CELLULOSE CHEMISTRY AND TECHNOLOGY

SELECTIVENESS AND EFFICIENCY OF COMBINED PERACETIC ACID AND CHLORINE DIOXIDE BLEACHING STAGE FOR KRAFT PULP IN REMOVING HEXEURONIC ACID

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Combined peracetic acid and chlorine dioxide bleaching stages of unbleached and oxygen delignified hardwood and softwood kraft pulps were compared with conventional chlorine dioxide and peracetic acid stages as to kappa number and viscosity reduction, selectivity and reduction of hexenuronic acid content. The combined stages were more efficient in kappa number reduction than those with only chlorine dioxide. Part of the increased kappa number reduction was due to an improved degradation of hexenuronic acid. The stages where chlorine dioxide was added before the peracetic acid (DT) showed a higher selectivity than those in which the chemicals were added simultaneously (D+T); in turn, the latter were more efficient than the “pure” chlorine dioxide (D, D_0) and peracetic acid stages (T). However, peracetic acid and chlorine dioxide seemed to react with each other, leading to the degradation of both bleaching chemicals. The mechanisms and practical implementation of these bleaching sequences are discussed.

Keywords: NaCl, active chlorine; D, chlorine dioxide bleaching stage; E, alkaline extraction stage; HexA, hexenuronic acid; O, oxygen delignification stage; T, peracetic acid bleaching stage

INTRODUCTION

Chlorine dioxide bleaching (D) is today the most important bleaching method for kraft pulps, besides oxygen delignification (O).[1] One reason is that it combines efficient delignification with high selectivity, *i.e.* low degradation of cellulose.[2] Chlorine dioxide bleaching works according to several principles:[3-7]

- ClO_2 oxidizes phenolic and non-phenolic aromatic rings in lignin into muconic acids and quinones under generation of ClO_2^- and ClO^-;
- ClO_2 attacks aliphatic double bonds and thereby reduces colour. Also, here, ClO_2^- might be a side product;
- ClO_2 works as a radical scavenger, neutralizing radicals generated during the bleaching reactions.[8] Thereby, cellulose is protected against depolymerization caused by aggressive radicals;
- ClO_2^-, formed as a side product in the oxidation of aromatic structures by ClO_2, is generated in a series of HClO and Cl_2 reactions, which are able to chlorinate and oxidize even the resistant double bonds in lignin and other pulp components.

The last reaction, chlorination,[5] is much more efficient at lower pH. Furthermore, the direct oxidation of non-phenolic lignin structures by ClO_2 is very slow, compared to the oxidation of phenolic structures. Therefore, powerful delignification by ClO_2, which degrades and activates the non-phenolic aromatic structures in lignin, is enhanced[9] by a relatively low pH. Consequently, the first chlorine dioxide stage in a bleaching sequence (D_0) is normally carried out at an end pH of 2 to 3. This gives efficient delignification, but generates also some chlorinated organic effluent products, which may create potential environmental problems.[10] Subsequent chlorine dioxide stages (D_1, D_2, etc.) are normally carried out at higher pH, often around 4. Under these conditions, less chlorination occurs, and although the oxidation of phenolic structures in lignin is still efficient, the delignifying effect is generally poorer than in D_0 stages.

Apart from degrading and dissolving the lignin remaining in pulp after the kraft cook, a bleaching sequence should optimally remove hexenuronic acid (HexA) from pulp. HexA is created from 4-O-metyl glucuronic acid residues, a side chain of xylans, during kraft cooks.[11,12] This structure is normally undesired in bleached pulps, since they contribute to brightness reversion,[12] by generating coloured degradation products.[13] Furthermore, HexA strongly chelates transition metal ions, which catalyze the degradation of hydrogen peroxide during bleaching, resulting in low selectivity. Chlorine dioxide itself is not very efficient in degrading HexA by direct oxidation, while the Cl_2 formed during D_0 stages is able to chlorinate HexA. This prevents the post-yellowing reactions of HexA,[13] but forms, on the other hand, chloro-organic compounds that may have negative environmental effects.[10] These problems of HexA removal by D-stages have led to the development of a hot chlorine dioxide bleaching stage (D*), where low pH and high temperature induced the degradation of HexA with less chlorination.[14] D* stage might however somewhat lower cellulose viscosity, *i.e.* its degree of depolymerization.[15]

