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Why oxalic acid protects cellulose during ozone treatments?

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Abstract

This study shows that oxalic acid is a very effective additive for the ozone treatments compared with other additives. The required concentration is very small and even lower than the concentration formed during the stage itself. Several different mechanisms for the action of oxalic acid as an additive during the ozone bleaching are examined. He is advisable to have a pH acid during Z stage, but it has been proved that pH value is not the only factor that positively influences. Oxalic acid has an additional effect due to different factors that increase the selectivity of the Z stage. This acid has a minor ^{o}OH scavenging capacity than others acids, however, it prevents the cellulose degradation to a greater extent. Moreover, less ^{o}OH are formed when oxalic acid is added. Oxalic acid decreases swelling of cellulose and stabilises ozone avoiding its decomposition, then ozone is not consumed by oxalic acid. Metal ions, which are detrimental during ozone stage, can be chelating by oxalic acid. The most interesting outcome is that oxalic acid could act as hydrogen donor inhibiting the formation of ^{o}OH radicals. Thus, in studying the effects of oxalic acid, we have determined the requisites for an additive to be optimally effective to protect cellulose during ozone treatments.

Keywords: Cellulose; Kraft pulp; *Eucalyptus*; Bleaching; Ozone; pH; Additives; Chain scission number; Oxalic acid

1. Introduction

Ozone is a good alternative for use as a new bleaching agent in TCF sequences. However, its application will remain limited until the properties of the resulting pulp are improved, since ozone gives rise to extensive degradation of cellulose, producing pulp with poor strength properties. There are basically two disadvantages to ozone bleaching (Z): (a) Production of ozonised pulp that is susceptible to alkaline degradation in the following bleaching stage. (b) Low efficiency and selectivity of the ozone bleaching stage.

Different post-treatments for application subsequent to the Z stage were studied (Roncero, Colom, & Vidal, 2002a) to increase the selectivity of the process and reducing the substantial degradation of viscosity that occurs during the hydrogen peroxide stage (P) following ozone bleaching. The improvement in viscosity is attributed to a reduction of the carbonyl groups formed during ozone bleaching that can lead to cellulose degradation in an alkaline stage, such as hydrogen peroxide bleaching (P). The effective reduction power of sodium borohydride post-treatment (R) was corroborated using the cellulose chain scission number. However, other studies (Roncero, Colom, & Vidal, 2003) suggest that the improvement may not be attributable exclusively to a reduction of carbonyl groups. The R post-treatment, in addition to successfully reducing carbonyl groups to alcohol groups, gives rise to the dissolution of organic material that might be lignin or amorphous cellulose corresponding to fibrils located on the surface of the fibre.

The next question to be dealt with was the determination of a suitable pulp treatment that would prevent or decrease the reaction of ozone with carbohydrates during the Z stage and thereby increase the efficiency and selectivity of this stage, producing pulp with better properties for the manufacture of paper. The aim is to avoid the physical availability of the ozone to the cellulose, either by controlling the nature of the medium to increase the ozone stability, or by preventing the formation of radical species that cause degradation of the cellulose, or by inhibiting the action of those radical species. For this purpose different pre-treatments and additives were studied (Roncero, Colom, & Vidal, 2002b,c)). In a general comparison of pre-treatments

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and additives, it was observed that additives produce a greater increase in the selectivity of the process. The improvement of selectivity is due mainly to a lesser degradation of carbohydrates rather than to greater delignification.

In the studies aimed at increasing the efficiency and selectivity of the Z stage, it appears that there are a number of factors that influence this stage. The results obtained clearly show an ‘additional’ positive effect of some additives that is not connected with pH.

Thus in this paper, the effect of pH on ozone bleaching is examined and the additional and beneficial effects of additives and particularly oxalic acid are determined.

2. Materials and methods

The unbleached material used is a *Eucalyptus globulus* kraft pulp from an industrial source with 12.5 of kappa number, 35.3% ISO brightness and 1062 ml/g of viscosity. The bleaching sequences used were XOZR and XOAZR, where X is an enzymatic pre-treatment with xylanases, O is an oxygen delignification, A is an additive, Z is an ozone bleaching and R is a reductive treatment with sodium borohydride. Pulp was characterised in terms of kappa number, brightness and viscosity ISO standards 302, 5351/1 and 3688, respectively. Crystallinity by X-ray diffraction method (XRD) was determined: the samples to be analysed were used to prepare laboratory sheets in accordance with ISO standard 5269-2, aiming to make the sheets as homogeneous as possible (Browning, 1967).

The term Additive (A) is used to refer to a reagent used in a low-consistency treatment preceding Z stage, without washing between the two stages, thus the additive was present throughout the ozone bleaching process. The reagents employed were (Roncero et al., 2002c): acetic acid (A1), acetone (A2), oxalic acid (A3), methanol (A4), formaldehyde (A5), sulfamic acid (A6), citric acid (A7), dimethyl sulfoxide (DMSO) (A8), formic acid (A9), EDTA (A10), salicylic acid (A11), benzoic acid (A12), carbon dioxide (A13), sodium carbonate (A14), boric acid (A15) and sulphuric acid (A16). The equipment and methods used for the different bleaching stages were published earlier (Roncero, 2001; Roncero, Queral, Colom, & Vidal, 2000).

3. Results and discussion

3.1. Does pH affect the Z stage?

Many studies have been made of the effect of pH on the Z stage and most of them have concluded that pH has a considerable effect on ozone bleaching. However, some authors (Colodette, Singh, Ghosh, & Singh, 1993; Johansson, Lind, & Ljunggren, 2000; Lambert, 1999) consider that it is not the most crucial parameter or the only one that should be controlled, giving rise to certain controversies on this subject. Lachenal and Bokström (1986) concluded that the improvement of selectivity of the Z stage when carried out at acid pH was due mainly to the elimination of metal ions, while the effect of the pH of the reaction itself was of little importance.

Nevertheless, we have reached that pH actually has a very substantial effect on the reactions that occur during ozone bleaching since the kinetic study shows that: (a) The rate constant of delignification (k_L) decreases considerably after $pH > 5$. (b) The rate constant of chromophore elimination ($k_{(K/S)}$) follows a similar trend to that of k_L. (c) The rate constant of cellulose degradation (k_{DP}) is almost twice as high at pH 10 as at pH 2.5. (d) The selectivity value (k_L/k_{DP}) is six times higher at pH 2.5 than at pH 10 (Roncero, Queral, Colom, & Vidal, 2002d).

The least effective additives used during the Z-stage are those that are applied at $pH > 3$. The cellulose chain scission number (CS) occurring in ozone bleaching in relation with pH is showed in Fig. 1. The CS is defined as (Bouchard, Morelli, & Berry, 2000; Lindholm, 1990):

$$CS = \frac{DP_0 - DP}{DP}$$

Where DP_0 is the polymerisation degree of the oxygen delignification sample (XO pulp) and DP is the polymerisation degree after R treatment (XOAZR and XOZR sequences). The viscosity is taken after a borohydride treatment (Roncero et al., 2002a) to eliminate the effect of alkaline degradation produced by the viscosity measurement itself. As the pH increases, degradation of cellulose also increases since CS increases, regardless of the additive used.

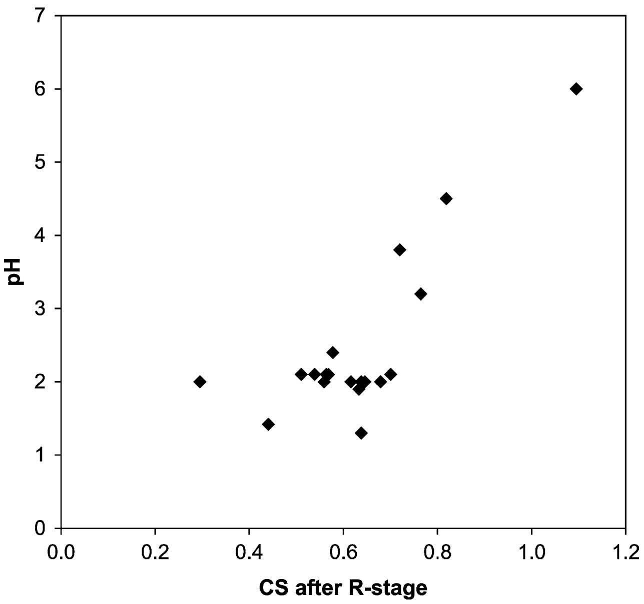

Fig. 1. CS values after R-stage versus pH.

