate of delignification, it simultaneously increases the rate of cellulose depolymerization.

At slightly acidic and neutral pH, cellulose degradation occurred via a second reaction path. Unlike the first reaction type, this reaction is highly dependent on peroxyacetic acid charge but is not highly temperature sensitive. Increasing the pH increases the rate of peroxyacetic acid decomposition,[5] and therefore the second type of carbohydrate depolymerization reaction may be caused by compounds formed from decomposed peroxyacetic acid. These compounds may be some highly reactive oxygen species, such as hydroxyl radicals, which may be formed by homolytic cleavage of the oxygen-oxygen bond in peroxyacetic acid.[13, 14]

At neutral pH, the selectivity may be improved by increasing the temperature of peroxyacetic acid treatment, which had no significant effect on cellulose depolymerization but increased the rate of delignification. Increasing peroxyacetic acid charge would also increase the rate of delignification[12] but the simultaneous increase in the rate of cellulose depolymerization indicates that the selectivity of delignification cannot be improved by increasing peroxyacetic acid charge.

Dissolved Carbohydrates

The carbohydrate composition of the initial pulp as monosaccharides was glucose 85.2% (w/w), xylose 7.6%, mannose 5.9%, arabinose 0.8%, galactose

TABLE 2.
Polysaccharide Compositions (% of all Polysaccharides) in the Initial Oxygen-Delignified SuperBatch (SB-O) Pulp and in Two Peroxyacetic Acid-Treated Pulps.

Pulp	Xylan	Glucomannan	Cellulose
SB-O	8.4	7.5	84.1
SB-O-Q-Paa $_{307}$	8.3	7.9	83.8
SB-O-Q-Paa $_{308}$	8.3	8.1	83.6

Numbers 307 and 308 refer to the reaction conditions in Table 1, delignification times were 180 min (307) and 45 min (308).

0.3%, and hexenuronic acids 0.2%, the composition being typical for a pine kraft pulp.[11, 15] The monosaccharide composition of the pulp after peroxyacetic acid treatment was almost the same as that of the initial pulp except that nearly all hexenuronic acid groups had been removed.[7] Hence the calculated polysaccharide composition of the pulp did not change much during peroxyacetic acid treatment (Table 2).

Because the change in carbohydrate composition of the pulp during the peroxyacetic acid treatment was small, even at 40% delignification, the determination of the monosaccharide or polysaccharide composition was not sensitive enough for a study of the effects of process parameters on pulp carbohydrates. Therefore, to get a more accurate measure of the changes in pulp carbohydrate composition during peroxyacetic acid treatment, the carbohydrate contents of the spent liquors were determined.

The content of dissolved carbohydrates was determined as monosaccharides present in the spent liquors from delignifications of 45 and 180 min (measured values are shown in Appendix I). Although xylose comprised less than 8% of all pulp carbohydrates, the xylose content of the spent liquors was on average 30% of total carbohydrate. On the other hand, glucose, which represented over 85%

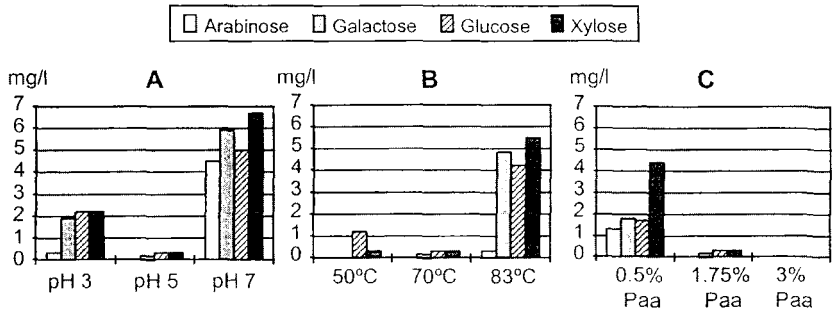

FIGURE 2. Effect of pH (**A**), Temperature (**B**), and Peroxyacetic Acid Charge (**C**) on the Content of Monosaccharides in Spent Liquor After 45 Minutes Delignification. (**A**: 68°C, 1.75% Paa; **B**: pH 5, 1.75% Paa; **C**: pH 5, 68°C)

of total pulp carbohydrate, represented only 20% of carbohydrates in the spent liquors. This was probably because in kraft pulp fibres xylan is present mainly on outer fibre surfaces,[16] from where it dissolves fairly easily in the liquor during peroxyacetic acid treatment. On the other hand, most of the glucose units in wood fibres originate from long cellulose chains located in the inner parts of the fibres[16] and therefore are not easily dissolved. Furthermore, cellulose has partly crystal structure which reduces its solubility.