Another drawback of the D-stages is that their effluents cannot included in system closure, due to the presence[16] of high amounts of Cl^-. Thus, there are both environmental and technical reasons for seeking alternatives to D-stages, especially to the D_0 stages. Among possible alternative methods for bleaching, the use of peracetic acid at a moderately acidic pH (T) should be mentioned. This is an electrophilic bleaching method that allows the hydroxylation of both double bonds and aromatic rings, including non-phenolic aromatics, and further oxidations to muconic acids, quinones and other components.[17] Peracetic acid is efficient in degrading HexA,[18] and is surprisingly selective for being used as a peroxide, *i.e.* it gives a relatively low degradation of cellulose. In spite of these good properties, the use of T-stages for bleaching kraft pulps is limited, probably mainly due to the high price and also to the fact that the T-stages are slower in delignification than the D_0 ones.

The present study investigates the effects of combined peracetic acid and chlorine dioxide stages – performed at higher pH, where chlorination is relatively low – on the pulp properties. Such stages may combine the advantages of the different bleaching methods – such as the ability of peracetic acid to hydroxylate the non-phenolic aromatic structures and HexA, and the high selectivity and efficient oxidation of phenols by chlorine dioxide.

MATERIALS AND METHOD

Materials

Peracetic acid and chlorine dioxide were manufactured at Invenntia AB, Stockholm, Sweden, according to standard procedures. Oxygen delignified softwood (mixed *Picea abies* and *Pinus sylvestris*) kraft pulp with a kappa number of 11.4 and viscosity of 900 were obtained from Mönsterås mill, Mönsterås, Sweden. A hardwood kraft pulp (*Eucalyptus globulus*), obtained from a South American mill, was used in both unbleached form (kappa number – 16.3 and viscosity – 1341) and oxygen delignified form (kappa number – 10.4 and viscosity – 920). After delivery, the pulps were washed with de-ionized water and stored in a refrigerator until used. All other chemicals used were of analytical grade.

Characterization of bleaching chemicals

The concentration of ClO_2, expressed as active chlorine, was determined by adding 3 mL of the ClO_2 solution to 10 mL 80g KI /L and 10 mL conc. H_2SO_4 diluted 10 times, and immediately titrating with 0.1 M $Na_2S_2O_3$. The amount of active chlorine (aCl) in the solution was then calculated by the following formula:

$$aCl\ [g/dm^3] = V_{titr} \cdot C_{titr} \cdot 35.5 / V_{sample}$$

where V_{titr} – volume of $Na_2S_2O_3$ used with concentration C_{titr} (0.1M), and V_{sample} – volume of sample containing bleaching chemicals in 1 mL.

The residual amounts of active chlorine resulted from bleaching experiments were determined by adding a 10 mL fluid sample to 10 mL 80 g KI/L and 10 mL conc. H_2SO_4 diluted 10 times, and immediately titrated with 10 mM $Na_2S_2O_3$; concentration was then calculated using the formula above.

The peracetic acid concentrations were determined as follows: 100 mL de-ionized water and 10 mL 10% sulphuric acid were mixed in a beaker, subsequently transferred to an ice bath to prevent evaporation. 0.200 g of sample was added together with a few drops of 3% manganese sulfate solution. The solution was titrated with a 20 mM potassium permanganate solution up to a faint pink colour (which was allowed to stay for about 10 s before fading). The amount of potassium permanganate used was noted for calculating the amount of H_2O_2 in the mixture. This was determined by adding 10 mL 80 g KI/L, followed by the incubation of the beaker at dark, for 3 to 5 min. Subsequently, the solution was titrated with 100 mM $Na_2S_2O_3$ until becoming colourless, with 2 g/L starch (Thyodene) added at the end of titration. The concentrations of hydrogen peroxide and peracetic acid were calculated according to:

Conc. (%) $H_2O_2 = 0.17005 \cdot a/W$

Conc. (%) $CH_3CO_3H = 0.38025 \cdot b/W$

where a – used amount of 20 mM $KMnO_4$ [ml], b – used amount of 100 mM $Na_2S_2O_3$, and W – sample weight [g].