3.2. What is the origin of this beneficial effect of lower pH?

Ozone has a higher oxidising potential than other oxidants used in bleaching and its oxidising potential decreases with an increase in pH (Biermann & Kronis, 1997). The ozone molecule, in comparison with its decomposition products, is an oxidising agent that reacts primarily with electron-rich systems, such as the double bonds and aromatic groups found mainly in lignin. However, it does not react, or reacts only slightly, with carbohydrates. Even so, ozone bleaching is not selective. The reason for the degradation of carbohydrates and therefore the decrease of selectivity, is generally held to be the presence of hydroxyl radicals (°OH) (Chirat & Lachenal, 1995; Ek, Gierer, & Jansbo, 1989; Eriksson & Gierer, 1985; Gierer, 1997; Gierer & Zhang, 1993; Jacobson, Lindlad, Ni & Nilvebrant, 1991; Johansson et al., 2000; Kang, Zhang, & van Heiningen, 1995; Kishimoto & Nakatsubo, 1998; Reitberger, Eriksson, Ek, & Ihren, 1995).

The °OH radical is a strong oxidant with a reduction potential of 2.72 V in acid media and 2.32 V in neutral solutions (Gierer & Zhang, 1993). Owing to its high electrophilic nature, it oxidises both organic and inorganic compounds rapidly. Hoigné and Bader (1983a,b), Nompex, Doré, De Laat, Bawa and Legube (1991) and Ek et al. (1989) studied the kinetic constants of ozone and the °OH radical reactions with lignin and carbohydrate models. The selectivity of the ozone is 10^5–10^6, while the selectivity of the °OH radical is only 5–6, indicating that the hydroxyl radicals formed during ozonisation of the pulp readily degrade carbohydrates.

The literature consulted (Eriksson & Reitberger, 1995; Gierer & Zhang, 1993; Ni, Kang, & Van Heiningen, 1996; Quesada, Rubio, & Gómez, 1998; Schuchmann & von Sonntag, 1989) states that the main paths of hydroxyl radicals formation are the following: (a) reactions of ozone with lignin; (b) decomposition of ozone catalysed by OH^- ions; (c) decomposition of ozone catalysed by the presence of metal ions.

In order to determine whether there is a greater decomposition of ozone at alkaline pH, ozonisation of distilled water buffered to different pH with sulphuric acid or sodium hydroxide was carried out in the low-consistency ozone reactor described in Roncero et al. (2000). The evolution of inlet ozone charge (CZG) and residual ozone (CZS) of the samples ozonised at different pH are shown in Fig. 2. CZG is the same in all cases for the different samples, since it obviously does not depend on the sample used. When the process becomes stable ($t > 50$ s), the higher the pH of the sample, the lower the CZS. This confirms that ozone decomposes more readily as pH increases, generating more °OH radicals.

Eriksson, Ragnar and Reitberger (1998) showed that the formation of hydroxyl radicals begins to become substantial at pH ≥ 3. As mentioned above, the least effective additives are those applied at pH of over 3 (Fig. 1), a circumstance that could be related to a greater formation of °OH. Another parameter that must be taken into account is the solubility of ozone depending on the pH of the solution. According to Bouchard, Nugent and Berry (1995), ozone is 2.2 times more soluble at pH 2 than at pH 7.

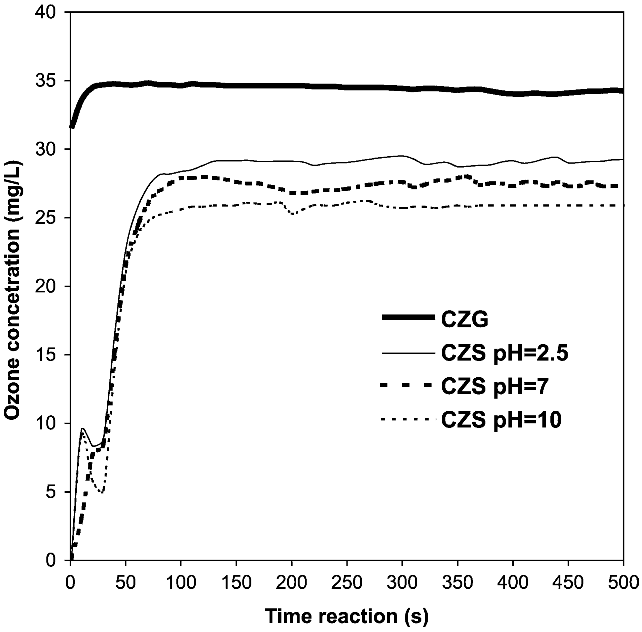

Fig. 2. Evolutions of generated ozone (CZG) and residual ozone (CZS) at different pH in distilled water.

Thus, pH has a substantial effect on ozone bleaching that could be related to the greater formation of °OH radicals at alkaline pH. Kishimoto and Nakatsubo (1998) state that °OH radicals are responsible for 40–70% of the degradation of carbohydrates. Therefore, the Z stage should be carried out under acid conditions, according to the results of the kinetic study (Roncero et al. 2002e), and of other authors (Eriksson et al., 1998; Jacobson et al., 1991; Liebergott, Van Lierop & Skothos, 1992; Lindholm, 1990; Ni et al., 1996; Ragnar, 2000). At this point we must consider the question as to whether the type of additive used to attain the desired pH has any effect on the bleaching.

3.3. Does the type of additive used at a specific pH affect the Z stage?

As can be seen in Fig. 1, different additives applied at around pH 2 give different CS values. This indicates that even when bleaching is carried out at a specific acid pH, the nature of the additive can affect the selectivity of this stage. Therefore, pH is not the only factor that can affect ozone bleaching.

The chain scission number of cellulose that can be avoided by application of a specific additive (CS_{NoA-R}) can be calculate from the viscosity values after R-stage (XOAZR and XOZR sequences) using the following formula:

$$CS_{NoA-R} = CS_{XOZR} - CS_{XOAZR}$$

Where:

$$CS_{XOZR} = \frac{DP_{XO} - DP_{XOZR}}{DP_{XOZR}}$$

$$CS_{XOAZR} = \frac{DP_{XO} - DP_{XOAZR}}{DP_{XOAZR}}$$

These values for the additives applied at pH ≈ 2 and with CS_{NoAR} similar to or higher than the additive sulphuric acid (A16) are shown in Fig. 3(a). All of the additives prevent the degradation of cellulose to a great extent, although not with the same efficiency, even when they are applied at the same pH. If the effect of the pH itself is subtracted, i.e. that of the sulphuric acid $(CS_{NoA-R})_{H2SO4}$ from the CS_{NoA-R} value for each additive, the cellulose chain scission number prevented by the nature of the additive itself $((CS_{NoA-R})_{NopH})$ is obtained according to the following formula:

$$(CS_{NoA-R})_{NopH} = CS_{NoA-R} - (CS_{NoA-R})_{H2SO4}$$

These values (Fig. 3(b)) clearly confirm that the nature of the additive also affects the lesser degradation of cellulose, with DMSO (A8) being the additive that most effectively prevents depolymerisation, followed by oxalic acid (A3). Taking into account the pulp properties and the high percentage of residual peroxide in the P stage (Roncero et al., 2002c), we can conclude that the additive with oxalic acid is the most effective of the additives studied.

Oxalic acid has a further positive effect in comparison with sulphuric acid, i.e. oxalic acid provides an additional benefit in ozone bleaching that cannot be attributed solely to the effect of the pH itself. This additional effect of oxalic acid is also demonstrated in the kinetic study carried out by Roncero et al. (2000) where: (a) The rate constant of delignification (k_L) increases quickly with low concentrations of oxalic acid and stabilises after concentrations of 5.4 ppm. (b) The rate constant of chromophore elimination ($k_{(k/s)}$) follows the same trend as that of delignification. (c) The rate constant of cellulose degradation (k_{DP}) decreases with the increased concentration of oxalic acid. (e) The selectivity of the process as defined by the ratio between k_L and k_{DP} increases with the increased concentration of oxalic acid in the sample.