Spent liquor from peroxyacetic acid treatment at pH 5 had a lower concentration of carbohydrates than spent liquors from treatment at pH 3 or 7 (Figure 2A and Appendix I). This was probably because at pH 5 the rate of acid hydrolysis was negligible. Also, the peroxyacetic acid was relatively stable and probably did not degrade to species that cause carbohydrate depolymerization and dissolution. At pH 3, acid hydrolysis, which caused cellulose depolymerization, was probably also responsible for the side-chain cleavage of carbohydrates and thus for carbohydrate dissolution. The side chains of

hemicelluloses, such as arabinose units in xylan and galactose units in galactoglucomannan, are known to be particularly susceptible to acid hydrolysis.[17] At neutral pH, peroxyacetic acid may have decomposed to produce carbohydrate-degrading species and thus carbohydrate dissolution.

The content of carbohydrates in spent liquor increased with increasing temperature, as shown in Figure 2B and Appendix I. The content of carbohydrates in spent liquors from treatment at temperatures of 70°C or lower was in most cases just above the detection limit, whereas that from treatment at 83°C was higher.

Increasing the peroxyacetic acid charge lowered the carbohydrate content in spent liquor, as shown in Figure 2C and Appendix I. It is therefore probable that peroxyacetic acid reacted with dissolved carbohydrates, although it is known that peroxyacetic acid does not oxidize the hydroxyl groups in pulp carbohydrates. However, the dissolved carbohydrates which were liberated by acid hydrolysis have reducing end group and therefore they may react with peroxyacetic acid.

Oxidation of Glucose by Peroxyacetic Acid

In order to study the reaction between peroxyacetic acid and carbohydrates, glucose was subjected to peroxyacetic acid treatment at pH 3.5 and 6.0. The total ion GC-MS chromatogram of the ion-exchanged and silylated reaction mixture showed several oxidation products from glucose (Figure 3). Identification of the peaks by mass spectrometry, based on a commercial mass spectrum library, showed that the oxidation/degradation products were gluconic acid, arabinonic acid, arabinose, ribose, threonic acid, erythronic acid, glyceric acid and glycolic acid. The one-carbon carboxylic acid (formic acid) was also found from the reaction mixture though by using another analytical procedure as explained in the experimental section. The formation of formic acid during peroxyacetic acid

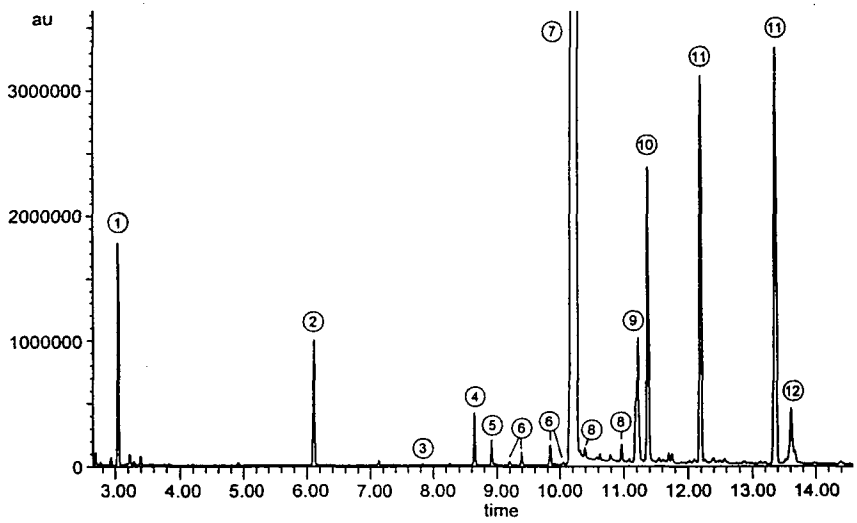

FIGURE 3. GC-MS Chromatogram of Products from Peroxyacetic Acid Oxidation of Glucose at pH 6. Identified Peaks: 1 = Glycolic acid, 2 = Glyceric Acid, 3 = Erythrose (?), 4 = Erythronic Acid, 5 = Threonic Acid (Isomer of Erythronic Acid), 6 = Arabinose, 7 = Xylitol (Internal Standard), 8 = Ribose (Isomer of Arabinose), 9 = Arabinonic Acid, 10 = Unidentified Compound, 11 = Glucose and 12 = Gluconic Acid. Arabinose, Ribose and Glucose Showed Several Peaks due to their α and β Anomers and Furanosidic and Pyranosidic Ring Structures.

delignification of pulp has also been observed by other scientists.[18, 19] Erythrose was also probably present (Figure 3), but due to its very low concentration in the sample and background noise in the mass spectra, its presence could not be verified with certainty. However, the fragment peaks in the mass spectrum indicated that peak 3 may originate from erythrose. The same oxidation products were detected when oxidation was performed at pH 3.5, although the concentrations were lower.