Bleaching with chlorine dioxide and peracetic acid

Bleaching of pulps was performed in a sealed plastic bag, at 8% pulp consistency, in thermostatic water baths. The bags were kneaded every 5 min. After completing incubation time (45 min), the bags were cooled for 10 min in cold water. An aliquot of the bleaching liquor was withdrawn for analysis of active chlorine and end pH before the pulps were washed with de-ionized water in a Büchner funnel. The final pH was between 4 and 4.5, if not specified otherwise. The amount of chlorine dioxide is the same in all steps, 10 kg aCl/BDt, except for the plain T-step, which has no chlorine dioxide. All steps included the use of 5 kg peracetic acid per BD, except for the plain D-step, which involved no peracetic acid.

Alkaline extraction (E) of pulp

Alkaline extraction was performed at 10% pulp consistency in the presence of 0.35% NaOH and 0.025% $MgSO_4$ in a sealed plastic bag, at 70 ºC for 60 min. The bag was kneaded regularly. After incubation, it was cooled under running water for 10 min and the pulp was washed several times on a Büchner funnel with de-ionized water.

Pulp characterization

Kappa number was determined according to SCAN-C 1:00, and viscosity – according to ISO 5351. The HexA content was analyzed by the method of Li and Gellerstedt.[19] These data permitted to calculate the kappa number contribution from compounds other than hexenuronic acid (mostly the remaining lignin).

RESULTS AND DISCUSSION

The effects of bleaching with a mixture of peracetic acid and chlorine dioxide were investigated and compared with plain peracetic acid and chlorine dioxide stages, using both unbleached softwood kraft pulp and unbleached and oxygen delignified hardwood kraft pulps. Bleaching was performed at pH 4.5-5, a value at which both peracetic acid and chlorine dioxide are efficient, while chlorination by the chlorine species formed during the reaction between ClO_2 and lignin is much lower at such a value as compared to chlorination at lower pH (D_0 stages).[5] Bleaching experiments with different bleaching times indicated that most kappa number reducing reactions occurred during the first 45 min (not shown), at 70 ºC. Bleaching of an oxygen delignified softwood kraft pulp with a combined peracetic acid stage (DT) and chlorine dioxide at different temperatures was also performed, and the results indicated that the bleaching effect increased considerably between 60 and 70 ºC, whereas an increase to 80 ºC only gave a moderate increase (Fig. 1). Thus, a 45 min bleaching time at 70 ºC was used in the study.

Plain chlorine dioxide bleaching stages (D) with different dosages of chlorine dioxide on oxygen delignified hardwood kraft pulp were compared with the stages in which a limited amount of peracetic acid was added after a 5 min reaction time (DT). The result implied that the addition of peracetic acid caused a moderate increase in bleaching efficiency (Fig. 2). Thus, it might be interesting to use simultaneously peracetic acid and chlorine dioxide for bleaching, but what is the best way to mix them? A comparative experiment was devoted to the three different ways of performing combined peracetic acid and chlorine dioxide bleaching, on unbleached hardwood kraft pulp:

- "(D+T)-mix" – chlorine dioxide and peracetic acid were mixed and incubated for 5 min before mixed with the pulp;
- "(D+T)" – the bleaching agents were mixed together with the pulp without any pre-incubation;
- "(DT)" – chlorine dioxide was added first to the pulp and the peracetic acid 5 min later.

The result of the experiments (Fig. 3) indicated that the (DT) stage had the best delignifying effect, followed by the (D+T) stage and the (D+T)-mix stage, and that this tendency was also present after a subsequent alkaline extraction stage (E). One explanation for the difference between the "(D+T)" and the "(D+T)-mix" stages might be that the two bleaching agents slowly react with each other, thereby reducing the amount of bleaching agents reacting with lignin. Figure 4 illustrates a possible reaction for such consumption. However, other mechanisms might be involved, providing an explanation for the difference between the (D+T) and (DT) stages. Possibly, an explanation might be that some of the chlorine dioxide is consumed while it is "alone" with the pulp, and thus less ClO_2 is left to react with the peracetic acid. Another possibility considers the synergistic effects manifested in the bleaching mechanisms between the two bleaching agents which, for some reason, are more efficient in the (DT) stage.