Research by Meng and Hsieh (2000) shows that at pH 2 attained using sulphuric acid or acetic acid there is no difference in ozone consumption, indicating that the type of acid used has no effect on ozone consumption. In order to verify this, ozonisation of distilled water buffered to pH 2.5 with sulphuric acid and to pH 10 with sodium hydroxide and with addition of different amounts of oxalic acid was carried out in the low consistency ozone reactor. The evolution of generated ozone (CZG) and residual ozone (CZS) for the samples ozonised at pH 2.5 with different concentrations of oxalic acid are shown in Fig. 4(a). As observed in the stationary zone ($t > 50$ s), as the concentration of oxalic increases, less ozone is decomposed as the higher CZS value indicates. The same behaviour is observed at pH 10 with different concentrations of oxalic acid (Fig. 4(b)). This indicates that oxalic acid reduces the decomposition of ozone regardless of the pH. Fig. 4(c) shows the CZG and CZS curves at pH 2.5 and 10, with and without oxalic acid. Less ozone decomposes at pH 2.5 than at pH 10 (effect of the pH) and the difference is more pronounced when oxalic acid is added (additional effect of the oxalic acid). The effect of lower pH on decomposition of ozone is more noticeable than the effect of the addition of oxalic acid. Therefore, this confirms that oxalic acid has an additional effect on the improvement of the Z stage selectivity and on the decomposition of ozone, regardless of pH.

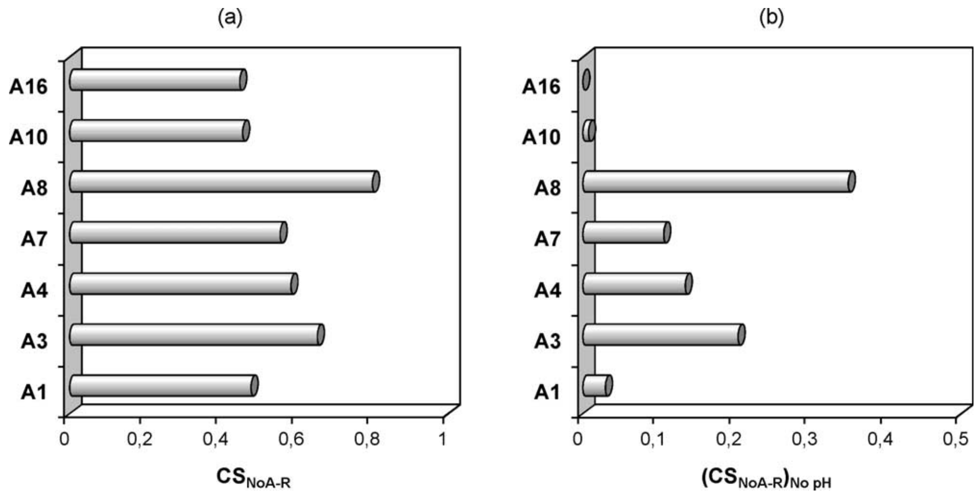

Fig. 3. (a) Chain scission number that can be avoided by application of a specific additive (CSNoA-R); (b) chain scission number in cellulose prevented by the nature of the additive itself without pH effect ((CSNoA-R)NopH). A1: acetic acid; A3: oxalic acid; A4: methanol; A7: citric acid; A8: DMSO; A10: EDTA; A16: sulphuric acid.

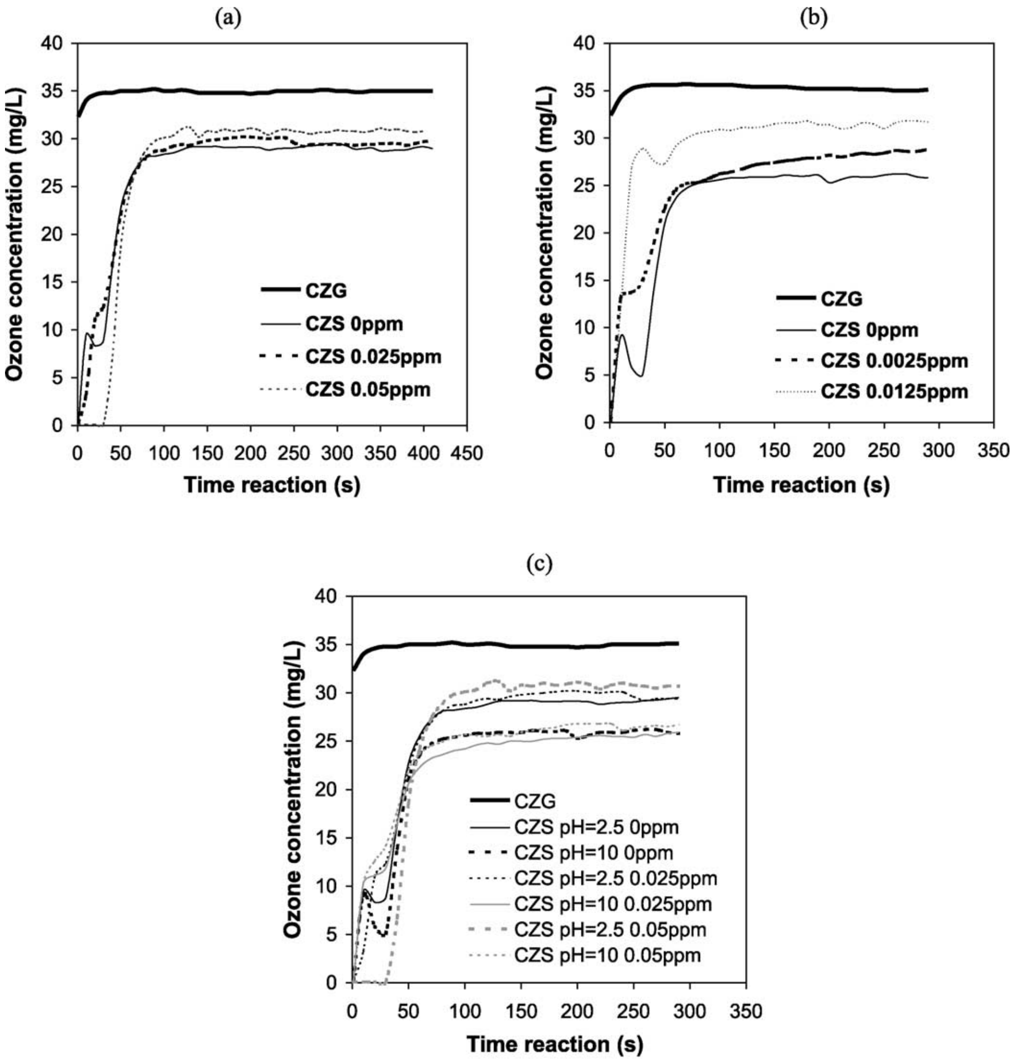

Fig. 4. Evolutions of generated ozone (CZG) and residual ozone (CZS) in distilled water with different oxalic acid doses, at pH 2.5 (a) and at pH 10 (b). CZG and CZS values, with and without oxalic acid, at pH 2.5 and pH 10 (c).

3.4. What is the cause of the additional effect of oxalic acid? What factors influence the beneficial effect of oxalic acid?

The cause of the additional effect of oxalic acid could be of a chemical nature, such as hydroxyl radical scavenging, chelating effect on metal ions, or catalysis of ozone and/or radicals reactions with lignin; and/or of a physical nature, such as modification of the solubility of ozone, stabilisation of ozone, or decreased swelling of cellulose. We will now attempt to clarify the beneficial and additional effects of oxalic acid, taking into account the results obtained and some of the aforementioned aspects.

3.4.1. Hydroxyl radical scavenger

The ^{o}OH radicals can be formed during the Z stage as a result of ozone reactions with lignin, by decomposition of ozone catalysed by OH^{-} and by metal ions. Considering that ozone bleaching is carried out at an acid pH, we can predict that ^{o}OH radicals will not be formed through decomposition of the ozone catalysed by OH^{-}. However, there remain two other principal pathways of ^{o}OH formation that can have an influence on the lower selectivity of ozone bleaching.

Therefore, one way of reducing the degradation of cellulose during ozone bleaching would be to scavenger or eliminate the ^{o}OH radicals or reduce their formation, which is already achieved in part by lowering the pH, although the nature of the acid used might also affect the reduction of ^{o}OH radicals. Numerous studies on the application in the Z stage of different additives with attributed ^{o}OH radical scavenging properties, such as methanol, ethanol, *ter*-butyl alcohol, ethylene glycol, DMSO, acetic acid, formic acid, oxalic acid, have been found in the literature (Bouchard et al., 2000; Cogo et al., 1996; Gierer & Zhang, 1993; Jacobson et al., 1991; Johansson et al., 2000; Kang, Zhang, Ni, & van Heiningen, 1995; Lind, Merényi, Ek, & Wägner, 1994; Magara, Ikeda, Tomimura, & Hosoya, 1998; Reitberger et al., 1995; Shimada, Ma, Akamatsu, & Hattori, 1994; Xu et al., 1995; Zhang, Kang, Ni, & Van Heiningen, 1997).

