



# *Institute of Paper Science and Technology*

## **FUNDAMENTALS OF OZONE BLEACHING**

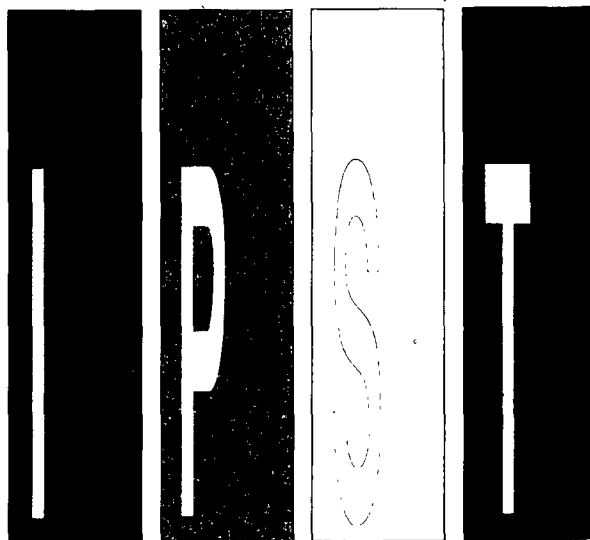
**Projects 3728, F015, and F013**

**6/93-7/96**

**to the**

**MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY**

**July 1997**



*Atlanta, Georgia*

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

FUNDAMENTALS OF OZONE BLEACHING

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6/93-7/96

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

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July 1997

# Fundamentals of Ozone Bleaching

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# FUNDAMENTALS OF OZONE BLEACHING

## FORWARD

This document is a compilation of the diverse studies in ozone bleaching that were directed by Dr. Lucinda B. Sonnenberg, Assistant Professor of Chemistry, in the Wood Chemistry group at the Institute of Paper Science and Technology from 1992 until 1997. It begins with an in-depth review of the fundamental chemistry of ozone bleaching, much of which is published as "Overview of Ozone Bleaching" (In Chlorine Use in the Pulp and Paper Industry, V. Turoff, Ed., Ann Arbor Press, In Press). This section is modified here to include references to the research performed at IPST, which is presented as five research reports in the second half of the paper. The intent is for the reader to be able to interpret the reported research results in the context of what is currently known about the complex chemistry of ozone bleaching.

Previously unpublished studies are presented in Research Reports 1 and 2: "Phase Effects in Reactions of a Lignin Model Compound with Ozone" and "Soluble Byproducts 1. Characterization and Secondary Reactions." Research Report 3, "Characterization of Pulp Ozonolysis Products and Studies in Ozone Delignification," is a substantially revised and expanded version of a paper presented in the Proceedings of the 1992 Tappi Environmental Conference; the expansion includes a condensed set results from the unpublished M.S. research of S. Michelle Nooney, IPST, 1994 ("Formaldehyde as a Byproduct of Pulp Ozonation"). Research Report 4, "Studies in High Consistency Ozone Delignification," is related to a previously published report in the Proceedings of the 1994 International Pulp Bleaching Conference. Research Report 5 covers the last unpublished studies; it presents the effects of pulping and oxygen delignification on ozone chemistry. The final report here attempts to incorporate all of the information that has been gained about ozone bleaching throughout the duration of the project.



## **REVIEW OF OZONE BLEACHING CHEMISTRY**

### **INTRODUCTION**

The pulp and paper industry is exploring ways to reduce its impact on the environment. Reducing the formation of chlorinated organic compounds and the volume of discharged effluent are key areas for improvement. Bleaching with oxygen-based chemicals can serve the pulp and paper industry well in meeting both of these objectives. Ozone is one promising oxygen-based alternative.

Interest in ozone bleaching by the U.S. pulp and paper industry first emerged in the 1970s when environmental legislation began in earnest. Considerable research was initiated; however, interest waned as it became clear that several problems could not be readily overcome with the existing technology. The problems included poor selectivity, poor uniformity, and the high expense of generating ozone. However, interest in oxygen-based bleaching resurged in the 1990s due to the discovery of chlorinated dioxins and furans in pulp and paper mill effluents, increasing environmental regulation, and increasing public pressure. As a result, several ozone plants have been recently built in the U.S., Canada, and Europe. Fourteen worldwide installations in 1995 have capacities ranging from 100 to 1600 tpd, and include three virgin fiber facilities in the U.S.

### **OZONE CHEMISTRY**

Ozone is an electrophilic, nonlinear, extremely potent oxidant with an oxidation potential of -2.07 eV ( $\text{O}_3 + \text{H}^+ + 2 \text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$ ). By comparison,  $\text{Cl}_2$  has an oxidation potential of -1.4 eV ( $\text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^-$ ). The high degree of reactivity of ozone and the heterogeneity of pulp allow numerous types of chemical reactions to take place during bleaching. Ozone reacts rapidly at sites of high electron density, such as the side chain double bonds and aromatic rings found in lignin, and more slowly at less activated sites, such as the C-H bonds typical in carbohydrates. The generally fast rates of ozone reactions make mass transport to the desired sites of attack critical for efficient and selective bleaching.

## Reactions With Carbohydrates

Carbon-hydrogen bonds in many saturated compounds are susceptible to cleavage by ozone, including the activated anomeric carbon-hydrogen bonds in carbohydrates. Highly reactive hydrotrioxide intermediates are produced from the ozonation of acetals<sup>1-3</sup>, including glucosidic acetals.<sup>4</sup> <sup>6</sup> Ozonation of ethers,<sup>7-9</sup> aromatic aldehydes,<sup>7,10,11</sup> and saturated hydrocarbons<sup>7,12</sup> also produces hydrotrioxides. When there is an oxygen atom adjacent to the insertion site, the hydrotrioxide may be stabilized by an intramolecular hydrogen bond, forming a six membered ring. Several mechanisms have been proposed for the formation of the hydrotrioxides, including a concerted 1,3 dipolar insertion (Fig. 1a), hydride transfer (Fig. 1b), hydrogen abstraction (Fig. 1c), and an initial attack at acetalic or etheric oxygens (Fig. 1d).

Most kinetic data, solvent effects, substituent effects, stoichiometry, and thermochemical calculations support either the concerted insertion,<sup>1,7,10,13</sup> or the hydride transfer.<sup>7,12</sup> However, attack by ozone on compounds with highly acidic  $\alpha$  hydrogens of -CHOR groups, forming tetroxide intermediates, has also been reported for a  $\beta$ -keto ether.<sup>9</sup> For compounds that do not have acetal oxygens, substituent effects suggest a moderately positively charged carbon transition state consistent with an insertion mechanism. When acetals are ozonated, the acetal oxygen stabilizes the positively charged transition state, thereby masking any substituent effects.<sup>1</sup> Small solvent effects and net retention of configuration also support the insertion mechanisms; however, these phenomena could occur with the hydride transfer mechanism if there is a solvent-caged radical pair intermediate. While entropies of activation have been reported to be consistent with both mechanisms,<sup>1</sup> Giamalva et al.<sup>7</sup> and Nangia and Benson<sup>12</sup> suggest that the experimental values are more consistent with a hydride transfer. The hydride mechanism is also more consistent with the energies of activation for ozonation of C-H bonds than with the insertion mechanism, which requires a highly ordered and energetic pentavalent carbon transition state.<sup>7,12</sup> Although there is evidence that radicals are present during ozonation, they are not likely to arise from hydrogen abstraction by ozone to form the hydrotrioxides, but result from the decomposition of the hydrotrioxides or other reaction pathways.<sup>7,12</sup>

Once the hydrotrioxide intermediates are formed, they may decompose either heterolytically (Fig. 2) or homolytically (Fig. 3). The ionic decomposition pathways depend on the other substituents on the hydrotrioxide-bearing carbon, solvents, and other reactants. The products can be either carbonyls and hydrogen peroxide (Fig. 2a), carbonyls and singlet oxygen (Fig. 2b), alcohols and singlet oxygen (Fig. 2c), or carbonyls and alkylperoxyl compounds (Fig. 2d).<sup>3,14</sup> Homolytic cleavage of oxygen-oxygen bonds of the hydrotrioxide can occur at two sites to form either alkylperoxyl and hydroxyl radicals (Fig. 3a), or alkoxy and hydroperoxyl radicals (Fig. 3b). These radical reactants may then further decompose, abstract a hydrogen, or couple. The radical decomposition reactions may not occur as readily as the ionic mechanisms in some instances,<sup>3,14</sup> however, they initiate the formation of radicals that may play an important role in subsequent chain reactions.

Deslongchamps et al. ozonated glycosides,<sup>4</sup> as well as other acetals,<sup>2</sup> primarily in nonaqueous solvents. They found that for conformationally rigid glycopyranosides that exist predominately in the C1 conformation, the  $\beta$ -anomers react with ozone while the  $\alpha$ -anomers do not. The  $\alpha$ -anomers can react with ozone only if they can attain a 1C conformation. The researchers proposed that reactivity with ozone is enhanced in structures with conformations in which a nonbonding orbital of each acetal oxygen is antiperiplanar to the insertion-point hydrogen. Stabilization of a positively charged transition state by correctly oriented nonbonding orbitals is required for the reaction to occur by the proposed 1,3 dipolar insertion mechanism. Either hydrotrioxide or hemioorthoester intermediates may be reaction intermediates. The sole products from ozonated methyl glycopyranosides were glyconate methyl esters. In these studies, the specificity of the decomposition of the intermediate by way of ring cleavage rather than glycoside cleavage was attributed to stereoelectronic requirements similar to those for hydrotrioxide formation. There must be two nonbonded electron pairs antiperiplanar to the departing alkoxy group in the tetrahedral intermediate, a condition which is fulfilled for the cleavage of the ring oxygen, but is not fulfilled for the glycosidic oxygen. Although these reactions by themselves would not result in chain cleavage, the ester linkage would cause the cellulose chains to be susceptible to cleavage by alkaline and acid hydrolysis.

Ozonations of glycosides in aqueous systems have produced different compounds which suggests there are other significant mechanisms of carbohydrate degradation when water is present. The major products from ozonation of aqueous solutions of  $\beta$ -methyl glycoside are gluconic acid and gluconolactone.<sup>5</sup> A decomposition pathway for the hydrotrioxide was proposed in which the glycosidic bond is cleaved, rather than the ring oxygen bond, to form gluconolactone which subsequently hydrolyzes to form gluconic acid. These two  $\beta$ -glycoside reaction mechanisms are illustrated in Fig. 4.

Oxidation of C6 to form glucuronic acid during ozonation of glucose and cellobiose has also been reported.<sup>16</sup> Other products from cellulose ozonation include formaldehyde<sup>16,17</sup> and glucose oligomers;<sup>16</sup> arabinose is a reaction product as well. Its formation has been attributed to a radical Ruff-type degradation in which the C2 hydrogen of gluconic acid is abstracted, a *gem* diol is formed at C2, and subsequent decarboxylation of C1 occurs. When anomeric mixtures of mannose and xylose were ozonated, similar products were found.<sup>17</sup>

Researchers have reported that ozone reacts with  $\alpha$ -anomers in aqueous solutions, albeit considerably slower than with  $\beta$ -anomers. Katai and Schuerch<sup>15</sup> proposed a mechanism similar to acid catalyzed hydrolysis of glycosidic bonds to explain the glucose that resulted as a major product from the ozonation of an  $\alpha$ -methyl glucoside. They proposed that ozone directly attacks the glycosidic oxygen to form a tetroxide intermediate, which then decomposes to glucose anomers via a carbocation intermediate and unspecified degradation products of the tetroxide. The authors felt that the anomeric methyl group was an unlikely site of attack, although other investigators<sup>7</sup> have shown that methyl ethers react slowly with ozone. Pan et al.<sup>5</sup> ozonated  $\beta$ -methyl glucoside and also found glucose, but only as a minor product, and proposed the same mechanism.

It is interesting that the methyl ester of gluconic acid was not identified in any of the aqueous reactions of ozone with methyl glycosides, in contrast to the nonaqueous reaction results of Deslongchamps et al.<sup>4</sup> Possible reasons include a lack of identification of this compound in the reaction mixtures, acid hydrolysis of the ester with a subsequent lactonization of the gluconic acid, or a solvent-mediated shift of the optimal reaction pathway.

## Reactions With Lignin

The strong electrophilic properties of ozone allow it to react efficiently and rapidly with sites of high electron densities in lignin, such as double bonds in the side chain and the aromatic rings. In addition, ozone may also attack the C-H bonds in aryl ether substituted side chains. Reactions of ozone with lignin are complex because of the diversity of potential sites of attack and because products of the initial attack are quite susceptible to further attack. Furthermore, other reaction byproducts, such as hydrogen peroxide, are also reactive.

Reactions of ozone with alkenes proceed by way of the Criegee mechanism (Fig. 5). The reaction begins with a 1,3 dipolar concerted addition reaction across the double bond to form a highly unstable 1,2,3-trioxolane, or primary ozonide (Fig. 5a). Although the primary ozonide may directly decompose into a carbonyl and hydroperoxide by attack of participating solvents (Fig. 5b), it is more likely to cleave at the C-C bond to produce a carbonyl and a carbonyl oxide zwitterion or radical pair (Fig. 5c). The directionality of the cleavage depends on the carbocation or radical stabilization capabilities of the substituents on each of the alkenyl carbons; thus, a higher degree of alkyl substitution on a carbon allows it to become the carbonyl oxide. Once the two fragments are formed, several pathways are possible.

For aldehydic carbonyl compounds in inert solvents, the two fragments may recombine to form 1,2,4-trioxolane, or a secondary ozonide (Fig. 5d), which can be readily isolated in many cases. When the secondary ozonide is exposed to water, it can hydrolyze to two carbonyl fragments and hydrogen peroxide, probably through a hydrotrioxide intermediate (Fig. 5e). Alternatively, it may decompose to a carboxylic acid and a carbonyl compound (Fig. 5f). In addition to recombining with the carbonyl compound, the carbonyl oxide can also undergo dimerization reactions to form bisperoxides.

Decomposition of the primary ozonide to the carbonyl and carbonyl oxide fragments is the reaction pathway that is most likely to predominate in the aqueous conditions normally used in ozone bleaching. The carbonyl oxide is trapped by water to form an  $\alpha$ -hydroxy hydroperoxide (Fig. 5g). The fate of the hydroperoxide depends on other substituents and solvents. The hydroxy group,

originally from the water, can become a carbonyl group, releasing hydrogen peroxide (Fig. 5e). Under acidic conditions, the peroxy oxygen can become protonated, forming hydrogen peroxide and a carbocation. The carbocation then reacts with water to form a *gem* diol that is likely to become further oxidized to a carbonyl compound (Fig. 5h). Also in acid, the terminal oxygen in the peroxy group can become protonated. If there is a group on the carbon which migrates easily, a rearrangement can occur to form a carbonyl and an alcohol (Fig. 5i). Finally, if one of the groups on the hydroxy hydroperoxide carbon is hydrogen, the peroxide can decompose to water and a carboxylic acid (Fig. 5j).

Aromatic compounds also react by the Criegee mechanism, although at a slower rate than alkenes. There are three sites of attack on each aromatic ring. Preferential sites of attack and higher rates of reaction will occur at those carbons with the highest electron density. Therefore, aromatic compounds with the most electron-releasing groups react most rapidly with ozone, and the ozonide forms at the carbons bearing the electron releasing groups. Once the ring cleavage product is formed, a muconic acid, the two aliphatic double bonds also become susceptible to attack.

At least three other reaction pathways have been proposed for aromatic compounds, particularly phenols. Phenols become hydroxylated and quinones have been reported as ozonation products. Standard electrophilic substitution mechanisms have been invoked to explain these products.<sup>22,23</sup> The electron deficient ozone oxygen attacks the aromatic pi electrons; an arenium ion forms which, for the ozone electrophile, is a trioxide carbocation. The trioxide anion loses oxygen and the ring either rearomatizes so that the net result is ring hydroxylation, or quinones form if good leaving groups are present. Epoxidation can also occur via electrophilic substitution at double bonds.<sup>24,25</sup> Hydrogen abstraction from phenolic hydrogens has also been proposed as an initiating reaction for the formation of quinones, and for polymerization reactions in nonaqueous solvents.<sup>26</sup>

Nearly all of these reactions have been reported for the ozonolysis of lignin model compounds and lignin. Common pathways of ozonolysis proposed for lignin type compounds are summarized in Fig. 6, which shows the complete oxidation of all unsaturated sites in an aromatic model. Ozonides, isolated from veratryl lignin model compounds ozonated in inert solvents, decompose to

small aldehydes, acids, and methyl esters upon warming.<sup>27</sup> Lignin model dimers give similar small, oxygenated products, as well as monomeric rings. Quinones and other "active oxygen" compounds have been reported<sup>27,28</sup> as ozonation products of lignin and lignin model compounds. The mechanisms discussed previously were used to explain the reaction products.

Most of the differences in reactivity between functional groups in lignin can be explained in terms of an initial reaction that is strongly electrophilic; the most electron donating substituents enhance reactivity, while electron withdrawing substituents inhibit it. These combined reactivity phenomena lead to interesting competitive pathways of ozone consumption. Gierer et al.<sup>24</sup> report that the order of ozone reactivity of lignin models is stilbenes > styrenes > phenols > muconic acids > nonphenols > aldehydes. Therefore, ozone will cleave the double bonds in stilbenes and styrenes before attacking any aromatic rings. Such reactions are likely to be important for delignification and for decolorization<sup>29</sup> of kraft residual lignin which is enriched in vinyl ethers compared to wood lignin. Once the side chain double bonds are cleaved, the aromatic rings are attacked. Phenolic lignin models react with ozone before nonphenolic lignin models; this is probably related to the electronic effects of the hydroxyl and methoxyl groups (e.g., Hammett constants  $\sigma_p$  for -OH and -OCH<sub>3</sub> are -0.38 and -0.28, respectively). Other substituents, of course, will also have an impact. Kojima et al.<sup>30</sup> attributed the reactivity of dimeric model compounds towards ozone to the total number of substituents on the two rings. Thus, a guaiacyl biphenyl (2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dialkyl diphenyl) with a total of 8 activating ring substituents reacted faster than phenylcoumaran with a total of 7 groups (3 alkyl, 2 methoxyl, 1 alkoxy, 1 hydroxyl), which in turn reacted faster than a  $\beta$ -aryl ether with a total of 5 alkoxy or alkyl ring substituents. Furthermore, when dimeric compounds are ozonated, the ring with the most activation will react first; many times it will be the only ring that reacts, but not always.<sup>31</sup>

As with any electrophilic reactions, substituents will help direct lignin reaction pathways. For example, model compound work has shown that aromatic ring cleavage will occur primarily (but not exclusively<sup>31</sup>) between oxygen-bearing C3 and C4 for softwood lignin models that have an electron-donating side chain. However, if the side chain is electron withdrawing, rates of ozonation decrease and cleavage increases at C2-C3 or C4-C5, producing more non-esterified small acids.<sup>27</sup>

The products of the initial ring attack, muconic acid derivatives, have opposing reactivity features: they are olefins which promotes their reactivity over the parent aromatic, but they also have electron withdrawing carbonyl groups as a result of the oxidation. These characteristics make the reactivity of muconic acid structures to ozone generally intermediate to phenolic and methoxylic aromatic compounds. Therefore, once ring cleavage occurs in dimeric compounds, if the remaining ring is phenolic, the second ring will be attacked. Conversely, if the second ring is methoxylic, the side chain will continue to be attacked by ozone and the second ring will remain intact.<sup>24</sup> Ozonolysis of the two double bonds in muconic acid structures produce the two-carbon oxygenated fragments typically found in lignin and lignin model ozonations, including glyoxal, glyoxylic acid, glyoxylic acid methyl ester, oxalic acid, monomethyl oxalate, and dimethyl oxalate. The primary pathways to these products from lignin phenolic monomers is given in Fig. 6. For the phenylpropane monomer shown, four moles of hydrogen peroxide can be generated, along with two moles of glyoxylic acid, one mole of glyoxylic acid methyl ester, one mole of formaldehyde, and one side chain carbonyl functional group, when the unsaturated sites are fully oxidized.

Under limiting ozone conditions, muconic acid derivatives may form lactones, rather than cleaving to smaller products. If there is an  $\alpha$  hydroxyl group on the side chain, the oxygen will bond with the C4-carbonyl carbon to form a  $\delta$ -lactone for both phenolic and nonphenolic compounds.<sup>30,31</sup> If an  $\alpha$ -hydroxyl group is not present on the side chain, a  $\gamma$ -lactone will form between C1 and the carboxylate oxygen of an oxidized phenolic at C4.<sup>24</sup>

The predominate pathways of lignin model ozonolysis are those that have been discussed. However, the potency of ozone and the complexity of both lignin and its reaction byproducts allow numerous other reactions to occur. The prevalence of one pathway over another depends on the reaction conditions and the specific features of the lignin. For example, while it appears that most hydroperoxide intermediates decompose by losing hydrogen peroxide, rearrangements may also occur.<sup>27,28</sup> In another pathway, hydroperoxides decompose to produce the carboxylic acids that are prevalent in ozone mixtures. However, it is difficult to differentiate the latter pathway from a simple oxidation of aldehydes to acids. Substitution reactions may produce epoxides from muconic acid derivatives,<sup>24</sup> hydroxylate phenols,<sup>31</sup> and produce quinones.<sup>28</sup> The formation of high



molecular weight material from ozonation of lignin model compounds indicates that ozone can initiate polymerization; Diels-Alder type reactions, radical coupling, and esterification have all been proposed as potential routes.<sup>31,32</sup>

Balousek et al.<sup>31</sup> ozonated a  $\beta$ -aryl ether model compound and found products that supported a reaction in which the ozone inserts into the  $\beta$ -carbon-hydrogen bond, forming a hydrotrioxide intermediate, similar to the reactions with glycosides discussed previously. They proposed a homolytic decomposition pathway to a hydroperoxy radical and a ketone, analogous to a mechanism reported by Plesnicar et al.<sup>14</sup> for  $\alpha$ -methyl benzyl ethers and alcohols. It is noteworthy that the insertion reaction was competitive with the rapid reactions with electron-rich alkenes and aromatics; it might be predicted to have a considerably slower reaction rate. However, if the lignin insertion reaction occurs under bleaching conditions, it is likely to effectively depolymerize the portions of the residual lignin macromolecule that still retain  $\beta$ -aryl ethers after cooking.

Many of the reactions that have been proposed as a result of model compound studies have been borne out by changes in the concentrations of functional groups when lignin and pulp are exposed to ozone. There is a pronounced increase in carboxylic acids in lignin in residual lignin of ozonated kraft pulp,<sup>18,21</sup> dissolved lignin fragments from ozonated kraft pulp,<sup>28</sup> as well as ozonation products of isolated wood lignins,<sup>28,33</sup> and isolated kraft lignin.<sup>27,34</sup> Carbonyl groups also increase in number with ozonations,<sup>18,28,29,34</sup> although the extent is variable and limited.

As expected, ozone depletes phenolic groups in kraft residual lignin,<sup>18,21,34</sup> similar to oxygen and chlorine dioxide.<sup>35</sup> The aromatic content of ozonated wood lignins is less than that of unozonated lignins.<sup>28,33,36</sup> However, the reactivity of wood lignin appears to be different from kraft residual lignin. Chirat et al.<sup>18</sup> found the aromatic carbon content of residual lignin from ozonated kraft pulp to be similar to the original residual lignin. The latter results suggests that most ring cleavages that occur during ozone bleaching kraft pulp ultimately cause dissolution of the lignin. This may be a function of the competitive nature of the muconic acid reactions versus the aromatic reactions. Such a conclusion is supported by the fact that molecular weight distributions of residual lignin of ozonated pulp are not substantially changed by moderate charges of ozone.<sup>34,35</sup> Further-

more, analyses of the dissolved fragments from ozonated pulp and groundwood show little intact aromatic compounds<sup>28,37</sup> and there appears to be more high molecular weight material in filtrates from ozonated pulp than from pulps treated with other bleaching reagents.<sup>38,39</sup> Together, the data suggest that the biggest impact of ozone on kraft lignin is the introduction of hydrophilic groups rather than substantial depolymerization.<sup>35</sup>

Methoxyl and methyl ester contents are somewhat variable for ozonated pulp, and the values depend on the substrate, conditions of ozonation, and the analytical methods used. Demethoxylation may arise from ester hydrolysis of cleaved rings, or from a radical demethoxylation pathway, both of which are likely to be highly dependent on the pH, metals content, and other variables of the reaction medium.

Freshly ozonated lignin appears to contain reactive intermediates that degrade over time. It has been suggested that this "active oxygen" consists of hydroperoxides, peroxides, ozonides, or quinones.<sup>28,40</sup> There is also evidence of free radicals in ozonated lignin mixtures,<sup>40</sup> and they may cause polymerization or other radical-initiated reactions.

### Selectivity

Selectivity refers to the preferential attack of a reagent on lignin versus carbohydrates. The rates of carbohydrate reactions determine selectivity under various ozone bleaching conditions. Carbohydrates may react with ozone directly, or react with lignin or carbohydrate byproducts, particularly radicals. Radicals, in turn, may be initiated from the decomposition of ozone, byproduct hydrogen peroxide, hydroperoxidic lignin byproducts, or intermediate hydrotrioxides. The contribution of each of these pathways of carbohydrate deterioration is currently unclear due to contradictory conclusions from numerous studies (e.g., references 41-44). When these processes are better understood, it may be possible to develop strategies to effectively prevent or minimize the most important pathways of carbohydrate deterioration. Furthermore, a clearer understanding of the maximum possible selectivity of ozone bleaching will be gained.

### ***Direct Reactions***

Selectivity depends, in part, on the reactivity of ozone directly with various functional groups. Second order rate constants for direct reactions of ozone with several compounds that have functional groups relevant to pulp are given in Table I. These rate constants and other kinetic parameters suggest that when lignin is present, ozone should be rapidly consumed by the lignin and cellulose should be fairly unreacted.

The data in Table I indicate the double bond of styrene and the activated benzene rings are very reactive, followed by the aliphatic unsaturated acids. Only the very small acids react more slowly than the carbohydrates. The data suggest that carbohydrates are protected from direct reactions with ozone by the presence of lignin and lignin degradation products. There is considerable data supporting this contention. Even benzaldehyde, a deactivated lignin structure, completely degrades before  $\beta$ -methyl glucopyranoside begins decomposing in ozonated mixtures.<sup>24</sup> Guaiacol and syringol are nearly completely consumed before the  $\beta$ -glucoside is degraded when mixtures of the compounds are ozonated.<sup>5</sup>

The model reactivities are reflected in pulp ozonation. When initial kappa numbers of pulp are high, viscosity is retained better than when ozonation occurs in later stages of a bleaching sequence and the initial kappa numbers are low.<sup>21,45,46</sup> Once a critical level of lignin has been removed from the pulp, ozone will begin to react to a greater extent with the C-H bonds of carbohydrates. The protecting effect of lignin appears to exist only to a point; at lower kappa numbers, lignin appears to promote carbohydrate degradation.<sup>46,47</sup> It has been suggested that ozone may abstract phenolic hydrogen atoms which initiates a radical pathway that forms the hydroxyl radical.<sup>48</sup> This may explain the superior selectivity of oxygen bleached pulps over kraft pulps since oxygen preferentially depletes phenolic structures in residual lignin.<sup>44</sup>

### ***Radical Reactions***

There are numerous species of radicals that may be associated with the ozonation of organic compounds in aqueous conditions. These radicals are involved in complex initiation, propagation,

and termination reactions that depend upon several reaction parameters. The pH, time, inorganic and organic substrates, as well as other reaction conditions can have a strong impact on the formation of radicals and the mechanisms by which they are destroyed.

The hydroxyl radical is clearly an important radical species that is formed directly from decomposition of ozone or reaction intermediates, or from chain reactions initiated by other radicals. The selectivity factor of the hydroxyl radical for lignin over carbohydrates is substantially higher than for the direct ozone reactions.<sup>49</sup> For this reason, the hydroxyl radical is often invoked as the species that is responsible for carbohydrate deterioration. Other species that may be formed include hydroperoxyl ( $\text{HOO}\bullet$ ), organic peroxy ( $\text{ROO}\bullet$ ), organic oxyl ( $\text{RO}\bullet$ ) and ozonide ( $\text{HOOO}\bullet$ ) radicals. While these latter compounds are less reactive than the hydroxyl radical,<sup>50</sup> they enter into complex chain reactions that may ultimately produce hydroxyl radicals.

During ozone bleaching, it is possible that radicals may form directly from ozone or they may arise from the homolytic decomposition of products from direct ozone reactions. The main pathways include metal-catalyzed decomposition of ozone, homolytic decomposition of lignin peroxides, metal-catalyzed decomposition of intermediate hydrogen peroxide, and hydrogen abstraction by ozone followed by decomposition of the resulting hydrotrioxide. Another potential source of radical initiation is the decomposition of the hydrotrioxide intermediates of carbohydrates and lignin. These pathways are briefly reviewed.

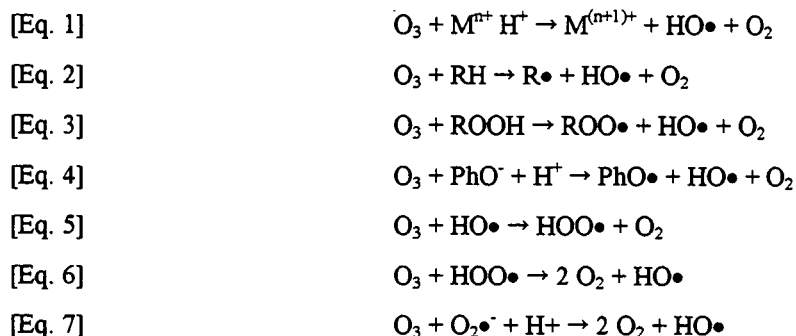
#### Radicals from Ozone Reactions

The decomposition of ozone to radicals is initiated by hydroxide ions and metals. Other pathways that produce radicals directly from ozone are reactions with other radicals and abstraction reactions. Under the acidic conditions used in pulp bleaching, the most likely to initiate radical formation from ozone are the metal catalyzed decompositions [Eq. 1] and the hydrogen abstraction reactions, similar to those discussed in the previous section [Eq. 2-4]. Radical chain reactions [Eq. 5-7] will consume more ozone and propagate more radicals. The protic radicals will exist predominately in their protonated form under typical bleaching conditions ( $\text{pK}_a$  of  $\text{HOO}\bullet = 4.9$ ); however, low levels of the superoxide radical anion are likely to be present even at low pHs and

may be sufficient to propagate radical pathways.<sup>48,51</sup> Many of the reactions proceed through ozonide intermediates.

Protonated phenols probably react primarily by nonradical mechanisms because of the rapidity of those reactions; however, as shown in Eq. 4, abstraction of an electron by ozone from phenolates may be a source of radicals.<sup>48,51</sup> The proportion of ionized phenols is probably only sufficient for these pathways to be significant when the bleaching conditions are above pH 3. Exceptions may be phenols with an  $\alpha$ -carbonyl group which reduces the pKa of phenols.<sup>51</sup>

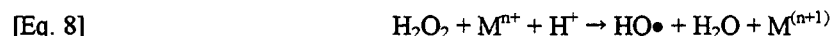
It has been suggested that a key radical intermediate is the superoxide radical anion that propagates hydroxyl radical formation by its reactions with ozone [Eq. 7], as well as reactions with hydrogen peroxide.<sup>51</sup> The superoxide arises from the decomposition of organic peroxy radicals. It has been proposed that by controlling the level of the superoxide radical anion, the radical chain reactions may be terminated, and selectivity improved.<sup>51</sup>



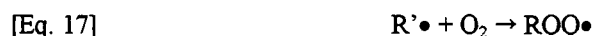
#### Decomposition of Peroxides and Hydrotrioxides

Another source of radicals is the decomposition of peroxide and hydrotrioxide intermediates produced from direct ozone reactions. Hydrogen peroxide arises primarily from the decomposition of hydroxy hydroperoxide intermediates of lignin (Figures 5e and 6). A comparatively minor source is the homolytic decomposition of hydrotrioxides (Fig. 3b). The main radical initiation mechanism from hydrogen peroxide is the classic, metal-catalyzed Fenton reaction [Eq. 8]. High

concentrations of  $\text{H}_2\text{O}_2$  during high consistency bleaching may cause this pathway to be more important under high consistency than at low consistency conditions.<sup>52</sup> Hydrogen peroxide may also propagate radicals by reacting with superoxide radical anions to form the highly reactive hydroxyl radical [Eq. 9].<sup>51</sup> Although ozone will react with  $\text{H}_2\text{O}_2$  at a high pH, the reaction is suppressed at low pH,<sup>53</sup> and probably is not a significant pathway for radical production during ozone bleaching.



Organic peroxides are most likely to arise from reactions of ozone with lignin (Fig. 5g). They may decompose to radicals by direct reactions with ozone [Eq. 3] or by metal catalyzed reactions [Eq. 10-11]. Propagation reactions in which the peroxides are involved include the abstraction of hydrogen from the peroxides by alkyl radicals [Eq. 12-13]. Peroxyl and alkoxy radicals then participate in additional chain carrier reactions [Eq. 14-16]. Equation 14 may be particularly important because it represents another pathway to the superoxide radical anion that has been proposed to be a key radical chain carrier, as mentioned previously.<sup>48,51</sup> Note that under oxygenated conditions, an additional pathway to peroxyl radicals may be through coupling of oxygen to organic radicals [Eq. 17].



Hydrotrioxides may arise from ozone insertion in C-H bonds in carbohydrates (Fig. 4) and in the side chains of lignin. Although these reactions are expected to be slow compared to other ozone reactions, they may play a part in the radical initiation under some conditions.<sup>54</sup> Numerous homolytic decomposition of hydrotrioxides are outlined in Fig. 3. The types of radicals formed are comparable to those already discussed ( $R\bullet$ ,  $RO\bullet$ ,  $ROO\bullet$ ,  $HO\bullet$ ) and enter into the same propagation reactions.

#### Hydroxyl Radical Reactions

Reactions of lignin with the hydroxyl radical are only marginally favored over carbohydrate reactions ( $k_{\text{lignin}}/k_{\text{carbohydrates}} = 5-6$ ).<sup>49</sup> Hydroxyl radicals react readily with lignin in pulps with high lignin content, although at least one study indicates there is little delignification due to these reactions.<sup>43</sup> Model compound studies with hydroxyl radicals and lignin show that phenols and etherified phenols react differently. Radical coupling occurs predominately when phenols are exposed to hydroxyl radicals, while hydroxylation and demethoxylation are the major reactions with etherified phenols.<sup>41</sup>

Hydroxyl radicals may react with carbohydrates by abstracting hydrogen atoms from either C1 or C2.<sup>52,55</sup> The resulting radicals may couple with oxygen to form intermediate organic peroxy radicals. Depolymerization might occur as a direct result of fragmentation of the intermediate radicals. Alternatively, if carbonyl groups are introduced at C2 as a result of hydrogen abstraction and oxygen coupling at C2, then depolymerization may take place through  $\beta$ -elimination when the carbohydrates are exposed to alkaline conditions.<sup>55</sup>

#### Mass Transfer Limitations

Because of its high reactivity, ozone mass transfer to lignin is critical during ozone bleaching. Diffusion of ozone across the immobile water layer adjacent to the cell wall can be a significant rate determining step for low consistency and poorly mixed medium consistency bleaching.<sup>56</sup> Diffusion within the cell wall is rate limiting in high consistency and well-mixed low consistency ozone delignification. Griffin et al.<sup>57</sup> have proposed a model of ozone delignification whereby an

advancing front of lignin-ozone reactions takes place across the cell wall to the lumen. They propose that the highly reactive hydroxyl radicals produced by ozone-lignin reactions immediately degrade the adjacent carbohydrates, and therefore, all cellulose decomposition takes place within the ozone-lignin front.

## **APPLICATIONS**

When ozone is applied to pulp, several process conditions must be optimized to maximize the desired reactions with lignin and minimize the harmful reactions with carbohydrates. Optimizing efficiency and selectivity generally focuses on: 1) minimizing ozone decomposition, 2) promoting uniform exposure of lignin to ozone, 3) minimizing exposure of carbohydrates to radicals and high ozone concentrations, and 4) minimizing reactions of ozone with dissolved byproducts. Important controlling parameters are consistency, charge, pH, concentration of ozone in the gas, time, temperature, carry-over, metals removal, mixing, additives, and position in sequences.

In general, ozone decomposition is reduced at conditions of low pH, medium or high consistency, effective metals removal, low charges, and low temperatures. Uniform bleaching is promoted by effective mixing and fluffing (at high consistency). Carbohydrates are protected from high ozone concentrations by using charges less than 0.5% by weight and by good mixing. Viscosity is sometimes better preserved at low and well-mixed medium consistency and by shorter reaction times. Exposure of cellulose to radicals can be reduced by additives that act as radical scavengers as well as by reducing ozone decomposition.

Bleaching efficiency can be reduced by carryover; for example, a COD load of 10 kg COD/adt was found to double the ozone demand in medium consistency pilot trials.<sup>58</sup> Lower kappa number pulps are generally considered suitable for ozone bleaching because of the relatively high cost of ozone. Oxygen delignification is often used prior to a Z stage because of the low expense of oxygen and because the residual lignin remaining from oxygen appears to react readily with ozone.



Excellent and extensive reviews of industrial applications of ozone bleaching have recently been published.<sup>59-61</sup> Important process variables in ozone bleaching and their impact on selectivity and efficiency are briefly reviewed below.