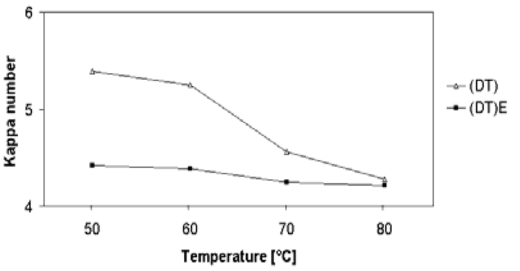

Figure 1: Effect of temperature on (DT)-bleaching of oxygen delignified mixed softwood kraft pulp (pH – 4.5, incubation time – 45 min)

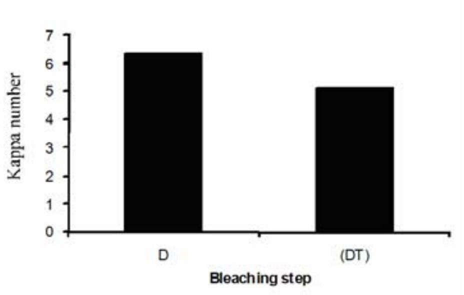

Figure 2: D stage compared to (DT) stage on oxygen delignified hardwood kraft pulp

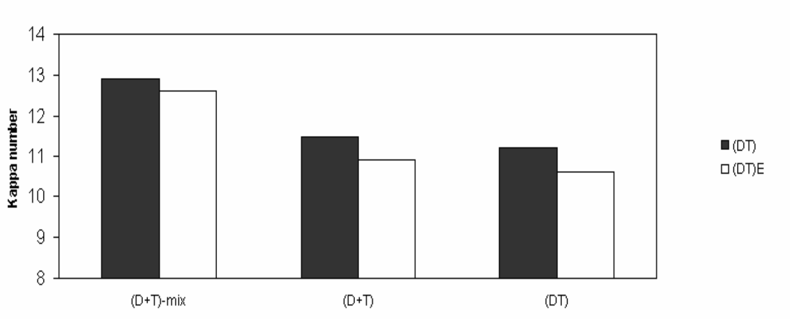

Figure 3: Effects of different mixing of bleaching agents. See materials and method for mixing conditions.

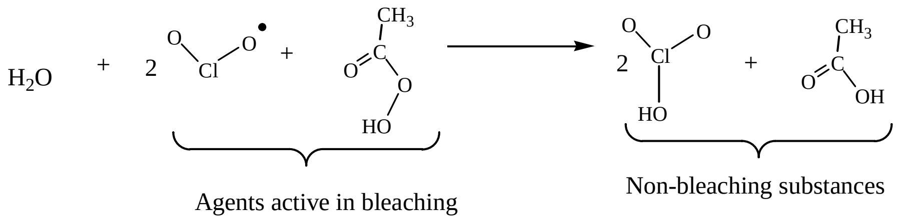

Figure 4: Hypothetical reaction of chlorine dioxide and peracetic acid in consuming bleaching agents

The effects on the degree of polymerization of cellulose, expressed as viscosity, were also determined. The results (Fig. 5) showed that both peracetic acid and chlorine dioxide bleaching caused small decreases in the degree of polymerization, which might be due to the decomposition of peracetic acid into hydroxyl radicals, similarly to peroxide, possibly catalyzed by transition metal ions.[20] Also, in the chlorine dioxide stages, aggressive radicals, such as the chloromonoxide radical, might occur.[8] However, the (DT) stages gave a lower loss of viscosity than the DT sequence, evidencing, in the case of softwood pulp, the lowest loss of viscosity of all bleaching stages tested (Fig. 5). Chlorine dioxide is known to work as a radical scavenger – which is, to a great extent, the reason why the selectivity of the D stages is so high.[8] An explanation for such results is that chlorine dioxide reacts with the radicals created by the peracetic acid (hydroxyl radicals etc.), thus preventing polysaccharide depolymerization. Also, in mixtures with ozone, the presence of chlorine dioxide has been found to diminish the viscosity decrease.[21] Thus, ClO_2 might possibly work as a radical scavenger in combined chlorine dioxide and peracetic acid bleaching, thereby protecting cellulose from depolymerization. Figure 6 describes a hypothetical mechanism for this effect. Thus, the effects of mixing peracetic acid and chlorine dioxide are complex, as to the reduction in kappa number and viscosity. Accordingly, the selectivity values of two different pulps were calculated for various bleaching stages (Table 1). The (DT) afforded a superior result, especially for softwood pulp, which may be partly explained by the radical scavenger effect[22] of ClO_2, however it appears that, in some way, peracetic acid also assists chlorine dioxide in delignification, when the peracetic acid is more efficient than ClO_2. One such aspect might be the attack on the non-phenolic aromatic structures[23] from residual lignin. It is known that chlorine dioxide oxidizes such structures very slowly,[7,8] whereas the peracetic acid has the capacity to hydroxylate the aromatic rings and, therefore, to convert the non-phenolic aromates to phenols which, in turn, may be oxidized by chlorine dioxide. Figure 7 illustrates a hypothetical mechanism for this situation, suggesting that the peracetic acid "activates" this type of lignin for a subsequent oxidation by chlorine dioxide. Interestingly, this presents similarities to the way white rot fungi are believed to degrade lignin, by the concerted action of two enzymes: cellobiose dehydrogenase and manganese peroxidase.[24] Such reactions might partly explain the high selectivity of the combined chlorine dioxide/peracetic acid stages.