Some of the reagents above mentioned are included in Fig. 3(b). This figure shows the number of cellulose chain scissions prevented by application of the corresponding additive ($(CS_{NoA-R})_{NopH}$). In the case of acetic acid (A1), oxalic acid (A3), methanol (A4) and DMSO (A8), the degradation prevented could be attributed to the elimination of hydroxyl radicals, since all of them are known to be radical scavengers. The additive that prevents the degradation of cellulose to the greatest extent is DMSO (highest $(CS_{NoA-R})_{NopH}$ value). Many authors report that DMSO is an efficient hydroxyl radical scavenger (Byvoet, Balis, Shelley, Montgomery, & Barber, 1995; Das, Bandyopadhyay, Bhattacharjee, & Banerjee, 1997; Gao, Tawa, Masaki, Okano, & Sakurai, 1998; Lind et al., 1994; Lomonosova, Kirsch, & Degroot, 1998). Therefore this lesser degradation of cellulose when DMSO is applied can be attributed to the elimination of those radicals. In fact, the kinetic constant of the ^{o}OH radical with DMSO is around 7×10^{9} l/mol/s (NDRL Radiation Chemistry Data Centre, 2002). However, in the previous study of different additives (Roncero et al., 2002c), it is not considered efficient, since, although it provides the greatest reduction of degradation of cellulose, the brightness obtained is clearly lesser to that of the other additives. According to Ragnar (2000), the hydroxyl radical is not a bleaching agent and therefore its elimination will not have any effect on whether greater or lesser brightness is obtained. Lind et al. (1994) noted that DMSO, in addition to being an effective radical scavenger, also reacts with ozone with a rate constant similar to the rate constant of the ozone reaction with pulp. This means that DMSO can prevent degradation of carbohydrates by hydroxyl radicals, but it can also compete with lignin in reactions with ozone, minimising or preventing the reaction of ozone with chromophore groups in the pulp to attain greater brightness.

Acetic acid and methanol are considered good hydroxyl radical scavengers. The kinetic constants of the hydroxyl radical with acetic acid and methanol, and also with citric and oxalic acid are shown in Table 1 (Leitner & Doré, 1997; NDRL Radiation Chemistry Data Centre, 2002; Zhang et al., 1997). Taking into account the concentration of the additive used, the approximate ^{o}OH radical scavenging capacity can be calculated. Methanol has the highest radical scavenging capacity, followed by citric acid, acetic acid, and finally oxalic acid. In order to attain the same ^{o}OH scavenging capacity as methanol, it would be necessary to add 20 times more of citric acid, 50 times more of acetic acid and 500 times more of oxalic acid. That methanol (A4) prevents the degradation of cellulose to a greater extent than acetic acid (A1) and citric acid (A7), confirming this finding (Fig. 3(b)). However, oxalic acid (A3), prevents the degradation of cellulose to a greater extent, even in comparison with methanol, which has a greater ^{o}OH scavenging capacity. Therefore, ^{o}OH scavenging cannot be the only factor attributed to the additional effect of oxalic acid. Thus, part of the degradation prevented by oxalic acid can be explained by a partial inhibition of the hydroxyl radicals, but this radical scavenging capacity cannot be the only reason for the greater efficiency obtained through use of this acid.

Table 1
Concentration, kinetic rate constants with hydroxyl radical ($k_{^{o}OH}$) and scavenging capacity of hydroxyl radical of the acetic acid, methanol, citric acid and oxalic acid

Additive	Concentration (mol/l)	$k_{^{o}OH}$ (l/mol/s)	Scavenging capacity ^{o}OH (s^{-1})
Acetic acid	0.31	1.6×10^{7}	0.05×10^{8}
Methanol	0.31	1.0×10^{9}	3×10^{8}
Citric acid	0.31	5.0×10^{7}	0.15×10^{8}
Oxalic acid	0.31	1.4×10^{6}	0.004×10^{8}

3.4.2. *Ozone stabiliser and decreased swelling of cellulose (decreased accessibility)*

According to Leitner and Doré (1997) ozone does not react with oxalic acid, and with methanol either (Lind et al., 1994). The addition of oxalic acid leads to lesser decomposition of ozone (Fig. 4). This indicates that oxalic acid could act as a stabiliser of ozone and/or increase its solubility, since this figure shows that in the presence of oxalic acid: (a) decomposition of ozone is reduced and therefore the formation of ^{o}OH radicals that facilitate the degradation of cellulose is also reduced, (b) there is a greater amount of ozone available for reaction with lignin, taking into account that ozone is more selective than ^{o}OH radicals, (c) ozone is not consumed by the oxalic acid.

In a previous research (Roncero et al., 2003), TCF ozone sequences with and without oxalic acid were studied and showed that when oxalic acid is applied the total chain scission number in the cellulose (CS_{total}) is reduced by 27% and the cellulose chain scission number because of the direct attack by ozone and/or hydroxyl radicals (CS_{G}) is reduced by 55.3%. This could be due to the effect above mentioned, i.e. that there is less decomposition of ozone in the presence of oxalic acid and therefore fewer ^{o}OH radicals which can cause degradation of cellulose.

There could also be less swelling of the cellulose and therefore lower accessibility of the cellulose to the oxidising reagents. Some authors (Bouchard et al., 2000; Kamishima, Fujii, & Akamatsu, 1984; Mbachu & Manley, 1981; Ruiz, Freer, Rodriguez, & Baeza, 1997) state that there is a decrease in swelling of the cellulose in the presence of organic acids. Kamishima et al. (1984) considered that the positive effects of oxalic acid and methanol are due to a lesser swelling of the cellulose, this would limit the access of the ozone and the radicals to the fibre or to specific areas of the fibre, resulting in less degradation of the cellulose. The swelling or the accessibility of the fibre in different media can be evaluated as the water retention value (WRV).

Table 2
Water retention value (WRV) of eucalyptus XO-pulp at different pH and oxalic acid

pH	Reagent	Oxalic acid (ppm)	WRV (%)
10.5	NaOH	–	123
2.5	H_2SO_4	–	120
2.5	H_2SO_4	125	118
2	–	200	116

The results are presented in Table 2, and show that the WRV is higher at pH 10 than at pH 2.5 (with sulphuric acid). When oxalic acid is added, the fibre has a lower water retention capacity, which might be related to a lesser swelling of the fibre in presence of this additive.

In fact, the crystallinity study (Fig. 5) shows that ozone treatments reduce crystallinity (CrI) slightly, both at pH 10 and pH 2.5 with sulphuric acid. At high ozone charges and pH 2.5, the ozone appears to react primarily with the more crystalline regions of the cellulose since CrI decreases while at pH 10 it appears to react indiscriminately with amorphous and crystalline cellulose. However, at pH 2.5 with oxalic acid, the degree of crystallinity is maintained, which indicates that oxalic acid could act to decrease accessibility of the crystalline cellulose, thereby preventing excessive degradation of the more ordered portion of the cellulose by the ozone and other radical species (Roncero et al., 2003).

The study of carbohydrates (Roncero et al., 2003) confirmed that cellulose is degraded during the Z stage, but when oxalic acid is applied this degradation appears to affect cellulose with lower molecular weight. Therefore, the presence of oxalic acid seems to prevent 'indiscriminate' degradation of the pulp by the ozone, i.e. oxalic acid appears to guide the ozone reactions towards more heterogeneous regions with lower molecular weight located mainly on the surface of the fibre, preserving the more crystalline regions with higher molecular weight located mainly in the middle walls (S_2) of the fibre, which could be related to a lower accessibility of the cellulose.

Moreover, the cellulose chain scission number increases by 16% in the presence of oxalic acid because of to the content of carbonyl groups ($CS_{C=O}$), indicating a greater formation of these groups. Chirat and Lachenal (1995) state that the formation of carbonyl groups in the cellulose chain is due solely to direct reaction with the ozone. Dence and Reeve (1996) deduce that carbonyl groups are formed mostly by direct reaction with the ozone, although some of them might be formed by hydroxyl radicals. It has been showed that ozone undergoes less decomposition in the presence of oxalic acid, which indicates that there is more ozone available to react with lignin or carbohydrates. Even if the lesser swelling of cellulose in the presence of oxalic acid is accepted, the accessibility of ozone to cellulose cannot be totally avoided. In accordance with the findings of Chirat and Lachenal (1995) and Dence and Reeve (1996), the greater amount of molecular ozone would give rise to a greater formation of carbonyl groups in the cellulose, which confirms the $CS_{C=O}$ results obtained (Roncero et al., 2003).