### Consistency

Early work on consistency showed high consistency produced the strongest pulps. However, as mixing technology has improved, results at low and medium consistency have improved. All three conditions have been used and each has its disadvantages. Low consistency disadvantages include a large water demand, large effluent volume and mixing limitations. In medium consistency, the gas to pulp ratio must be small enough to be adequately mixed, yet the ozone concentration must be high enough to delignify. Either the  $O_2/O_3$  stream must be pressurized or a high concentration of ozone in the  $O_2/O_3$  flow must be used; each option has its drawbacks.

Lindholm<sup>62,63</sup> found that low consistency is more selective than high consistency which was attributed to better homogeneity at low consistency. Carbohydrates may degrade more during high consistency bleaching because of the heterogeneity of the system, which causes localized areas of high ozone concentration and low lignin concentration. During low consistency bleaching, the reaction medium is more homogeneous, the ozone can be more readily dispersed, and reaction products may contribute to carbohydrate-protecting effects.<sup>64</sup> In medium consistency pilot studies, selectivity was between that of high and low consistency.<sup>58</sup> However, lab results show best selectivity at medium consistency with high intensity mixing.<sup>65,66</sup>

Delignification efficiency (the amount of ozone required per unit kappa number drop) has been found to be worst at low consistency in lab studies,<sup>63,66-68</sup> although one study reported delignification efficiency to be unaffected by consistency.<sup>65</sup> More ozone is consumed at lower consistencies.<sup>63,66</sup> Since the consumed ozone does not result in more delignification, more decomposition or secondary reactions must occur at the lower consistencies. The combination of improved delignification at high consistency and improved viscosity retention at low consistency has driven the interest in medium consistency ozonation.

## Charge and pH

Increasing the charge of ozone from 1-2% by weight decreases the kappa number and increases the brightness at the expense of viscosity. Without a cellulose protector, a 1% charge of ozone has been considered to be the maximum for optimal cellulose quality.<sup>67,69</sup> In practice, ozone charges generally do not exceed 0.7%, even for softwoods which require higher charges.

A pH between 2 and 3 is optimal for pulp ozonation.<sup>58,63,67</sup> Delignification is improved at low pH and the strong acidity does not contribute to substantial losses of viscosity. Viscosity loss is minimal up to pH 4. Beyond pH 4, viscosity loss occurs and brightness is reduced.<sup>58</sup> Low pH may be optimal because of three factors. Decomposition reactions that produce radicals are inhibited; metals that promote ozone decomposition may be removed in acid washes; and primary O<sub>3</sub>-lignin reactions may be favored.<sup>63</sup> The dependency of delignification on pH has been found to be complicated when pulps have a higher residual lignin content.<sup>46</sup> Furthermore, recent work suggests that high pHs can be tolerated during ozone bleaching under appropriate conditions.<sup>43</sup>

## Concentration

The concentration of ozone produced in O<sub>2</sub>/O<sub>3</sub> streams is important because it affects pulp quality and because it affects the optimization of various other process variables, particularly reaction time. In general, concentrations below 10% have been used due to safety considerations and limitations on ozone generation. More recently higher ozone concentrations up to 15% have been effectively employed (e.g., reference 70).

The dependency of pulp quality on concentrations of ozone varies depending on whether very low concentrations are used (<3%) or higher concentrations are used (10%). When increasing the concentration up to 2-3% by weight, lower concentrations improved viscosity using high consistency conditions.<sup>68</sup> However a 10% concentration was found to be more selective than a 2.2% concentration, also using high consistency; the higher ozone concentrations resulted in greater delignification.<sup>71</sup> Medium consistency ozonations are also more selective at higher ozone concentrations.<sup>58</sup> Other researchers have found little effect of ozone concentration on kappa number or viscosity,<sup>59,60,72</sup> but higher concentrations reduced reaction times for delignification.<sup>59,60</sup>

## Time

Reaction time is particularly important at low and medium consistencies. When constant ozone charges have been applied to softwood pulps at different reaction times, longer reaction times resulted in higher ozone consumption and improved delignification for low and medium consistency ozonations. With long enough reaction times, delignification at low and medium consistency nearly matched that achieved under high consistency conditions.<sup>65</sup> At high consistency, longer reaction times suppress carbohydrate degradation but do not affect the drop in kappa number.<sup>68</sup>

Hardwood pulps appear to have a different time dependency than softwoods. Laboratory experiments using medium consistency showed that hardwood pulp ozone consumption increases with reaction times, but brightness and delignification actually decrease.<sup>65</sup> Pilot studies using medium consistency ozone bleaching of hardwood dissolving pulp also found that longer reaction times consume more ozone with no increase in delignification.<sup>58</sup>

Selectivity is best in the beginning of high consistency ozone bleaching and drops off later.<sup>21,71</sup> Increases in the concentrations of radicals or radical precursors, coupled with a decrease in the amount of available lignin to consume the radicals, are possible reasons for this observation.

It is important to note that the dependence of bleaching behavior on reaction time may be a significant variable in comparing some laboratory studies to mill practices. While laboratory studies generally employ reasonably long reaction times, technical bleaching may be conducted in seconds (medium consistency) or minutes (high consistency).

## Temperature

Lower temperatures promote selectivity probably by reducing carbohydrate reactions.<sup>73</sup> High temperatures promote ozone decomposition, which creates the cellulose-degrading radicals, although below 25°C, ozone decomposition is minimal.<sup>74</sup> Delignification is fairly constant up to about 55°C for medium consistency hardwood ozonation; kappa numbers rise slightly at higher temperatures.<sup>58</sup> Liebergott et al.<sup>60,61</sup> reported slight increases in kappa and slight reductions in

viscosity when temperatures were raised from about 20 to 80°C. These effects have been attributed to increased ozone decomposition with temperature. For low consistency operations, temperature will also affect ozone solubility, which may in turn affect bleaching efficiency.<sup>75</sup>

### **Carryover/Filtrates**

The effects on ozone efficiency of carry over and of dissolved organic material in filtrates are important because of the implications for brownstock washing and filtrate recycle, respectively. Although ozone reacts with organic material in ozonation filtrates, Lindholm and Vilpponen<sup>76</sup> found that it will react with pulp preferentially. Consequently, ozonating pulp using recycled ozonation filtrates at high or low consistency does not affect delignification efficiency. In fact, viscosity protection at low consistency has been attributed partly to the presence of degradation products.<sup>64</sup> By contrast, a COD carry over load of 10 kg C/adt was found to double the ozone demand in medium consistency pilot trials.<sup>58</sup>

### **Mixing**

Doubling mixing times reduced kappa numbers and increased efficiency in the medium consistency ozonation of hardwood pulps.<sup>58</sup> Increasing mixing intensity improved viscosity protection and delignification (when adequate reaction times were used) in medium consistency bleaching.<sup>65</sup> There is higher ozone consumption at higher mixer speeds when ozonating at medium consistency. As the ZE stage (after ozone and alkaline extraction) brightness increases, viscosity and lignin levels decrease with increasing mixer intensity for softwoods and hardwoods.<sup>65</sup>

### **Additives/Solvents**

Large numbers and types of compounds have been evaluated for their potential as carbohydrate protectors and have been compiled by Liebergott et al.<sup>59,60,67</sup> Nothing that is commercially feasible has been found to be highly effective and Liebergott notes that the problem of finding a cheap

effective commercial inhibitor of carbohydrate depolymerization during ozone delignification remains to be solved.<sup>67</sup>

Methanol has been found to protect cellulose; DMSO protected carbohydrates at high consistency without inhibiting delignification in one set of studies,<sup>68</sup> but another study found no effect of DMSO at high consistency or low consistency.<sup>64</sup> It is interesting that some chemicals that protect cellulose in oxygen bleaching don't work with ozone which suggests that some carbohydrate damage from ozonation does not arise from radicals.

The acids used to reduce pH may affect ozone efficiency. Although acetic acid inhibits metal-catalyzed decomposition of ozone, some studies have shown that there is no difference between sulfuric acid and acetic acid ( at low consistency) on viscosity, strength<sup>68</sup> or delignification efficiency.<sup>64</sup> More recent studies suggest that ozonating in 90% acetic acid under low consistency conditions improves selectivity, particularly when ozonating down to low kappa numbers.<sup>44,77</sup> Oxalic acid also improves selectivity at low and high consistencies at pH <2.<sup>64</sup>

Protective effects of lignin and lignin fragments have been noted<sup>64,77-79</sup> and attributed to radical scavenging by these materials.<sup>46</sup> On the other hand, cellulose reacts with ozone more readily in the presence of small amounts of lignin than under lignin-free conditions which may result from cellulose attack by radical intermediates generated by lignin oxidation.<sup>46,47</sup>

## Sequences

Placement of an ozone stage in several different points in a bleach sequence have been investigated over the years. Most bleaching sequences now use an oxygen stage prior to ozonation and place the ozone stage early in the sequence. Examples of sequences recently implemented in pilot plants include OZP (Graz, Austria), OZEP (Baienfurt, Germany), OZEP, OZED, O(pZE)P (Paprican), and (O)Z with any sequence (Espanola, Ontario). Two recent commercial installations have employed (EOP)ZP (Lenzing, Austria) and OZ(EO)D or OZEP (Franklin, VA). Se-

quences such as ZPZP, ZEP, chelation followed by OO(ZE)P(ZE)P, OO(ZE)PP, ZEDED, and others have also been studied.

Comparison of the different positions of ozone in a bleaching sequence is influenced by the position of alkaline extraction stages. The carbonyls formed from cellulose ozonation are susceptible to further reaction under alkaline conditions, resulting in depolymerization and viscosity reduction. Some studies show that ozone selectivity is lost in an alkaline post-treatment stage,<sup>46,71</sup> resulting in a recommendation that ozone be introduced last or that a strong reducing agent be added to the alkali stage. Other studies show inconsistent or negligible effects on viscosity at charges of 1% ozone or below and 1 to 1.5% NaOH charge in the extraction stage.<sup>59,60,65</sup> Lachenal et al.<sup>78,79</sup> have noted that although ZE produces pulp with lower viscosity than Z, the latter is still better than an O stage at low kappa numbers. Alkaline extraction reduced brightness when comparing an OZD to an OZED sequence.<sup>59,60</sup>

Washing between Z and E stages resulted in slightly higher kappa numbers than when there was no washing between Z and E.<sup>67</sup> Washing between a D stage and a Z stage was also found to be unnecessary.<sup>78,79</sup>

Generally, an oxygen delignification stage prior to ozone application is better than the reverse sequence.<sup>59,60,71,78,79</sup> Because ozone does not react well with bark and shives, better quality pulp results when oxygen precedes ozone. Also, it is economically more feasible to use oxygen to remove the bulk of lignin and to follow up with ozone. A peroxide stage between an O stage and a Z stage has been shown to improve pulp bleachability.<sup>68</sup>

Ozone has been used to replace chlorine, chlorine dioxide or hypochlorite stages in traditional sequences. Using a chlorine dioxide stage immediately adjacent to an ozone stage to achieve a constant kappa number improves selectivity over ozone alone. The high selectivity of chlorine dioxide is utilized in this sequence. Furthermore, a DZ sequence results in higher viscosity pulp than a ZD sequence.<sup>78,79</sup> Two possible reasons have been put forth. In a DZ sequence, the chlorine dioxide may modify the residual lignin so that lignin becomes more reactive to ozone. Alternatively,

in a DZ sequence may result in fewer cellulose-degrading radicals arising from lignin oxidation, thereby reducing carbohydrate degradation from that source. An O(DZ)ED sequence produced good viscosity pulp with a very low AOX in effluent.<sup>78,79</sup> Hypochlorite or ozone followed by peroxide resulted in similar viscosity losses in medium consistency bleaching.<sup>58</sup> However, when one D stage is replaced by ozone in a DEDED sequence, the brightness ceiling is lowered.<sup>46</sup>

## **ENVIRONMENTAL BENEFITS**

The environmental effects of waste waters from oxygen-based bleaching, relative to those from chlorine-based bleaching, vary due to the influence of a number of factors. Some of these include differences in wood species, quality of pulp produced, the extent and specifics of water recycling, target species for toxicity assays, other bleaching stages used, the receiving water quality, and even the specific experimental techniques used (including sample preservation and storage). It is also important to recognize that the bleach plant is only one input into whole mill effluents; dilution and chemical transformations will take place. Furthermore, the ultimate environmental loading from a mill will depend on the effectiveness of biological treatment, which varies greatly.

Despite the variability, it is clear that replacing a C or D stage with ozone drastically reduces the formation of AOX and specific chlorinated compounds. While effluent AOX ranges from 0.1 to 1.0 kg ptp for mills using chlorine dioxide without oxygen,<sup>80</sup> some values reported for AOX from ozone bleaching filtrates include nondetect for a (QZ)(Q)(PO) mill sequence,<sup>81</sup> 0.0002 kg/tonne for a Z(PO) laboratory sequence,<sup>82</sup> and 0.09 kg/ADMT (D filtrate) from a mill OZED sequence.<sup>83</sup> The actual benefit to the environment from low AOX discharges is unresolved. In general, at discharges less than 2 kg/ton, AOX does not correlate with toxicity or other environmental effects, while discharges above 2 kg AOX/ton do correlate with environmental impacts.<sup>80</sup> Chlorodioxins, chlorofurans, and chlorophenols, which can have a significant environmental impact, are not detected; however, traces of chloroform remain, in some TCF cases.<sup>83</sup> A potentially significant environmental advantage to TCF bleaching is the expected decline in the releases of chlorine and chlorine dioxide, two important Toxics Release Inventory chemicals. It is unclear how emissions of other volatile compounds from the bleach plants using TCF and ECF sequences differ.

The oxygen demand in effluents will vary considerably depending on how much lignin and carbohydrates are removed from the pulp in the bleach plant, and on how much water is recycled back to recovery. An OZED sequence with nearly complete recycle of the OZE stages produces mill discharges of COD and BOD that are at least 90% less than discharges from a CEDED sequence and 70-90% less than an O(DC)ED sequence.<sup>84</sup> No water recycle with OZED sequences results in comparable or slightly higher levels of organic carbon,<sup>85</sup> possibly due to larger quantities of carbohydrates in TCF filtrates than in ECF filtrates. Laboratory studies in which TOC, COD, and BOD have been measured in untreated and treated filtrates suggest that the organic material produced in ozone-containing sequences is more easily degraded by microbes than ECF filtrates.<sup>82</sup> These findings are consistent with the higher BOD/COD ratios of waste waters containing ozone filtrates than for waste waters with C or D stage filtrates.<sup>82,86</sup>

The toxicity of ozone filtrates has been found to be higher, lower, and the same as conventional filtrates, depending on the specific study. For example, exposure of several marine organisms to untreated filtrates from D(EO)DD and Z(PO) sequences (using 50 and 22 m<sup>3</sup> water/ tonne pulp, respectively), showed that ozone filtrates were generally more toxic than the untreated D filtrates.<sup>82</sup> Target organisms included scallops, algae, urchins, fish, and bacteria. Peroxides in the untreated ozone filtrates may have been a primary source of toxicity in the TCF filtrates. Similarly, laboratory Z filtrates in a TCF sequence had a higher chronic toxicity to fathead minnows and *Ceriodaphnia* than ECF filtrates, but no acute lethal toxicity. Fathead minnows tend to be more sensitive to chlorine-containing effluents, while *Ceriodaphnia* are more sensitive to OZ filtrates.<sup>87</sup> By contrast, other studies of hardwood mill effluents indicate filtrates from a QZEopAEP sequence were slightly less toxic than those from a DEopDED sequence (using 16 and 25 m<sup>3</sup> water/ton, respectively).<sup>88</sup> Cates et al.<sup>89</sup> recently showed Microtox toxicity decreased in the order: ECF softwood > ECF hardwood > TCF softwood > TCF softwood. A clearer understanding of how the toxicological properties of ozone filtrates compare to conventional filtrates depends on the identification and quantification of the primary toxicants in all filtrates.



Despite the complexity of the issue of toxicity of effluents, it is clear that fewer potential toxicants and other compounds will reach the aquatic environment when most of the bleach plant waste is recycled back to the recovery, and zero or near-zero effluent is discharged. Ozone bleaching is one way to achieve those goals. It remains to be determined whether emerging alternative approaches to mill closure, such as Champion's bleach plant filtrate recycle (BFR) of ECF filtrates,<sup>90</sup> will offset some of the current environmental advantage of ozone bleaching.

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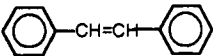
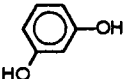
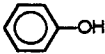
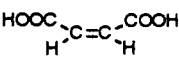
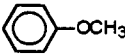
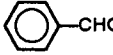

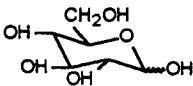
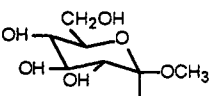
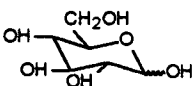


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## FIGURES AND TABLES

Table 1. Second Order Rate Constants for Direct Reactions with Ozone<sup>a</sup>

Compound	Structure	pH	k M <sup>-1</sup> ·s <sup>-1</sup>	Scavengers
Styrene		3 in CCl <sub>4</sub> <sup>b</sup>	3 x 10 <sup>5</sup> 1 x 10 <sup>5</sup>	t-Butanol -
Resorcinol		2	> 3 x 10 <sup>5</sup>	Propanol
Phenol		1.7-2	1.3 x 10 <sup>3</sup>	Propanol
Maleic Acid		2 6	1 x 10 <sup>3</sup> 5 x 10 <sup>3</sup>	t-Butanol
Anisole			2.9 x 10 <sup>2</sup>	Propanol
Benzaldehyde		1.7	2.5	Propanol
Acetaldehyde		2	1.5	-
Glucose		2	0.5	-
Methyl β Glucoside <sup>c</sup>		3	0.5	-
Saccharose		2	0.1	t-Butanol
Glyoxilic Acid		1.5 - 5	0.2	t-Butanol
Formaldehyde		0.2	0.1	-

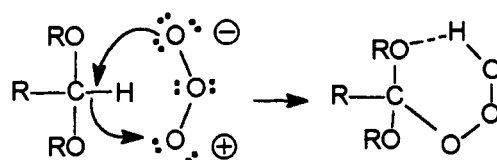
<sup>a</sup> Values are taken from References 91 and 92 unless otherwise indicated.

<sup>b</sup> Reference 93

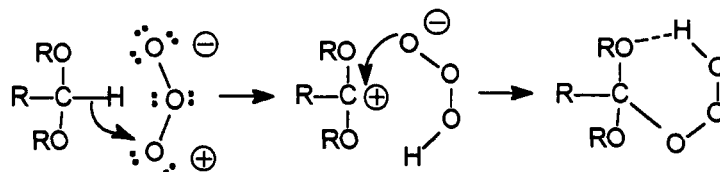
<sup>c</sup> Reference 5



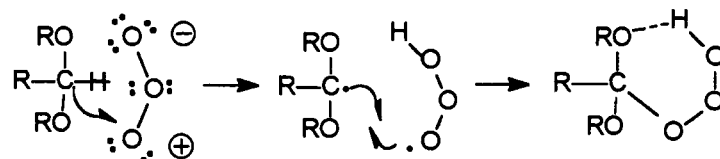
(a) 1,3 Dipolar Insertion



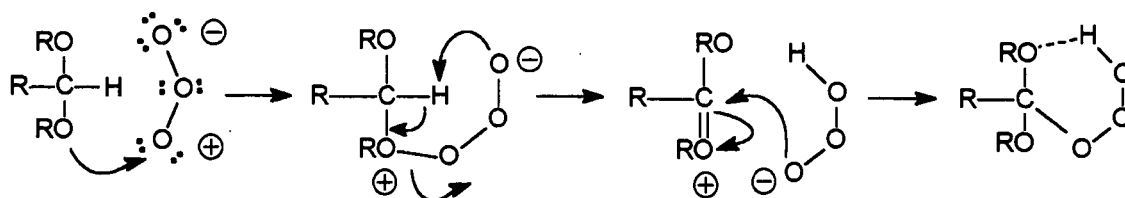
(b) Hydride Transfer



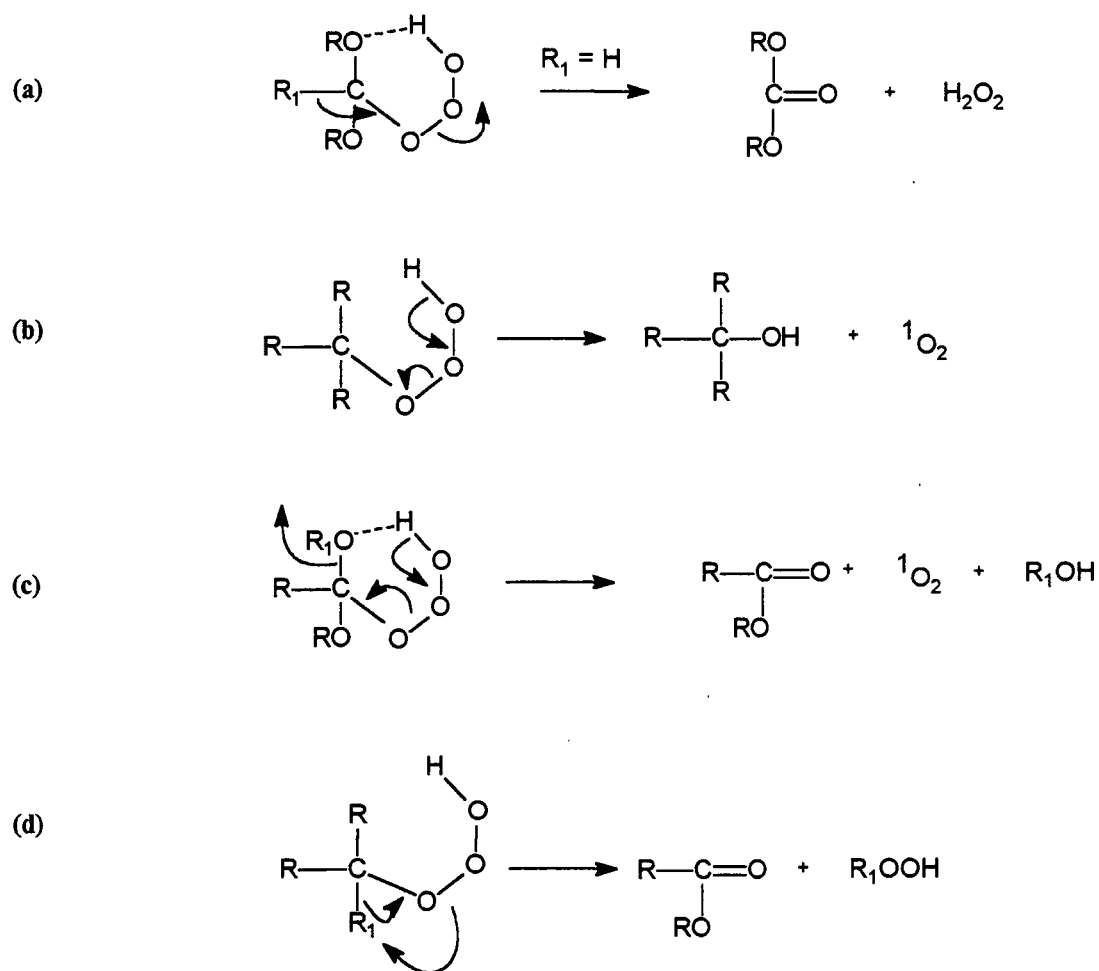
(c) Hydrogen Abstraction



(d) Oxygen Attack



**Figure 1. Potential Mechanisms of Hydrotrioxide Formation**



**Figure 2. Ionic Mechanisms of Hydrotrioxide Decomposition**

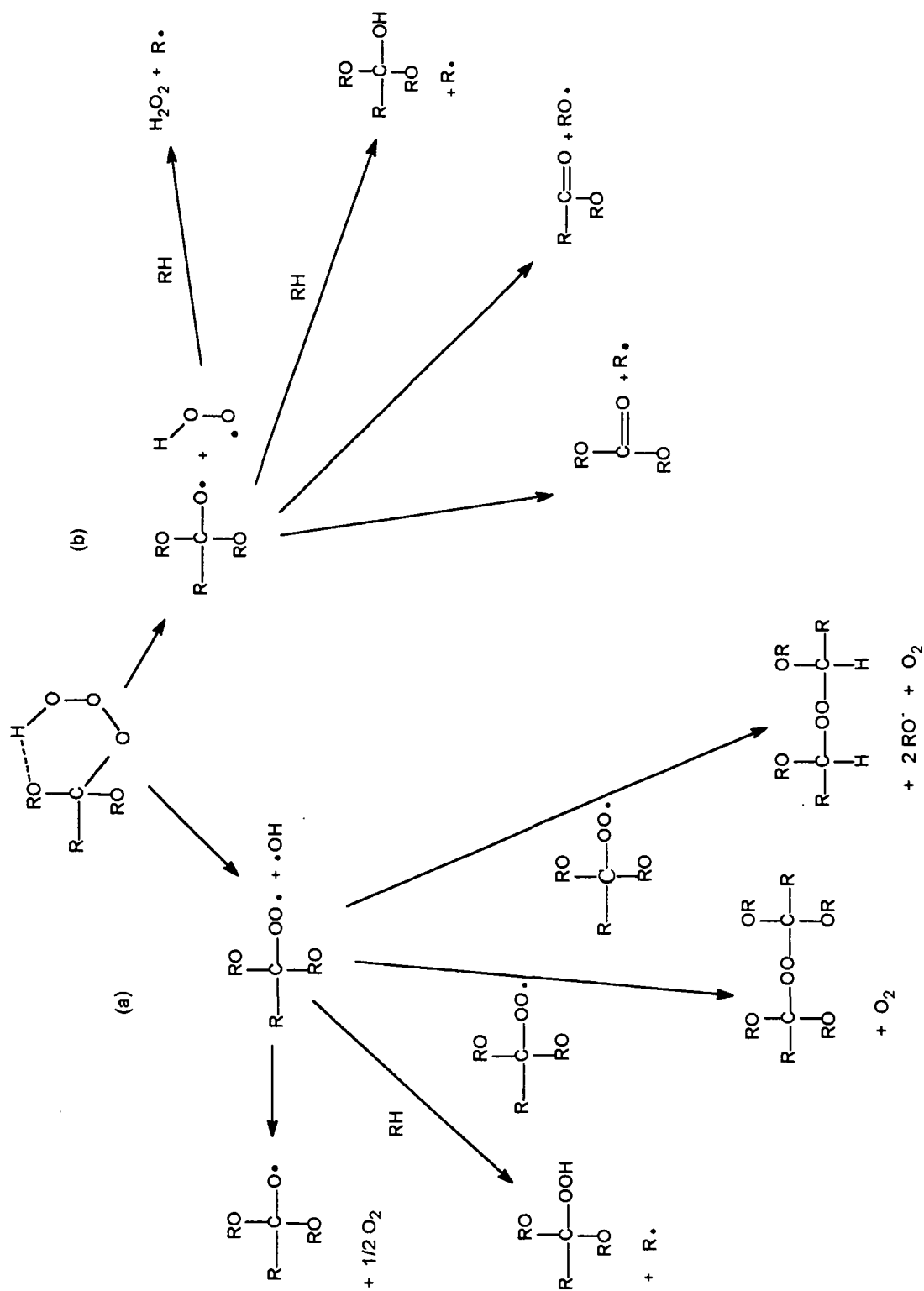
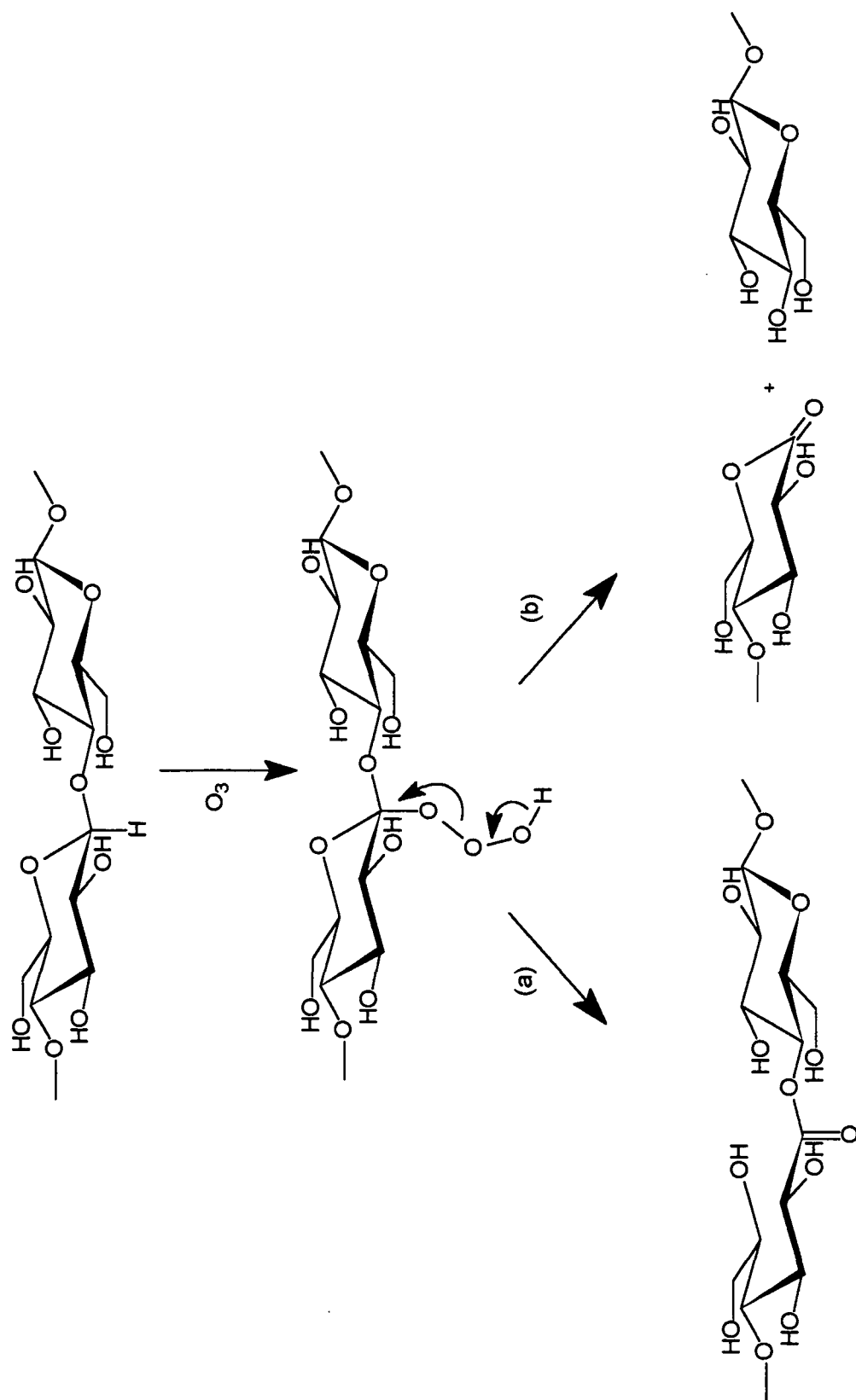


Figure 3. Radical Mechanisms of Hydrotrioxide Degradation



**Figure 4. Ozone Cleavage of Glycosides**

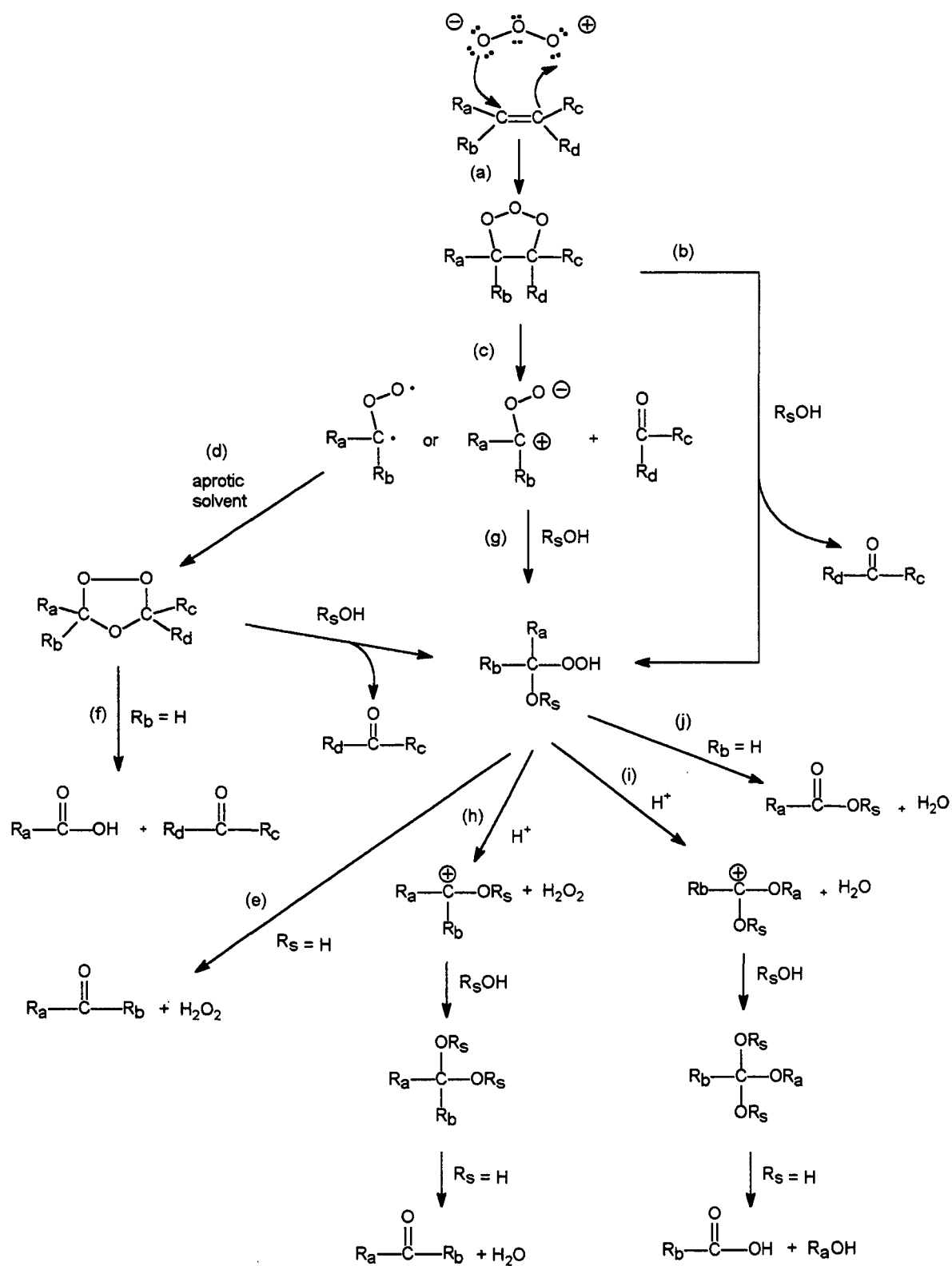


Figure 5. Common Reactions of Ozone with Double bonds ( $R_s$  refers to solvent).

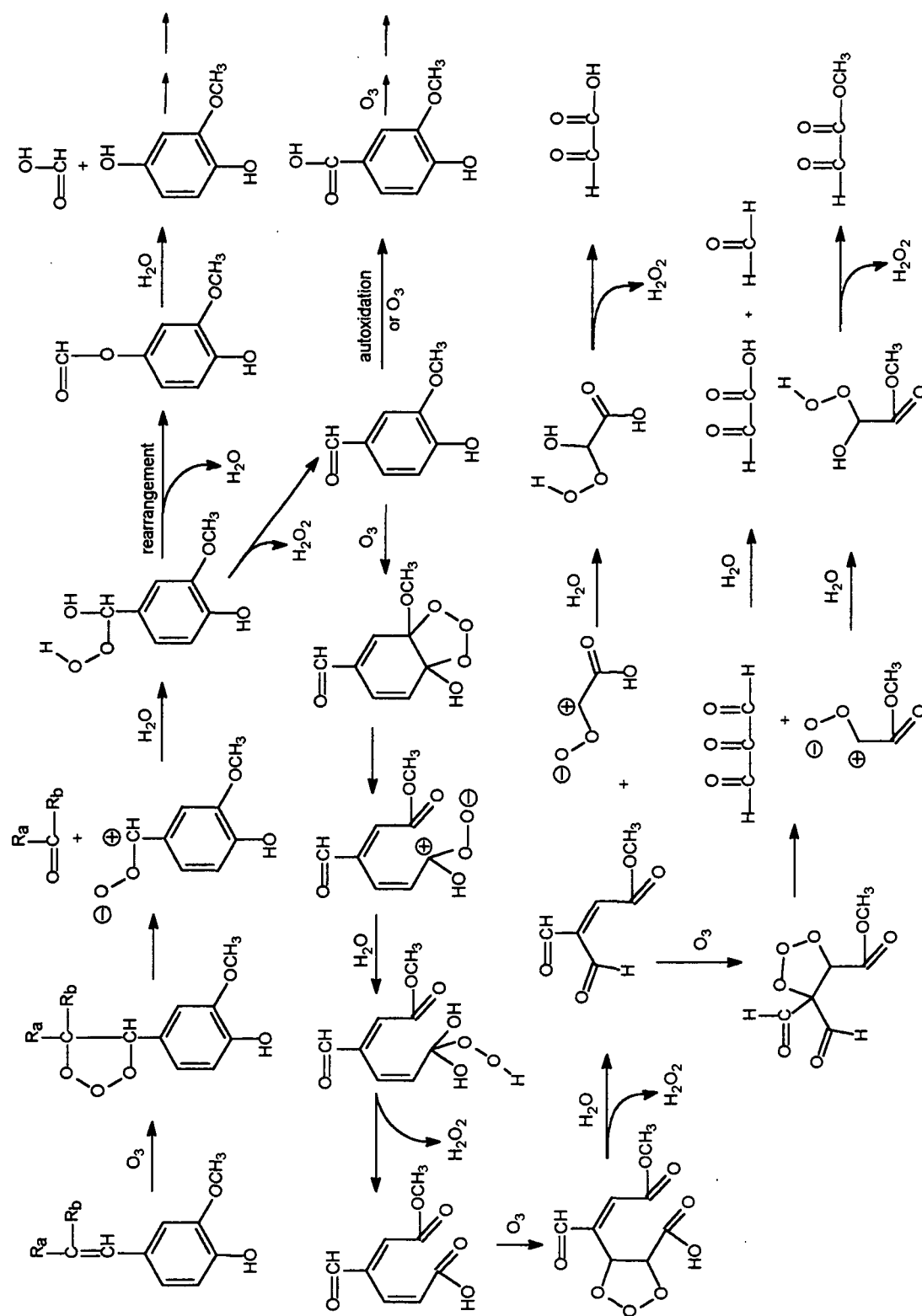


Figure 6. Reactions of Ozone with Aromatic Lignin Models

## RESEARCH REPORTS

# RESEARCH REPORT I: PHASE EFFECTS IN REACTIONS OF A LIGNIN MODEL COMPOUND WITH OZONE

## INTRODUCTION

The mechanisms of ozonolysis of lignin model compounds have been investigated by many researchers in order to develop effective delignification techniques. Many of the studies have been conducted in water-organic cosolvents as a way to dissolve lignin models so that limitations to accessibility and mass transfer are minimized. Chemical reaction pathways can then be better ascertained. For example, Gierer et al. (1985) conducted landmark studies of eight lignin models in aqueous methanol systems. Balousek et al. (1981) examined the degradation of lignin models in 80% aqueous acetone. The latter researchers found that the solvent consumed ozone, but the reaction pathways were similar to those that occur in acetic acid. Kojima et al. (1978) conducted lignin model experiments using ethanol as a solvent. The effects of the solvent, phase, and carbohydrates on reaction pathways of lignin models has not been fully addressed. It is possible that these conditions will affect the chemical mechanism of reactions of ozone with lignin models.