The reaction products indicate that treatment of monosaccharide by peroxyacetic acid at pH 6 oxidizes the aldehydic end group to a carboxylic acid

group, as was suggested earlier.[7] In addition, the C_1-C_2 bond in the monosaccharide may be cleaved by peroxyacetic acid. The first reaction step in glucose oxidation is then probably the oxidation of the aldehyde end-group to a carboxylic acid group, leading to formation of the corresponding aldonic acid, in this case gluconic acid. This step may proceed via the Baeyer-Villiger reaction, which is catalysed by either bases or strong acids.[13] Decarboxylation and cleavage of the C_1-C_2 bond in gluconic acid leads to formation of a lower aldose. According to the reaction products, two isomers of lower aldose are possible and in this case both arabinose and ribose were formed. Several other methods for carbohydrate chain shortening have been reported,[20] e.g. with hydrogen peroxide (Ruff degradation) or with oxygen under alkaline conditions. However, no chain shortening reaction caused by peroxyacetic acid has been reported earlier. In the cleavage of the C_1-C_2 bond, carbon dioxide is probably liberated, and it has in fact been shown[21] that carbon dioxide is liberated during peroxyacetic acid delignification. The lower aldose formed is probably oxidized further to arabinonic acid and the chain reaction may then continue according to Figure 4.

The reactions suggested may be responsible for the significant consumption of peroxyacetic acid during pulp delignification, since every step consumes one equivalent of peroxyacetic acid. Oxidation of one mole of glucose can theoretically consume 11 moles of peroxyacetic acid. During the oxidation of glucose at pH 6 all peroxyacetic acid was consumed. Most of the peroxyacetic acid was consumed in glucose oxidation reactions because the spontaneous decomposition of peroxyacetic acid consumes less than half of the peroxyacetic acid charge under equivalent conditions.[22] At pH 3.5, peroxyacetic acid consumption was only 3.9% of the charge indicating that only few oxidation reactions occurred as was also concluded from the low amount of oxidation products. During pulp bleaching with peroxyacetic acid, it is obvious that