Even so, the increase in the formation of carbonyl groups is not very high. Therefore, the theory of lesser swelling and then lesser accessibility could be compatible with the greater stability of ozone in the presence of oxalic acid. However, these properties of oxalic acid could also be attributed to methanol, since Bouchard et al. (2000) and Kamishima et al. (1984) state that methanol decreases the swelling of the cellulose. Brolin, Gierer and Zhang (1993), Gierer and Zhang (1993) and Ruiz et al. (1997) also note that acetic acid is an excellent stabiliser of ozone. Since there are differences in the improvement of selectivity by these additives, it is clear there is a further factor attributable to oxalic acid that makes it more selective than the other additives.

3.4.3. Catalysing effect on reactions of ozone and/or radicals with lignin

A kinetic study (Roncero et al., 2000) shows that as oxalic acid is added, the kinetic constant of delignification

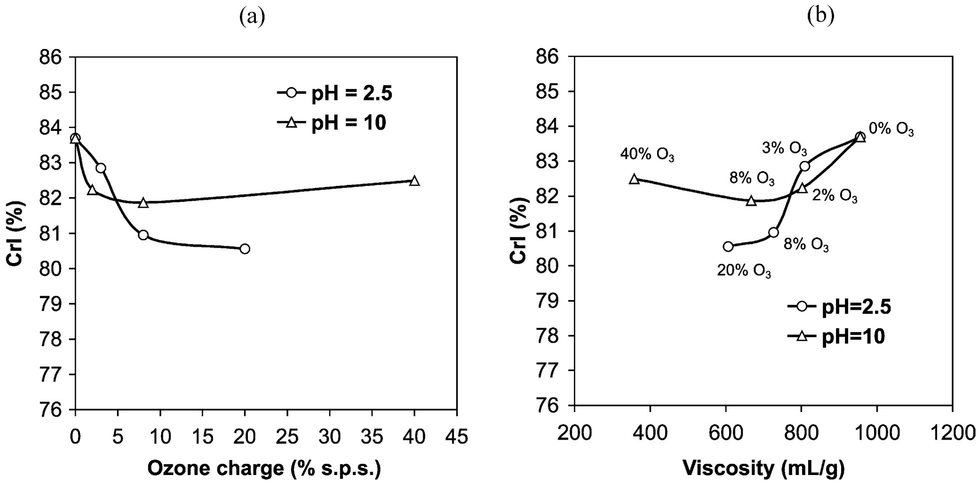

Fig. 5. CrI (%) of XOZ pulp, at different ozone charges and at pH 2.5 and 10, vs. ozone charge consumption (a) and pulp viscosity (b).

(k_L) increases rapidly, although it eventually stabilises, while the kinetic constant of degradation of cellulose (k_{DP}) decreases constantly. Therefore, oxalic acid has a catalytic effect on reactions of ozone and/or radicals with lignin, while it partially inhibits reactions with carbohydrates. This could be related to the lesser swelling of the cellulose in the presence of oxalic acid, as mentioned above. However, Kamishima et al. (1984) also suggest that the mechanism for protection of carbohydrates in the presence of methanol is due to the combined effects of the increased rate of delignification and the decrease in the reactivity of the cellulose with the ozone. This means that there should be no difference between these two additives, which does not agree with the results obtained in this work, since these results show that oxalic acid is more selective than methanol.

3.4.4. Inhibitor of ^{o}OH radical formation

It is known that decomposition of ozone gives rise to formation of hydroxyl radicals. However, *is this the first radical that is formed?* According to Reitberger et al. (1995) the first radical formed is the superoxide anion radical (O_2^{o-}), and this has recently been proved (Eriksson et al., 1998). These authors state that the main cause of the low selectivity of the Z stage is the chain reaction mediated by the superoxide anion radical that gives rise to the formation of hydroxyl radicals. In other words, the first radical to form is the O_2^{o-} anion, which then reacts with the ozone (kinetic constant of $10^9\ M^{-1}\ s^{-1}$), generating the ^{o}OH radical according to the following reactions:

$$\begin{array}{l} O_2^{\circ-} + O_3 \rightarrow O_3^{\circ-} + O_2 \\ O_3^{\circ-} + H^+ \rightarrow {}^{\circ}OH + O_2 \\ \hline O_2^{\circ-} + O_3 + H^+ \rightarrow {}^{\circ}OH + 2O_2 \end{array} \qquad \text{(Exp.1)}$$

In turn, the hydroxyl radicals formed in this way can then react with the ozone, giving rise to a chain reaction that generates more ^{o}OH radicals according to the following reactions:

$$\left.\begin{array}{l} {}^{\circ}OH + O_3 \rightarrow HO_2^{\circ} + O_2 \\ HO_2^{\circ} \leftrightarrow O_2^{\circ-} + H^+ \\ O_2^{\circ-} + O_3 \rightarrow O_3^{\circ-} + O_2 \\ O_3^{\circ-} + H^+ \rightarrow {}^{\circ}OH + O_2 \end{array}\right\} \qquad \text{(Exp.2)}$$

According to some authors (Gierer, 1997; Reitberger et al., 1995; Ragnar, 2000), ^{o}OH radicals are species that do not diffuse, i.e. they have a short lifetime and cannot move around in the solution or penetrate the fibres. Therefore, these species will react near the place where they are formed. On the other hand, the O_2^{o-} radical is a species with a long lifetime and it therefore survives long enough to diffuse into the fibre. Gierer (1997) and Ragnar (2000) state that the O_2^{o-} radical is selective, since it does not react or reacts only negligibly with carbohydrates, meaning that in theory its existence does not constitute a problem in connection with the degradation of carbohydrates. However, once it is inside the fibre, the O_2^{o-} radical can give rise to the formation of ^{o}OH radicals (Exp. 1) that cause degradation of the cellulose. Therefore, the O_2^{o-} radical increases the generation of ^{o}OH radicals and furthermore serves as a vehicle for movement of the ^{o}OH into the fibres and to other places that it would not reach on its own, where it can react with cellulose.

If the O_2^{o-} radical is eliminated, fewer hydroxyl radicals will be formed. Therefore, one way of controlling the formation of ^{o}OH, and thus the ozone bleaching selectivity, is by scavenging or eliminating the O_2^{o-} radical. This would prevent the formation of ^{o}OH radicals when the O_2^{o-} penetrates the fibres. The HPLC study of carbohydrates (Roncero et al., 2003) shows that during the Z stage cellulose degradation takes place, but that when oxalic acid is applied, we have cellulose of low molecular weight. Furthermore, the study of crystallinity (Fig. 5) shows that the CrI is maintained when oxalic acid is applied, which indicates that there is less accessibility to crystalline cellulose. In general, cellulose is more crystalline the deeper it is within the fibre and is more amorphous on the surface of the fibre. If the entry of O_2^{o-} into the fibre is avoided, the ^{o}OH formation in the interior places, decreasing the attack on the crystalline cellulose and thereby maintaining crystallinity. The ^{o}OH radicals produced by other ways will be formed on the surface of the fibre, and since ^{o}OH radicals do not diffuse, they will react in situ, attacking the surface of the fibre where the more amorphous regions or the cellulose with lower molecular weight are located. These hypotheses agree with the HPLC and crystallinity results (Roncero et al., 2003).