The purpose of this study was to determine whether the pathway and efficiency of ozonolysis of a lignin model compound change as a function of the reaction phase. A water-insoluble dimeric lignin model compound (LMC), shown in Figure 1, was ozonated when dissolved in acetone/water (at acid and neutral pH), when in particulate form suspended in water (at acid and neutral pH), and when adsorbed onto cotton linters (at acid pH and high consistency). The effect of consistency of the spiked cotton linters on the efficiency of ozonolysis of the model was also determined. The extent of degradation of the model compound was measured at different ozone charges to evaluate efficiency. Major reaction products were identified to evaluate changes in reaction pathway.



## **METHODS**

### **Ozonation of the LMC**

All ozonations were carried out in a Welsbech T2 ozone generator and a modified rotary evaporator. Immediately after ozonation, samples were purged with nitrogen. The amount of ozone applied was determined by iodometric titration of a sodium thiosulfate solution into which a reference stream was bubbled. Ozone charges were varied by modifying the voltage of the ozonator; thus, the times of the ozonations were held constant at two minutes. All ozonations were carried out at room temperature.

For the dissolved phase experiments, the LMC was dissolved in a 10:90 mixture of acetone and water. In the acid experiments, the water was acidified to pH 2 with  $\text{H}_2\text{SO}_4$ ; in the neutral experiments, the pH was 6. Approximately 100 mg of the LMC (345  $\mu\text{mole}$ ) was ozonated in 5 mL of solvent. For the particulate phase, the same procedure was carried out, except the acetone was omitted. Fine particles of the LMC were suspended in the water; the solution was vigorously mixed throughout the ozonation. For both dissolved and particulate phase experiments, blank samples were processed to determine ozone consumption by solvents.

For the adsorbed phase experiments, pre-extracted cotton linters were soaked in a dichloromethane solution of LMC at a ratio of approximately 25 mg LMC/g dry linters. The linters were then dried by rotary evaporation at room temperature, evenly wetted with acidified water, filtered and frozen until use. The initial quantity of LMC on the linters was measured directly. Approximately 80% of the LMC in the dichloromethane solution was retained on the linters. Ozonations were carried out on 2.5 g samples of the linters at 30% consistency. Blank samples were processed to determine ozone consumption by the cotton linters.

### **Quantitation of the LMC**

Several methods were examined to quantify the LMC: dichloromethane extraction followed by gas chromatography (GC) analysis of derivatized and underivatized extracts, direct aqueous injection into the GC, and high pressure liquid chromatography (HPLC). The GC analyses em-

ployed flame ionization (FID) or mass spectrometric (MS) detectors. For most experiments, the derivatized (diazomethane methylation of carboxyl groups) samples were quantified by GC/FID using internal standard techniques. The internal standard is shown in Figure 1. For some samples, dehydration of the LMC or compounds bearing the  $\beta$  hydroxy group occurred during methylation; the dehydration products were included in the quantitation of the parent compound.

### **Identification of Reaction Products**

The retention time and mass spectrum of the LMC were used to identify its signal in the chromatograms. Other aromatic reaction products were tentatively identified by fragmentation analysis of the mass spectra. Spectral matching with standards and literature spectra was possible for some low molecular weight reaction products, including glyoxilic acid and its methyl ester and vanillin. Product distributions are compared solely on the basis of relative peak areas in chromatograms; comparisons between ozone conditions are valid while absolute quantitation of the products is not.

## **RESULTS AND DISCUSSION**

### **Lignin Model Degradation - Efficiency of Ozonolysis**

The percent degradation of the lignin model compound under different conditions are shown in Figures 2 and 3. Results are reported on the basis of moles of ozone consumed per mole of starting material. Ozone consumption data are provided in Table 2. Variability of duplicates is likely due to the variability in ozone and lignin model compound measurements.

Approximately the same amount of the LMC degraded when similar amounts of ozone were applied to the adsorbed lignin model and to the dissolved model compound (see designated points in Figure 2). However, the adsorbed lignin model consumed more ozone than the dissolved model to achieve the same degree of degradation. Ozonation of linters blanks showed that direct consumption by the linters did not account for the higher ozone consumption, although approximately 0.2 mmole ozone was consumed per gram dry linters. Secondary ozonolyses (i.e., reaction of

primary reaction products with ozone) may occur more readily in the presence of the linters than in their absence. The concentration of the primary products in the water layer surrounding the high consistency fibers would likely be higher than in the bulk solution in the homogeneous dissolved phase experiments, resulting in faster reaction rates. However, the concentration of the LMC would also be higher in the linters system, also resulting in faster rates of reaction, unless the LMC accessibility to ozone was hindered. Accessibility is likely to be even more significant for lignin in high consistency pulp than in this case of surface-applied LMC. Differences in product distributions of the linters and non-linters systems, discussed below, are consistent with the occurrence of secondary reactions.

The model compound suspended in water degraded very little or not at all. The particulate nature of the model when it was suspended may have limited uniform access to the ozone. It was the only sample in which there was no correlation of LMC degradation with ozone charge. While neutral pH promoted degradation of the particulate LMC, there was not a clear pH effect on the degradation of the dissolved model.

A second experiment was performed in which the effect of consistency and the effect of dissolved glucose on ozonation efficiency was examined (Figure 3). Low consistency conditions exhibited the worst efficiency, similar to Funk et al. (1992), Liebergott et al. (1991), and Kassebi et al. (1982). High consistency linters again consumed more ozone than linters-free systems, to achieve comparable degrees of degradation. There was no effect of dissolved carbohydrates on LMC degradation, consistent with the significantly different reaction rates (see Part I Table 2). These data also support the hypothesis that ozone accessibility to lignin is a key limiting factor in heterogeneous systems.

### **Reaction Products - Effects on Reaction Mechanism**

Common to all of the reaction mixtures is a lactone derived from cleavage of the A ring of the model with a subsequent condensation of the carboxylic acid product of ring cleavage and the  $\beta$ -hydroxy group to form the lactone (Figure 4). These types of compounds have been frequently

reported in dimeric lignin model ozonations conducted in solution (Kojima et al. 1981, Eriksson and Gierer 1985).

For the dissolved model compound, when ozone charges were increased three-fold (9:1 to 30:1 molar ratio of applied ozone to dissolved lignin model), the primary product changed from the lignin model to the lactone. Thus, the major reaction of ozone with dissolved model is simply cleavage of the A ring. When more ozone is applied, more LMC is degraded. Small quantities of other products may arise from the cleavage of the side chain at various sites while the B ring remains intact. Guaiacol is another common product, possibly arising from either ring, but likely from the B ring, since the A ring is so reactive.

The product distribution of the adsorbed model compound differs somewhat from the dissolved compound. The lactone and other aromatic fragments are present, however, at lower concentrations. In addition, there were several small peaks with short retention times in chromatograms of the adsorbed phase extracts that were not present in the chromatograms of the dissolved phase extracts. These peaks arise from low molecular weight compounds, some of which were identified as methylated and unmethylated oxalic acid, glyoxylic acid, malonic acid and methoxyfuran. Other tentatively identified reaction products found in all systems are shown in Figure 5.

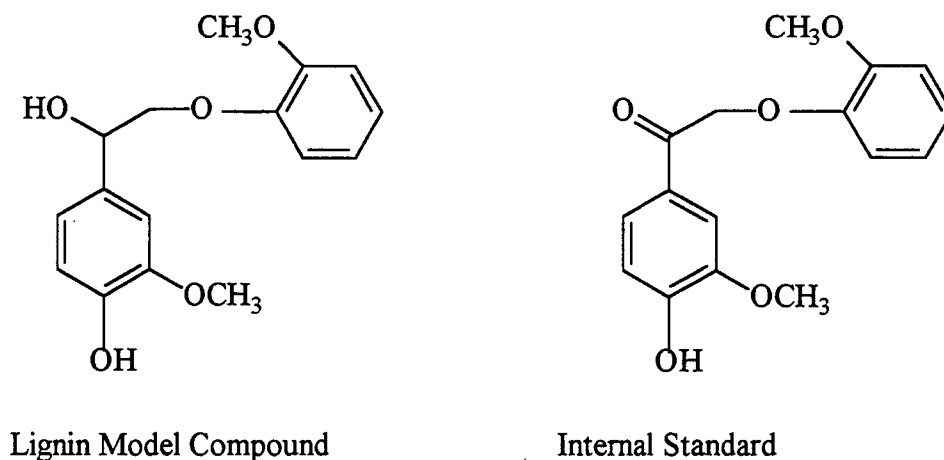
Ozonation of the LMC on linters at high consistency may affect the ozonation pathways of lignin because primary lignin reaction products are more concentrated and react more quickly. Alternatively, the linters may consume ozone and produce chain cleavage and small oxidation reaction products (see Report 3). Each of these scenarios would result in enhanced ozone consumption per mole LMC degraded and the formation of low molecular weight compounds, both of which were observed in this study. While low molecular weight acids and aldehydes may arise from ozonolysis of both linters and unsaturated primary lignin products, the rates of the reactions of the two substrates are likely to be quite different (Hoigne' and Bader 1983a, Hoigne' and Bader 1983b, page XX this document). The majority of the small products are likely to arise from lignin decomposition because of their substantially greater second order rate constants for direct reactions with ozone. This is supported by the fact that more ozone was consumed in the LMC-

alcohol. Further, or concurrent, reactions produce several products arising from cleavage of the side chain at various sites, while the least substituted ring remains intact.

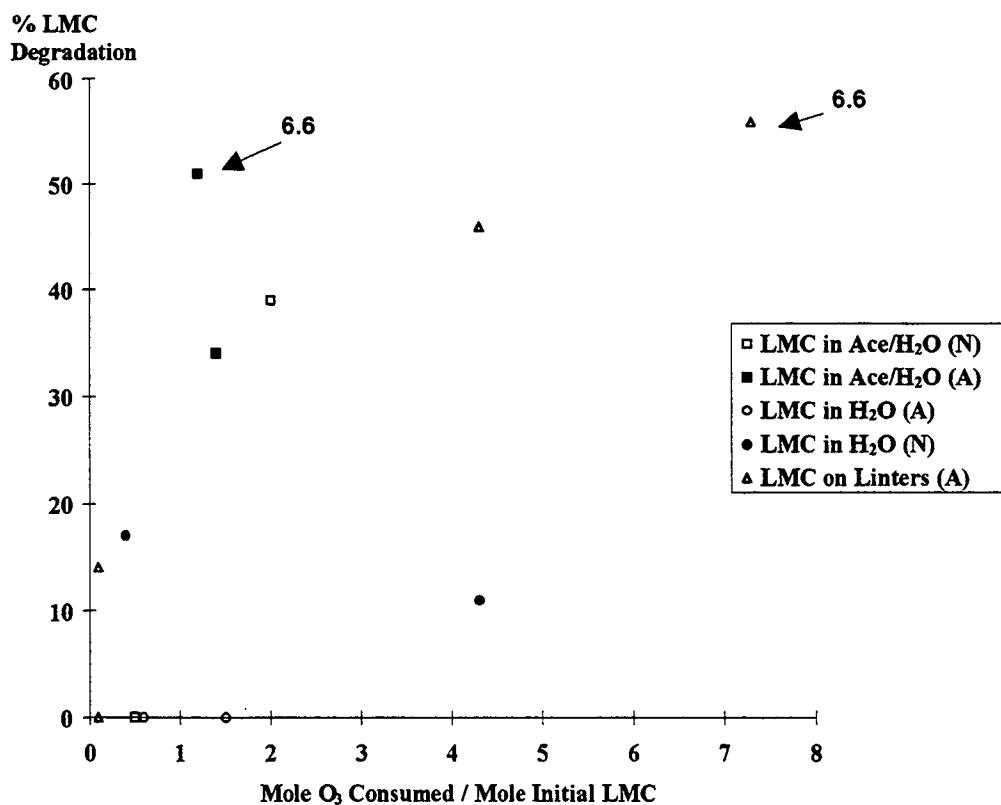
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## FIGURES AND TABLES



**Figure 1.** Lignin model compound, 1-(4'-hydroxy-3'-methoxyphenyl)-2-(2''-methoxyphenoxy)-1-ethanol, and internal standard used for fundamental ozonolysis studies.



**Figure 2.** Influence of the phase on LMC degradation and on ozone consumption. Numerals in the graph are moles of ozone applied per mole of LMC degraded for the designated samples. (A = acidic, N = neutral).

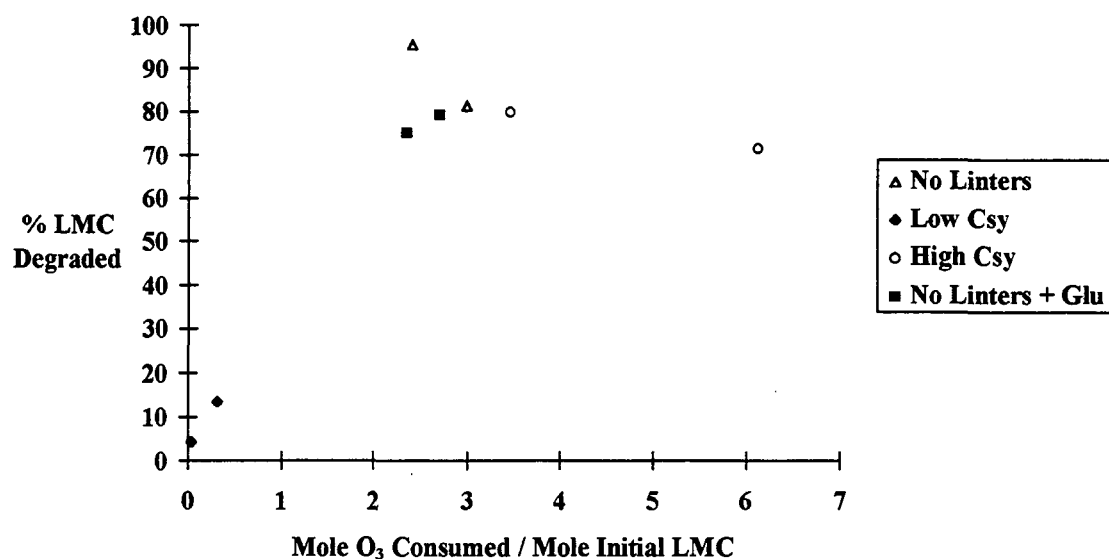


Figure 3. Influence of consistency (Csy) and dissolved carbohydrates on LMC degradation and on ozone consumption; Glu = glucose.

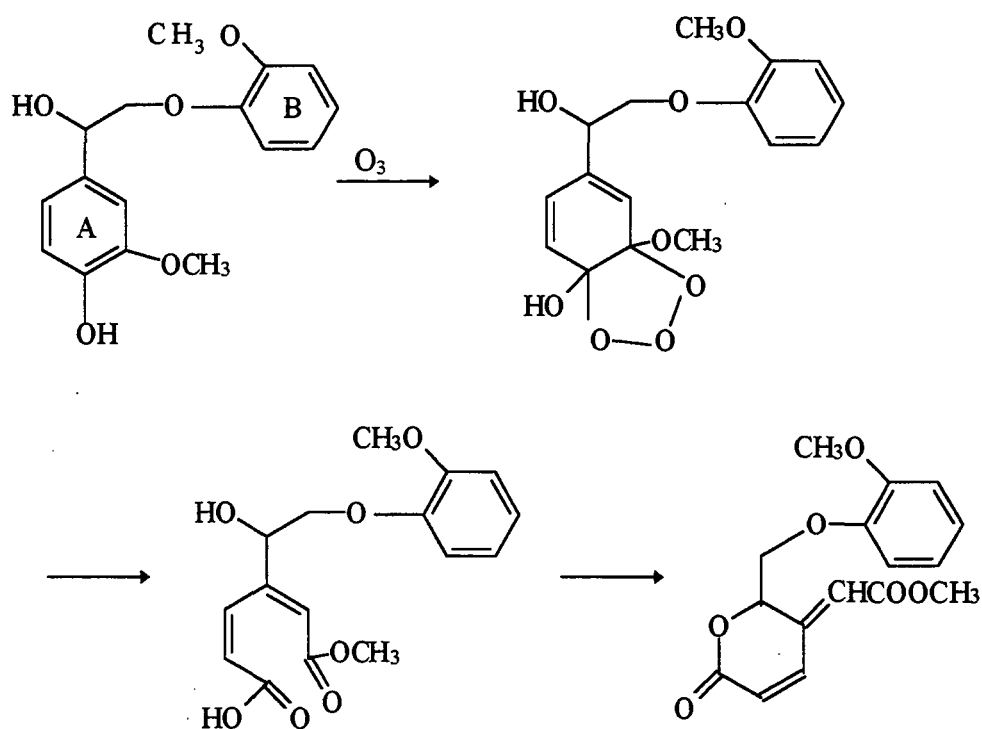
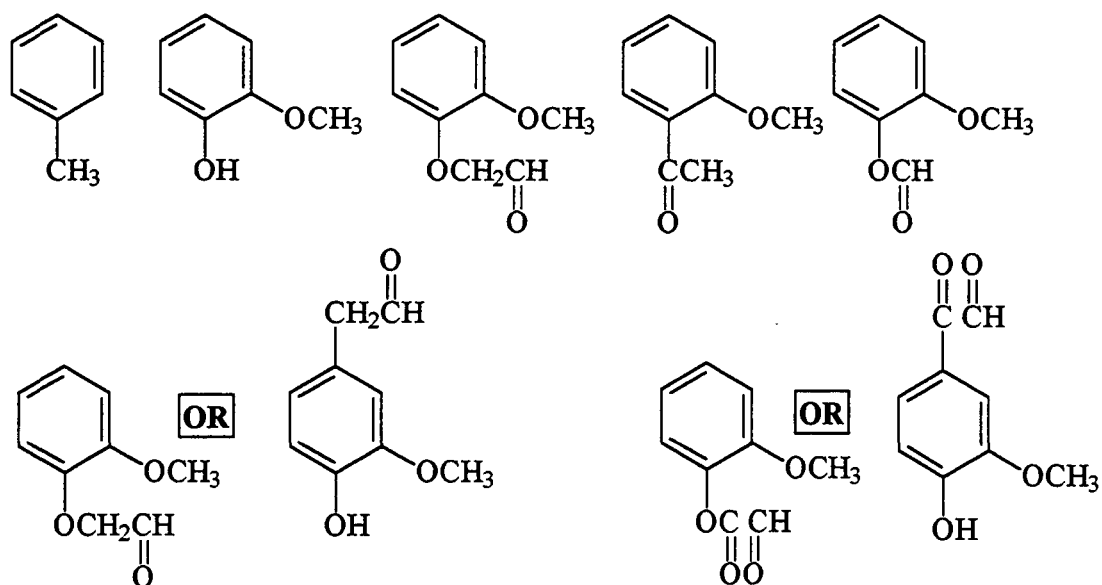


Figure 4. Ring cleavage of the LMC followed by lactone formation.



**Figure 5.** Reaction products tentatively identified from the ozonation of LMC in solutions, in addition to the LMC lactone.



**Table 1. Ozone consumption of the LMC in different phases and ozone charges. Consumption by solvents and linters is excluded.**

Sample	Initial Ozone (mole O <sub>3</sub> /mole LMC)	% Ozone Consumption
LMC in Water		
Neutral	6.5	67
	0.6	66
Acid	6.5	23
	6.8	9
LMC in Acetone/Water		
Neutral	5.1	39
	0.8	63
Acid	6.9	20
	6.8	18
LMC on Cotton Linters		
	6.7	64
	6.6	111
	0.3	33
	0.3	33

## RESEARCH REPORT 2: SOLUBLE BYPRODUCTS 1. CHARACTERIZATION AND SECONDARY REACTIONS

### **INTRODUCTION**

Characterizations of the byproducts of pulp ozonation have shown that two general types of products are formed (see Research Report 3). One type consists of small, gas chromatographable compounds, particularly short-chain and long-chain aliphatic acids and diacids. The other type of ozonation byproduct is methanol-soluble, water insoluble, and possibly composed of large, polar lignin fragments. Few monomeric lignin compounds are detected, and evidence for lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). These highly oxidized, low molecular weight compounds may represent inefficient ozone bleaching. If they arise from lignin reactions, their precursors consume ozone beyond that required to gain solubility. If they arise from carbohydrates, ozone is consumed to weaken the fiber.

Studies of ozonolysis of lignin model compounds indicate that reaction pathways are affected by the presence of cotton linters; the linters reduce efficiency and produce different byproducts (see Research Report 1). Secondary reactions may occur when there is a high concentration of the primary products in the water layer surrounding the linters fibers and there is limited accessibility of the parent LMC. This is a phenomenon that would most likely occur in the initial phase of high consistency ozonation. As surficial lignin is depleted, the rates of reaction with the carbohydrates may become competitive with the rate of mass transfer of the ozone to intrafiber lignin.

In this investigation, characterization of pulp ozonation byproducts focuses on the role of secondary reactions in pulp ozonation. Secondary reactions are defined as reactions of ozone with lignin beyond that required for dissolution of lignin or reactions with carbohydrates. We hypothesized that more secondary reactions will produce more oxidized, acidic filtrates with a higher proportion of low molecular weight material. Filtrates with a high ozone demand will have a higher

potential for secondary reactions and inefficient bleaching. Thus, we measured molecular weight distributions of ozonation byproducts at different charges, the acidity of the soluble byproducts (as a measure of oxidation state), and the ozone demand of different filtrates.

## **METHODS**

### **Ozone**

In one set of experiments, ozonation of southern pine kraft pulp (kappa number =27.9) was carried out in a modified rotoevaporator apparatus at approximately 25% consistency and at pH 2. Ozone was generated by a Welsbach Ozone Generator. The three ozonated pulps consumed 0.8, 1.0%, and 1.4% ozone on o.d. pulp. Filtrates were generated by rinsing ozonated pulp three times with an alkaline solution composed of 0.02 M NaHCO<sub>3</sub>, 0.01 M NaCl, and enough NaOH to adjust the pH to 10.5 (the mobile phase for liquid chromatography analyses). The solution composition was selected on the basis of optimizing size exclusion analyses. The pH of these solutions was near neutral.

In a second set of experiments, a softwood kraft pulp (kappa number =22) was ozonated at several ozone charges ranging from 0.3% to 1.4% on oven dried (o.d.) pulp at about 25% to 30% consistency, also at pH 2. In these samples, filtrates were generated by stirring the ozonated pulps (20 g) in 100 mL of approximately 10<sup>-2</sup> M NaOH. The final pH of these samples ranged between 2 and 4. Acidity was calculated on the basis of these measurements.

### **Molecular Weight Distributions**

Size exclusion chromatography (SEC) was performed two ways. In one method, separations were carried out with a high pressure liquid chromatograph (Hewlett Packard Model 1090) equipped with a photodiode array detector (several wavelengths were monitored) and a TSK-Gel PW 4000 column (Toyopearl). In one case, fractions were collected every minute from the HPLC eluent and measured for total organic carbon (TOC) (Beckman Tocamaster) in an effort to correlate UV activity with concentration of TOC. A typical mobile phase was 0.02 M NaHCO<sub>3</sub>,

0.01 M NaCl, and enough NaOH to adjust the pH to 10.5. No improvements in chromatography were obtained by adding polyethylene glycol or methanol to the mobile phase or altering the pH.

Size exclusion was also performed by medium pressure chromatography using Sephadex G-15 and G-75 stationary phases eluted with 0.1 N LiCl and with on-line TOC detection (Schwantes 1994, Schwantes and McDonough 1994). In these analyses, filtrates were generated by washing pulps in 0.1 N LiCl at pH  $\approx$  5.

Molecular weight distributions were also obtained by ultrafiltration (UF) in some experiments. An Amicon 250 mL ultrafiltration unit equipped with a YM1 or UM2 membrane (MW cutoff  $\approx$  1000) was used. Samples were diluted 100-fold prior to diafiltration in order to minimize aggregation effects. Diafiltration is the displacement of sample solvent with fresh solvent while maintaining a constant volume. The sample solvent volume turned over approximately 50-60 times.

It may be important that the ultrafiltrations of the first set of UF experiments were conducted at near neutral pHs. Despite our attempts to minimize charge exclusion by adjusting the ionic strength of the solution, ionized compounds may have been retained to a greater degree than their molecular weight would dictate. The apparent higher molecular weight fraction for these samples may be erroneously high. In the second set of UF experiments, the acidic pH is likely to have minimized charge exclusion.

### **Ozone Demand**

The values for ozone demand are operationally defined. In these experiments, ozone was bubbled through acidified effluents at a constant rate (50 mg O<sub>3</sub>/min) for two minutes. The amount of ozone delivered and the amount remaining after exposure to the effluent were measured by iodometric titration of potassium iodide traps.

## **Total Organic Carbon Measurements**

Most total organic carbon measurements were performed on a Beckman Tocamaster TOC analyzer using manual injections. For some individual analyses and for the on-line TOC chromatography detection a Shimadzu Model 5050 TOC analyzer was used. For most samples, analysis for total carbon were preceded by acidification and nitrogen purge. Some raw samples were measured for total and inorganic to determine TOC; in general, this method produced more variable results. The eluate from the medium pressure chromatography columns contained an insignificant percentage of inorganic carbon.

## **RESULTS AND DISCUSSION**

### **Recovery of TOC**

In all instances of ozone delignification, the TOC of the filtrates increased with ozone charge reflecting increasing delignification. However, considerable amounts of organic carbon were not recovered (Figure 1). The minimum amount of dissolved lignin that should have been detected was estimated by examining the drop in kappa number with ozone application. This value was compared to the amount of dissolved lignin that was detected, estimated from TOC values. In these calculations, it was assumed that the percent lignin in solution was equal to 0.15 times the drop in kappa number, lignin contains approximately 65% carbon by weight, and it has a molecular weight of 180. These estimates indicated that variable percentages of TOC were lost. In one set of experiments, TOC loss was not related to ozone charge. In a second set of experiments the loss correlated inversely with charge (Figure 2). While the route of organic carbon loss is unproven, the most likely route is from volatilization of low molecular weight compounds.

It is somewhat counter to intuition that the percentage of TOC loss decreases as ozone charge increases. However, the similarity of the slopes in the two curves in Figure 2 show that there is a fairly constant quantity of TOC lost, even with increasing charge. At low charges, this lost portion represents a substantial fraction, approximately 80%, of the total organic carbon removed from the pulp. At high charges, while the absolute amount of unrecovered carbon is similar to

that at low charges, it represents a much smaller proportion of the total organic carbon removed from the fiber, approximately 40%.

It should be noted that in the first set of experiments, there was no correlation between TOC loss with charge. However, there were limited data points (three), and consistency of the ozonation was generally lower. A larger water layer around the fiber may limit the volatilization that takes place during ozonation. It is also possible that the higher pH of the filtrates inhibited volatilization of acidic compounds.

### **Molecular Weight Distributions by Ultrafiltration**

Initial UF experiments indicated that, at charges at 1% or below, approximately equal amounts of apparently LMW (<1,000 daltons) and HMW material are formed. As the charge increased, the percentage of HMW material increased. Interpretation of these data needs to be undertaken with caution, however, because of the TOC loss and also because of the effect of ionized compounds on the separation process. When these experiments were performed a second time with numerous ozone charges and at a pH that would not ionize most carboxylic acids, the proportion of apparent HMW material ranged from about 20% to 45% with no apparent relationship to charge (Figure 3). When the loss of TOC was taken into account and assumed to be LMW, the HMW proportion ranged from 10% to 25% and increased with charge, as previously observed (Figure 4).

### **Molecular Weight Distributions by Size Exclusion Chromatography (SEC)**

The size distributions of the soluble lignin fragments in the alkaline rinsates of unbleached and ozonated pulp were also evaluated by HPLC-SEC. In Figure 5, the size exclusion chromatograms of the alkaline rinsates of an unbleached pulp and pulps ozonated at three charges; the UV detection wavelength is 254 nm. Compounds elute in the order of high molecular weight to low molecular weight. There is a general increase in the intensity of all peaks, roughly corresponding to increase in delignification. This method also indicates an increase in high molecular weight material, relative to the LMW material, with increasing ozone charge. It should be noted that the

sharp peak eluting at approximately 10 minutes in Figure 5 is likely to be an artifact of the work-up procedures.

A problem with most chromatography methods that employ TOC characterization is the unambiguous detection of organic material that is eluting from the columns. Monitoring the 254 nm wavelength is a common and useful way to monitor some types of sites of unsaturation. However, not all unsaturated compounds absorb at 254 and not all material in filtrates is unsaturated. Although monitoring shorter wavelengths tends to be more noisy, it is also more sensitive to many compounds that are not usually detected at other wavelengths. Figure 6 shows the chromatograms with 210 nm wavelength UV detection. Comparisons of the chromatograms shows that there are alkali-soluble components of the unbleached pulp that are successively removed with increasing charges of ozone. The negative peaks at low wavelengths correspond to elution of compounds that absorb less than the mobile phase. A negative peak at approximately 40 minutes also decreases with charge, possibly indicating the removal of another soluble byproduct.

The results from the HPLC-SEC at 210 nm analyses indicate that secondary reactions occur during pulp bleaching with ozone. Interestingly, it is not likely that these secondary reactions are the major sources of the oxidized, LMW compounds found by UF at low ozone charges. The latter compounds did not increase with charge, but remained relatively constant. Analyzing the UF retentates by HPLC-SEC showed that the substrate of the secondary reactions were smaller than 1000 daltons (Figure 7), which is consistent with the results from the ozone demand experiments in which most consumption of ozone was by LMW material at high charges (see below).

A shift to LMW material (and increased TOC loss) with increasing charge is expected if secondary reactions of ozone with dissolved byproducts is a major pathway of ozone consumption. While the SEC evidence points to its occurrence, there is an overall production of mostly high molecular weight material with increasing charge. Therefore, the fraction that is detected at 210 nm and disappears with increasing ozone charge must not represent an overall significant fraction of the dissolved TOC and may not be a significant source of ozone consumption during pulp ozonations.

These results again illustrate the difficulty in obtaining unambiguous information about molecular size distributions, in part because of the methods of detection. For a single sample, fractions of the eluent from the HPLC-SEC were collected every minute and analyzed for TOC. The histogram in Figure 8 roughly indicates a molecular weight distribution based organic carbon detection. It can be seen that while a general bimodal distribution is also indicated by the TOC chromatograms, there is little similarity with the UV chromatograms beyond that feature. Furthermore, in later work using column chromatography with a different stationary phase and with on-line TOC detection, a different distribution was obtained (Figure 9). This method shows a generally uniform distribution of compounds, but with a slight prevalence of LMW material, consistent with the second UF method of determining molecular weight distributions.

### **Oxidation State of Byproducts**

The pH of the whole and HMW fraction of the filtrates decreased with charge (Figure 10). The increase in acidity of the filtrates is related to the increase in TOC. As more acids are released into the filtrate, the pH decreases. However, another aspect of filtrate acidity is the relative acidity of the individual components of the filtrates. Compounds with a low pKa will produce a low pH effluent. We normalized the hydrogen ion content of the filtrates to the TOC (moles/moles) and used these values as a measure of the relative acidity of the organic carbon produced in the filtrates (Figure 11). The lignin fragments that are produced at low charges have a higher relative acidity than the material produced at higher charges.

### **Ozone Demand**

The ozone demand of ozonation effluents was measured to determine the potential for secondary reactions in which dissolved byproducts react with ozone. The results were expressed in two units: mole ozone consumed per mole organic carbon in the filtrate (Figure 12) and mg ozone consumed by the filtrate per gram of pulp that was ozonated (Figure 13). It is important to recognize that the ozone demand measurements were made in the absence of pulp; therefore, these



data represent maximum possible values. There is likely to be significant competition for the ozone by the lignin in the pulp.

The alkaline rinsate from the unbleached pulp exerted a strong ozone demand per gram of organic carbon in the rinsate, reflecting the relatively unoxidized state of the alkali-soluble pulp component (Figure 12). By contrast, the ozone filtrate constituents consumed little ozone per mole organic carbon, consistent with the high oxidation state of the primary ozone products. Kamyr has reported that the reactivity of ozone with carryover from cooking, oxygen delignification, peroxide, and ozone decrease in that order (Szopinski and Stromberg, 1993). The molar ozone consumption in our work was comparable to values reported by the Austrians for  $O_3$  consumption by liquor carryover in the E(OP)ZP bleaching of sulfite pulp: 3 kg ozone consumed per kg TOC in the carryover, which corresponds to a 0.08 ozone:carbon molar ratio (Peter and Ekholm, 1993). There is some disparity in studies of carryover effects. Lindholm (1988) found that ozonation filtrates used for low consistency ozone bleaching had no effect on bleachability, except an increase in selectivity. Szopinsky et al. (1993) also found no consumption of ozone by Z stage filtrate components. However, Coledette et al. (1993) have found that Z stage filtrates reduce efficiency while selectivity remains the same.

The quantity of organic carbon in the filtrates from the different ozonation conditions must be taken into account (Figure 13) when assessing ozone consumption. Although the demand for ozone per mole carbon is low for the filtrates from the high charge ozonations, the quantity of dissolved organic carbon is high enough so that the high-charge filtrates consume more ozone overall than the low-charge or unbleached filtrates. These data also indicate an interesting preferential consumption of ozone by low molecular weight compounds in the high-charge filtrates.

These results indicate that there is a potential for ozone consumption in secondary reactions of soluble byproducts. However, an important variable in ozone consumption by filtrates is likely to be the relative oxidation states of the filtrate and pulp components. The oxidation states depend not only on the oxidant used to generate the filtrates, but also on the charges of the oxidants used,

pH, and other reaction variables. Possibly, the more soluble effluent components will generally have a higher oxidation state and therefore be less reactive toward ozone than pulp components.

## CONCLUSIONS

The combined results suggest that there is a labile, oxidized portion of the pulp that is readily dissolved at low charges and some of which is volatilized. Common ozonation products that are volatile include aldehydes and ketones (see Research Report 3); complete oxidation to CO<sub>2</sub> may occur to some extent, as well. It is likely that these initial reactions occur at the surface at the fiber. As ozone charge increases, the rate of mass transfer increases and penetration into the fiber is accompanied by primary reactions that produce more compounds that are high molecular weight. The production of low molecular weight, acidic byproducts at low ozone charges is likely to be the result of the reactions of ozone at the terminal points in lignin and carbohydrate molecules. As a result, depolymerization at low charges may be minimal.

There appear to be two avenues by which potentially inefficient ozone bleaching can occur. At low ozone charges, oxidation beyond that required for dissolution for lignin and/or carbohydrate reactions occur, producing the acidic, low molecular weight products noted above. The extent of these types of reactions appears to be fairly constant with charge and they are not likely to be preventable by modifying ozonation conditions.

The second avenue occurs at high ozone charges. There is evidence from HPLC-SEC-UV that soluble, low molecular weight byproducts react further with ozone. These reactions are probably promoted by high consistency conditions (see Research Report 1). However, the bulk characteristics of the dissolved organic material from higher charges (> 1%) are more consistent with depolymerization rather than secondary reactions. Therefore, secondary reactions of soluble, low molecular weight byproducts from pulp ozonation will likely consume only a small fraction of the ozone applied. If an unoxidized source of soluble organic material is present, or if very high charges are used that produce large quantities of dissolved organic material, the significance of such secondary reactions increases.