However, except for lignin, the carbohydrate-derived structures are also important contributors to the kappa number, of which hexenuronic acid is the most important. Chlorine dioxide can degrade hexenuronic acid, but relatively slowly. Thus, the effects of combined stages on the hexenuronic acid and on the remaining lignin part of the kappa number were investigated (Fig. 8). The combined bleaching stages were more efficient than ClO_2 alone, for removing both the remaining lignin and hexenuronic acid, although the relative effects were stronger on the hexenuronic acid part of the kappa number. Since the hexenuronic acid content in pulp is associated with brightness reversion,[12,13] the addition of peracetic acid to one or several D-stages might improve the brightness stability of the pulp, especially with hardwood kraft pulps.

Table 1
Selectivity of bleaching stages

Bleaching method	Pulp	Kappa number	Viscosity (mL/g)	Specificity*
None	Unbl. hardwood	16.3	1341	
D	Unbl. hardwood	13.0	1270	0.046
T	Unbl. hardwood	13.4	1248	0.031
DT	Unbl. hardwood	10.4	1206	0.044
(D+T)	Unbl. hardwood	11.5	1259	0.059
(DT)	Unbl. hardwood	10.4	1265	0.078
None	Ox. softwood	11.4	920	
D_0	Ox. softwood	5.3	874	0.16
D	Ox. softwood	5.3	890	0.28
T	Ox. softwood	8.8	889	0.11
DT	Ox. softwood	3.6	870	0.19
(D+T)	Ox. softwood	6.1	899	0.41
(DT)	Ox. softwood	4.7	903	0.74

*Change in kappa number divided by the change in viscosity

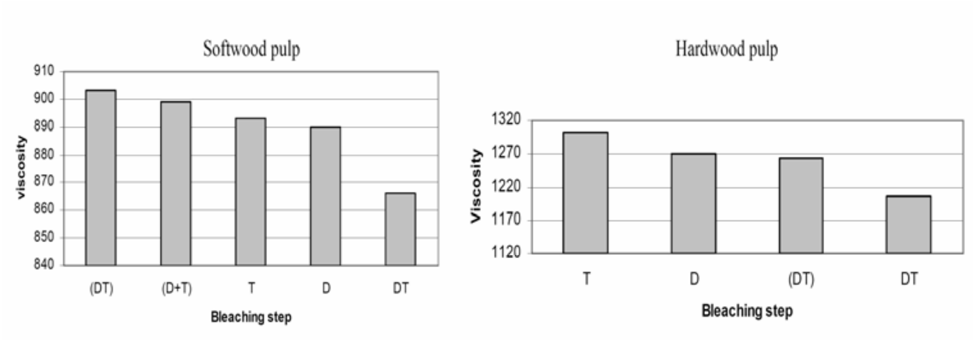

Figure 5: Viscosity after different bleaching steps on oxygen delignified mixed softwood kraft pulp and unbleached hardwood pulp. The original viscosity of the softwood pulp was of 900 and that of the hardwood pulp – 1341.