3.4.5. How can the action of the O_2^{o-} anion radical be avoided?

The O_2^{o-} can be eliminated through contribution of protons to the system, i.e. by maintaining an acid pH, giving rise to formation of hydrogen peroxide:

$$O_2^{o-} + H^+ \overset{pK_a \approx 4,8}{\leftrightarrow} HO_2^{o} \qquad \text{(Exp.3)}$$

$$HO_2^{o} + O_2^{o-} \rightarrow HO_2^{-} + O_2 \xrightarrow{H^+} H_2O_2 + O_2 \qquad \text{(Exp.4)}$$

Reaction 3 takes place with a kinetic constant of approximately $10^9\ M^{-1}\ s^{-1}$, which is similar to that of the O_2^{0-} radical reaction with ozone (Exp. 1). The HO_2^{0} radical formed (Exp. 3) can react with ozone in accordance with reaction 5 generating ^{o}OH radicals, but with a very low kinetic constant ($10^4\ M^{-1}\ s^{-1}$) (Eriksson et al., 1998):

$$HO_2^o + O_3 \rightarrow {}^oOH + 2O_2 \tag{Exp.5}$$

Consequently, for effective elimination of the O_2^{o-} radical (Exp. 3 and 4) the medium must have a high protonic activity. However, a very low pH can give rise to hydrolysis of carbohydrates. Thus, the ‘additional’ positive effect of oxalic acid in comparison with other acids (such as sulphuric acid) could be due its providing a high protonic activity at a particular pH. Our hypothesis is that oxalic acid could act as a *hydrogen donor* for the O_2^{o-} radical in the following reaction:

$$H_2A + O_2^{o-} \rightarrow HO_2^o + HA^- \tag{Exp.6}$$

The HO_2^o radical formed can react with the ozone to produce ^{o}OH radicals (Exp. 5), but at a much lower rate ($10^4\ M^{-1}\ s^{-1}$) than its reaction with the O_2^{o-} radical ($10^9\ M^{-1}\ s^{-1}$), to give hydrogen peroxide (Exp. 4). Thus the formation of ^{o}OH radicals would be reduced, allowing greater selectivity during ozone bleaching. It is important for the H–AH bond to be sufficiently weak to allow the O_2^{o-} to remove the proton easily. Acids with a low pK_a value have this requisite. Oxalic acid is an ideal candidate, since its first pK_a value is 1.23. Another important property of oxalic acid is that it does not react with ozone or reacts with it only at low rates (Leitner & Doré, 1997), meaning that it might very possibly react at a higher rate with the superoxide radical than with ozone.

The enzyme studies of application of fungi and ligninolytic enzymes found in the literature consulted (Dutton & Evans, 1996; Kuan & Tien, 1993; Shimada, Akamatsu, Tokimatsu, Mii, & Hattori, 1997; Zapanta & Tien, 1997) state that oxalic acid is involved in the enzyme hydrolysis reactions, acting as a hydrogen donor and also as a chelating agent of metal ions.

Another study of the use of antioxidants to stabilise synthetic pigments (Uquiche & Romo, 2000) indicates that citric acid acts as a hydrogen donor to reactivate the antioxidants and also as a chelating agent of metal ions. Our previous study (Roncero et al., 2002c) showed that citric acid also gives good results applied as an additive in Z stages. It could also be behaving as a hydrogen donor, but its protective effect in connection with the cellulose chain scission number is not as significant as in the case of oxalic acid (Fig. 3). This could be due to the fact that the first pK_a of citric acid is 3.14, making it more difficult for the O_2^{o-} radical to remove the proton, in comparison with oxalic acid.

3.4.6. Chelating agent of metal ions

The hypothesis that oxalic acid acts as a hydrogen donor to the O_2^{o-} to prevent the formation of the ^{o}OH is a very interesting and altogether acceptable one. However, a problem can arise caused by this elimination of O_2^{o-} radicals by means of proton contribution, which generates hydrogen peroxide (Exp. 3, 4 and 6). It is known that hydrogen peroxide can decompose in the presence of metal ions, giving rise to formation of ^{o}OH radicals according to the following reaction (Backa, Gierer, Reitberger, & Nilsson, 1992; Gierer, Jansbo, & Yoon, 1998; Grönroos, Pitkänen, & Vuolle, 1998; Hyde & Wood, 1997; Lambert, 1999; Ragnar, 2000):

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + OH^- + {}^oOH \tag{Exp.7}$$

The metal ions are presented in water and also in the pulp.

In addition, the O_2^{o-} radical can also react with hydrogen peroxide to form ^{o}OH radicals (Gierer et al., 1998; Guillén, Muñoz, Gómez-Toribio, Martínez, & Martínez, 2000):

$$O_2^{o-} + H_2O_2 \rightarrow O_2 + OH^- + {}^oOH \tag{Exp.8}$$

It has been also previously mentioned that metal ions can catalyse the decomposition of ozone, forming ^{o}OH radical. However, Eriksson and Reitberger (1995) and Ragnar (2000) note that ozone is not as sensitive as hydrogen peroxide to the presence of metal ions, owing mainly to the high reaction rate of the ozone with the residual lignin.

Lambert (1999) states that, under normal conditions in the Z stage, the ozone reacts more rapidly with the Fe^{2+} (Exp. 9 and 10) than the hydrogen peroxide (Exp. 11, Fenton reaction), giving Fe^{3+} and therefore preventing formation of the ^{o}OH radical.

However, the Fe^{3+} can react with the hydrogen peroxide (Exp. 12) forming the O_2^{o-} radical which can give rise to formation of ^{o}OH radicals (Exp. 1).

$$Fe^{2+} + O_3 \rightarrow (FeO)^{2+} + O_2 \tag{Exp.9}$$

$$(FeO)^{2+} + Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{Exp.10}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^oOH + OH^- \tag{Exp.11}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2^{o-} + H_3O^+ \tag{Exp.12}$$

Acid pre-treatment can be used to eliminate metal ions from the hydrophilic portions of the pulp, but those found in the lipophilic portions (lignin) can remain after the acid or chelating treatment. Therefore, it is preferable for the acid or chelating agent to be present during ozone bleaching, since some of these metal ions can be released or become more accessible, as a consequence of the oxidising reactions. In the study of pre-treatments (Roncero et al., 2002b) and additives (Roncero et al., 2002c), the additives are more effective, since they are present during the Z stage. Moreover, the effect of pH in the Z stage is significant, being more noticeable at acid pH, since metal ions can be eliminated.

Oxalic acid could play a role in this effect. In addition to providing the optimal pH during bleaching and being present during this stage, it can act as a chelating agent of the metal ions that are released from regions where they were trapped and were largely inaccessible prior to the oxidation reactions taking place during the Z stage.

EDTA (A10) is an effective chelating agent of metal ions and sulphuric acid also eliminates them. Even so, they do not surpass oxalic acid in the increase of selectivity of the Z stage, as seen in Fig. 3. Possibly, oxalic acid has a greater or more effective capacity as a chelating agent of metal ions present in the water and the pulp, inhibiting their potential degradatory effects in cellulose. Cameselle, Núñez and Lema (1998), Hyde and Wood (1997) and Luhta and Åkerholm (1998) showed that oxalic acid forms strong complexes with iron, which is thoroughly acceptable, since it possesses an important chelating characteristic, i.e. it has two carboxyl ends groups (Devenyns, Chauveheid, & Mårtens, 1998).

In summary, it has been shown that oxalic acid has an additional effect in comparison with the acids and chelating agents used in previous studies. This additional effect could be due to different factors such hydroxyl radical scavenger, ozone stabiliser, decrease of swelling of the cellulose, catalyst of reactions of ozone and/or radicals with lignin, it does not react with ozone, it acts as an efficient hydrogen donor and as a chelating agent.

4. Problem of the formation of oxalic acid

The formation of oxalic acid in the pulp bleaching process has recently been the subject of a number of studies. Oxalic acid can readily form solid crystals of calcium oxalate that can precipitate and cause serious problems with deposits and scale in the process circuit. This problem becomes even more serious when closure of circuits is carried out, since the amount of oxalic acid in effluents can steadily increase (Bergnor-Gidnert, Tomani, & Dahlman, 1998; Da Costa, Correia, Bissiati, & Molinar, 2000; Elsander, Ek, & Gellerstedt, 2000; Luhta & Åkerholm, 1998; Nilvebrant & Reimann, 1996; Rudie, 2000). According to Quesada et al. (1998), oxalic acid is formed as a degradation product of low molecular weight during ozonisation of lignin at high ozone concentrations, meaning that it is a final product of degradation. Luhta and Åkerholm (1998) found, in their industrial trial, that the amount of oxalic acid formed during the Z stage was relatively small, which they attributed to small amounts of hexenuronic acid present in their pulps.

Furthermore, the kinetic study (Roncero et al., 2000) shows that a concentration of 5.4 ppm (corresponding to 0.0486 kg oxalic acid/tonne medium consistency pulp) is enough to obtain the beneficial effect of this additive. Table 3 shows some of the values for oxalic acid formed during the Z stage as given in the literature consulted (Lindeberg, 1996; Nilvebrant & Reimann, 1996). These values show that the concentration of oxalic acid generated is higher than the concentration applied to improve selectivity. Thus, if it is accepted that oxalic is an effective additive in the bleaching stage, the effluent could be recirculated within the Z stage itself to make use of the oxalic acid formed during this stage.