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## FIGURES AND TABLES

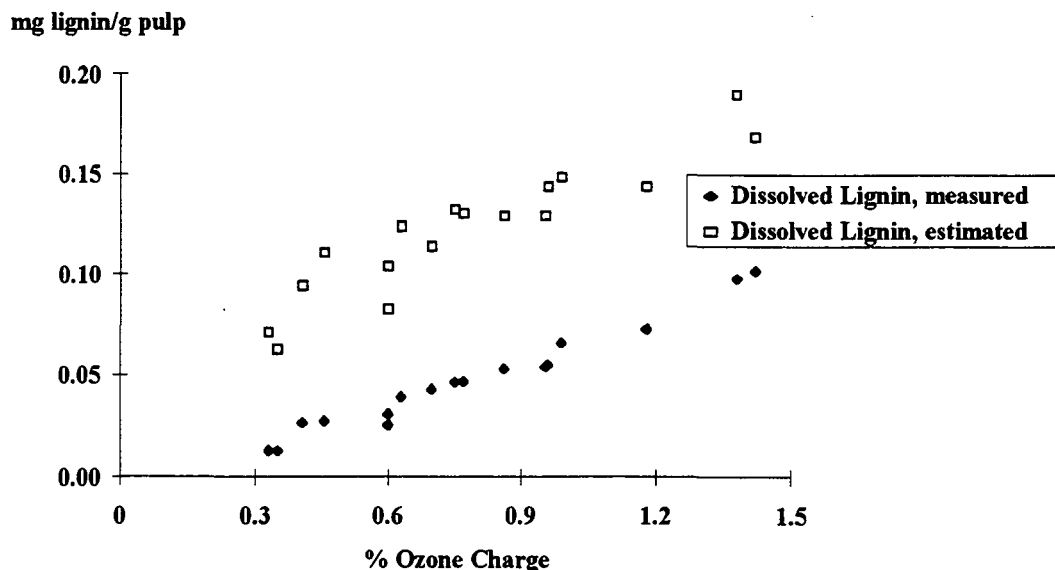


Figure 1. Discrepancy between values of dissolved lignin in filtrates based on total organic carbon measurements (measured) and lignin reduction in pulp (estimated).

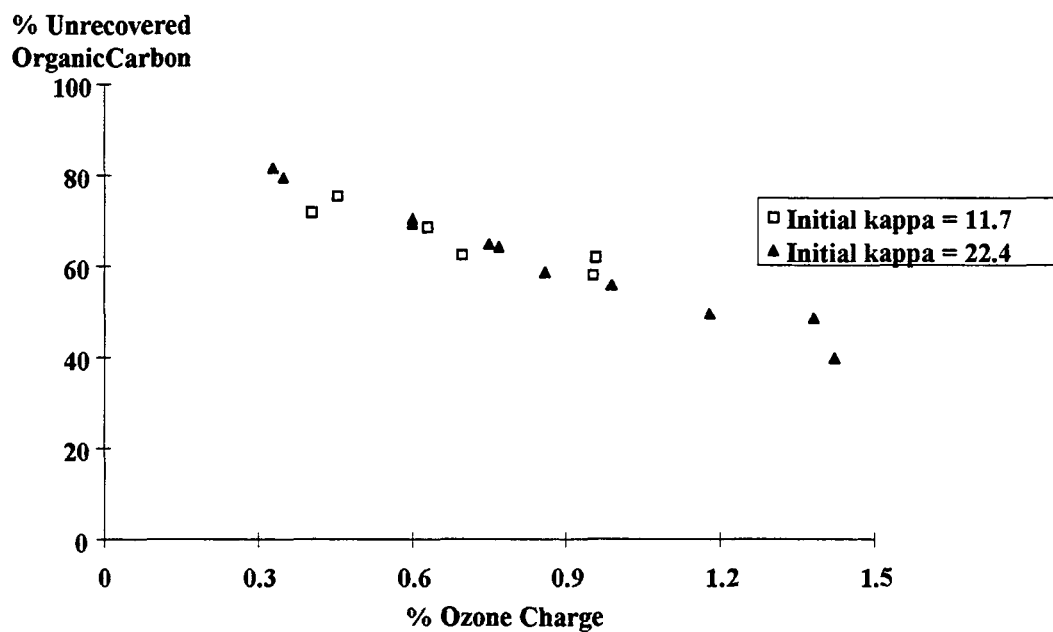


Figure 2. TOC loss with ozone charge.

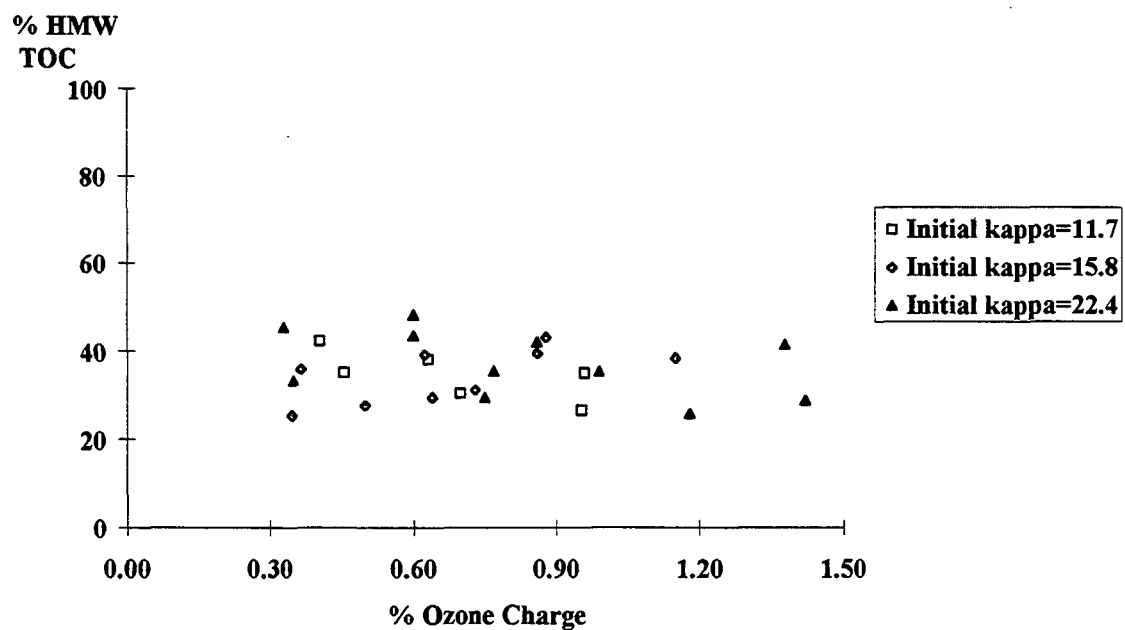
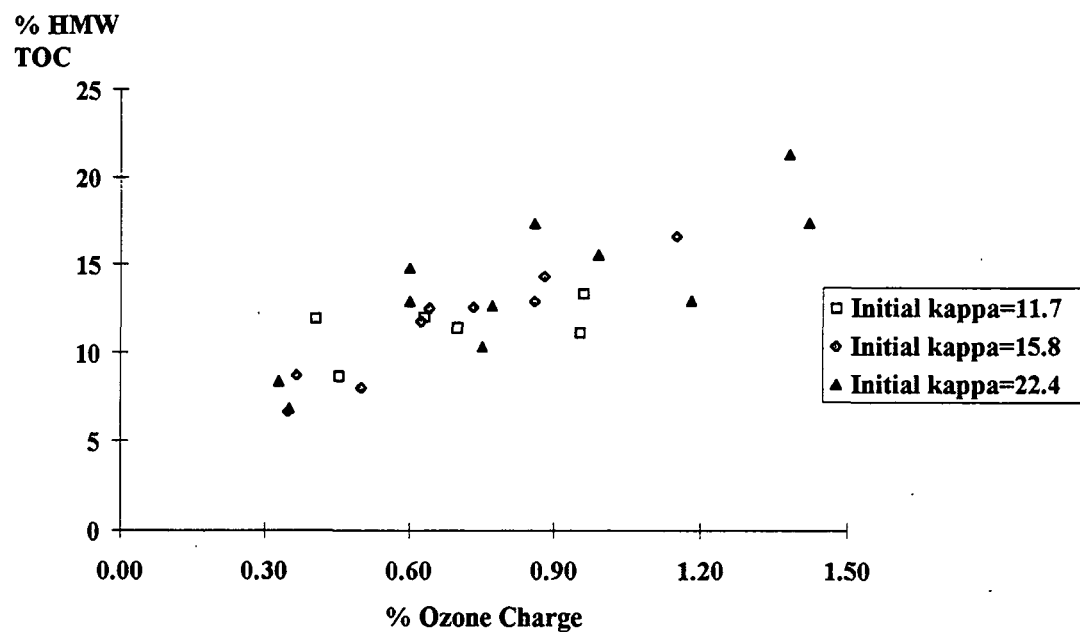
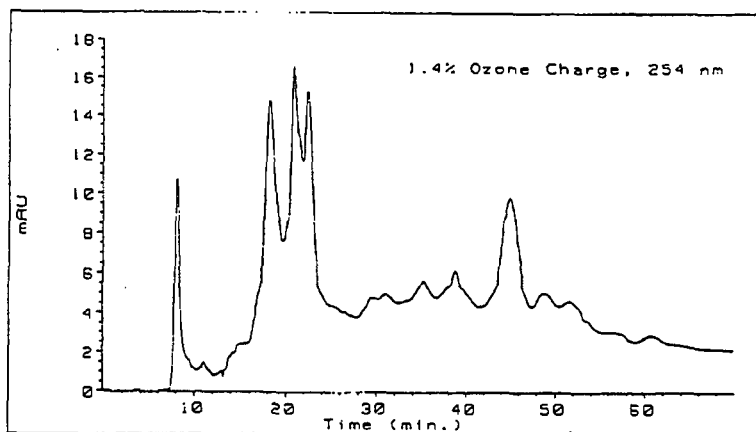
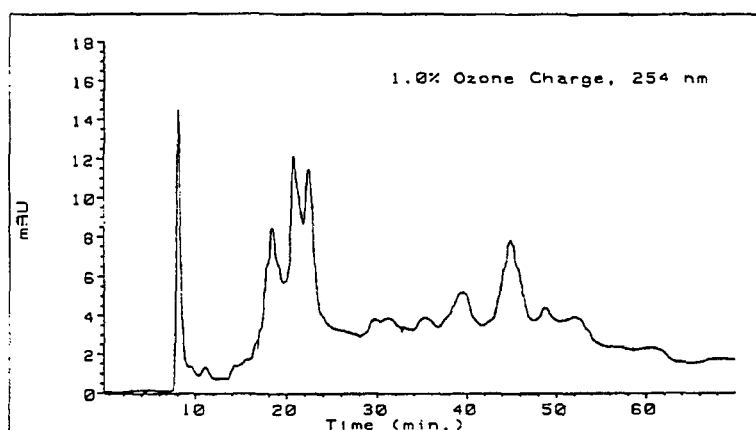
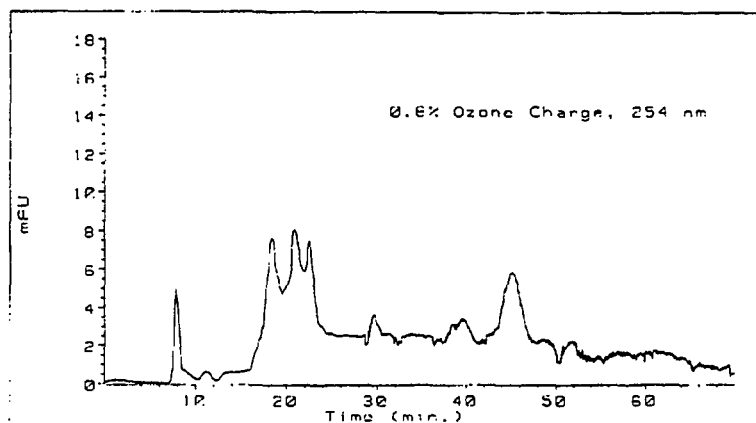


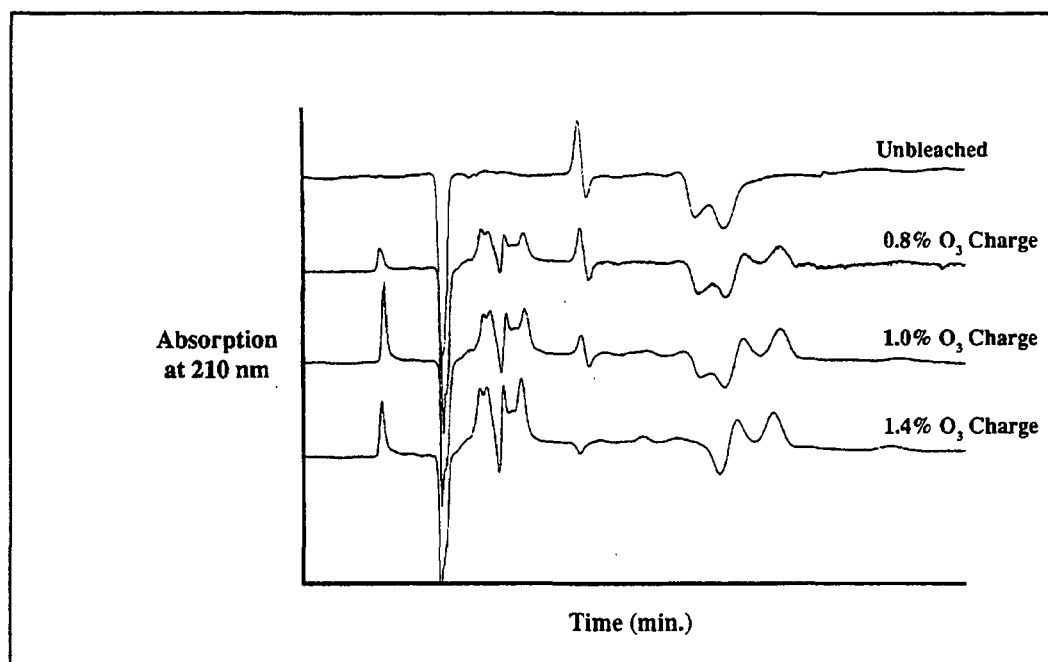
Figure 3. Percent of HMW organic carbon produced from ozonation.



**Figure 4.** Calculated percent of HMW organic carbon produced from ozonation, accounting for unrecovered TOC as LMW.



**Figure 5.** HPLC size exclusion chromatograms of alkali-soluble pulp ozonolysis products. High molecular weight compounds elute before low molecular weight compounds. Detection is by UV at 254 nm. Units are milli absorbance units.



**Figure 6.** HPLC Size exclusion chromatograms of alkali-soluble pulp ozonolysis products. Detection is by UV at 210 nm.

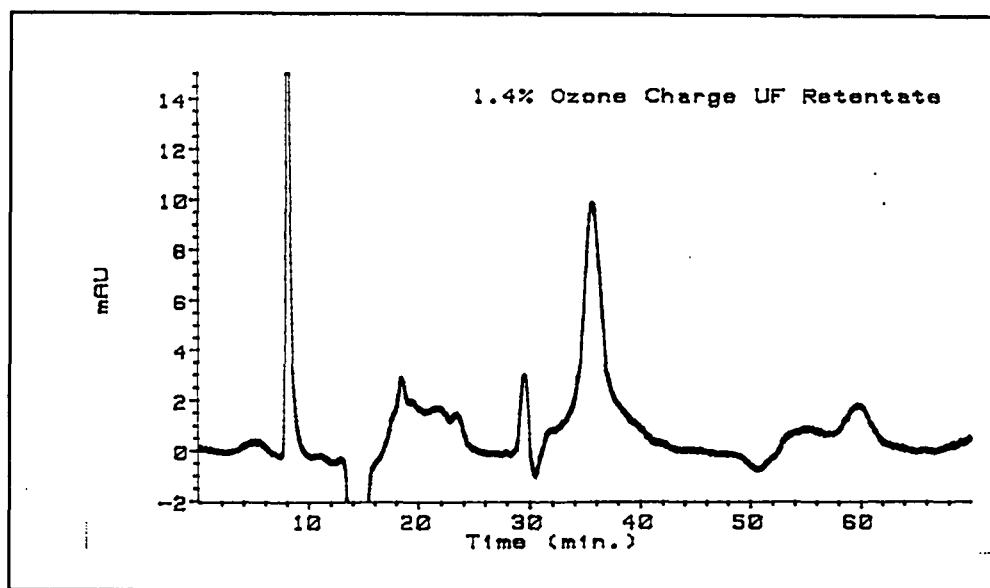
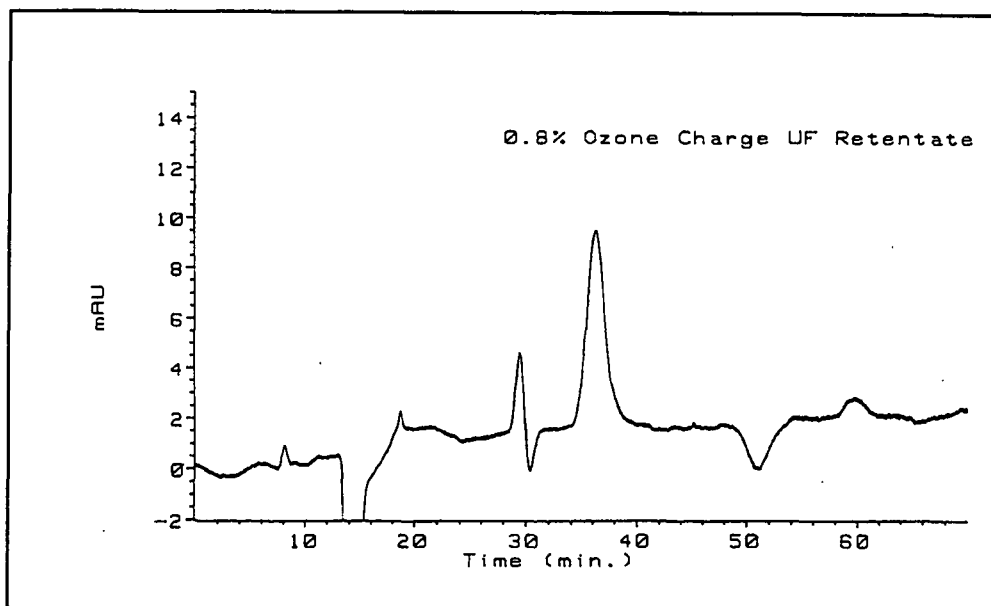
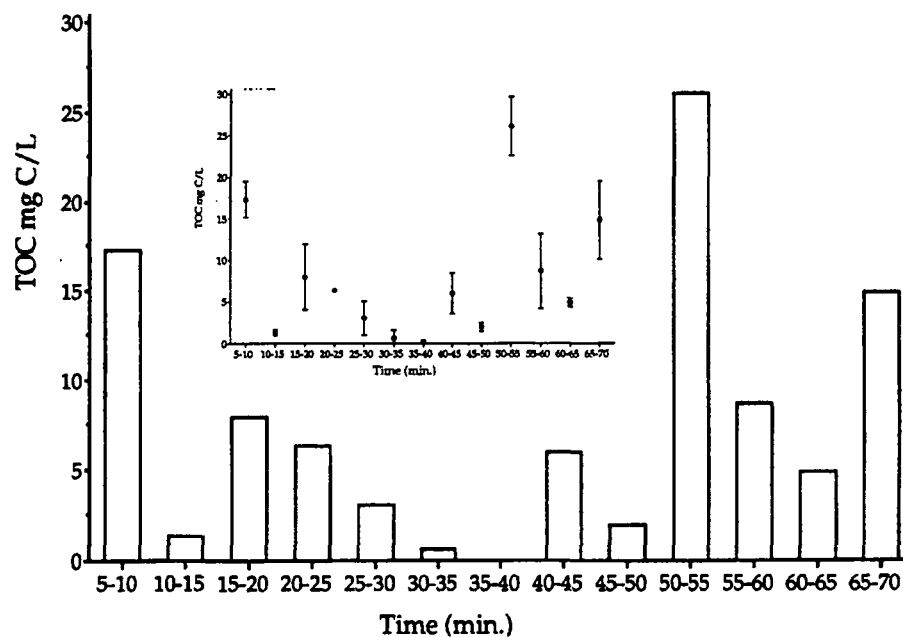
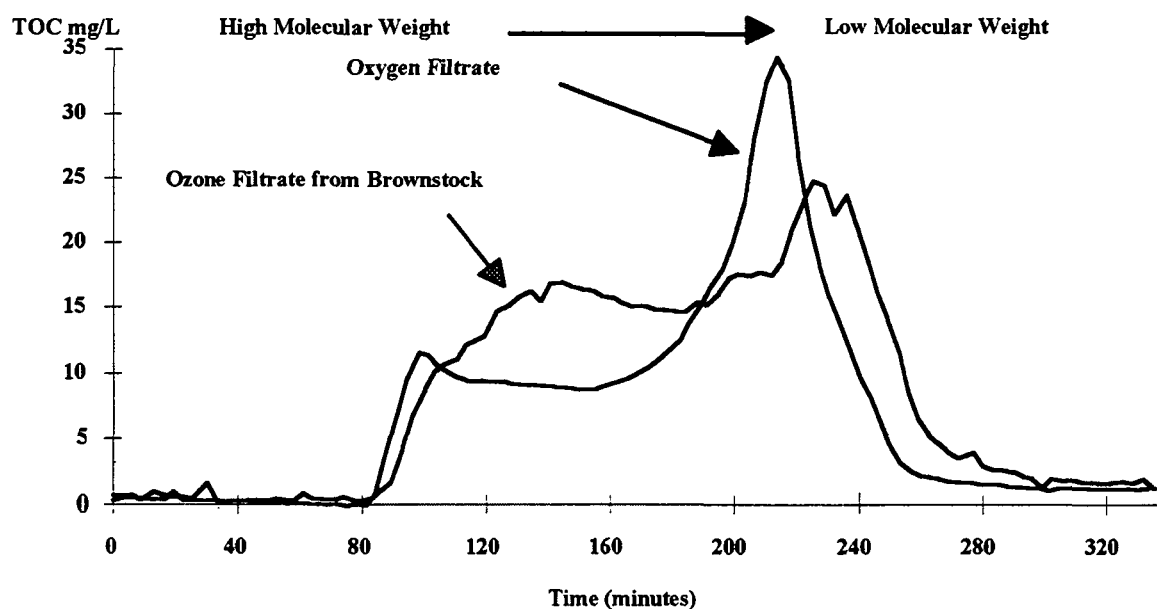


Figure 7. HPLC Size exclusion chromatograms of UF retentates.





**Figure 8.** Histogram of TOC values of HPLC-SEC fractions. Inset shows 95% confidence intervals from triplicate TOC analyses of each fraction.



**Figure 9.** Column size exclusion chromatograms of alkali-soluble pulp ozonolysis products. Detection is by on-line TOC.

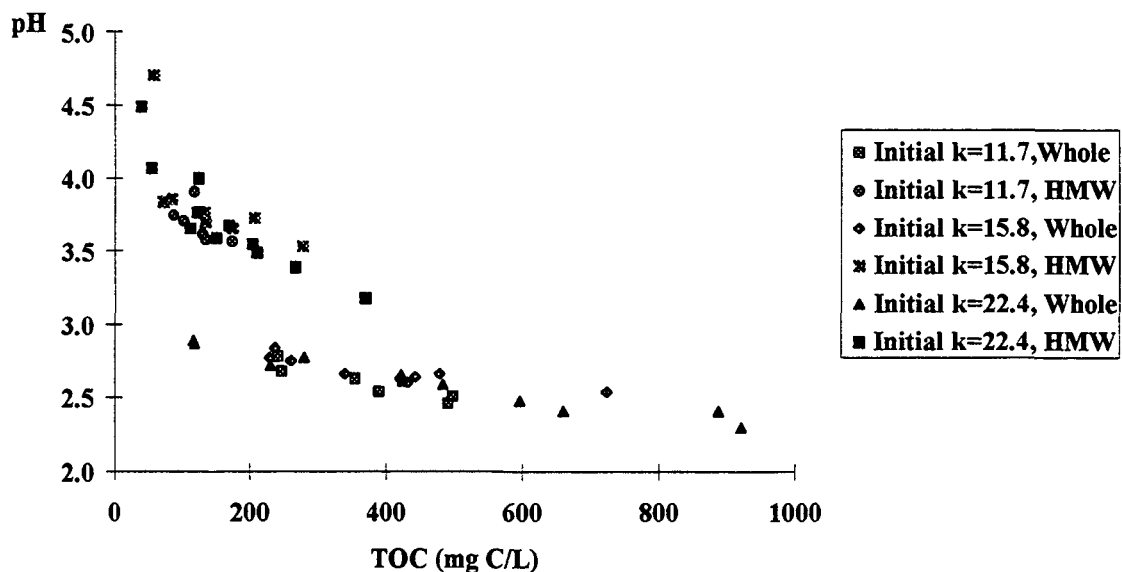


Figure 10. The pH of whole ozonation filtrates and the high molecular weight fraction at different ozone charges.

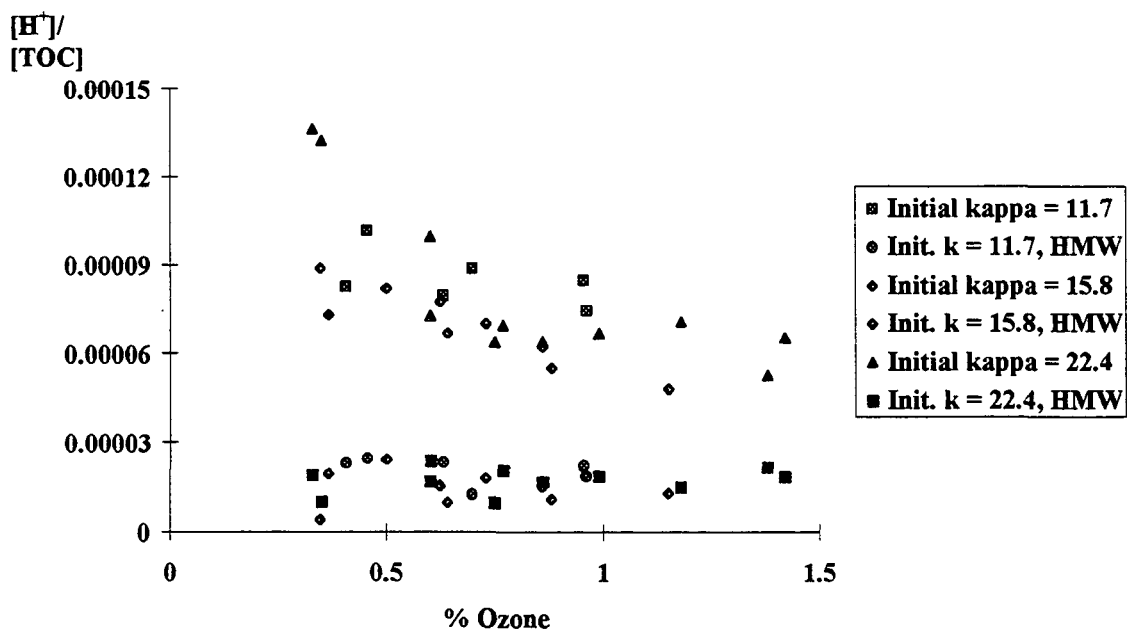


Figure 11. The acidity/mole of dissolved organic carbon produced by ozonation.

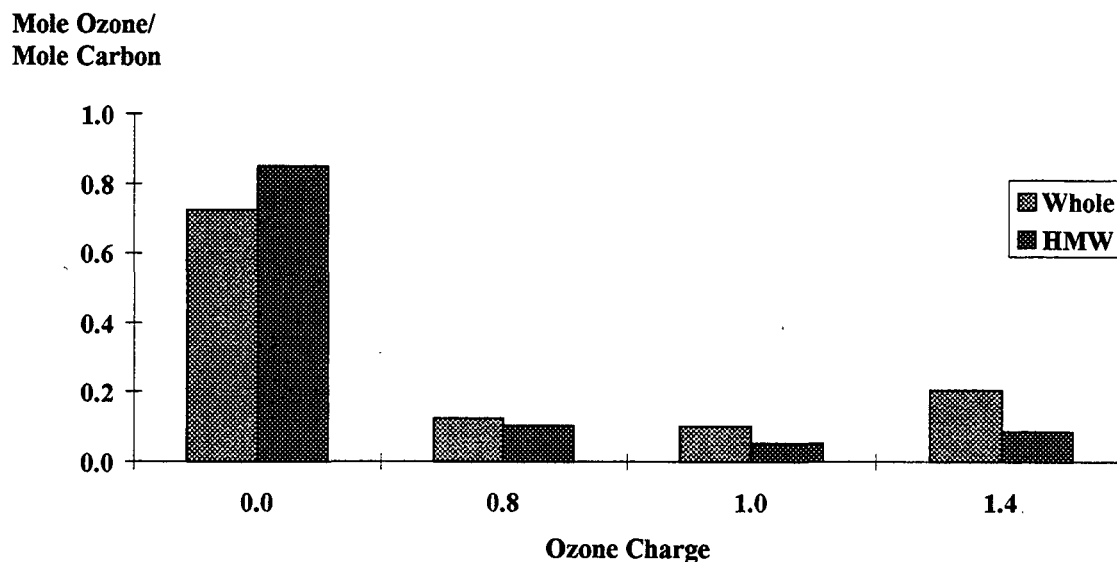


Figure 12. Ozone demand of ozonation filtrates (mole  $O_3$  consumed/mole organic carbon in filtrate).

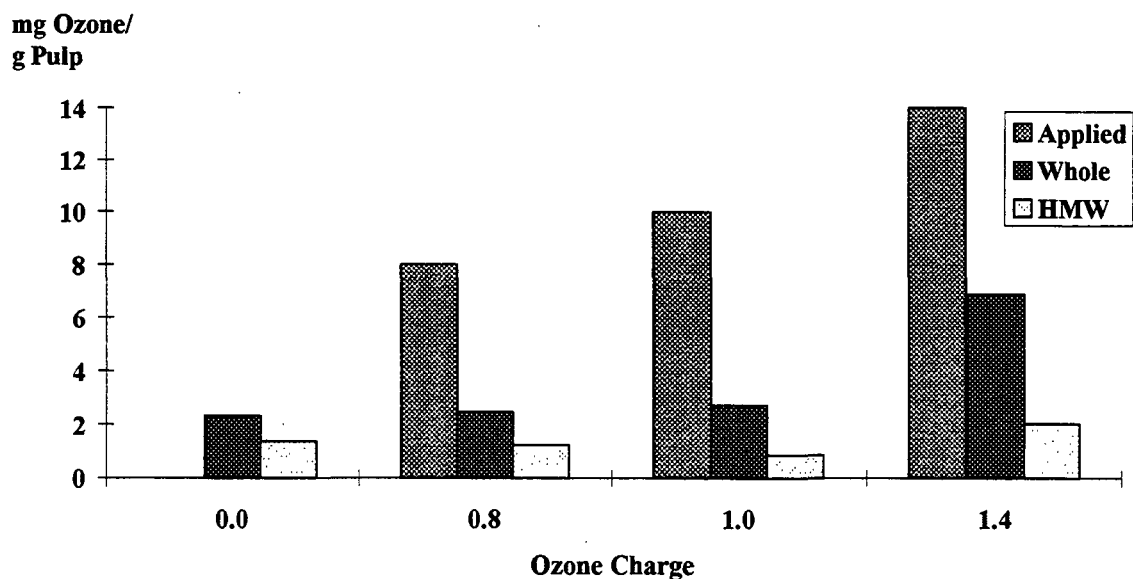


Figure 13. Ozone demand of ozonation filtrates (mg ozone consumed per g pulp).

## RESEARCH REPORT 3: SOLUBLE BYPRODUCTS 2. LOW MOLECULAR WEIGHT COMPOUNDS

### INTRODUCTION

Because of increasing pressure to reduce or eliminate chlorinated organics in effluents and pulps, the paper industry is developing bleaching processes which do not utilize chlorine or chlorine dioxide. Ozonation and oxygen delignification are two such promising techniques. Although there is considerable information regarding byproducts from chlorinating pulp,<sup>1,2</sup> less is known about the byproducts from oxygen-based bleaching. Knowing the components of effluents from these bleaching techniques can be invaluable in assessing the effluents' potential toxicity and evaluating treatment strategies. In addition, the composition of the effluents can help elucidate prevalent reaction pathways.

There are many ways to approach the task of effluent characterization. Functional groups (e.g., carboxyl content), physicochemical properties (e.g., Koc), broad physical and chemical characteristics (e.g., molecular weight distribution ozone demand, see Report 2) can be examined. Specific small products can also be identified. Each approach provides important information about these complex mixtures.

Small compounds are of particular environmental interest because they have a higher potential for toxicity than higher molecular weight material, usually because they are more bioavailable.<sup>3</sup> Aldehydes are potentially important because they are produced by reactions of ozone with sites of unsaturation and because some aldehydes are toxic.<sup>4</sup>

The distribution of small, gas chromatographable products associated with ozonated pulp is the focus of the work reported here. Emphasis is placed on carbonyl compounds. Because initial characterizations of ozone byproducts indicated showed few characteristics of lignin fragments, information about the fraction of the pulp that is the source of the byproducts was sought by pre-extraction with several solvents. These included an acid solution, alkaline solution, and a non-

polar organic solvent. After ozonation, extracts from several different pulps were analyzed by gas chromatography-mass spectrometry. A northwestern softwood kraft pulp and a southern softwood kraft pulp (with and without prior oxygen delignification) were examined.

## **METHODS**

### **Oxygen and Ozone**

The northwestern softwood pulp had an initial kappa number of 27.9; the southern softwood pulp had an initial kappa number of 27.6. Approximately 10 o.d. g pulp samples (acidified to pH=2 with H<sub>2</sub>SO<sub>4</sub> solutions) were ozonated at high consistency (30-35% on o.d. pulp) in a rotoevaporator adapted for ozone application from a Welsbach Model T-28 ozonator. Ozone charges varied from 1.2% to 1.7%, except as otherwise noted. Oxygen delignification was conducted for 1 hour at 110°C, 10% consistency, 2% NaOH and 0.5% MgSO<sub>4</sub>.

### **Pulp Extractions**

In initial studies, after the pulp was ozonated, the aqueous filtrates and pulp were both extracted with diethyl ether; the extracts were derivatized and analyzed. Two fractions were obtained: a methanol-soluble, water insoluble fraction (from the pulp) and a methanol-soluble, water-soluble fraction (from the filtrate). Numerous short chain diacids and similar polar chemicals were detected. The notoriously poor recovery of these chemical classes out of water prompted the use of methanol as an extraction solvent in a second series of experiments. In addition, methanol is a good solvent for lactones, lignin dimers, and unsaturated aliphatic acids. Most ozonated pulps in the second series of experiments were extracted with and derivatized in methanol; the methanol extracts were then analyzed directly by GC/MS. Most of the ozonated pulps were soxhlet extracted overnight in methanol. Water was azeotropically removed from the methanol extracts (to ensure solubilization of all compounds and good derivatizations) by rotoevaporation of a ternary mixture of the methanol, water, and chloroform. Methylene chloride pre-extractions were based on TAPPI Method T204 om-88, except the pulp was not air-dried.

## Derivatizations

The carboxylic acids and phenols in methanol and ether extracts were methylated by diazomethane generated by the Fales method.<sup>5</sup> The methanol extracts were either derivatized directly by *in situ* generation of diazomethane, or an ethereal solution of diazomethane was added to the methanol extract. It should be noted that extraction of the acidic pulp with methanol also caused methylation of some carboxylic acids, probably by way of an acid-catalyzed Fisher esterification.

Pentafluorobenzyl oxime derivatives were prepared by adding approximately 15 g of *O*-(2,3,4,5,6-penta-fluorobenzyl)hydroxylamine hydrochloride to 1 mL of concentrated methanol extracts. After standing overnight at room temperature, the methanol solution was acidified with 2 mL of pH=1.3 H<sub>2</sub>SO<sub>4</sub> solution and extracted with hexane. Derivatization of standards using these conditions indicates that methylation of acids occurs in this procedure as well.

## Analyses

The samples were analyzed with an HP 5890 II GC, equipped with an HP 5971A MSD driven by a G1030A Chemstation. Electron impact (70 eV) spectra were obtained for masses 40 to 400 AMU. Identifications were made by matches with compounds in NBS and EPA/NIH libraries, fragmentation analysis and relative retention times. Glyoxylic acid methyl ester, glyoxal, oxalic acid dimethyl ester and vanillin identifications were confirmed by spectra and retention times of standards.

## Formaldehyde Studies

A separate study of formaldehyde production was carried out by S. Michelle Nooney, a Master's student, in 1994. In these experiments, two softwood kraft pulps, one with a kappa number of 22.4 and another oxygen delignified to a kappa number of 13.3, were ozonated at high consistency at charges ranging from 0.3 to 3.8% on o.d. pulp. Cotton linters samples were ozonated as well. Following ozonation, the consistency was lowered to 3% and aliquots of the solution were taken for PFBHA derivatization (described above).

In addition to analyzing dissolved forms of formaldehyde, we also attempted to measure gas-phase formaldehyde. Gas phase derivatization was carried out by passing the gas stream from the ozonator through Waters Sep-Pak dinitrophenylhydrazine (DNPH) silica cartridges. The cartridges were eluted with 3 mL of acetonitrile over one minute. Derivatives were analyzed using a Hewlett Packard 1090 liquid chromatograph equipped with a photodiode array detector (at 360 nm) and 4.6 x 100 mm C<sub>18</sub> reverse phase column. The mobile phase consisted of 65% water, 30% acetonitrile, and 5% tetrahydrofuran.