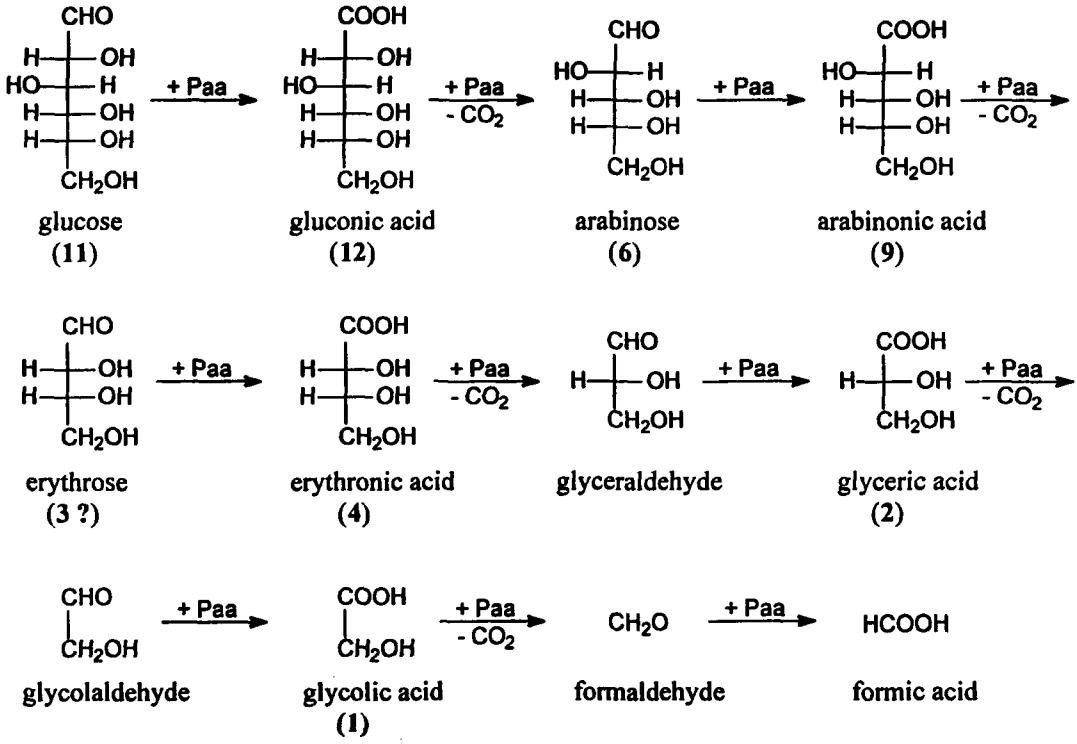

FIGURE 4. Suggested Reaction Pathway for Glucose Oxidation With Peroxyacetic Acid (Paa). All Compounds Except Formaldehyde, Glycolaldehyde and Glyceraldehyde were Identified and the Numbers in Parenthesis Indicate the Peak Number in the Chromatogram (Figure 3).

oxidation of dissolved monosaccharides and of end-groups in carbohydrate polymers consumes peroxyacetic acid, especially under slightly acidic conditions. The overall content of carbohydrates in the spent liquor is small, however, and thus the proportion of peroxyacetic acid consumed in these carbohydrate oxidation reactions may have a minor importance in pulp bleaching.

CONCLUSIONS

The reactions of carbohydrates during peroxyacetic acid treatment under bleaching conditions were strongly dependent on treatment pH. The reaction followed different pathways under neutral and acidic conditions.

Under neutral or slightly acidic conditions, an increase in peroxyacetic acid charge increased the depolymerization and dissolution of carbohydrates, possibly due to reactions initiated by radicals formed from peroxyacetic acid. However, the fall in pulp viscosity was small and almost independent of temperature. At acidic pH peroxyacetic acid is much more stable than at neutral pH and thus radical formation is less prominent. As a consequence, carbohydrate degradation occurred via a different reaction path than under neutral conditions. In peroxyacetic acid treatment at acidic pH, the dissolution of carbohydrates, both hemicelluloses and cellulose, can be explained by acidic hydrolysis. After all peroxyacetic acid treatment may be performed without any viscosity loss: under acidic conditions, temperature should be below 60°C and under neutral conditions peroxyacetic acid charge should be below 1% on pulp in order to prevent cellulose depolymerization.

Neither the carbohydrate content nor carbohydrate composition of the pulps was significantly affected by peroxyacetic acid treatment, and therefore the total content of dissolved carbohydrates was negligible in relation to pulp yield, even

under conditions where a high degree of delignification was obtained. However, the dissolved carbohydrates as well as the end-groups in the carbohydrate polymers may be oxidized by peroxyacetic acid. Therefore the determination of carbohydrates in spent liquors from peroxyacetic acid treatment is not an accurate way to determine the amount of carbohydrates removed from pulp fibres during the treatment.

ACKNOWLEDGEMENTS

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APPENDIX I

Contents of carbohydrates as monosaccharides (mg/l) found in spent liquors from peroxyacetic acid delignification. Delignification conditions are shown in Table 1.

	Time, min	Arabinose	Galactose	Glucose	Xylose	Mannose
301	45	0	0	0	0	0
301	180	0.7	2	2	2.8	0
302	45	0.3	0.3	1.4	2.1	0
302	180	2.5	4.9	4	5.5	0
303	45	0	0	0	0	0
303	180	0	0	0	0	0
304	45	0	0.3	0.3	0.3	0
304	180	0.3	6.2	6.1	5.8	0
305	45	1.5	2.4	2.4	3.1	0
305	180	6.9	7.5	7.2	10.9	2.2
306	45	5.7	3.6	3.5	5.8	0
307	45	1.3	3	3.3	4.7	0
307	180	4.4	12.5	13.5	16.2	3.8
308	45	2.9	6.6	6	6.2	0
308	150	6.5	12.5	12.9	15.2	0
309	45	0.1	1.9	2.2	2.2	0
309	180	4.8	6.9	8.3	10	3
310	45	4.5	5.9	5	6.7	0
311	45	1.3	1.8	1.7	4.4	0
311	180	4.9	8.2	8.7	7.5	0
312	45	0	0	0	0	0
312	180	0.1	3.1	2.8	6.2	0
313	45	0	0	1.2	0.3	0
313	180	0	0.3	0.3	0.3	0
314	45	0.1	4.8	4.2	5.5	0
314	180	15.7	11	11.6	13.6	0.1
315	45	0	0	0.3	0.3	0
315	180	2.6	6.4	5.7	6.7	0
316	45	0	0.3	0.3	0.3	0.1
316	180	0.3	6.7	7.3	7.6	0