Table 3
Oxalic acid formation during Z-stage

Ozone applied (% o.d.p.)	Oxalic acid (kg/t pulp)[a]	Oxalic acid (kg/t pulp)[b]
0.1	0.15	–
0.25	–	0.05
0.3	0.54	–
0.5	0.88	0.5
0.75	–	1.5
1	–	2.5

[a] Lindeberg, 1996

[b] Nilvebrant & Reimann, 1996

5. Conclusions

The most effective additive studied is oxalic acid, which produces an effect additional to the other additives and independently of the pH. From the studies carried out, it is deduced that this additional effect of oxalic acid could be due to the fact that this additive might give rise to a combination of factors that increase the selectivity of the Z stage. These factors are: hydroxyl radical scavenger, ozone stabiliser, decrease of swelling of the cellulose, catalyst of reactions of ozone and/or radicals with lignin, hydrogen donor inhibiting the formation of hydroxyl radicals and chelating agent of metal ions. Thus, in studying the effects of oxalic acid, we have determined the requisites for an additive to be optimally effective in cellulose ozone treatments.

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References

Backa, S., Gierer, J., Reitberger, T., & Nilsson, T. (1992). Hydroxyl radical activity in brown-rot fungi studied by a new chemiluminescence method. *Holzforschung*, *46*(1), 61–67.

Bergnor-Gidnert, E., Tomani, P. E., & Dahlman, O. (1998). Influence on pulp quality during the removal of hexenuronic acids. *International Pulp Bleaching Conference, Helsinki*, *Book 1*, 185–193.

Biermann, C. J., & Kronis, J. D. (1997). Bleaching chemistry, oxidation potentials of bleaching agents. *Progress in Paper Recycling*, *6*(3), 65–70.

Bouchard, J., Morelli, E., & Berry, R. M. (2000). Gas-phase addition of solvent to ozone bleaching of kraft pulp. *Journal of Pulp and Paper Science*, *26*(1), 30–35.

Bouchard, J., Nugent, H. M., & Berry, R. M. (1995). The role of water and hydrogen ion concentration in ozone bleaching of kraft pulp at medium consistency. *Tappi Journal*, *78*(1), 74–82.

Brolin, A., Gierer, J., & Zhang, Y. (1993). On the selectivity of ozone delignification of softwood kraft pulps. *Wood Science and Technology*, *27*(2), 115–129.

Browning, B. L. (1967). Crystallinity and accessibility. In J. Wiley (Ed.), *Methods of wood chemistr* (p. 499) USA: Interscience Publishers, Chapter 24.

Byvoet, P., Balis, J. U., Shelley, S. A., Montgomery, M. R., & Barber, M. J. (1995). Detection of hydroxyl radicals upon interaction of ozone with aqueous-media or extracellular surfactant—The role of trace iron. *Archives of Biochemistry and Biophysics*, *319*(2), 464–469.

Cameselle, C., Núñez, M. J., & Lema, J. M. (1998). Bioblanqueo de caolines con Aspergillus niger. *Afinidad*, *LV(478)*, 397–406.

Chirat, C., & Lachenal, D. (1995). Effect of hydroxyl radicals on cellulose and pulp and their occurrence during ozone bleaching. *The Eighth International Symposium on Wood and Pulping Chemistry, Helsinki*, *1*, 293–299.

Cogo, E., Baig, S., Briois, L., Molinier, J., Coste, C., Bailli, A., & Thieblin, E. (1996). Optimisation des conditions d'ozonation de la pâte à papier à haute consistance en présence de *tert*-butanol. *ATIP*, *50*(6), 219–227.

Colodette, J. L., Singh, U. P., Ghosh, A. K., & Singh, R. P. (1993). Ozone bleaching research focuses on reducing high cost, poor selectivity. *Pulp and Paper*, *67*(6), 139–147.

Da Costa, M. M., Correia, F. M., Bissiati, J. I., & Molinar, P. (2000). Estudos de solubilização química de incrustações no estágio D_2 da seqüência ECF-$D_0EoD_1D_2$. *O Papel*, *2*, 52–59.

Das, D., Bandyopadhyay, D., Bhattacharjee, M., & Banerjee, R. K. (1997). Hydroxyl radical is the major causative factor in stress-induced gastric-ulceration. *Free Radical Biology and Medicine*, *23*(1), 8–18.

Dence, C. W., & Reeve, D. W. (1996). *Pulp bleaching. Principles and practice*. Atlanta: Tappi Press.

Devenyns, J., Chauveheid, E., & Mårtens, H. (1998). Uronic acids and metals control. *International Pulp Bleaching Conference, Helsinki*, *Book 1*, 151–157.

Dutton, M. V., & Evans, C. S. (1996). Oxalate production by fungi, its role in pathogenicity and ecology in the soil environment. *Canadian Journal of Microbiology*, *42*, 881–895.

Ek, M., Gierer, J., & Jansbo, K. (1989). Study on the selectivity of bleaching with oxygen-containing species. *Holzforschung*, *43*(6), 391–396.

Elsander, A., Ek, M., & Gellerstedt, G. (2000). Oxalic acid formation during ECF and TCF bleaching of kraft pulp. *Tappi Journal*, *83*(2), 73–77.

Eriksson, T., & Gierer, J. (1985). Studies on the ozonation of structural elements in residual kraft lignins. *Journal of Wood Chemistry and Technology*, *5*(1), 53–84.

Eriksson, T., Ragnar, M., & Reitberger, T. (1998). Studies on the radical formation in ozone reactions with lignin and carbohydrate model compounds. *International Pulp Bleaching Conference, Helsinki*, *Book 1*, 119–126.

Eriksson, T., & Reitberger, T. (1995). *Formation of hydroxyl radicals from direct ozone reactions with pulp constituents* (*Vol. 2*). *The Eighth International Symposium on Wood and Pulping Chemistry, Helsinki*, pp. 349–354.

Gao, D. Y., Tawa, R., Masaki, H., Okano, Y., & Sakurai, H. (1998). Protective effects of Baicalein against cell-damage by reactive oxygen species. *Chemical and Pharmaceutical Bulletin*, *46*(9), 1383–1387.

Gierer, J. (1997). Formation and involvement of superoxide (O_2^{o-}/HO_2^o) and hydroxyl (OH^o radicals in TCF bleaching processes: A review. *Holzforschung*, *51*(1), 34–46.

Gierer, J., Jansbo, K., & Yoon, B.-H. (1998). On the participation of hydroxyl radicals in oxygen and hydrogen peroxide bleaching processes. *Personal Communication*.

Gierer, J., & Zhang, Y. (1993). *The role of hydroxyl radicals in ozone bleaching processes* (*Vol. 2*). *Seventh International Symposium on Wood and Pulping Chemistry, Beijing*, pp. 951–960.

Grönroos, A. J., Pitkänen, M., & Vuolle, M. (1998). Radical formation in peroxide-bleached kraft pulp. *Journal of Pulp and Paper Science*, *24*(9), 286–290.

Guillén, F., Muñoz, C., Gómez-Toribio, V., Martínez, A. T., & Martínez, M. J. (2000). Oxygen activation during oxidation of methoxyhydroquinones by Laccase from *Pleurotus Eryngii*. *Applied and Environmental Microbiology*, *66*(1), 170–175.

Hoigné, J., & Bader, H. (1983a). Rate constants of reactions of ozone with organic and inorganic compounds in water-I. Non-dissociating organic compounds. *Water Research*, *17*, 173–183.

Hoigné, J., & Bader, H. (1983b). Rate constants of reactions of ozone with organic and inorganic compounds in water-II. Dissociating organic compounds. *Water Research*, *17*, 185–194.

Hyde, S. M., & Wood, P. M. (1997). A mechanism for production of hydroxyl radicals by the brown-rot fungus *Coniophora puteana*: Fe(III) reduction by cellobiose dehydrogenase and Fe(II) oxidation at a distance from the hyphae. *Microbiology*, *143*, 259–266.

Jacobson, B., Lindlad, P.-O., & Nilvebrant, N.-O. (1991). *Lignin reactions affect the attack of ozone on carbohydrates* (*Vol. 2*). *International Pulp Bleaching Conference, Stockholm*, pp. 45–58.

Johansson, E. E., Lind, J., & Ljunggren, S. (2000). Aspects of the chemistry of cellulose degradation and the effect of ethylene glycol during ozone delignification of kraft pulps. *Journal of Pulp and Paper Science*, *26*(7), 239–244.

Kamishima, H., Fujii, T., & Akamatsu, I. (1984). Mechanism of carbohydrate protection with oxalic acid and methanol during ozone bleaching of unbleached kraft pulp. *Journal of Wood Research Society*, *30*(11), 927–935.