Quantitation was carried out by external standard methods.

## **RESULTS AND DISCUSSION**

### **Solubility Characteristics of Ozonation Byproducts**

Two series of experiments were performed with ozonated pulp, one was based on ether extractions and the second was based on methanol extractions. These procedures essentially fractionated byproducts based on their solubilities, providing valuable information about their chemical characteristics.

In initial investigations of ozonation byproducts from a northwestern softwood pulp, two fractions of byproducts were obtained: a water-soluble, ether-soluble fraction (from extraction of filtrates) and a water-insoluble, ether-soluble fraction (from extraction of pulp). These fractions were obtained for ozonated pulps and unozonated control pulps.

The unozonated control samples underwent the same procedures except no ozone was applied to the pulp. Products in the control extracts were assumed to represent adsorbed, weakly bound, or acid-labile pulp constituents. The chromatograms of the control samples, shown in Figures 1c and 1d, show the scarcity of low-molecular weight, water-soluble material in the unoxidized pulp. Higher molecular weight (but still chromatographable), water-insoluble components associated with the untreated pulp are the most abundant compounds. The distribution is reversed in the ozonated pulp extracts (Figures 1a and 1b); more compounds were detected in the water than on

the pulp. The high molecular weight compounds that were present in the unozonated pulp are removed by the ozone. The ozone shifted the distribution of gas chromatographable compounds from higher molecular weight, water-insoluble compounds to smaller, water-soluble compounds.

In the second series of experiments, fractionations were based on methanol and water solubilities. A significant portion of the byproducts is methanol-soluble but not water-soluble. At least some of the water-insoluble material is also insoluble in nonpolar solvents such as ether and hexane. Furthermore, high pressure liquid chromatography indicated the water-insoluble fraction was not readily chromatographable. This poorly solubilized, poorly chromatographed fraction is likely to contain polar, high molecular weight lignin fragments.

The water-soluble products are different; they appear to be mostly low molecular weight aliphatic compounds, judging by gas chromatography (discussed below) and by proton NMR spectra (data not shown). Also, chromatography of the water-soluble fraction resulted in dozens of fairly well resolved peaks, consistent with discrete, low molecular weight compounds.

These combined observations suggest ozone produces smaller, chromatographable compounds, as well as large, polar, non-chromatographable lignin fragments. Since these ozonations were carried out at high charges ( $\geq 1\%$ ), the results are consistent with studies reported in Report 2 in which it was shown that ozonation byproducts generally consist of two classes. Low molecular weight material that is highly oxidized is readily formed at low ozone charges and at high charges, moderately polar, high molecular weight material is produced as well.

### **Reactions of Ozone with Extractives**

The changes in characteristics of chromatographable compounds with ozonation support the hypothesis that at least some precursors to the ozonation products are loosely-associated, water-insoluble, and relatively high molecular weight compounds in the untreated pulp. These types of pulp constituents may compete with fiber lignin for ozone. These reactions may also be a source of volatile, low molecular weight products that were discussed in Research Report 2.



A pulp was pre-extracted three separate ways in an attempt to remove nonlignin and noncellulose compounds that are potential precursors to ozonation products. A northwestern softwood pulp was treated with acid, with base, and with dichloromethane. These pulps were ozonated under acidic conditions and then extracted with methanol. Acid washes were expected to cause cleavage and removal of aryl ethers and some esters. Alkaline washes were expected to cleave esters, reduce physical entrainment, and remove low molecular weight (<1,000 daltons) phenolic and carboxylic acids. The organic solvent was expected to remove fairly low molecular weight, non-polar compounds, such as fats and waxes, fatty acids, resin acids, and some polyphenolic extractives. By comparing ozonation product distributions of the three pulps, we attempted to determine the chemical characteristics of some of the precursors to the chromatographable products.

The data yielded some evidence of ozone consumption by unsaturated fatty acids. A probable source of nonanedioic acid, a commonly identified reaction byproduct, is the Criegee cleavage of the double bond in unsaturated fatty acids. Octadecenoic (oleic), hexadecenoic (palmitoleic), octadecadienoic (linoleic) and/or octadecatrienoic (linolenic) acids may be cleaved by ozone to form nonanedioic acid. Pre-extraction by dichloromethane is expected to remove these unsaturated, non-polar precursors. Removal of the precursors is reflected in the low amounts of nonanedioic acid in the pre-extracted pulps compared to the unextracted pulps (Figure 2). Thus, some ozone must be consumed in reactions of fatty acids during ozone bleaching. The results show that secondary (i.e., non-delignifying) reactions occur during ozone bleaching. The significance of the ozone consumption in these reactions compared to delignifying reactions remains unknown.

There are few unique products in the methanol extracts of the differently treated pulps (Figure 2). The major differences lay in the relative amounts of the different classes of compounds. Pre-extraction with dichloromethane did cause a shift in the distribution of compounds, in addition to reducing nonanedioic acid production. Surprisingly, palmitic and stearic acids were the most abundant products in the dichloromethane-extracted sample. Samples that were not pre-extracted with dichloromethane also had significant quantities of the two fatty acids, but in addition there were higher quantities of other LMW products.

It is difficult to explain the abundance of stearic acid and palmitic acid found after ozonating dichloromethane-extracted pulp. It is unlikely that ozone breaks covalent bonds to produce these aliphatic acids. In comparison to methanol, dichloromethane may be inefficient in removing extractives. It should be noted that the methanol extracts of ozonated northwestern softwood pulp that was pre-extracted with dichloromethane consistently behaved differently in their reactions than the other softwood extracts for unknown reasons. For example, upon methylation with diazomethane, there was significant precipitation of material, which did not occur with the other extracts.

Ozonated acid and alkali washed pulps produced similar product distributions (Figures 2b and 2d). The absolute amounts of products appears to be less in the alkaline washes, but these results can only be considered semi-quantitative. The data show that nonlignin and noncellulose precursors to ozonation products can be released from the fiber by cleavage of ester bonds, physical modification of the fiber, and/or by solubilization of acids.

### **Identity of Chromatographable Ozonation Byproducts**

Aliphatic acids, ranging from six carbons to 24 carbons, were a significant component in almost all of the extracts of ozonated pulp. The methyl esters of the acids, designated in Figure 3, have very characteristic mass spectra, including strong 74 and 87 peaks (Figure 4). Acids with 17 and 19 carbons were identified and were probably derived from the ozonolysis of unsaturated, longer chain fatty acids. However, the presence of a small peak identified as the methyl ester of octadecenoic acid suggests that not all unsaturated fatty acids are cleaved by ozone at the charges used (1%-2% on o.d. pulp).

Several diacids were detected (Figure 3). Most of the diacids probably arose from cleavage of double bonds in fatty acids, which would produce longer chain aliphatic acids, or from cleavage of the aromatic rings in lignin, which would produce much shorter chain aliphatic acids. Of the longer chain diacids (propanedioic to nonanedioic), nonanedioic acid was the most prominent.

The latter compound is likely formed when the double bonds in unsaturated acids are cleaved by ozone, as discussed above.

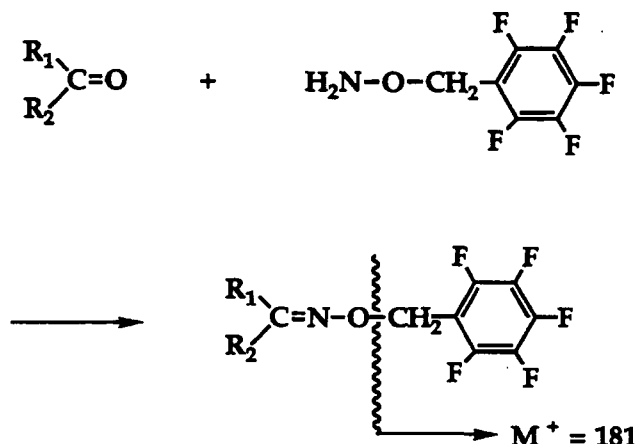
Oxalic acid dimethyl ester and glyoxylic acid methyl ester peaks were also prominent in the chromatograms of the methanol extracts of ozonated pulp. The analytical method that was used does not distinguish between oxalic acid and its methyl esters or between glyoxylic acid and its methyl ester in the extracts. All of these compounds can form through muconic acid type intermediates upon ozonolysis of aromatics (Figure 5). Their presence may indicate the extent to which aromatic ring cleavage occurs. Since the formation of these compounds may not represent delignification *per se*, their presence in high concentrations may indicate inefficient ozone consumption. Glyoxal is another ozonolysis product that may arise from aromatics which is addressed with discussions on carbonyl compounds. The production of formaldehyde is addressed below, as well.

It is notable that few monomeric lignin fragments were identified in any of the extracts. Vanillin and vanillic acid were the two most significant. The ozonation products contrast with chlorination effluents in which aromatics are important constituents.<sup>1</sup> Another variation from chlorination effluents is the lack of catechols in the ozonation byproduct mixtures. This may occur because ozone does not demethylate aromatic methoxyl groups, while chlorine does.<sup>6</sup> The scarcity of lignin monomers is consistent with ozone producing polar, high molecular weight material by depolymerization reactions along with small fragments of the aromatic ring from lignin.

Most of the differences in the distribution of the northwestern and southern pulps reflect the differences in their fatty acids content. Two major chromatographable constituents of the southern softwood pulp effluent were octadecanoic acid (stearic acid) and hexadecanoic acid (palmitic acid) whereas the northwestern softwood pulp produced higher quantities of other compounds. The differences in the extractives contents of the two sources of pulp is further exemplified by the lack of aliphatic acids in the southern pulp that are presumed to be fatty acid ozonolysis products in the northwestern pulp, e.g., heptadecanoic and nonanedioic acids. In addition, the 20, 22 and 24 carbon fatty acids detected in the northwestern softwood pulp were not found in the southern softwood pulp.

## Carbonyl Compounds

Ozone often reacts with double bonds in Criegee-type reactions to produce aldehydes and ketones. Other carbonyl compounds may also be formed from ozone attack on activated hydrogens.<sup>7</sup> One way to selectively look for these compounds, and to improve their recovery, is to derivatize them with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA). PFBHA reacts with aldehydes and, to some extent, ketones, to form the readily identifiable fluorinated oximes.<sup>8,9</sup>



Pentafluorobenzyl oxime derivatives have a signature mass spectrum, consisting of a dominant 181 base peak (C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub><sup>+</sup>) that is monitored. It is useful to compare an ion chromatogram for mass 181 with mass 59, which is strongly characteristic of methyl esters, to estimate the number of compounds that are bifunctional. These comparisons show that most of the carbonyl compounds also have a carboxylic group, with only a few exceptions.

Chromatograms from PFBHA-derivatized extracts of the pretreated pulps described in the previous sections are shown in Figure 6. All chromatograms are dominated by one peak, the oxime derivative of glyoxylic acid methyl ester. Products from oxygen delignified pulp also exhibited similar chromatograms. This compound was identified in the extracts without PFBOA treatment only after its oxime derivative was detected in this series of experiments. These chromatograms suggest that glyoxilic acid and/or its methyl ester is the most prevalent carbonyl compound in all ozonation extracts.

The PFBHA samples show that glyoxal is also an important carbonyl compound (Figure 8). Glyoxal may arise from cleavage of unsubstituted double bonds of muconic acid derivatives (Figure 4). Identification of glyoxal in the underivatized samples was not possible because it elutes with methanol.

In this study, the PFBHA was added to the methanol extracts of the pulps and the reaction was quenched with acidic water. In literature methods,<sup>9,10</sup> the derivatization is performed in water. In the case of a glyoxal standard, the methanol appears to induce the formation of an oxime derivative different from that produced in water. The other standards derivatized in this study (acetone, formaldehyde, vanillin, and methylated glyoxylic acid) produced oxime derivatives with the expected mass spectra. Future work in this area should either be performed in water or provide thorough documentation of the derivative formation in methanol.

The relatively strong molecular ion of the vanillin oxime, shown in Figure 9, is characteristic of aromatic derivatives.<sup>9</sup> Few other oxime peaks exhibited as strong a molecular ion, suggesting that vanillin is the major aromatic aldehyde produced by ozonation. These data are supported by the chromatograms and spectra from the underivatized extracts.

### **Formaldehyde Formation**

Formaldehyde is another carbonyl compound of interest. Although it was detected in the PFBHA extracts described above, it was also present in the blanks in small amounts. In addition, the sample work-up was not conducive to good recovery of formaldehyde. For these reasons, and because of the potential problematic nature of formaldehyde emissions, a more careful study was warranted. In the following studies, formaldehyde was analyzed in ozonated pulp rinsates and in the gas stream leaving the ozonation chamber during pulp ozonation. These studies were carried out by S. Michelle Nooney at IPST in 1992-1994 in partial fulfillment of Master's degree requirements.

### *Formaldehyde in Aqueous Phase*

Formaldehyde was consistently detected in the rinsates of the ozonated pulp. A typical chromatogram is shown in Figure 10, which shows the carbonyl products produced from ozonation of the kraft pulp at 3.8% charge. In addition to formaldehyde, glyoxilic acid methyl ester, glyoxal, and a fourth, unidentified carbonyl compound were detected. The quantity of formaldehyde in these samples is considerably higher than in the previous studies described, probably reflecting the more careful work-up procedures to retain these polar, volatile compounds.

Blank samples indicated background contamination of formaldehyde. Analysis of the laboratory water showed that it contained approximately 30  $\mu\text{g/L}$  formaldehyde. This value was subtracted from the cotton linters values to correct for the water contamination. The remainder of the formaldehyde detected in the kraft pulp blank was assumed to arise from the pulp, prior to ozonation. The blank values were subtracted from those generated for the kraft pulp to correct for pulp and water contamination. The oxygen delignified pulp did not exhibit the same background contamination as the kraft pulp; formaldehyde values for the oxygen delignified pulp were corrected only for the water contamination.

Background-corrected values for formaldehyde concentrations in the pulp and linters rinsates are given in Table 1. There is a significant relationship between ozone charges and formaldehyde concentrations in the kraft pulp. Formaldehyde production increases with charge up until 2.5% charge, at which point the production levels off and then declines. The results suggest that at low charges, ozone quantities limit formaldehyde production (not lignin) and at very high charges, formaldehyde is oxidized to formic acid or completely converted to  $\text{CO}_2$ . Interestingly, there was no significant difference in formaldehyde production between the kraft and oxygen delignified pulp. We conclude, then, that lignin quantity is not an important factor in formaldehyde production.

The production of significant quantities of formaldehyde upon ozonation of cotton linters also indicates that there may be important nonlignin precursors to formaldehyde formation. Although formaldehyde is not often cited as a product of cellulose ozonation in mechanistic studies, these

data suggest that there is an important route of formation from cellulose. Indeed, over half of the total production of formaldehyde may be from cellulose reactions. It is important to bear in mind, however, that it is likely that competition between lignin and cellulose in pulp will affect the reactivity of the latter. The formaldehyde concentrations shown for ozonated linters represent maximum possible levels of contribution to formaldehyde production by cellulose reactions.

### ***Formaldehyde in Gas Phase***

There was a surprising lack of formaldehyde in air emissions. No formaldehyde was detected in any samples analyzed by LC, however, traces of formaldehyde derivatives were found GC analyses. There are two possible reasons for these findings. First, when formaldehyde is present in low quantities in aqueous solution, it may exist as methylene glycol,  $\text{CH}_2(\text{OH})_2$ .



While high consistency ozonation would be expected to minimize the formation of the glycol, it is possible that the water layer surrounding the fiber is adequate for this equilibrium to become significant. In this case, the formaldehyde will behave like the nonvolatile methylene glycol and remain in the aqueous phase.

A second possible reason for not detecting formaldehyde in gas phase may simply be an experimental artifact. The hydrazone derivatives in the cartridge are susceptible to deterioration by ozone. The formaldehyde may have formed the hydrazone derivative, which was then destroyed by residual ozone in the stream. Future work in this area should include a careful analysis of the interference of gas-phase formaldehyde by ozone.

### ***Regulatory and Environmental Implications***

Quantitative analysis of formaldehyde in the effluent of ozonated pulp result in an estimated production of 0.07 to 0.17 mg per gram pulp. Based on these estimates, approximately 63 kg of formaldehyde would be produced in filtrates per day at a bleach plant that produces 900 metric

ADT/day of pulp that is ozone bleached at high consistency and 0.7% charge. Due to its biodegradability and relatively low effluent levels, formaldehyde is not likely to be problematic, regardless of its listing as a hazardous substance under the Federal Water Pollution Control Act.

Based on the low concentrations found in the effluents and the low volatility of the glycol, it is probable that insufficient quantities of formaldehyde are emitted into the atmosphere during ozone bleaching to exceed the levels regulated by the Clean Air Act Amendments. The bleach plant would have to emit 25 kg per day in order to exceed the limit mandated by the Act

Employee exposure to formaldehyde in the bleach plant exceeding the PEL (permissible exposure level) established by OSHA is more probable than exceeding the levels regulated by the Clean Air Act. Given that ambient formaldehyde concentrations in the air may range from 1-10 ppb, and indoor air may contain as much as 100 ppb, the additional formaldehyde generated during ozonation could feasibly result in exposures in excess of 0.75 ppm. However, conclusive data are not available to support this supposition and further work on gas-phase ozone emissions is recommended.

## **CONCLUSIONS**

During pulp bleaching, ozone reacts with nonlignin, noncellulose pulp constituents that are weakly bound to the fiber to produce soluble, low molecular weight compounds. Some of these reactions may be accounted for by the reactions of unsaturated fatty acids to form fairly long chain acids, particularly nonanedioic acid. Beyond this type of substrate, we were unable to clearly establish the chemical characteristics of other nonlignin and noncellulose precursors. The significance of ozone consumption in these types of reactions, as compared to delignifying reactions, remains unknown.

Pulp ozonation produces basically two types of byproducts. One type consists of a polar, high molecular weight fraction. A second fraction consists of soluble, low molecular weight, chromatographable acids and aldehydes. The small byproducts found in ozonation filtrates include ali-



phatic acids ranging from 6 to 24 carbons. They probably arise from cleavage of unsaturated fatty acids. In addition, several small diacids, such as glyoxylic acid (methyl ester) and oxalic acid, were detected that are likely to arise from lignin ring cleavage; this interpretation is supported by the low quantities of aromatic lignin monomers that are detected. Examination of the carbonyl compounds produced from pulp ozonation showed that glyoxylic acid (methyl ester) and formaldehyde were the two most abundant carbonyl compounds found in pulp filtrates. Formaldehyde appears to have both lignin and cellulose precursors.

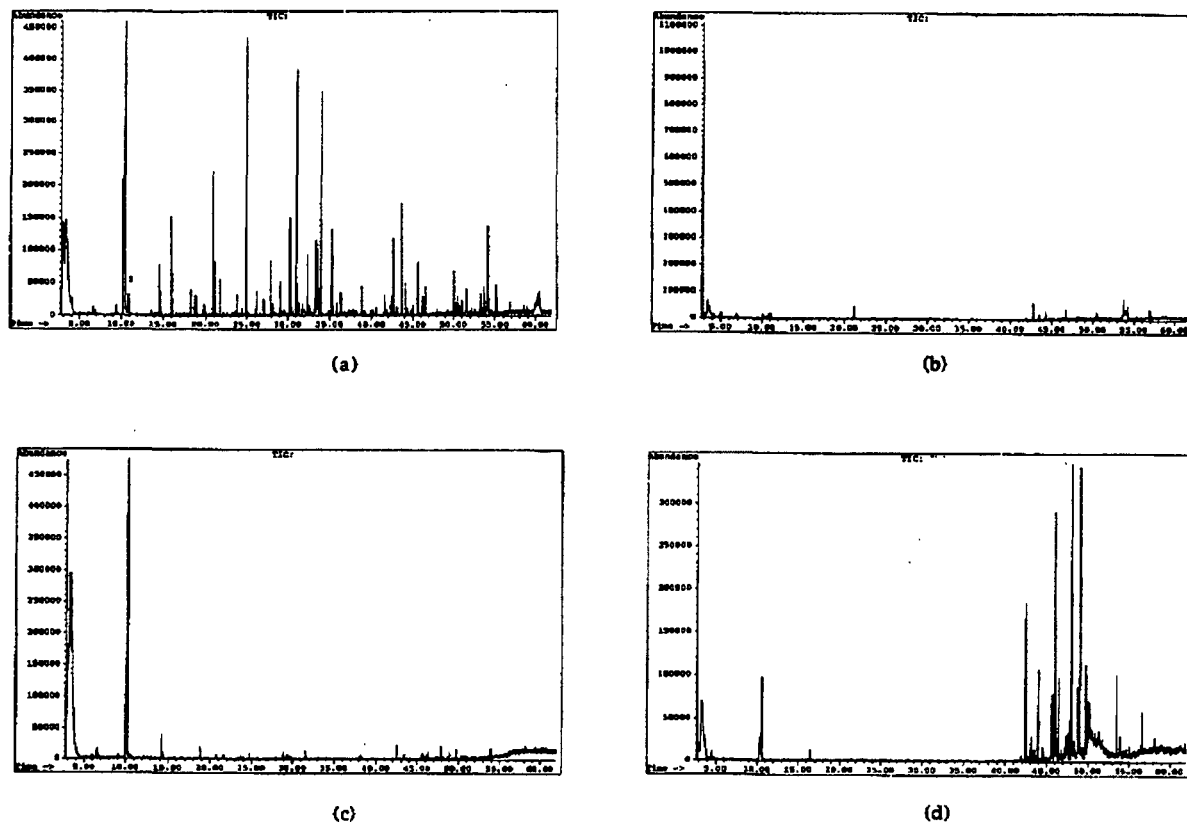
Thus, ozone may be involved in at least four classes of reactions during high charge ozone bleaching. It depolymerizes lignin to produce a polar, high molecular weight fraction. This pathway is probably most important at high charges of ozone. Ozone also cleaves the aromatic rings of lignin and degrades the muconic acid derivatives to very small diacids and aldehydes. While these reactions do destroy lignin, it is not likely to be an efficient mode of delignification since more ozone is consumed than is necessary to impart solubility. Ozone reacts with extractives to form aliphatic acids. Finally, ozone may react with the carbohydrate fraction to form small compounds such as formaldehyde.

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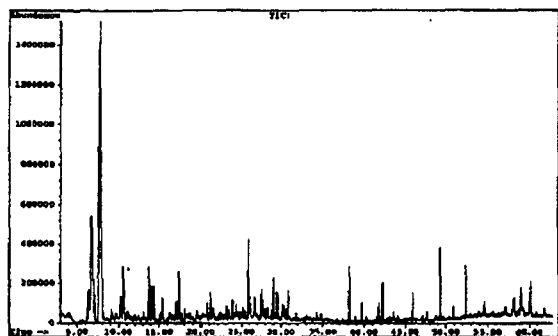
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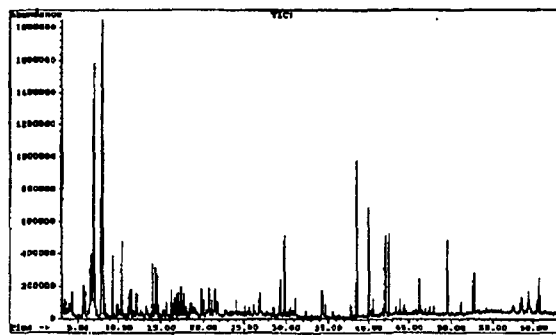
## FIGURES AND TABLES



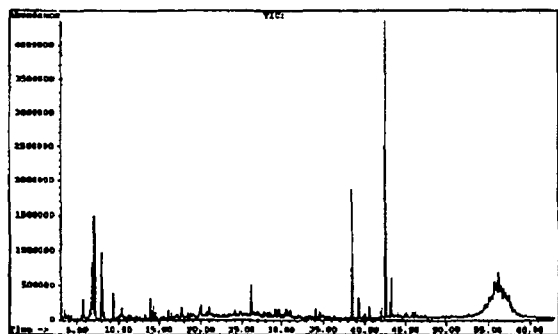
**Figure 1.** Chromatograms of methylated ether extracts of a) ozonated pulp filtrate, b) ozonated pulp, c) control pulp filtrate, and d) control pulp.



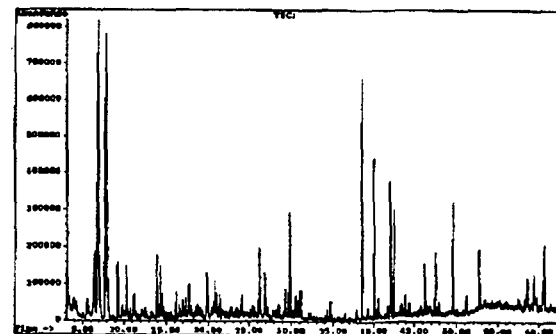
(a)



(b)

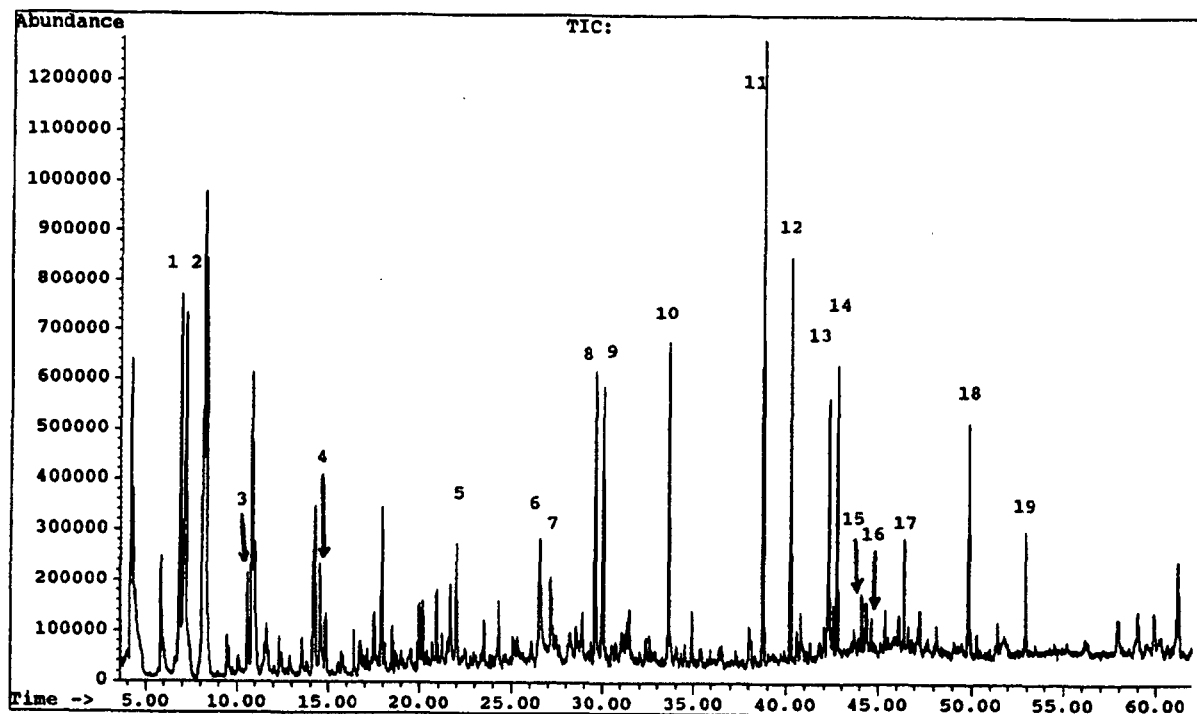


(c)



(d)

**Figure 2.** Chromatograms of methylated methanol extracts of ozonated pulp, a) southern softwood, pre-washed with acid, b) northwestern softwood, pre-washed with acid, c) northwestern softwood, pre-extracted with dichloromethane, and d) northwestern softwood, pre-washed with base.



<u>Peak</u>	<u>Name</u>
1	2-Oxo-ethanoic acid methyl ester (glyoxylic)
2	Ethanedioic acid dimethyl ester (oxalic)
3	Propanedioic acid dimethyl ester (malonic)
4	Butanedioic acid dimethyl ester (succinic)
5	Hexanedioic acid dimethyl ester (adipic)
6	4-Hydroxy-3-methoxy benzaldehyde (vanillin)
7	9-Oxo-nonanoic acid methyl ester
8	4-Hydroxy-3-methoxy benzoic acid methyl ester (vanillic)
9	Nonanedioic acid dimethyl ester (azelaic)
10	Hexadecanoic acid (palmitic)
11	Hexadecanoic acid methyl ester (palmitic)
12	Heptadecanoic acid methyl ester
13	Octadecenoic acid methyl ester
14	Octadecanoic acid methyl ester (stearic)
15	Nonadecanoic acid methyl ester
16	Nonadecanoic acid methyl ester
17	Eicosanic acid methyl ester (arachidic)
18	Docosanoic acid methyl ester (behenic)
19	Tetracosanoic acid methyl ester (lignoceric)

Figure 3. Chromatogram of a methanol extract of ozonated northwestern softwood pulp showing pulp ozonolysis byproducts.

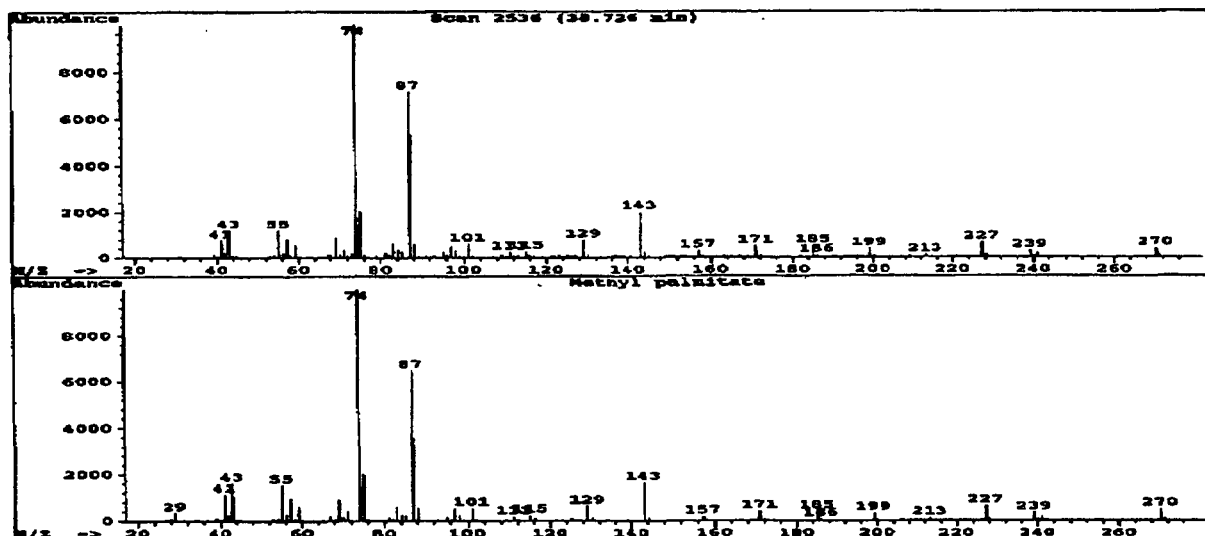


Figure 4. Mass spectra from peak number 11 (Figure 3) and from NIST/EPA/ MSCD 54 K Mass Spectral Database.

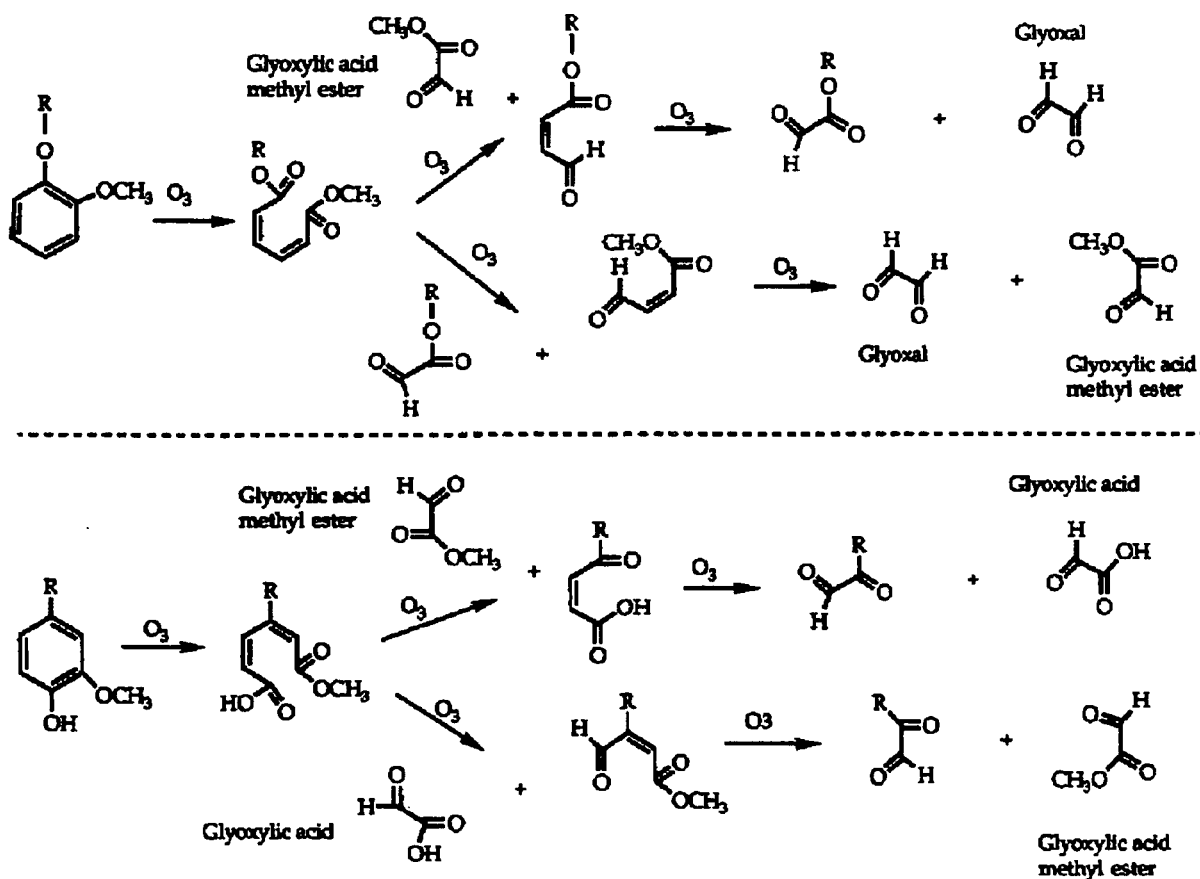
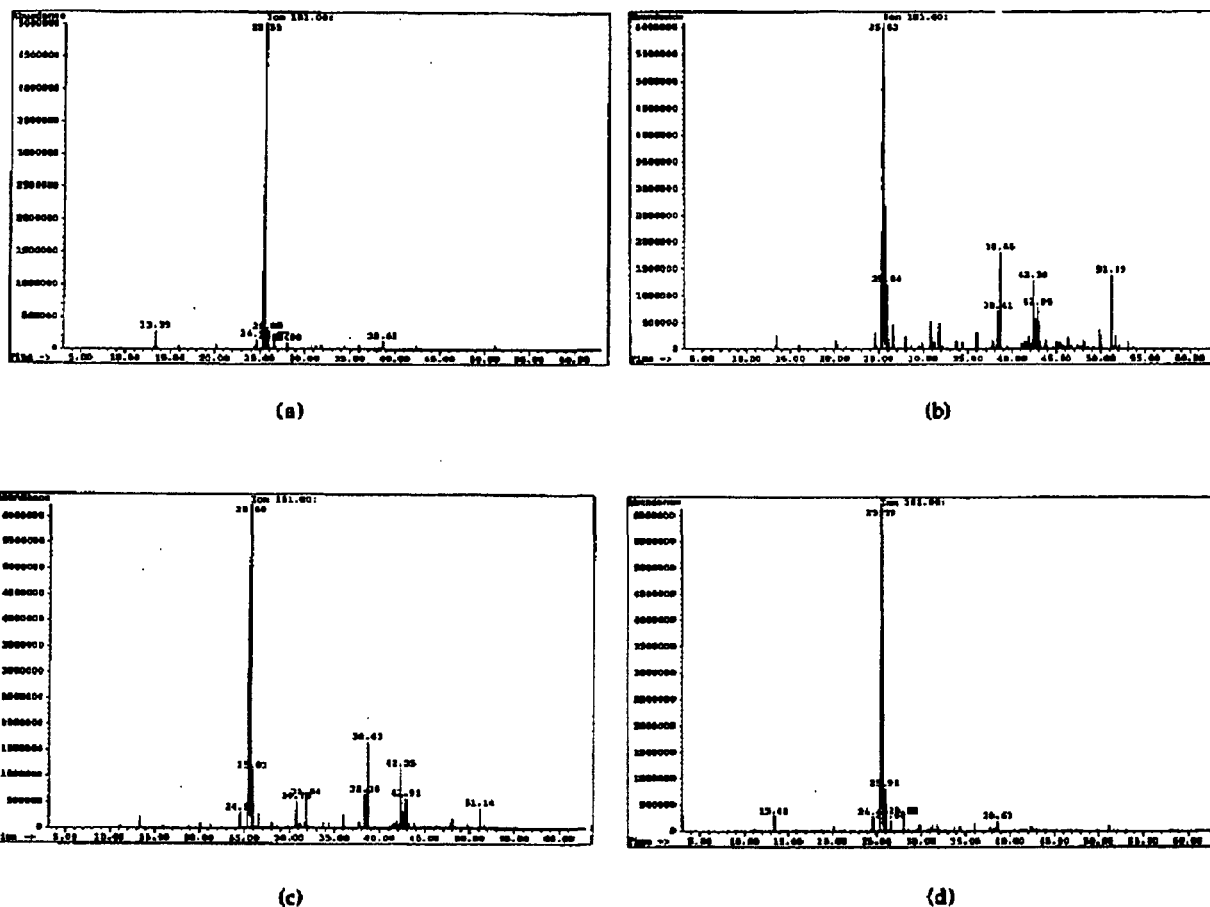
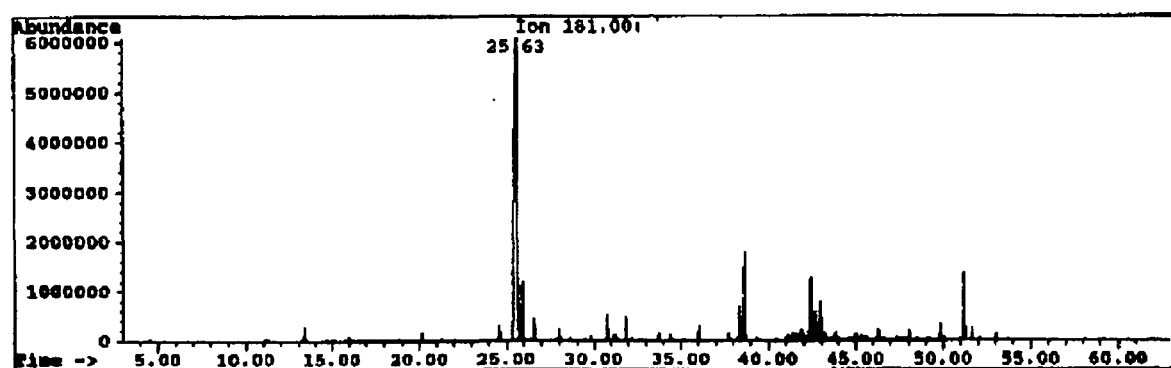


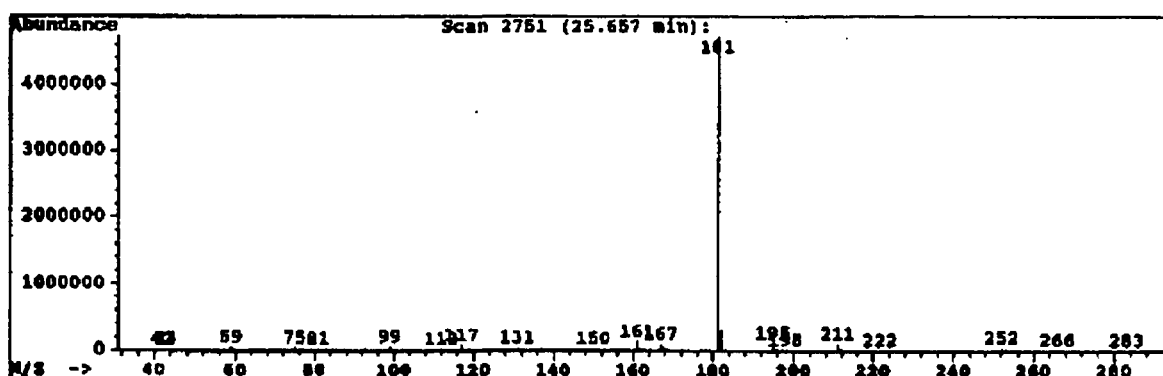
Figure 5. Potential pathways for carbonyl compound formation from ozonation of lignin.