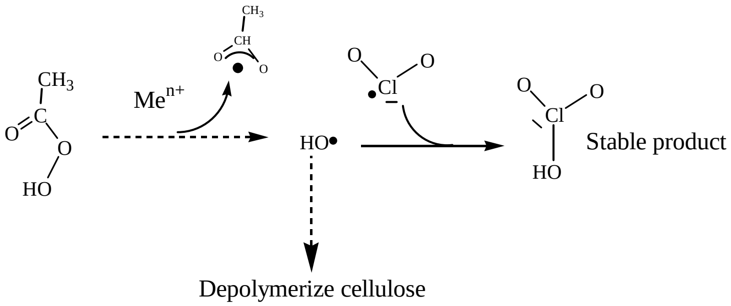

Figure 6: Hypothetical reactions behind the “protecting” effect of ClO_2 on the viscosity loss in mixed chlorine dioxide/peracetic stages.

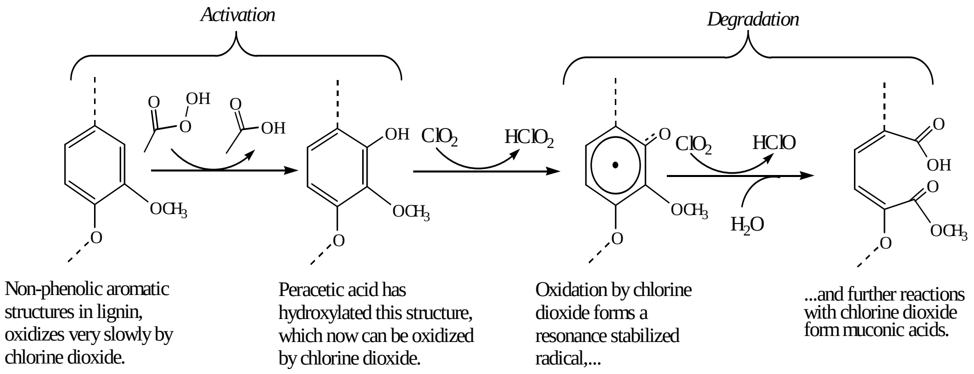

Figure 7: Hypothetical pathway for the degradation of non-phenolic lignin structures in mixed chlorine dioxide/peracetic acid stages.

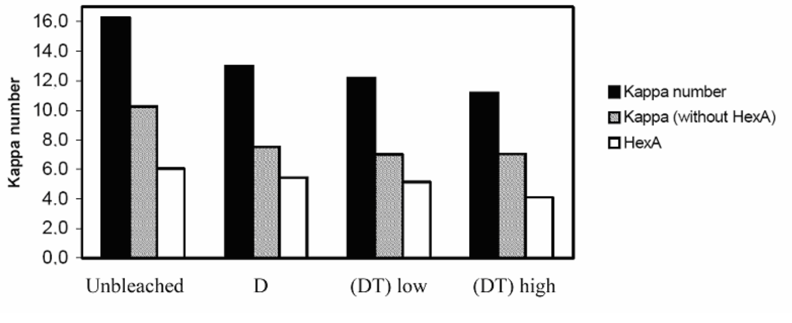

Figure 8: Effect on kappa number and hexenuronic acid content in combined bleaching stages. The pulp used is an unbleached hardwood kraft pulp. 10 [kg aCl/BDt] chlorine dioxide, 3 [kg/BDt] peracetic acid for (DT) “low” stage, and 5 [kg/BDt] peracetic acid for the (DT) “high” stages were used.

CONCLUSIONS

The results of this study imply that the addition of moderate amounts of peracetic acid to the D-stages induces interesting effects, such as an increased selectivity of the bleaching and degradation of hexenuronic acid, although more thorough studies are required for optimizing the existing methods. A (DT) stage, where the chlorine dioxide is added before the peracetic acid, seems however to be a better choice than a (D+T) stage. At present, the market price for peracetic acid is much higher than that for chlorine dioxide, and it is doubtful whether the benefits of peracetic acid addition can justify the extra cost. However, if the market price for peracetic acid decreases due to an increased consumption or improved production methods, the technique might be interesting, particularly for special purposes, and also when high brightness stability, or a combination of high strength and high brightness are desired.

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