Kang, G., Zhang, Y., Ni, Y., & van Heiningen, A. R. P. (1995). *Influence of lignins on the degradation of cellulose during ozone bleaching* (*Vol. I*). *The Eighth International Symposium on Wood and Pulping Chemistry, Helsinki*, pp. 345–352.

Kishimoto, T., & Nakatsubo, F. (1998). Non-chlorine bleaching of kraft pulp. *Holzforschung*, *52*(2), 185–190.

Kuan, I.-C., & Tien, M. (1993). Stimulation of Mn peroxidase activity: A possible role for oxalate in lignin biodegradation. *Proceedings of National Academic Sciences, USA*, *90*, 1242–1246.

Lachenal, D., & Bokström, M. (1986). Improvement of ozone prebleaching of kraft pulps. *Journal of Pulp and Paper Science*, *12*(2), 50–53.

Lambert, F., 1999. *Nouvelles utilisations de l'ozone dans le blanchiment des pâtes à papier chimiques*. PhD Thesis, Institut National Polytechnique de Grenoble, Grenoble, Francia.

Leitner, N. K. V., & Doré, M. (1997). Mécanisme d'action des radicaux OH^0 sur les acides glycolique, glyoxylique, acetique et oxalique en solution aqueuse, incidence sur la consommation de peroxyde d'hydrogène dans les systèmes H_2O_2/UV et O_3/H_2O_2. *Water Research*, *31*(6), 1383–1397.

Liebergott, N., Van Lierop, B., & Skothos, A. (1992). A survey of the use of ozone in bleaching pulps, Part 1. *Tappi Journal*, 145–152.

Lind, J., Merényi, G., Ek, M., & Wägner, K. (1994). The chemistry of ozone during pulp bleaching. *Journal of Wood Chemistry Technonogy*, *17*(3), 297–326.

Lindeberg, O. (1996). *Concurrent bleaching and metal management by addition of EDTA to chlorine dioxide and ozone stages, degradation of EDTA and formation of oxalic acid* (*Book 1*). *International Pulp Bleaching Conference, Tappi*, pp. 323–330.

Lindholm, C.-A. (1990). Effect of pulp consistency and pH in ozone bleaching—Part 6. Strength properties. *Nordic Pulp Paper Research Journal*, *1*, 22–27.

Lomonosova, E. E., Kirsch, M., & Degroot, H. (1998). Calcium vs. iron-mediated processes in hydrogen-peroxide toxicity to L929 cells—Effects of glucose. *Free Radical Biology and Medicine*, *25* (4/5), 493–503.

Luhta, U., & Åkerholm, M. (1998). *Formation of oxalic acid in the kraft pulping process of Metsä–Rauma* (*Book 1*). *International Pulp Bleaching Conference, Helsinki*, pp. 289–294.

Magara, K., Ikeda, T., Tomimura, Y., & Hosoya, S. (1998). Accelerated degradation of cellulose in the presence of lignin during ozone bleaching. *Journal of Pulp and Paper Science*, *24*(8), 264–268.

Mbachu, R. A. D., & Manley, R. St. J. (1981). The effect of acetic and formic acid pretreatment on pulp bleaching with ozone. *Tappi Journal*, *64*(1), 67–70.

Meng, M. X., & Hsieh, J. S. (2000). Improved ozone efficiency at reduced charges—An electrochemical model and new experimental approach. *Tappi Journal*, *83*(9), 1–11.

NDRL Radiation Chemistry Data Center, 2002 (On line). Web, URL ⟨http://allen.rad.nd.edu⟩ (March 27, 2002).

Ni, Y., Kang, G. J., & Van Heiningen, A. R. P. (1996). Are hydroxyl radicals responsible for degradation of carbohydrates during ozone bleaching of chemical pulp? *Journal of Pulp and Paper Science*, *22*(2), J53–J57.

Nilvebrant, N.-O., & Reimann, A. (1996). *Xylan as a source for oxalic acid during ozone bleaching*. *Fourth European Workshop on Lignocellulosics and Pulp, Stresa*, pp. 485–491.

Nompex, P., Doré, M., De Laat, M., Bawa, M., & Legube, B. (1991). Ozonisation of selected molecules constituting cellular matter. *Ozone Science Engineering*, *13*, 256–286.

Quesada, J., Rubio, M., & Gómez, D. (1998). Actuación directa del ozono molecular sobre la lignina y sus compuestos modelo. *Afinidad*, *55*(478), 413–421.

Ragnar, M., 2000. *On the importance of radical formation in ozone bleaching*. Doctoral Thesis, Kungliga Tekniska Högskolan (KTH), Estocolmo, Sweden.

Reitberger, T., Eriksson, T., Ek, M., & Ihren, G. (1995). *On the importance of radical species in TCF-bleaching* (*Vol. I*). *The Eighth International Symposium on Wood and Pulping Chemistry, Helsinki*, pp. 301–307.

Roncero, M. B., 2001. *Achievement of a TCF sequence with the application of ozone and enzymes for the bleaching of wood and non-wood pulps. Improvement of Z stage. Effects on components and morphology of fibres*. Doctoral Thesis. Polytechnical University of Catalonia, Terrassa, Spain.

Roncero, M. B., Colom, J. F., & Vidal, T. (2002a). Application of post-treatments to the ozone bleaching in an eucalypt kraft pulp to increase the selectivity. Part A. *Appita Journal*, *55*(4), 305–309.

Roncero, M. B., Colom, J. F., & Vidal, T. (2002b). Increasing seletivity of ozone bleaching of eucalyt kraft pulp. Part B. *Appita Journal*, *51*(3), 243–254.

Roncero, M. B., Colom, J. F., & Vidal, T. (2002c). Increasing the selectivity and efficiency of the ozone bleaching in a TCF sequence. Part C. *Appita Journal*, in press.

Roncero, M. B., Colom, J. F., & Vidal, T. (2003). Cellulose protection during ozone treatments of oxygen delignified eucalyptus kraft pulp. *Carbohydrate Polymers*, *51(3)*, 243–254.

Roncero, M. B., Queral, M. A., Colom, J. F., & Vidal, T. (2002d). The Role of pH in the ozone bleaching kinetics. *Wood Science and Technology*, in press.

Roncero, M. B., Queral, M. A., Colom, J. F., & Vidal, T. (2000). The role of oxalic acid in the ozone bleaching kinetics of an XO-kraft pulp. *Journal of Wood Chemistry and Techology*, *20*(2), 147–167.

Rudie, A. (2000). Calcium in pulping and bleaching. *Tappi Journal*, *83*(12), 36–37.

Ruiz, J., Freer, J., Rodriguez, J., & Baeza, J. (1997). Ozone organosolv bleaching of radiata pine kraft pulp. *Wood Science and Technology*, *31*(3), 217–223.

Schuchmann, M. N., & von Sonntag, C. (1989). Reactions of ozone with D-glucose in oxygenated aqueous solution—Direct action and hydroxyl radical pathway. *JWSRT-Aqua*, *38*, 311–317.

Shimada, M., Akamatsu, Y., Tokimatsu, T., Mii, K., & Hattori, T. (1997). Possible biochemical roles of oxalic acid as a low molecular weight compound involved in brown-rot and white-rot wood decays. *Journal of Biotechnology*, *53*, 103–113.

Shimada, M., Ma, D.-B., Akamatsu, Y., & Hattori, T. (1994). A proposed role of oxalic acid in wood decay systems of wood-rotting basidiomycetes. *FEMS Microbiology Reviews*, *13*, 285–296.

Uquiche, E., & Romo, C. (2000). Estabilizado de carotenoproteínas recuperadas de desechos líquidos de krill antártico (Euphausia superba) mediante el uso de antioxidantes. *Afinidad*, *57*(486), 135–138.

Xu, J., Cogo, E., Briois, L., Duprat, S., Molinier, J., Coste, C., & Kalck, P. (1995). Towards a selective ozone bleaching stage by addition of organic oxygenates. *Pulp and Paper Canada*, *96*(9), 49–53.

Zapanta, L. S., & Tien, M. (1997). The roles of veratryl alcohol and oxalate in fungal lignin degradation. *Journal of Biotechnology*, *53*, 93–102.

Zhang, Y., Kang, G., Ni, Y., & Van Heiningen, A. R. P. (1997). Degradation of wood polysaccharide model compounds during ozone treatment. *Journal of Pulp and Paper Science*, *23*(1), J23–J39.