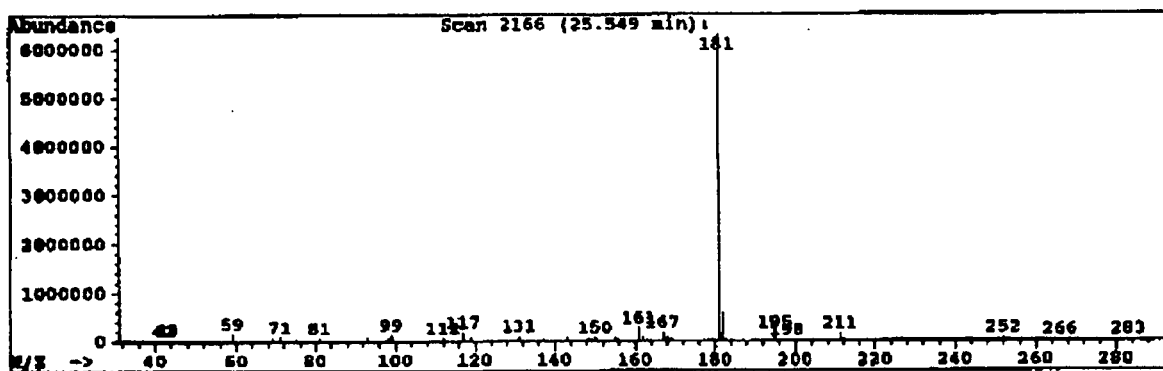
**Figure 6.** Ion chromatograms (mass = 181) of PFBHA-derivatized extracts of ozonated a) southern softwood, pre-washed with acid, b) northwestern softwood, pre-washed with acid, c) northwestern softwood, pre-extracted with dichloromethane, and d) northwestern softwood, pre-washed with base.



(a)



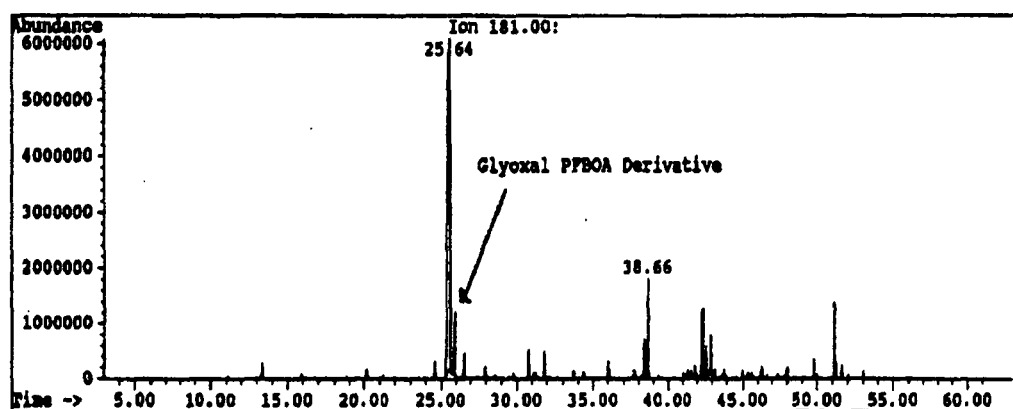
(b)



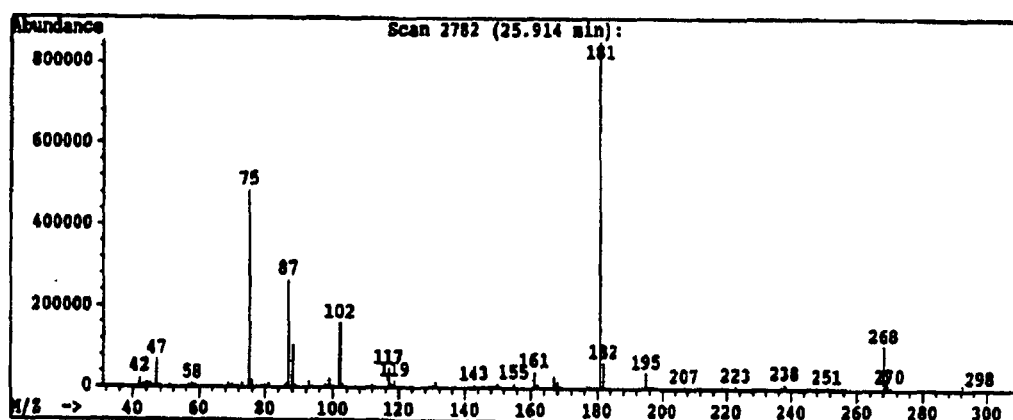
(c)

Figure 7. Glyoxylic acid methyl ester oxime derivatives; a) chromatogram of a PFBHA-derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated peak, and c) mass spectrum of a glyoxylic acid methyl ester standard derivatized in methanol.

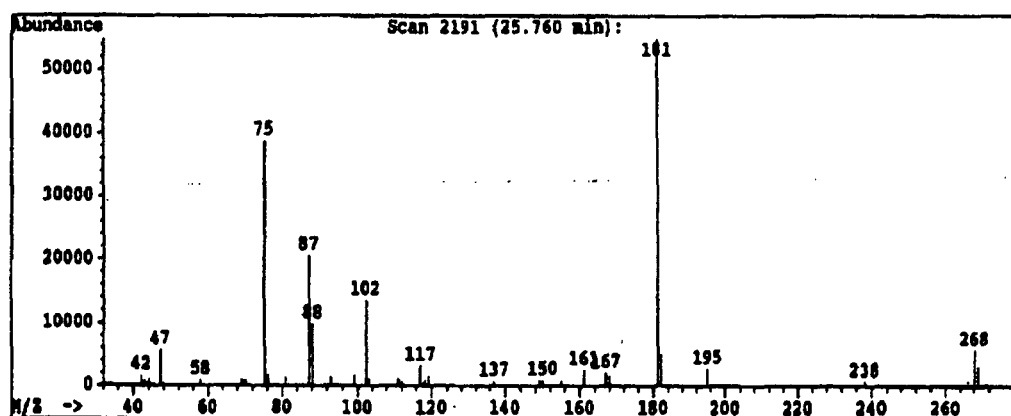




(a)

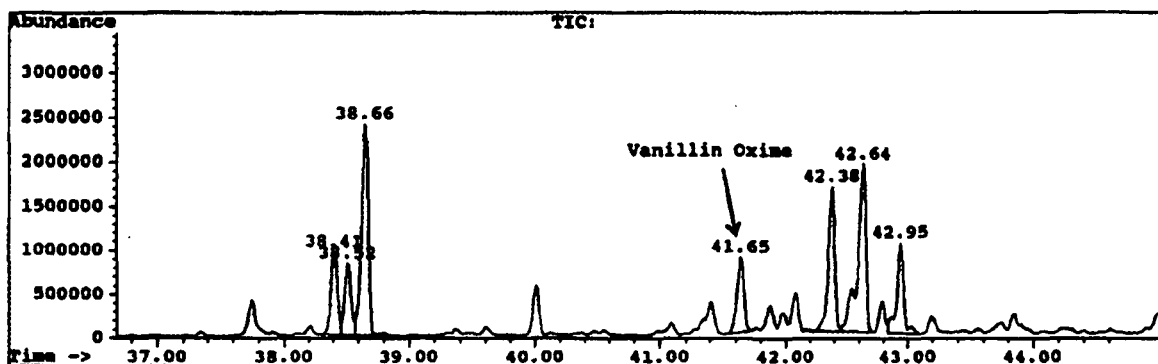


(b)

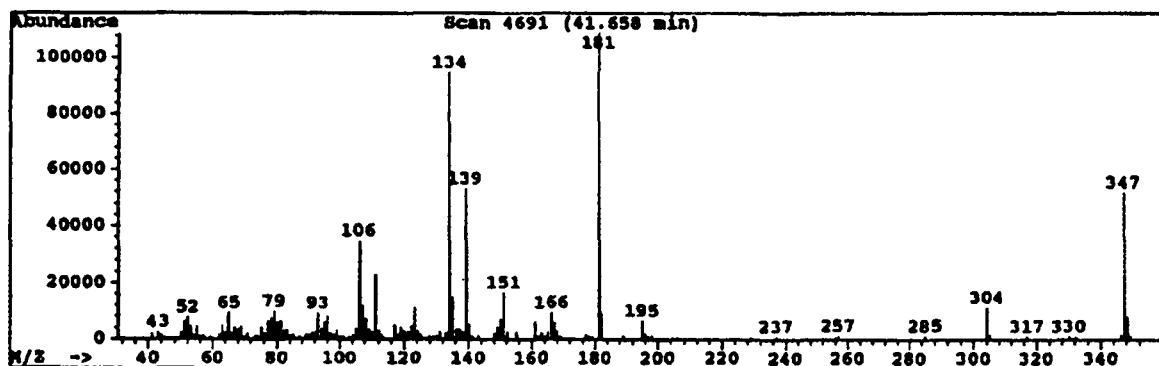


(c)

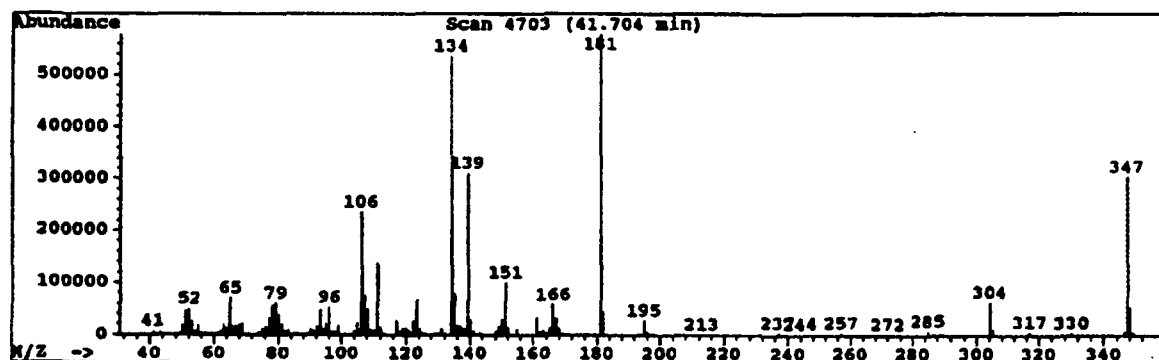
Figure 8. Glyoxal oxime derivatives; a) chromatogram of a PFBHA-derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated peak, and c) mass spectrum of a glyoxal standard derivatized in  $\text{CH}_3\text{OH}$ .



(a)



(b)



(c)

Figure 9. Vanillin oxime derivatives; a) chromatogram of a PFBHA-derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated peak, and c) mass spectrum of derivatized vanillin standard in  $\text{CH}_3\text{OH}$ .

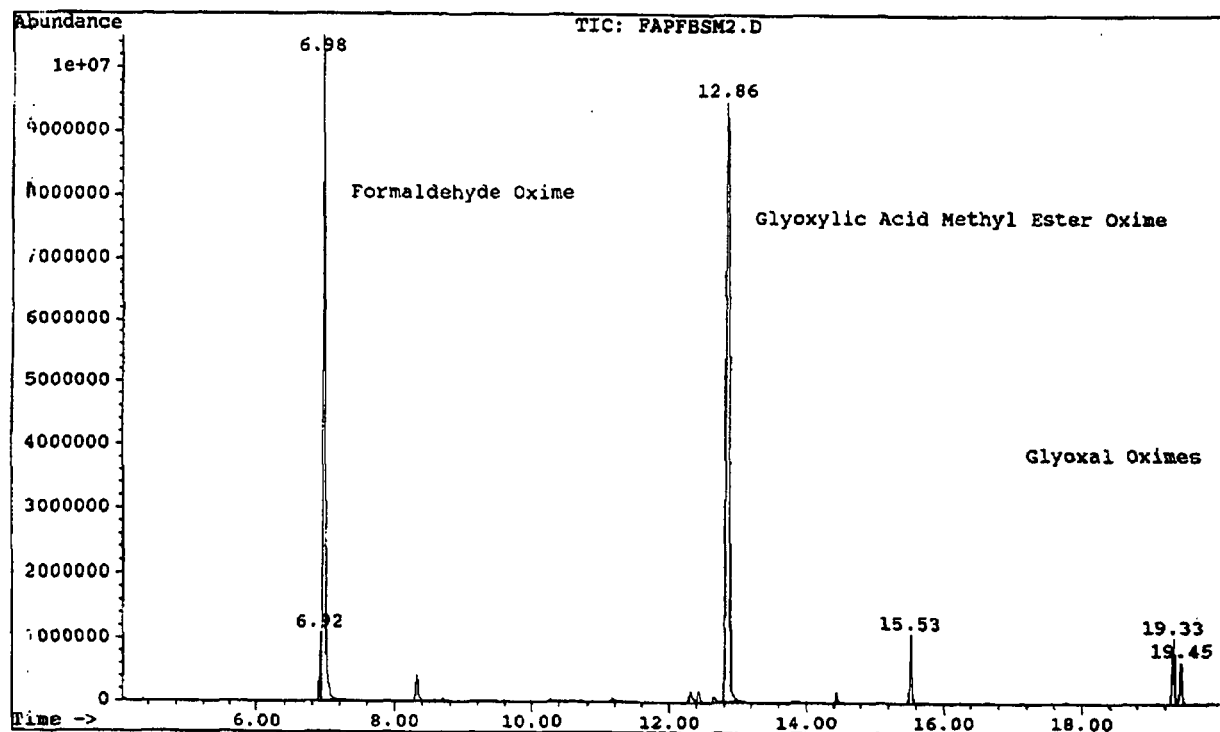


Figure 10. Typical chromatogram of quantitative PFBHA-derivatized extracts of ozone filtrates, showing formaldehyde production.

Table 1. Formaldehyde concentrations in ozone filtrates from ozonating pulp and linters at different charges.

Softwood Kraft		Oxygen Delignified		Cotton Linters	
% Ozone Charge	Filtrate Conc. mg/L	% Ozone Charge	Filtrate Conc. mg/L	% Ozone Charge	Filtrate Conc. mg/L
0.8	2.6	0.8	2.5	0.3	1.9
0.9	2.4	0.8	2.3	0.3	1.3
0.9	2.4	0.8	3.7	0.3	1.2
0.9	2.3	1.6	3.3		
1.0	2.5	1.7	3.3		
1.7	3.3				
1.8	3.0				
2.4	5.5				
3.2	6.0				
3.8	5.1				
3.8	5.1				

## RESEARCH REPORT 4: OZONE REACTIONS WITH LIGNIN AND CARBOHYDRATES IN KRAFT AND OXYGEN DELIGNIFIED PULPS

### INTRODUCTION

Ozone bleaching is currently under intense investigation as nonchlorine bleaching alternatives are being sought by the pulp and paper industry. Considerable information has been gathered about the fundamentals of ozone bleaching over the past twenty years, including model compound studies that examine the mechanism of delignification<sup>1-3</sup> and carbohydrate degradation (4-6), and applied studies that examine the influence of factors such as pH, consistency, dissolved lignin, additives, and temperature on bleaching behavior.<sup>7-10</sup> The state of ozone bleaching has recently been extensively reviewed.<sup>11-13</sup> However, basic information is still needed about ozone delignification under emerging ozonation practices.

One emerging practice is the placement of an oxygen stage before ozone to reduce ozone requirements.<sup>14</sup> Lindholm<sup>15</sup> and Chandra and Gratzl<sup>16</sup> have compared ozone bleaching behavior of unbleached and 50% oxygen delignified pulps. These researchers have found that delignification efficiency (reduction in lignin per unit ozone consumed) is greater in unbleached pulps than in 50% oxygen delignified pulps. Carbohydrate degradation has been reported both to be higher for oxygen treated softwood pulps<sup>15</sup> and lower for oxygen treated pulps<sup>16</sup> at low consistency. In support of the former results, Chirat et al.<sup>17</sup> found that the initial rate of carbohydrate degradation increases with decreasing initial kappa.

Questions remain about the impact of an oxygen stage on the efficiency and selectivity of ozone bleaching and on the mechanism of ozone delignification. The purpose of this research is to gain a better understanding of high consistency ozone delignification of oxygen bleached pulps. Pulp quality and structural characteristics of ozonated pulps were examined.

## **EXPERIMENTAL**

### **Approach**

A softwood kraft pulp (kappa number = 22) was oxygen bleached to 30% and 50% delignification in the laboratory. Three pulps were ozonated, including the kraft pulp (K[22]), the 30% oxygen delignified pulp at kappa number = 16 (K-O[16]), and the 50% oxygen delignified pulp at kappa number = 12 (K-O[12]). The ozonated pulps were analyzed for kappa number, viscosity, carboxylic acids, phenols, and methoxyl groups. Selected pulps were delignified with mild acid chlorite and subjected to a second carboxylic acid analysis to determine the cellulose carboxylic content.

### **Delignification**

The kraft pulp was oxygen delignified in 250 o.d. g batches in a laboratory reactor at 12% consistency, 120°C, 100 psig O<sub>2</sub>, with 0.1% MgSO<sub>4</sub> for 30 minutes. A 2% NaOH charge was used for the 50% delignified pulp and a 1% charge was used to obtain the 30% delignified pulp. After the reactions, the pulp was thoroughly washed with deionized water.

Prior to ozonation, the pulps were soaked in a sulfuric acid solution with a final pH of 2 for approximately 10 minutes, filtered to approximately 25% consistency, and fluffed. Twenty o.d. g batches of pulp were ozonated in a laboratory reactor (modified rotary evaporator) at room temperature for one to six minutes with O<sub>2</sub>/O<sub>3</sub> flows of 0.5-2.0 L/min. Charges ranged from 0.3 to 1.4 %. Potassium iodide traps were titrated iodometrically to determine ozone concentrations.

### **Analyses**

The kappa numbers and viscosities were measured using Tappi Methods T236 and T230. The number of scissions (DP<sub>o</sub>/DP - 1) was based on  $DP = 961.4 \log e - 245.3$  where  $e$  is the viscosity from Tappi method T230.<sup>19</sup> Carboxylic acids were measured by conductimetric titration of 1.5 o.d. g pulp with 0.05 N NaOH under nitrogen. Methoxyl measurements were based on the Zeisel method and phenols were analyzed by periodate oxidation.<sup>20</sup> Chlorite delignifications (1 g sodium chlorite/g pulp) were carried out in the dark, at room temperature, overnight, and at pH = 4.

Size exclusion chromatography was used to evaluate the molecular weight distributions of ozone filtrates and oxygen filtrates. These analyses were performed using the methods of described in Research Report 2.

## **RESULTS AND DISCUSSION**

### **Pulp Quality**

Unbleached softwood kraft pulp (K[22]), 30% oxygen delignified pulp (K-O[16]), and 50% oxygen delignified pulp (K-O[12]) were ozone bleached at several charges. The final kappa numbers and unreduced viscosity are shown in Figure 1. It is clear that oxygen delignification prior to ozone bleaching produces pulps with higher viscosity than when high kappa kraft pulps are ozone bleached. Furthermore, examination of ozone delignification as a function of carbohydrate degradation (kappa drop versus viscosity drop) shows that moderately oxygen bleached pulp exhibits the best selectivity during ozonation, followed by the 50% oxygen delignified pulp. The kraft unbleached pulp showed the worst selectivity (Figure 2). The two elements of selectivity, delignification and carbohydrate degradation, were examined separately.

### ***Carbohydrate degradation***

Carbohydrate degradation was evaluated by estimating the number of ozone-induced scissions as a function of ozone charge (Figure 3). The carbohydrates in the 50% oxygen delignified pulp underwent significantly more degradation at comparable ozone charges than the other two pulps, which is consistent with the findings of some other researchers.<sup>16</sup> The carbohydrates in the K-O[16] pulp had a response to ozone similar to the response of the kraft pulp. These results suggest that the protective role of lignin in ozone bleaching,<sup>21</sup> must have a threshold beyond which further delignification prior to ozonation causes substantial harm to the carbohydrates. The harm may occur directly or through lignin intermediates.<sup>21</sup> These results are consistent with a study by Chirat et al.<sup>17</sup> in which initial DP loss with ozonation was higher for a pulp with an initial kappa number of 7 than a pulp with an initial kappa number of 14 (Figure 4).

The susceptibility of the carbohydrates to ozone depolymerization was also quantified as the number of scissions induced per unit of ozone consumed (Figure 5). For all of the pulps, at higher ozone charges, there were fewer scissions per unit ozone consumed. It appears that ozone will attack a particularly labile carbohydrate fraction, even at low charges. Once the labile fraction is removed, the remaining carbohydrates are more resistant to increasing charges of ozone. The susceptibility of the carbohydrates to depolymerization by ozone was greatest for the KO[12] pulp; the other two pulps were similar. When susceptibility was examined as a function of "ozone kappa factor" (initial kappa number/O<sub>3</sub> charge), the relationships were similar (data not shown).

The issue of practical interest is the total degradation of carbohydrates from both oxygen and ozone to obtain a given kappa number. In general, to achieve a given kappa, there are fewer total scissions in oxygen delignified pulp than in kraft pulp. For example, as shown in Figure 6, to obtain a kappa number of 10, 30% oxygen delignification followed by ozonation caused 0.35 scissions compared to 0.50 scissions caused by ozonation of the kraft pulp. The resilience of the carbohydrates in the oxygen delignified pulp occurs despite the fact that the oxygen induces scissions as well as the ozone and that we are operating in the portion of the ozonation curve where there are high numbers of scissions per unit of ozone consumed (Figure 5). The reason viscosity is retained in the moderately oxygen delignified pulp is that the ozone is generally responsible for most of the scissions and there is a much smaller ozone requirement to reach a given kappa for the oxygen bleached pulp than the kraft pulp.

### ***Delignification Efficiency***

The next issue to be examined is delignification, which determines selectivity along with carbohydrate degradation. At low ozone charges, we found that oxygen delignified pulps had larger drops in kappa numbers than the kraft pulp (Figure 7). When ozone charges exceeded 0.5%, the efficiencies were comparable. At higher charges (>1.0%) the unbleached pulp may be more efficiently delignified than the 50% oxygen delignified pulp. Previous work has shown that at high ozone charges, depolymerization occurs whereas at lower charges, oxidation to small molecular weight compounds is important. These combined results suggest that oxygen will enhance ozone

bleachability when low ozone charges are applied, possibly by depolymerizing lignin so that ozone may oxidize its terminal point. No differences in efficiency are observed at high ozone charges because ozone will depolymerize lignin at high charges and the advantage of depolymerization by oxygen is negated.

For comparison, Lindholm<sup>15</sup> found 50% oxygen delignified pulp was less efficiently delignified than kraft pulp when they were ozonated at high charges ( $> 1\%$ ). Chandra and Gratzl<sup>16</sup> also found a decrease in delignification efficiency for a 50% oxygen delignified pulp at unspecified ozone charges.

The efficiency of delignification can also be quantified as the amount of lignin lost per unit of ozone consumed (Figure 8). The greater delignification efficiency of the oxygen bleached pulps at low charges is again seen. As occurred with the carbohydrate reactions, the kappa drop per unit ozone consumption decreased with increasing charge for all of the pulps. Efficiency may decrease at higher ozone charges because of the recalcitrance of the residual lignin, reduction in the accessibility of ozone to the lignin, or because there is an increase in nondelignifying ozone reactions at higher charges.

It is interesting and somewhat unexpected from a chemical reactivity standpoint that the oxygen delignified pulp showed better delignification than the kraft pulp. The introduction of electron withdrawing groups such as carbonyls and carboxylic acids would be expected to decrease ozone reactivity. Furthermore, removal of highly activating substituents such as phenolic hydroxyls would also be expected to reduce the ozone reactivity. Chemical reactivity is less important than having depolymerized residual lignin.

### **Structural Characteristics of Pulps**

In an attempt to better understand how ozone delignifies different pulps, we measured phenolic, carboxylic acid and methoxyl functional groups on the ozonated pulps (Table 1). For pulps with kappa numbers greater than 10, estimates of lignin concentrations were based on the kappa num-



bers ( $\% \text{ lignin} = 0.15 \times \text{kappa number}$ ). Another estimate of the concentration of functional groups in lignin was derived from ratios of the whole pulp functional group concentration to whole pulp methoxyl concentration. However, it is important to note that the methoxyl content appeared to fluctuate somewhat relative to the kappa number.

Carboxylic acids were measured in whole pulps and in pulps delignified with acid chlorite. The carboxylic acid content of lignin was calculated as the difference between the carboxylic acid concentration of the carbohydrates and the whole pulp. The carbohydrates in all cases bore the majority of the carboxyl groups, but the concentration of the acids in lignin increased with charge.

Oxygen delignification increased the carboxylic acid content in lignin which has been observed in other studies,<sup>18,22</sup> but only by a small amount; compare 0.1 meq COOH /g lignin in the K[22] pulp to 0.3 meq COOH/g lignin in the K-O[16] pulp. Although introduction of carboxylic acids by oxygen would be expected to reduce the chemical reactivity of lignin to ozone, the oxygen delignified pulps showed a higher delignification efficiency than the kraft pulp at low ozone charges. Oxygen-induced carboxylic groups on the fiber may promote fiber swelling, allowing better accessibility of the ozone to the lignin, or they may act to increase the solubility of the attached lignin fragments.

Low charges of ozone to the K[22] and K-O[16] pulps also increased the carboxylic acids in the lignin. In some cases, increases in ozone charge decreased the carboxylic acid concentrations in residual lignin, suggesting that the carboxylated fractions became dissolved. Clearly, carboxylic acids are formed in the lignin by both ozone and oxygen, without necessarily causing dissolution. The 30% oxygen delignified pulp had higher carboxyl concentrations than the kraft pulp both before and after ozonation. The higher carboxyl contents in the ozonated lignin suggest that the K-O[16] pulp reacted more readily with the ozone than the kraft pulp.

In contrast to the response of lignin to the two oxidants, carboxylic acids in carbohydrates were reduced by oxygenation and ozonation. These data suggest that the carboxylated portions of the carbohydrates are labile to further oxidation and dissolution and are readily removed, while the

rate of carboxylic acid formation in the carbohydrates is slow. The initial drop in carboxylic acid content of the carbohydrates with ozonation at low charges corresponds with the previously discussed result that there is a high efficiency of carbohydrate degradation at low ozone charges that levels off at higher ozone charges. Furthermore, these reactions may contribute to the formation of soluble, oxidized, low molecular weight material at low ozone charges that has been observed in our other work.

Phenolic groups in pulps and lignin were also estimated. The susceptibility of phenolic structures to oxygen delignification was affirmed by the reduction of phenol content with oxygen delignification, also observed elsewhere.<sup>18,22</sup> Low charges of ozone further depleted the phenolic structures from the lignin. It is interesting to note that the reduction in phenolic content with oxygen delignification and low ozone charges corresponded with an increase in lignin carboxylic acid content, perhaps representing lignin ring cleavage. Ring fragmentation prior to dissolution is also indicated by our previous work in which we found little evidence of intact aromatic byproducts from pulp ozonation.<sup>23</sup>

### **Molecular Size of Byproducts**

Much of the data presented suggest that depolymerization by oxygen may be a significant component of ozone bleachability. Previous work (Research Report 2) shows that ozone filtrates contain byproducts with a more uniform molecular weight distribution than filtrates from pulps treated with other bleaching reagents, including oxygen, chlorine dioxide, and chlorine.<sup>24</sup> Other researchers have reported that molecular weight distributions of residual lignin<sup>25, 26</sup> and dissolved lignin are not substantially changed by moderate charges of ozone. Together with our previous results, the data suggest that the biggest impact of ozone at low charges on kraft lignin is the introduction of hydrophilic groups rather than substantial depolymerization.<sup>26</sup>

A separate series of experiments was performed in order to investigate the importance of oxygen depolymerization of lignin on ozone chemistry. A kraft pulp and oxygen delignified samples of the kraft pulp were ozone bleached. The filtrates from each were analyzed for their molecular

size distributions using size exclusion chromatography. The data show (Figure 9) that increasing oxygen delignification allows ozone to produce a higher proportion of low molecular weight compounds. This is likely to result because oxygen depolymerizes residual lignin, without dissolving it, and then ozone readily solubilizes the depolymerized fragments. With increasing oxygen delignification, there are higher quantities of lignin fragments than can easily become solubilized by the introduction of hydrophilic functional groups. While this is beneficial in terms of delignification, it is likely that a similar phenomenon occurs with the carbohydrates and detracts from selectivity and/or yield.

## **CONCLUSIONS**

Pulp that was 30% oxygen delignified exhibited better selectivity during ozonation than either 50% oxygen delignified pulp or kraft pulp. Carbohydrates in the 30% oxygen delignified pulp were as nearly as resistant to degradation as the carbohydrates in the kraft pulp because there was sufficient lignin to protect them from ozone attack. At low ozone charges, lignin in the oxygen delignified pulps was more easily removed than the kraft pulp. Examination of the molecular weight distributions of ozone filtrates suggests that oxygen produces a depolymerized residual lignin that is readily solubilized by ozone by the introduction of hydrophilic groups. The efficiency advantage of oxygen delignified pulps at low ozone charges is not seen at higher charges. At high charges, ozone begins to depolymerize lignin (Research Report 2). As a result, the beneficial depolymerization effect of oxygen under low ozone charges is lost at high ozone charges.

A picture of ozonation emerges in which oxidized, labile portions of both carbohydrates and lignin in unozonated pulp are readily removed at low ozone charges producing soluble, acidic fragments. Concurrently, phenolic rings are cleaved and carboxylic acid groups are introduced onto the residual lignin. The beneficial role of oxygen lies in its ability to depolymerize lignin. The depolymerized residual lignin then becomes readily solubilized upon oxidation by ozone to carboxylic acids.

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## FIGURES AND TABLES

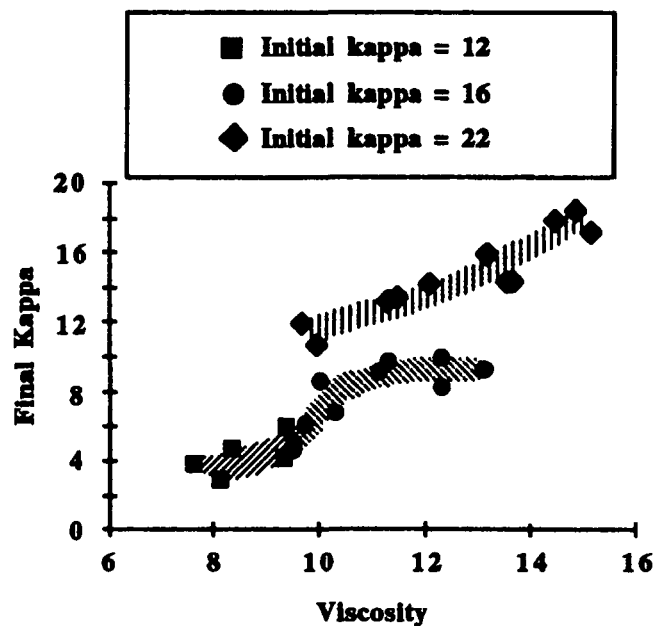


Figure 1. Kappa number and viscosity of kraft, 30% oxygen delignified, and 50% oxygen delignified pulps after ozonation at charges ranging from 0.3 to 1.4% on o.d. pulp.

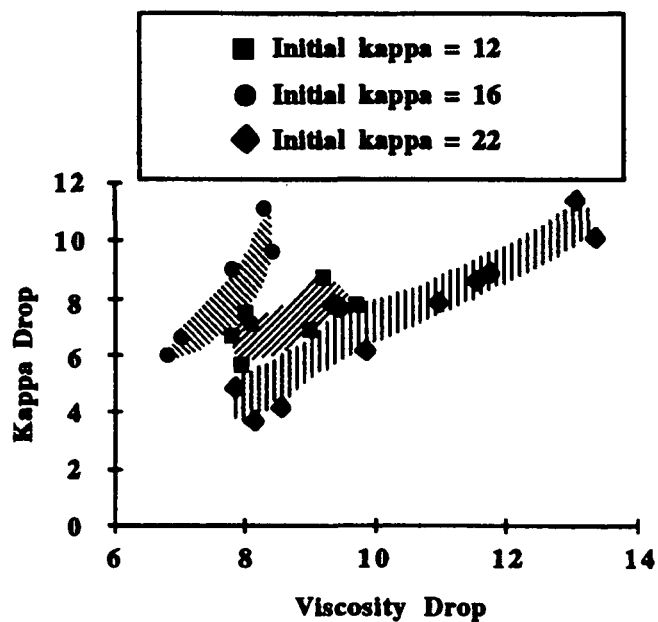


Figure 2. Selectivity of  $O_3$  bleaching of kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.

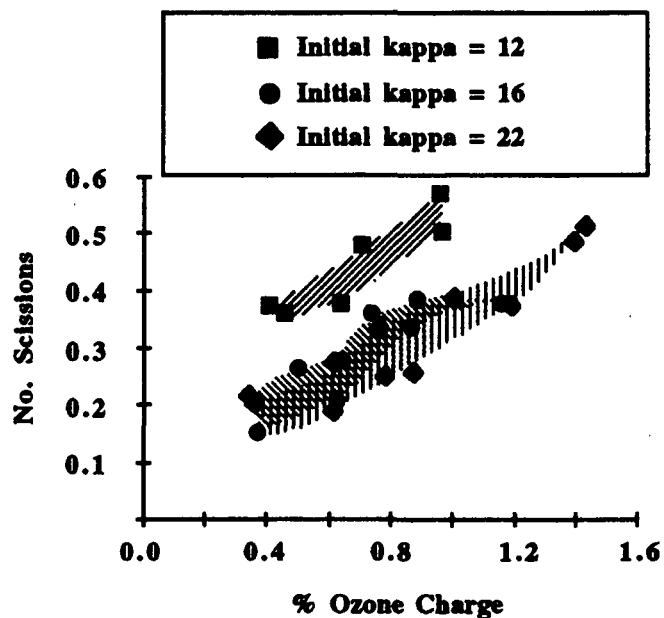


Figure 3. Carbohydrate degradation by ozone bleaching in kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.

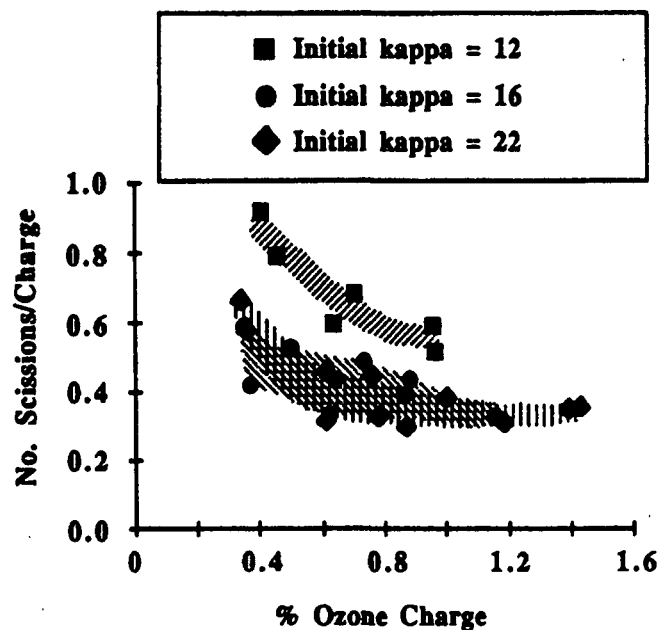


Figure 4. Number of scissions per unit ozone charge in kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.

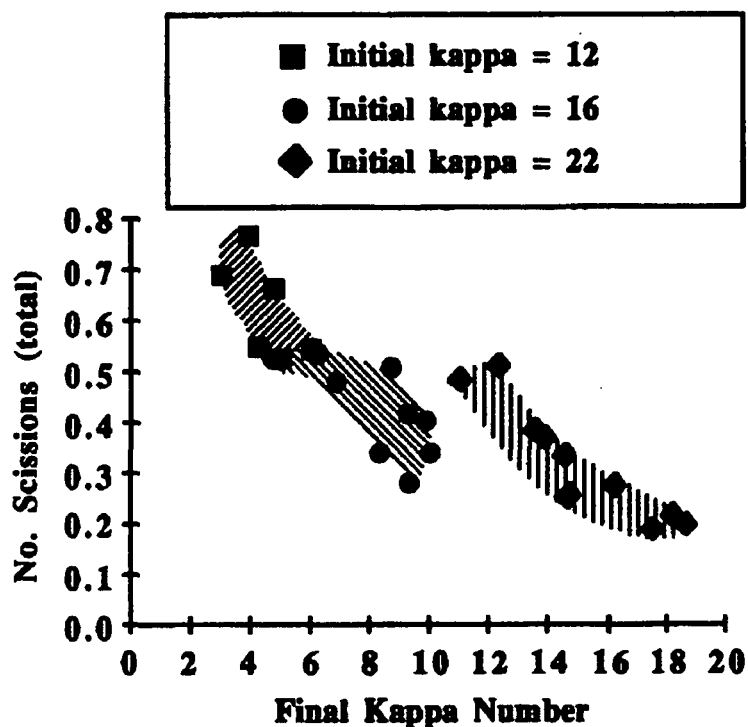


Figure 5. Total carbohydrate degradation from oxygen and ozone bleaching in kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.

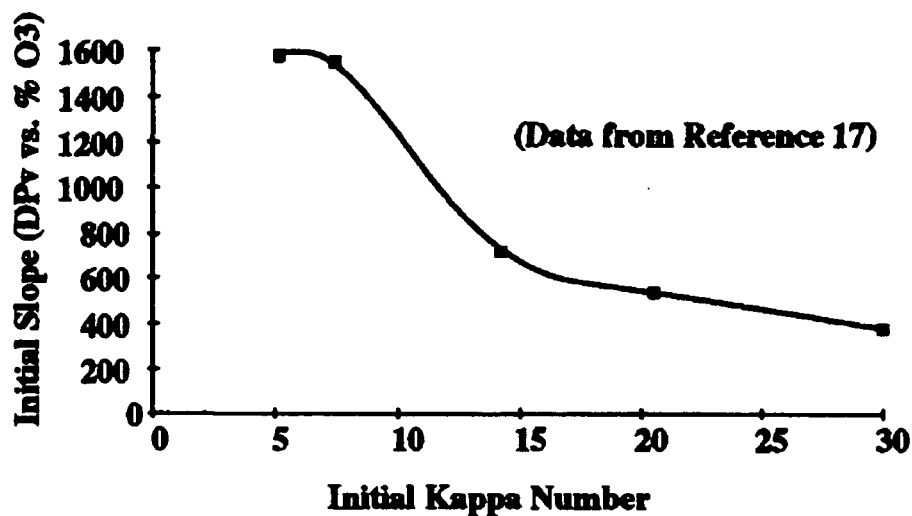


Figure 6. Initial rates of carbohydrate degradation as a function of initial kappa number (data from Reference 17).



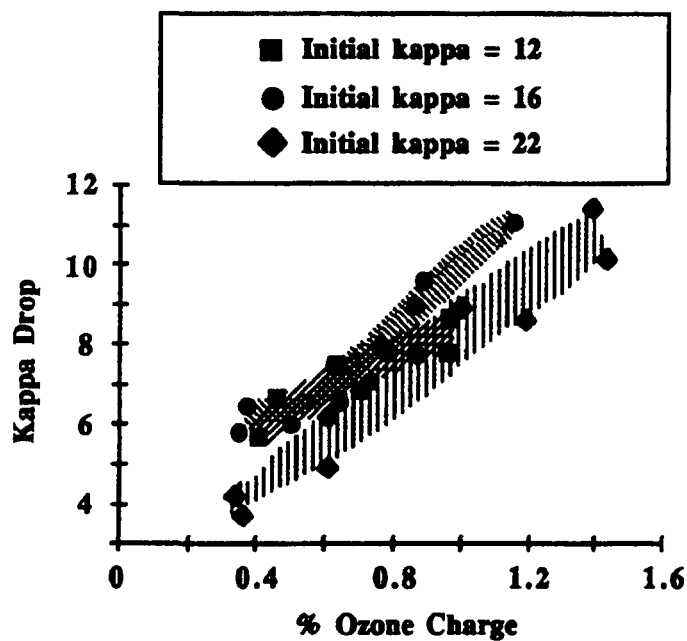


Figure 7. Ozone delignification in kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.

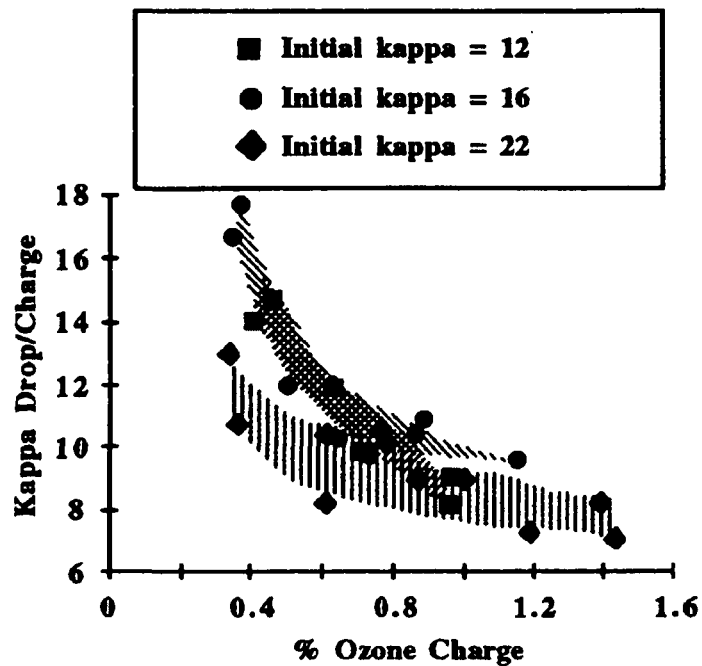
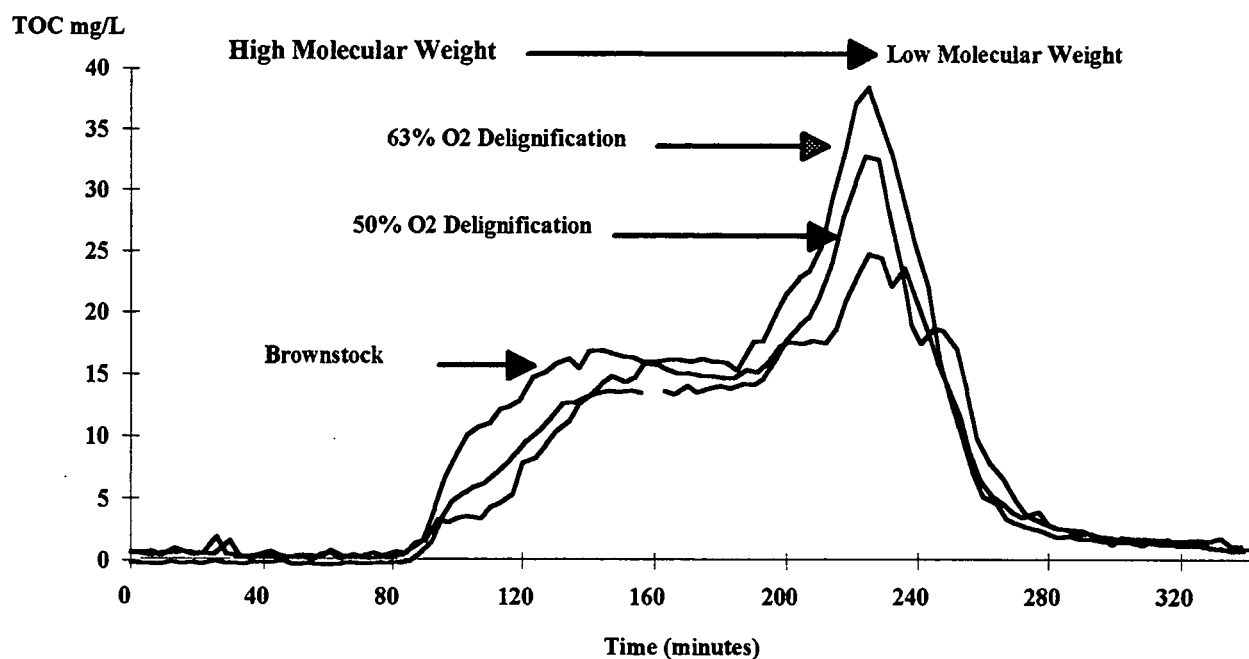


Figure 8. Efficiency of ozone delignification in kraft, 30% oxygen delignified, and 50% oxygen delignified pulps.



**Figure 9. Molecular Weight Distributions of Dissolved Organic Carbon in Ozone Filtrates of Brownstock and Oxygen Delignified Pulp**

**Table 1. Functional Groups (milli equivalents) on Ozonated Kraft and Oxygen Delignified Pulps**

% O <sub>3</sub> Charge	Final kappa number	CO <sub>2</sub> H/ 100 g pulp	lig. <sup>a</sup> CO <sub>2</sub> H / 100 g pulp	carb. <sup>b</sup> CO <sub>2</sub> H / 100 g pulp	CO <sub>2</sub> H/ g lignin <sup>c</sup>	OCH <sub>3</sub> / 100 g pulp	PhOH/ 100 g pulp	PhOH/g lignin <sup>c</sup>	PhOH/ OCH <sub>3</sub>	lignin CO <sub>2</sub> H/ OCH <sub>3</sub>
Kraft Pulp	k = 22.4									
0	22.4	6.5	0.2	6.3	0.1	15	8.4	2.5	0.56	0.01
0.33	18.1	7.0	1.4	5.6	0.5	18	6.6	2.4	0.37	0.08
0.35	18.6	6.7	1.0	5.7	0.4	16	-	-	-	0.06
0.60	17.4	5.8	0	5.8	0	13	6.3	2.4	0.48	0
0.60	16.1	6.3	-	-	-	14	-	-	-	-
0.86	13.5	5.7	-	-	-	11	-	-	-	-
1.38	11.2	5.0	-	-	-	8	4.7	2.9	0.59	-
1.42	10.9	5.2	0.8	4.4	0.4	8	-	-	-	0.10
O <sub>2</sub> Delig.	k = 15.8									
0	15.8	5.3	0.6	4.7	0.3	11	5.3	2.2	0.48	0.06
0.35	10.0	6.0	1.9	4.2	1.2	8	-	-	-	0.23
0.37	9.3	5.8	0.9	4.9	0.6	8	2.9	2.1	0.36	0.11
0.62	8.3	5.3	-	-	-	11	4.1	d	0.37	-
0.64	9.2	5.3	-	-	-	10	-	-	-	-
0.86	6.8	4.9	-	-	-	8	-	-	-	-
0.88	6.2	4.7	-	-	-	7	-	-	-	-
1.15	4.7	4.5	0.3	4.2	d	7	2.1	d	0.30	0.04
O <sub>2</sub> Delig.	k = 11.7									
0	11.7	5.9	0.2	4.1	d	7	2.8	1.6	0.40	-
0.41	6.0	4.3	-	-	-	8	-	-	-	0.03
0.45	5.0	4.4	0.7	3.7	d	8	1.7	d	0.21	-
0.70	4.8	4.4	-	-	-	4	-	-	-	-
0.95	3.9	4.1	0	4.0	d	4	1.4	d	0.35	-
0.96	3.0	4.0	-	-	-	4	-	-	-	0

<sup>a</sup> Milli equivalents of COOH associated with the lignin per 100 g of pulp; calculated by subtracting the right hand column from the left hand column.

<sup>b</sup> Value was determined by measuring the milli equivalents of COOH associated with 100 g of delignified (acid chlorite-treated) pulp.

<sup>c</sup> Calculated from column 3, after estimating the lignin content in 100 g of pulp from the kappa number (% lignin by weight = 0.15 x kappa number).

<sup>d</sup> Lignin estimates from kappa numbers below 10 are invalid.

## RESEARCH REPORT 5 : EFFECTS OF PULPING METHODS AND OXYGEN ON OZONE BLEACHING CHEMISTRY

### INTRODUCTION

Several earlier studies addressed the types reactions that ozone undergoes to produce characterized byproducts. In one series of ozone studies, the soluble byproducts from the ozonation of pulp at different ozone charges were examined (Research Reports 2 and 3). At low charges, ozone produced soluble, acidic fragments, including small fatty acids, short-chain and long-chain aliphatic acids, and diacids; little aromatic material was retained in solution. The impact of oxygen on ozone chemistry was initially recognized when it was determined that compared to brownstock, ozonation of oxygen delignified pulps produced soluble byproducts with a higher proportion of low molecular weight material. The results suggested that oxygen may depolymerize residual lignin and carbohydrates. It was hypothesized that ozone can then readily solubilize the pulp components by introducing carboxyl or other hydrophilic groups. These facile reactions produce the low molecular weight, acidic byproducts observed even at low ozone charges.

There is data in the literature that address the effects of oxygen (1,2) and ozone (3-5) individually on the structure of lignin and cellulose. However, there is little information about the interaction of the chemistries of these two oxidants when they are applied to a pulp in sequence. Thus, in a second study, the interaction of oxygen and ozone bleaching was more closely examined (Research Report 4). A softwood kraft pulp was oxygen bleached to 30% and 50% delignification in the laboratory. The three pulps (the kraft brownstock and the two oxygen delignified pulps) were ozonated at charges ranging from 0.3% to 1.4% on o.d. pulp. At low ozone charges, the moderately oxygen delignified pulp exhibited superior selectivity compared to the kraft or 50% oxygen delignified pulp. In the moderately oxygen delignified pulp, the carbohydrates appeared to benefit from the protecting effect of the residual lignin, while lignin removal was enhanced, possibly by depolymerization or introduction of carboxylic groups by oxygen. There was no advantage to moderate oxygen delignification at higher ozone charges (greater than 0.5%).

The study of the impact of oxygen and pulping processes on the chemistry of ozone bleaching was extended in this third series of experiments. The goal of the current set of studies is to determine the responses of three brownstock pulps from different cooking regimes to oxygen and ozone treatment. Pulp quality was assessed as well as chemical structure for the brownstocks, oxygen delignified, and ozonated pulps. From these data, the dependence of oxygen and ozone bleachability on structural features of the different pulps may be ascertained.

## **METHODS**

### **Approach**

Three mill pulps from the same source (kraft, kappa number = 22 [K-22]; conventional kraft, kappa number = 31 [K-31]; and polysulfide anthraquinone, kappa number = 22 [PSAQ]) were oxygen bleached in the laboratory to different levels. Each of the brownstock pulps and oxygen delignified pulps were then bleached with ozone. The brownstock, oxygen delignified, and ozone bleached pulps were analyzed for kappa number, klason and acid soluble lignin, viscosity (including sodium borohydride treated), functional groups, zero-span tensile strength, brightness, and ozone yield. Ozone filtrates were analyzed for total organic carbon, dissolved sugars, elemental composition, acidity, and lignin.

### **Oxygen Delignification and Bleaching**

Details of the methods used to achieve levels of oxygen bleaching ranging from 33% to 62% delignification in a laboratory batch reactor are given in Table 1. The mass of pulp that was oxygen delignified, the charge of NaOH, time, temperature, pressure, final pH and the final kappa number after oxygen bleaching are given. Bleaching was carried out at 12% consistency, using 0.1% MgSO<sub>4</sub>. Two controls were included. In one, oxygen was replaced by nitrogen and in a second, nonalkaline conditions were used.

Details of the methods used to ozone bleach the pulps are given in Table 2, including the mass of pulp bleached, consistency of ozonation, percent charge (consumed), and percent consumption of the total applied ozone. The pulps were prepared for ozonation by soaking in a slurry of ap-

proximately 3% consistency and lowering the pH to 2 with sulfuric acid. The pulps were filtered, centrifuged for 10 minutes, and fluffed using a rotary shaft mixer. All ozonations were carried out using a Welsbech T2 ozone generator and a modified rotary evaporator. The pulps were ozone bleached in duplicate at approximately 0.4% charge and 40% consistency. Duplicate ozonations were performed and the results for each are reported in tables as Z1 and Z2. Immediately after ozonation, samples were purged with nitrogen. The amount of ozone applied was determined by iodometric titration of a sodium thiosulfate solution into which a reference stream was bubbled; the amount of ozone remaining after ozone consumption was also measured to determine consumption. All ozonations were carried out at room temperature. Additional details about the method used for ozone bleaching are included in Appendix 1.

## Analyses

The following analyses were conducted on pulp. Kappa numbers were measured using TAPPI procedure T236. Acid soluble and klason lignin were measured by TAPPI method T222. Viscosity was measured using T230. Reductions of the pulp prior to viscosity measurements were carried out by soaking the pulp in a 2.5% NaBH<sub>4</sub> solution at 2% consistency, allowing it to react for several hours at room temperature, increasing the NaBH<sub>4</sub> to 5%, and then allowing the pulp to react several more hours. Phenols were analyzed by periodate oxidation (6). The method of measurements of methoxyl groups were based on the Zeisel method and performed by Chemlig, Inc. Carboxylic acids were measured by conductometric titration of 1.5 o.d. g pulp with 0.05 N NaOH under nitrogen. Zero-span tensile strength and directional brightness were measured by TAPPI methods T231 and T452, respectively.

After ozonation, the high consistency pulp was diluted and neutralized to approximately pH=7 with a measured amount of 0.1 N NaOH. The slurry was soaked overnight and then titrated further as the pH dropped with time. These values were considered total acidity, i.e., the acidity from the carboxylic acids in the pulp plus the dissolved byproducts. Neutralization requirements of the sulfuric acid remaining in the pulp after ozonation were insignificant. Further information is

given in Table 3, including filtrate volumes, neutralization equivalents, and the pH before and after neutralization.

The following analyses were conducted on the neutralized ozone filtrates. Total organic carbon was determined by taking the difference between measurements of total carbon and inorganic carbon using a Shimadzu Model 5050 TOC analyzer which uses catalytic combustion. In some cases, acidified, nitrogen-purged filtrates were measured for total carbon only. Dissolved sugars were measured using derivatization and spectrophotometry in a method modified from Dubois (7). Dissolved lignin was measured by spectrophotometry in a method adapted from TAPPI procedure T222. Elemental composition was provided by Huffman Laboratories. Additional details are provided in Appendix 1.

## **RESULTS AND DISCUSSION**

In addition to the figures presented, all numerical results are given in Tables 4-9.

### **Selectivity**

#### ***Carbohydrate Deterioration***

Several different measurements were used to gauge carbohydrate quality. Traditional viscosity tests have been routinely used to determine whether processes cause harm to cellulose and therefore, viscosity values are reported here. However, it has been widely reported that the presence of alkali-labile functional groups in ozonated pulp interferes with viscosity measurements, yielding misleadingly low values. For that reason, most pulps were chemically reduced prior to a second viscosity analysis. The sodium borohydride treatment reduced the carbonyl groups that may promote  $\beta$ -elimination reactions and cellulose chain cleavage during the alkaline viscosity assay. These reduced viscosity values were also used to assess carbohydrate degradation.

The purpose of most viscosity measurements is to indirectly assess suitability of a pulp to produce strong paper. Although the large number of samples prohibited standard tear and tensile testing in

these studies, zero-span tensile tests were performed to evaluate paper strength. Results are reported in breaking length (km).

### Viscosity

The viscosities of unreduced pulps were examined as one measure of carbohydrate degradation from oxygen and ozone bleaching. The viscosity data clearly indicate that each brownstock pulp responds differently to oxygen and ozone. In Table 4, the absolute viscosity values are given. The reduction in viscosity with oxygen treatment ( $\Delta v$ ) is shown in Figure 1. Oxygen degraded the carbohydrates in the K-31 pulp more than in the other pulps while the PSAQ pulp was the most resilient to oxygen. All three pulps showed an increasing loss in viscosity with increasing oxygen delignification.

By contrast to oxygen, ozone caused the greatest loss of viscosity in the K-22 pulp (large  $\Delta v$ ) and it least affected the K-31 pulp, as shown in Figure 2. The PSAQ pulp viscosity was only moderately affected by ozone. The protecting effect of the lignin in the K-31 pulp is most likely responsible for the carbohydrate preservation in these pulps. However, the kappa numbers of the PSAQ and the K-22 pulp after the oxygen stage were similar enough that lignin content is unlikely to be the cause for greater ozone depolymerization of cellulose in the K-22 pulp than the PSAQ pulp. The stabilization of the PSAQ pulp to ozone and oxygen does not appear to be related to oxidized carbohydrate reducing-end groups. This was our conclusion because the concentrations of carboxylic groups on the pulp are similar between the PSAQ pulp and the low lignin kraft pulp (see below). In Figure 2, the curves suggest that oxygen delignification up to approximately 45% causes changes in all three of the pulps such that carbohydrate depolymerization by ozone is inhibited (i.e.,  $\Delta v$  for ozone decreases between 30 and 45% oxygen delignification). The responses above 50% delignification were variable.

The net result of each of these processes on the carbohydrates in the three pulps is shown in Figure 3. The starting viscosity was low in the PSAQ pulp, but there was an extremely small viscosity reduction by oxygen along with the moderate reduction during ozonation. These results indi-



cate that PSAQ carbohydrates are more resistant to depolymerization by oxygen and ozone than the two kraft pulps, using viscosity as a measure of cellulose depolymerization.

Despite disparate starting kappa numbers and viscosities, and despite different susceptibilities to bleaching, final results after oxygen and ozone bleaching were similar for the three pulps (Figure 4). Careful examination of Figure 4 illustrates that although there was little viscosity lost during processing of PSAQ pulp, the initial viscosity was so low that advantages in oxygen and ozone selectivity could not compensate. As a result, there is a minor disadvantage to the PSAQ pulping process when low kappa numbers are achieved.

#### Reduced Viscosity

We observed the expected higher viscosity in the borohydride-reduced ozonated pulps compared to unreduced pulps (average difference between reduced and unreduced = 2.4 cP for the K-31 pulps) (Table 4). Unexpectedly, reduced K-31 pulps that were oxygen bleached, but not ozonated, had significantly higher viscosities than their unreduced counterparts (average difference between reduced and unreduced = 1.7 cP for K-31). These results suggest that oxygen produces the same functional groups that cause depolymerization reactions when ozonated pulps are exposed to alkali. By contrast to the K-31 pulp, the unozonated, oxygen bleached K-22 pulp did not show a significant effect of borohydride reduction on viscosity values; however, reduced ozonated pulps were on average 2.1 cP higher than the unreduced ozonated K-22 pulps. Reduced viscosity values for unozonated PSAQ pulp were not available.

Conclusions about effects of oxidants on carbohydrates drawn from viscosity measurements of reduced pulps are similar to those drawn from viscosities of unreduced pulps (Figures 5-7). Overall, viscosity is better preserved when ozone is used after oxygen to bleach down to low kappa numbers rather than when oxygen alone is used. There are clear differences in the reactivities of the pulps toward oxygen and ozone. Oxygen degraded the K-31 pulp more than the K-22 pulp, while ozone degraded the K-22 pulp more. In the K-31 pulp, the viscosity loss from ozone was the least for pulps oxygen delignified between 43 and 55% (Figure 6). Together, the effects

of oxygen and ozone stages resulted in the reduced K-22 pulps exhibiting slightly better viscosity retention than the reduced K-31 pulp.

Minor differences were found between the three reduced pulps at kappa numbers below 6 (Figure 7). The reduced viscosities decreased in the order K-31>K-22>PSAQ at the low kappa numbers. The reduced viscosity data show that bleaching with oxygen and ozone produces carbohydrates in PSAQ pulps that are slightly more degraded than the other two kraft pulps.

### Breaking Length

Another measure of deleterious impact of bleaching reagents on carbohydrate structure is loss of strength. Breaking length values were calculated from dry zero-span tensile strength data. All three pulps showed a significant loss of strength from oxygen (Table 5 and Figure 8). The K-22 and PSAQ pulps showed a pronounced drop in strength with low levels of oxygen (2.4 and 2.2 km, respectively). Increasing oxygen delignification to 60% caused only a comparatively small drop in strength (0.7 and 0.1 km, respectively). This result contrasts with the viscosity results which more closely correlated with the level of oxygen delignification.

The behavior of the K-31 pulp was more complicated. Of the three pulps, the K-31 pulp had the largest loss of strength from low levels of oxygen delignification (3.2 km). However, the K-31 samples that were oxygen delignified to between 40 and 50% had strengths comparable to the K-31 brownstock. These results support earlier work with other kraft pulps in which it was found that moderate oxygen delignification can produce higher quality pulps than either low or high levels of oxygen delignification.

Ozone bleaching at 0.4% charge did not cause substantial strength losses in any of the pulps. Strength values of ozonated pulps were similar to the values after oxygen delignification (Table 5). The final strength values indicated that the ozonated PSAQ pulp generally had the least strength of the three, particularly at low kappa numbers (Figure 9). The K-22 pulp showed the same pattern of strength loss with bleaching as the PSAQ, but the strength values were 1-2 km higher for the kraft pulp. The strength relationships of the ozonated K-31 pulp were complex,

reflecting the complex pattern of strength loss with oxygen. Exposing the K-31 pulp to low levels of oxygen to produce a kappa number between 15 and 16 substantially reduced its strength, even below the ozonated K-22 brownstock (not exposed to oxygen) that had a comparable lignin content (point A on Figure 9). However, higher levels of oxygen delignification of the ozonated K-31 pulp produced a low lignin pulp with similar or higher strength than the oxygen and ozone bleached K-22 pulp of comparable lignin content (point B on Figure 9).

The reduced viscosity values correspond with the breaking length values in most respects. However, once exposed to oxygen, the pulp breaking length does not seem to be as sensitive to increasing levels of oxygen delignification as viscosity.

### ***Delignification***

Lignin in each of the three pulps, as well as the carbohydrates, responds differently to ozonation (Figure 10 and Table 6). Reduction in lignin content as expressed by kappa number is given as  $\Delta k$  in Figures 10-13. The unoxygenated PSAQ was the most efficiently bleached by ozone ( $\Delta k=10$ , compared to approximately 7 for the other two pulps). Unfortunately, oxygen delignification caused a significant reduction in the efficiency of lignin removal by ozone such that at high oxygen delignification levels, ozone bleaching of the PSAQ pulp was the least efficient of the three pulps ( $\Delta k=5$ , compared to 6 for K-22 and 7 for K-31). Differences in ozone efficiency between the two low lignin pulps were minimized by oxygen bleaching. The dependence of efficiency of the ozone stage on oxygen delignification in the K-31 pulp was variable. However, it is noteworthy that there is an increase in the efficiency of pulps oxygen delignified between 30 to 45%. This observation corroborates our earlier work which suggests there is an optimal oxygen delignification level that can promote subsequent lignin dissolution by ozone.

### ***Total Lignin in Pulp***

Accurate lignin values are important for determining the efficiency of delignification, as well as for quantifying functional groups on lignin. Correlations with kappa number are frequently used to estimate lignin content (e.g.,  $0.15 \times \text{kappa number} = \% \text{ lignin}$ ). However, there is some question

as to the validity of the estimate at low kappa numbers. Insoluble and soluble lignin was measured in several pulps (Table 6). The deviation of kappa number from the total lignin was not more pronounced at low kappa numbers for any of the pulps, contrary to expectations. However, the relationship was slightly different for the three types of pulps. For example, the K-22 kappa numbers underestimated the measured total lignin content by up to 0.2% at high kappa numbers, while kappa numbers overestimated the lignin in the PSAQ pulp by about the same amount. The discrepancies between kappa number and total lignin are small enough so that lignin estimates by kappa number are valid, even at low kappa numbers.

### *Overall Selectivity*

The selectivities of oxygen and ozone for the three differently treated brownstock pulps, based on the decrease in kappa numbers and unreduced viscosity values ( $\Delta k/\Delta v$ ), are shown in Figures 11-13. The selectivity of each oxidant is shown (Figures 11 and 12), as well as the combined selectivity of the two (Figure 13). The very low susceptibility of the PSAQ pulp to carbohydrate deterioration by oxygen caused it to be the most selectively oxygen delignified (Figure 11). The selectivity of ozone was greatest toward the K-31 pulp, probably because of the protecting effect of lignin on the carbohydrates and because of the reasonably efficient ozone delignification of this pulp (Figure 12). Results based on reduced viscosity values showed similar ozone selectivities for the K-22 and K-31 pulps.

The combined result of the oxygen and ozone processes is that the PSAQ was the most selectively bleached by oxygen and ozone (Figure 13). This arises both because of its resilience to oxygen degradation, and its delignification efficiency by ozone. However, the selectivity was not great enough to overcome the poor pulp quality at the beginning of the oxygen and ozone process. The kraft pulps were similar, although there appeared to be a slight advantage of the K-31 over the K-22 pulps, based on unreduced viscosity results. Results based on reduced viscosity values of the K-22 and K-31 showed the similarity in the two kraft pulps, but the advantage was slightly greater for the K-22 pulp. These findings illustrate the importance of judicious application of the oxygen

stage prior to ozone because of the greater harm to the carbohydrates in that stage compared to the ozone stage, particularly for low lignin pulps.

## **Functional Groups in Pulp**

### ***Carboxylic Acids***

Carboxylic acid contents of pulps and filtrates were examined in order to determine how these functional groups affect dissolution of carbohydrates. Earlier work showed that concentrations of carboxylic acids increase in lignin as a result of oxidation, but most of the acids reside on the carbohydrates for oxygen and ozone bleached pulps (Research Report 4). The concentrations of carboxylic acids on the different oxygenated and ozonated pulps in these studies are given in Figure 14 and Table 7. The K-31 pulp contained the highest levels of acids, even accounting for differences in lignin content; higher concentrations of hemicelluloses with glucuronic acids may have contributed to the higher carboxylic acid content. The pulps with lower lignin levels were similar, but the PSAQ had slightly more carboxylic groups than the K-22 pulp.

Oxygen delignification did not significantly affect carboxylic acid content on the pulp. However, after each of the pulps was ozonated, there was a significant drop in the carboxylic acid content on the pulps. Furthermore, the removal of the acid groups on the pulp by ozone sharply increased for the pulps that were oxygen delignified between 40-55% in the two low lignin pulps.

It is interesting that ozonation caused a decline in carboxylic content on pulps, since ozone is expected to create significant quantities of acid groups. By measuring the equivalents of base required to neutralize a slurry of ozonated pulp, we estimated the total quantity of acids produced by ozone (pulp plus the dissolved byproducts) (Figures 15-17 and Tables 7 and 8). In general, ozonation produced a fairly constant total quantity of acids in the two low lignin pulps, as may be expected because they were ozonated at constant charge. Importantly, the proportion of the carboxylic acids in the dissolved phase increased with the extent of oxygen delignification, up to about 50% oxygen delignification for all of the pulps. For the K-31 pulp, the dissolved fraction continued to increase up to the highest levels of oxygen delignification. Thus, much of the reduc-

tion in carboxylic content in the pulp that we observed with ozonation simply represents dissolution of fragments that contain these functional groups. Previous work suggests that these solubilized fragments arise predominately from the carbohydrate fraction of the pulp.

Together, the results suggest that oxygen treatment between 40 and 50% delignification induces changes in the carbohydrate structure, such as depolymerization, so that low levels of ozone can readily oxidize the depolymerized portions. The carboxylic acid-bearing fragments become soluble, in some cases perhaps leaving behind a pulp that is less depolymerized and higher quality. The dissolution of carbohydrates should be reflected in lower yields; unfortunately, our ozone yield measurements were not reproducible enough to determine whether this occurred. If a significant fraction of the ozone is consumed in the solubilizing, oxidation reactions, then fewer chain cleavage reactions can occur in the carbohydrates that remain in the fiber. As a consequence of all of these factors, viscosity is retained in moderately oxygen delignified, ozonated pulps.

### ***Phenols and Methoxyls***

Residual lignin in oxygen delignified and ozonated pulps was examined by measuring phenol and methoxyl groups in whole pulps. The current data agree with other results in which oxygen depletes phenolic structures in lignin and then subsequent ozonation produces residual lignins more similar to kraft residual lignins (Figure 18). The oxygen appears to cleave the phenols, possibly leaving undissolved muconic acid fragments that contribute to the kappa number. Ozonation then readily cleaves these unsaturated aliphatic chains at the double bonds, producing the small chain acids and aldehydes previously identified in ozonation filtrates. When ozone cleaves a phenolic ring, as well as a methoxyl-substituted ring, the same rapid series of reactions occurs and the nonaromatic muconic acid fragments dissolve. The lignin remaining with the ozonated pulp is then more similar to the parent structure than lignin in oxygen bleached pulps. These results correspond with our earlier findings that initial delignification is efficient and rapid and produces acidic, low molecular weight products.

## ***Carbonyls***

It is important to consider carbonyl compounds, as well as carboxylic acid groups, in determining factors that cause dissolution. As mentioned earlier, the challenge of meaningful, accurate, and reproducible carbonyl analyses is not insignificant. Considerable effort was put toward developing a reliable wet-chemical means to determine carbonyl compounds on pulp, with little success. These studies are summarized in Appendix 1.

## **Dissolved Byproducts**

The oxidation level of the solids in ozone filtrates is an indication of bleaching efficiency; high oxidation levels may represent over bleaching. Weight percentages of carbon, hydrogen and oxygen for selected ozone filtrates are given in Table 8. Molar ratios of H/C and O/C are shown in Table 9. These data indicate that high levels of oxygen are frequently accompanied by a high degrees of saturation. These results are consistent with ozonation products that are nonaromatic, aliphatic, and highly oxygenated, just as we have previously found in our low molecular weight characterizations. The data for the K-22 and PSAQ pulps also indicated that oxygen delignification caused the ozone to produce more oxidized byproducts, also consistent with other experiments. It should be noted that the O/C values were very high (between 0.8 and 1), which suggests the presence of numerous carboxylic acid groups.

An estimate of the dissolved sugar content in the ozone filtrates was made by determining reactive aldehydes (Table 8). The estimate is likely to be a maximum value because of potential interferences from lignin-derived aldehydes. From the glucose values (1-2 mg glucose/g pulp ozonated) a minimum yield for ozonated cellulose was calculated to be 99.8%. This value corresponds reasonably well with our yield data (Table 5) which indicated little yield loss from these low ozone charges. There was not a substantial difference between the filtrates, but the K-22 filtrates had slightly lower carbohydrate levels than the other pulps. The total organic carbon that is measured in filtrates can be roughly accounted for by estimates of the concentrations of dissolved sugars and dissolved lignin.

### ***Papermaking Properties***

A significant result was the loss of zero-span tensile strength in the control samples (Table 5). The addition of oxygen or alkali for the K-22, K-31 and PSAQ experimental pulps did not substantially reduce strength more than the temperature and pressure in the controls, regardless of the degree of oxygen delignification. Furthermore, there was comparatively little loss of strength due to ozonation; most strength loss in the oxygen delignified, ozonated K-22 pulps arose during the oxygen bleaching. These results suggest that depolymerization is not likely to be the sole cause for strength loss; fibril orientation (8) may be a factor in these strength tests.

Cooking with oxygen to lower kappa numbers caused lower brightness levels for both K-22 and PSAQ pulps (Table 5 and Figure 20). However, ozone effectively boosted the brightness of the K-22 pulp beyond that expected from simple lignin removal. Ozone is expected to effectively destroy chromophores by its high degree of reactivity with unsaturated sites.

### **CONCLUSIONS**

Oxygen depolymerizes both lignin and carbohydrates. In the case of lignin, the depolymerized residual lignin leads to increased ozone delignification efficiency for some moderately oxygen-bleached pulps. The advantage appears to be lignin-dependent, though. Pulps that are low in lignin content prior to oxygen bleaching may not exhibit an advantage due to the recalcitrant nature and low concentrations of the residual lignin.

Oxygen appears to also depolymerize carbohydrates without necessarily dissolving the fragments. The depolymerized portions of cellulose may lead to easy dissolution during subsequent pulp ozonation. The dissolution phenomenon is particularly evident at 40-50% oxygen delignification. At this level of oxygen application, there is enough carbohydrate depolymerization to allow low ozone charges to easily dissolve fragments by the introduction of carboxylic acids. Damage to the carbohydrates remaining in the fiber at these oxygen levels is minimal. The result is dissolution of acidic, weak, fiber constituents and a high pulp quality. Precise yield measurements and molecular size distributions of cellulose would verify this hypothesis.



Pulping conditions significantly affect the reactivity of each pulp constituent to oxygen and ozone. Pulping with polysulfide anthraquinone produces a pulp with low viscosity; however, the PSAQ pulp is resistant to a reduction in viscosity by oxygen and fairly resistant to deterioration by ozone. The stabilization of the PSAQ pulp to oxygen and ozone does not appear to be related to oxidation of carbohydrate reducing end groups. The conventional high lignin kraft pulp exhibited the most viscosity loss by oxygen, while the K-22 pulp was quite susceptible to viscosity loss by ozone. These findings illustrate the importance of judicious application of the oxygen stage prior to ozone, particularly when ozone bleaching down to intermediate lignin levels (i.e., when there is substantial delignification in post-ozone stages) or when variable pulping conditions are used.

Despite disparate starting kappa numbers and viscosities, and despite different selectivities of bleaching reagents, all pulps with a kappa number of about 6 had viscosities of approximately 12. By all measures, PSAQ pulp produced inferior carbohydrates. Thus, the advantage of high selectivity toward PSAQ pulps by oxygen and ozone cannot compensate for its initial poor quality.

Oxygen delignification, in addition to depolymerizing, produces a residual lignin that is depleted in phenols. The depletion of these activated (toward ozone attack) functional groups did not systematically deactivate the lignin toward ozone, suggesting that chemical reactivity is not important in ozone bleaching. Subsequent ozonation produced a residual lignin that is more similar to the brownstock in phenolic content. The oxygen cleaves the phenols, leaving undissolved muconic acid fragments that contribute to the kappa number; ozonation then readily cleaves these unsaturated aliphatic chains at the double bonds, producing small, soluble, acidic products. When ozone cleaves a phenolic ring, as well as an etherified phenolic ring, the same rapid reactions of the ring cleavage products occurs and causes dissolution of the nonaromatic fragments. The lignin remaining with the pulp is then more similar to the parent structure. Thus, bleaching stages after ozone should not have a substantially different chemical reactivity than residual lignin in kraft pulps.

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## FIGURES AND TABLES

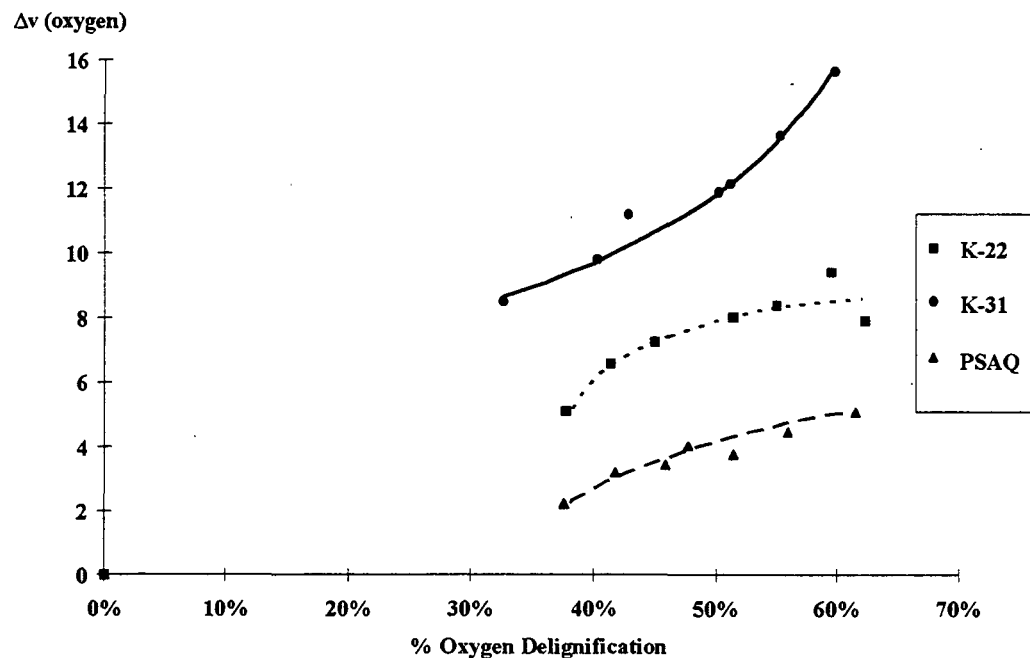


Figure 1. Viscosity reduction ( $\Delta v$ ) from oxygen delignification for kraft and PSAQ pulps.

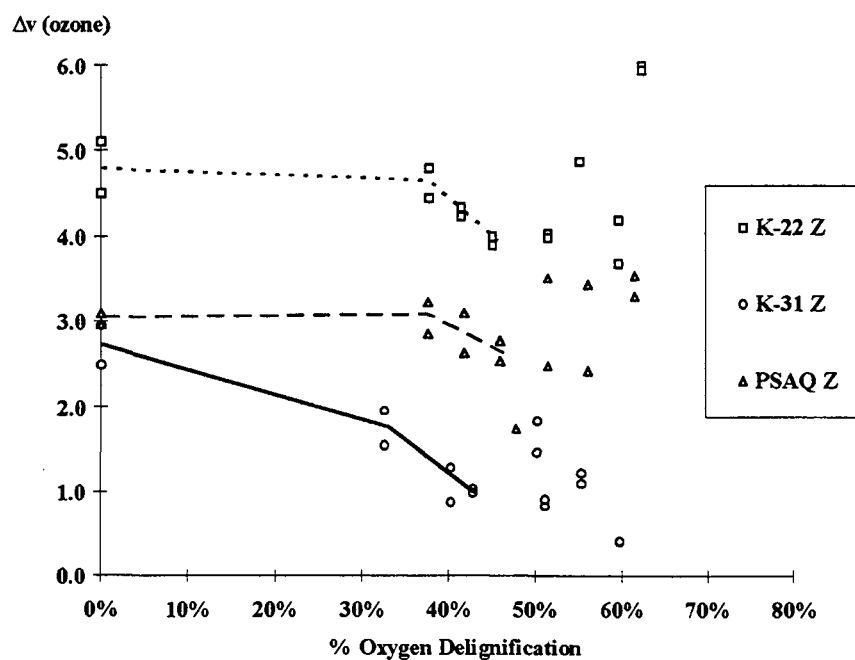


Figure 2. Viscosity reduction ( $\Delta v$ ) from ozone for kraft and PSAQ pulps after oxygen delignification. Points on the y-axis are pulps with no oxygen delignification.

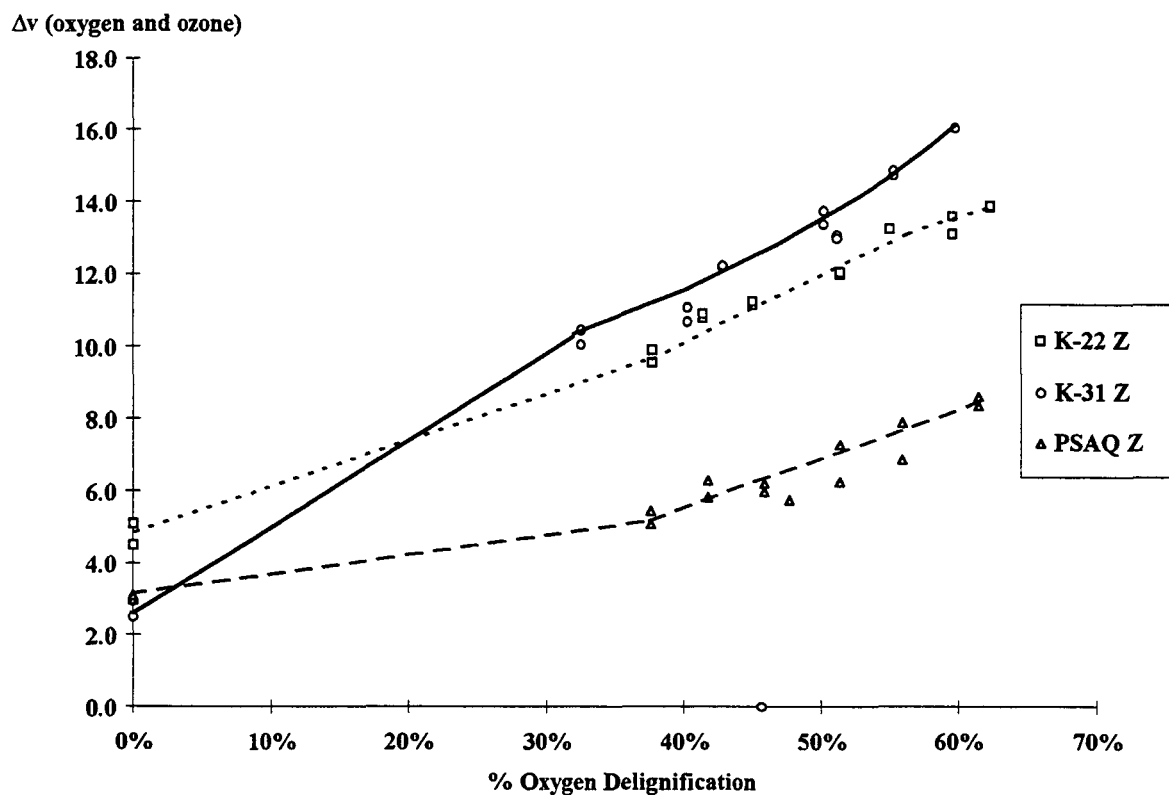


Figure 3. Total viscosity reduction ( $\Delta v$ ) from oxygen and ozone for kraft and PSAQ pulps. Points on the y-axis are pulps with no oxygen delignification.

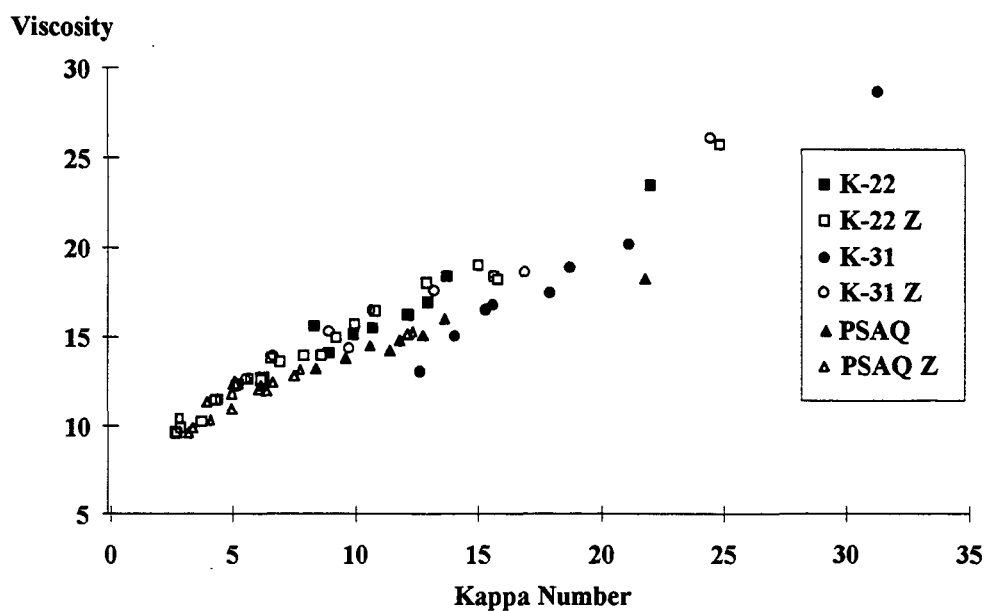


Figure 4. Selectivity curves for kraft and PSAQ before and after oxygen and ozone. The Z suffix represents ozonated pulps (open symbols).

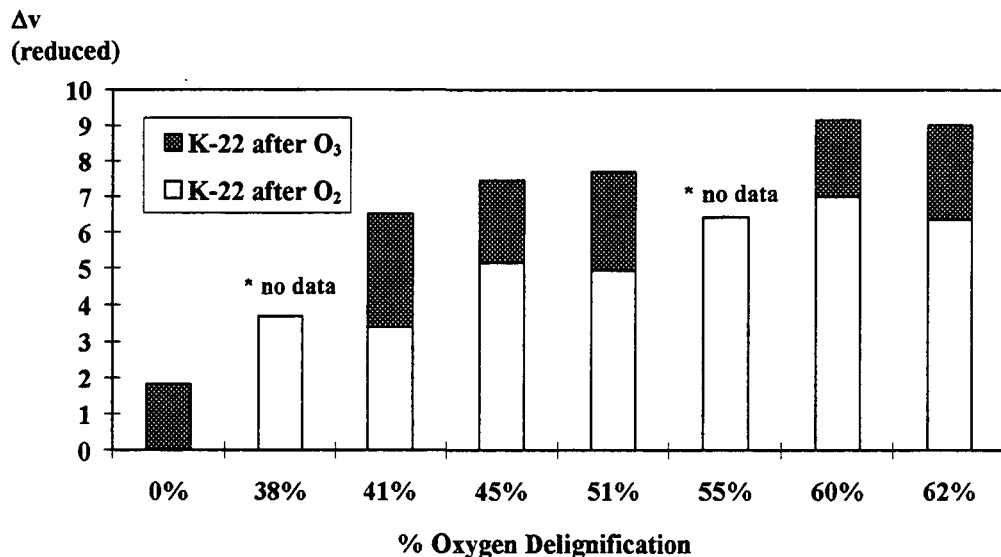


Figure 5. Viscosity reduction ( $\Delta v$ ), using sodium borohydride-reduced viscosity values, from oxygen and ozone delignification for a low lignin kraft pulp.

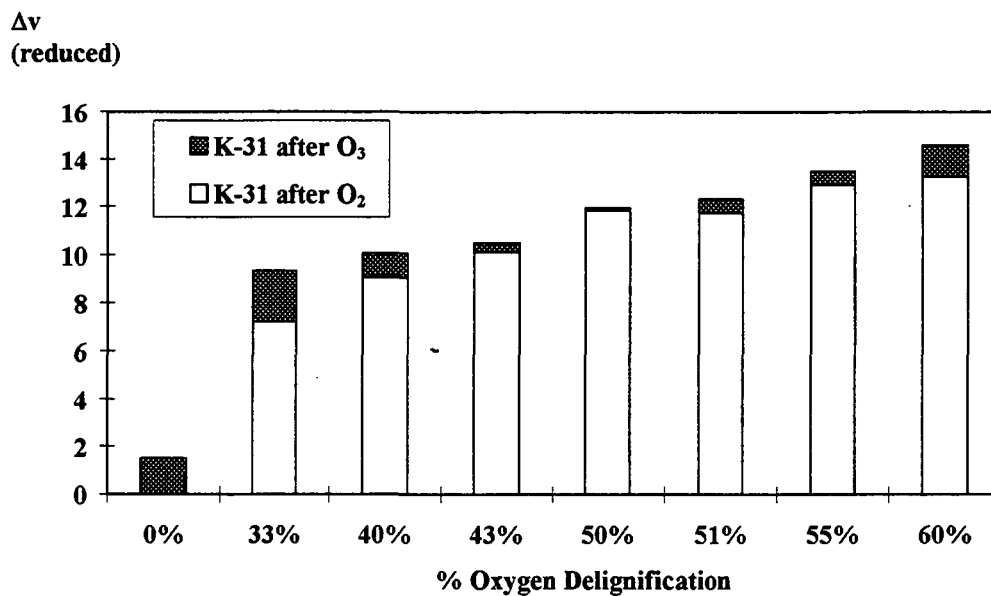


Figure 6. Viscosity reduction ( $\Delta v$ ), using sodium borohydride-reduced viscosity values, from oxygen and ozone delignification for a high lignin kraft pulp.

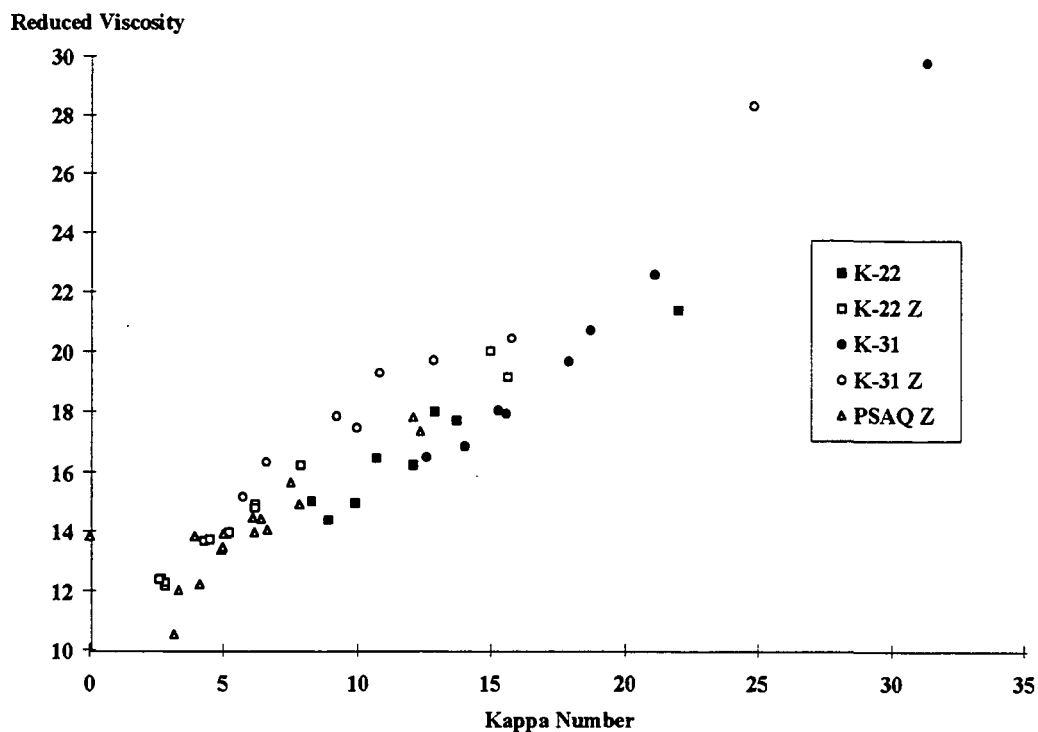


Figure 7. Selectivity curves for kraft and PSAQ before and after oxygen and ozone, using  $\text{NaBH}_4$ -reduced viscosity values. The Z suffix represents ozonated pulps (open symbols).

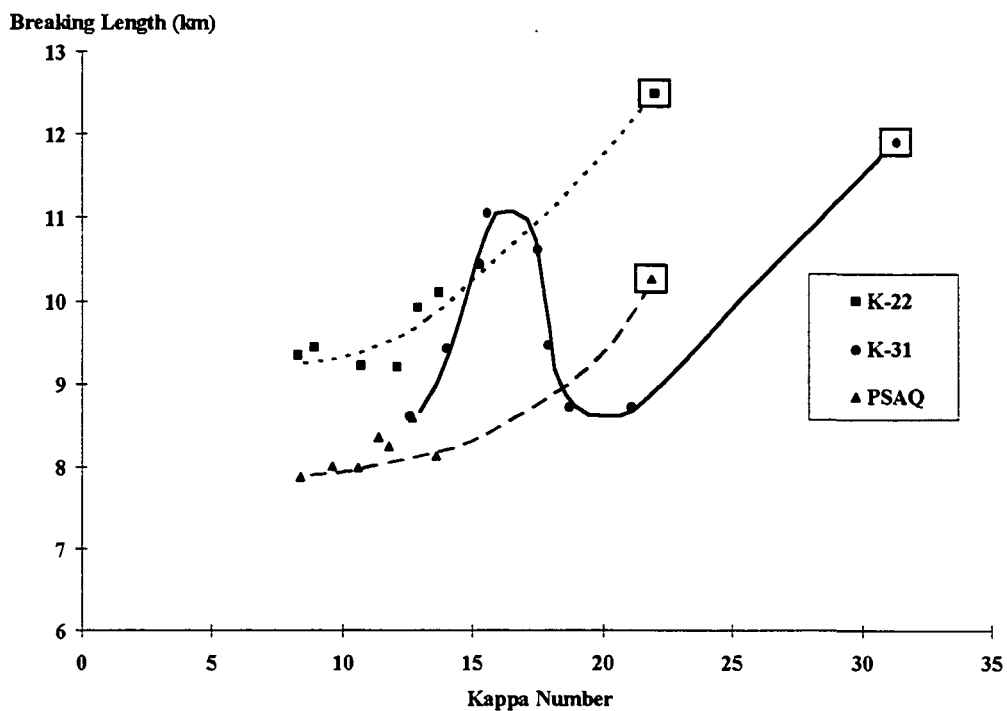


Figure 8. Breaking length of kraft and PSAQ pulps after oxygen delignification. Boxed points are brownstocks.

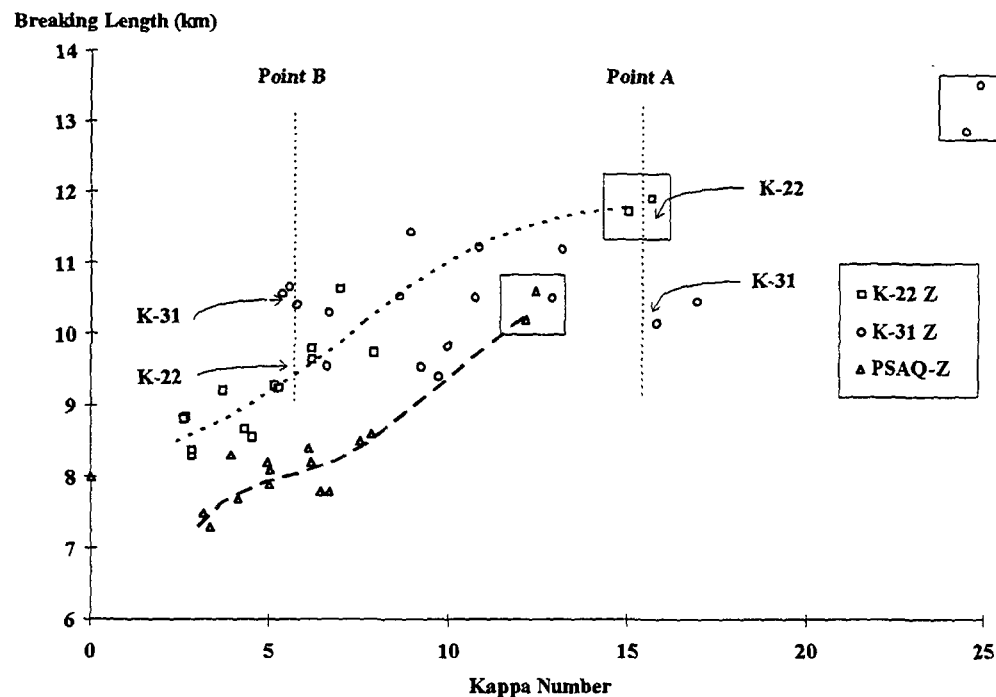


Figure 9. Breaking length of kraft and PSAQ pulps after ozone. The K-31 pulp strength showed little correlation with kappa number. Boxed points are ozonated brownstocks. Points A and B are discussed in the text.

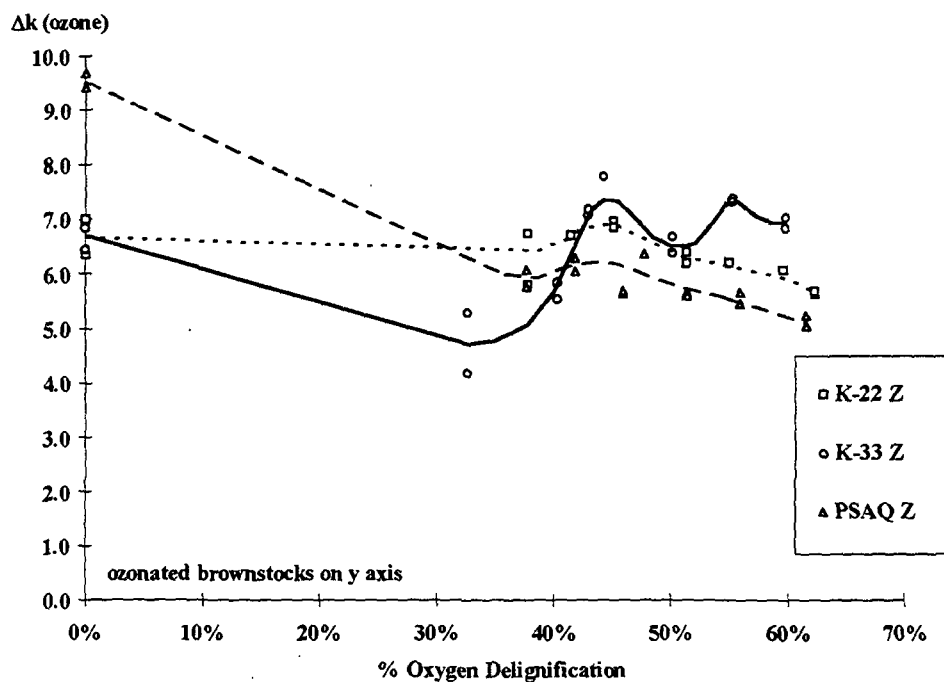


Figure 10. Kappa number reduction from ozone for kraft and PSAQ pulps. Points on the y-axis are pulps with no oxygen delignification.

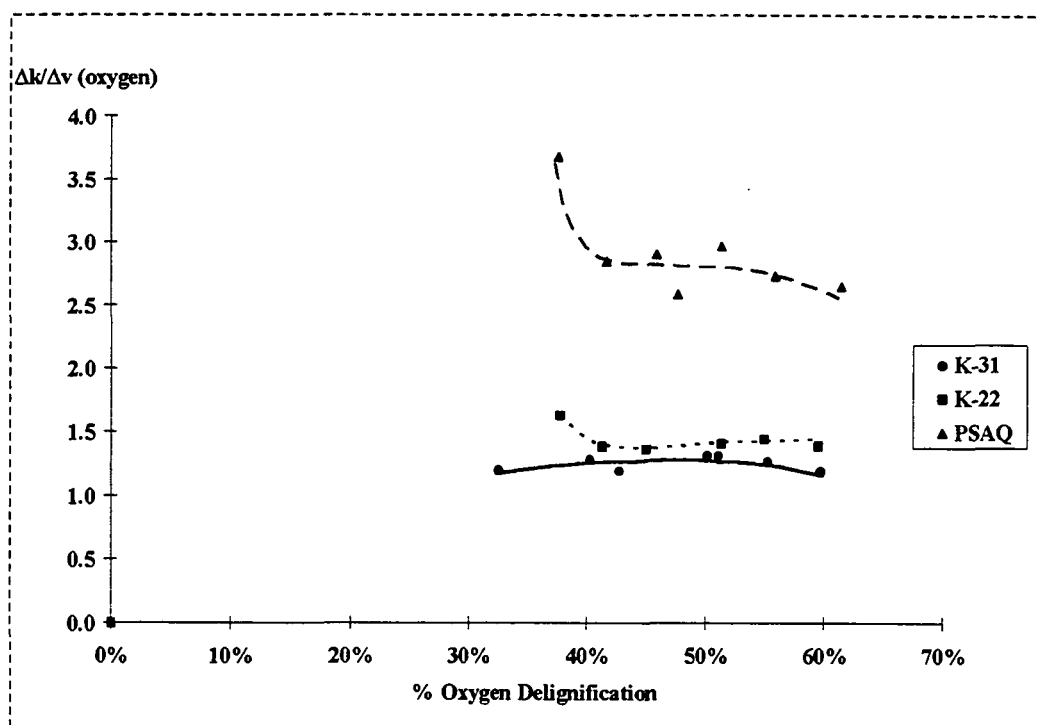


Figure 11. Selectivity ( $\Delta k/\Delta v$ ) of oxygen to kraft and PSAQ pulps, without ozone.

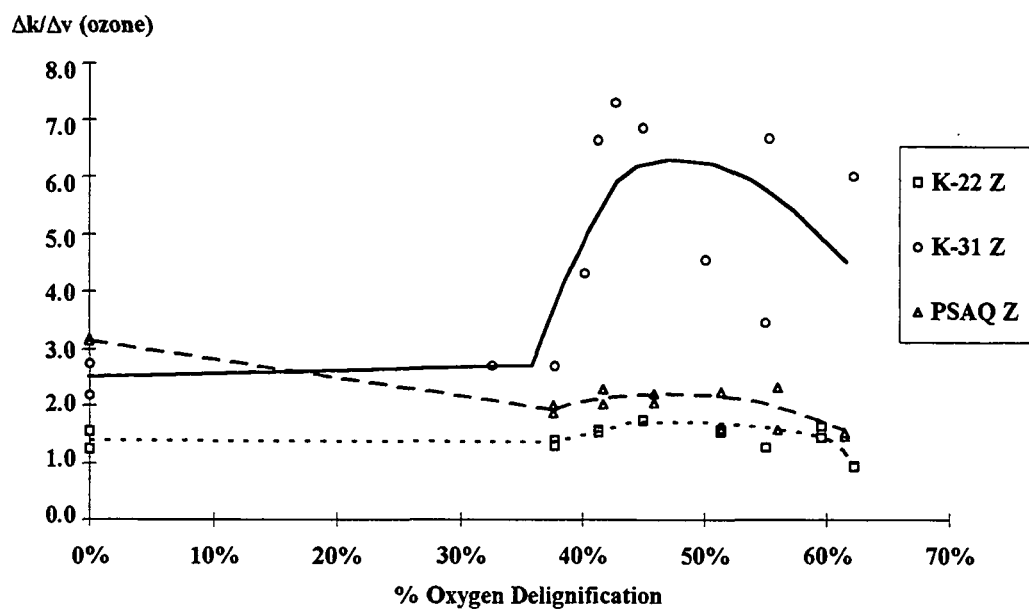


Figure 12. Selectivity of ozone to kraft and PSAQ pulps after oxygen delignification. Points on the y-axis are pulps with no oxygen delignification.



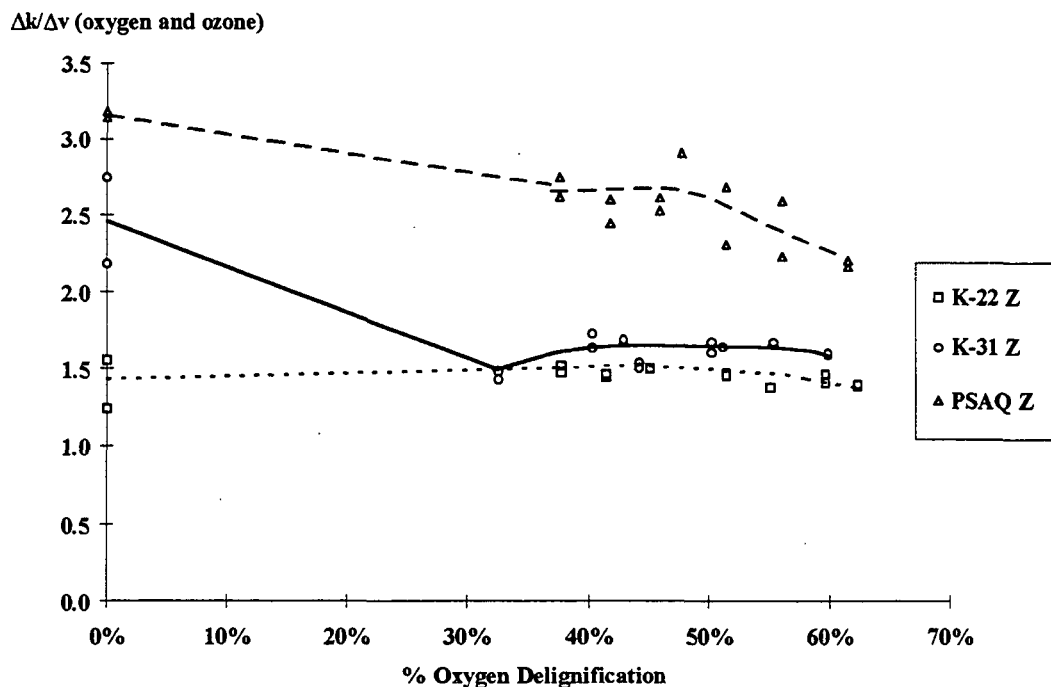


Figure 13. Total selectivity of oxygen and ozone to kraft and PSAQ pulps. Points on the y-axis are pulps with no oxygen delignification.

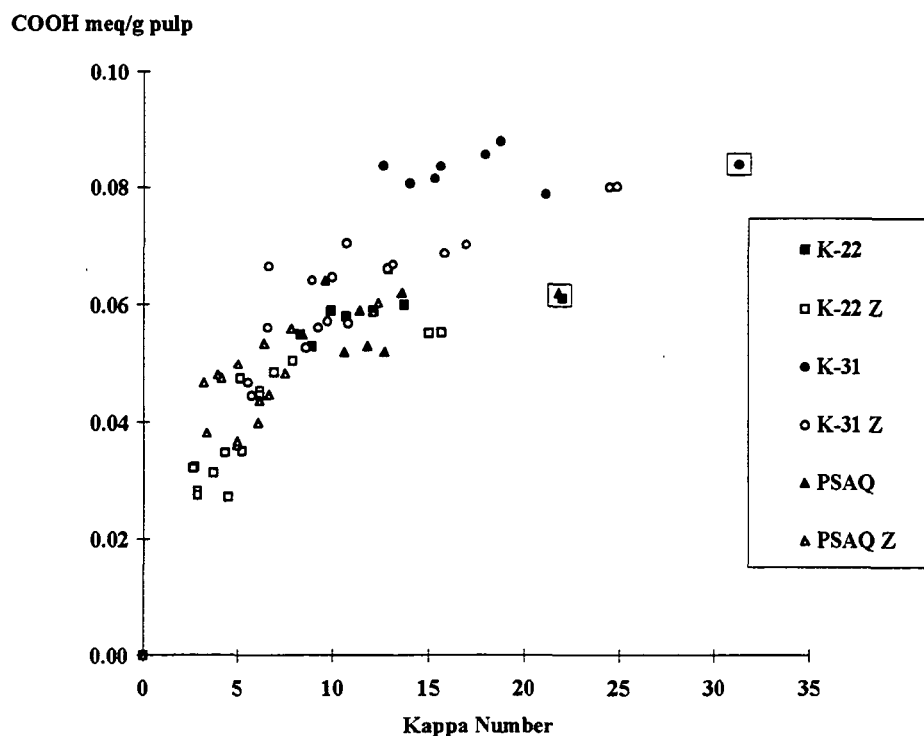


Figure 14. Carboxylic acid content of kraft and PSAQ pulps before and after oxygen and ozone. Z suffixes represent ozonated pulps (open symbols). Boxed points are brownstocks.

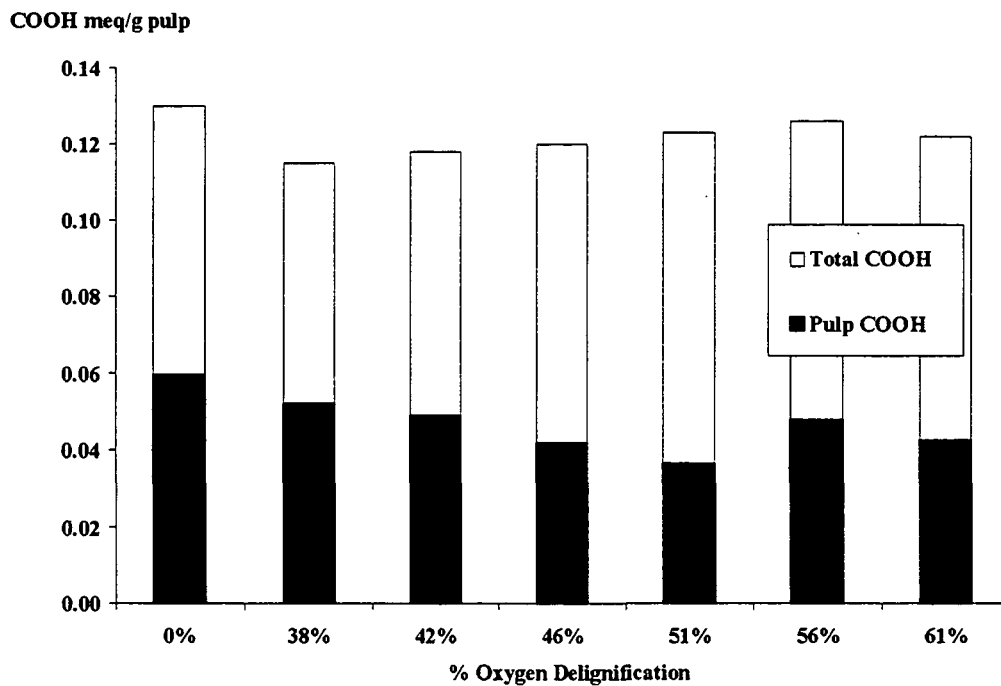


Figure 15. Total (pulp and dissolved) and pulp carboxylic acid concentrations for ozonated PSAQ pulp.

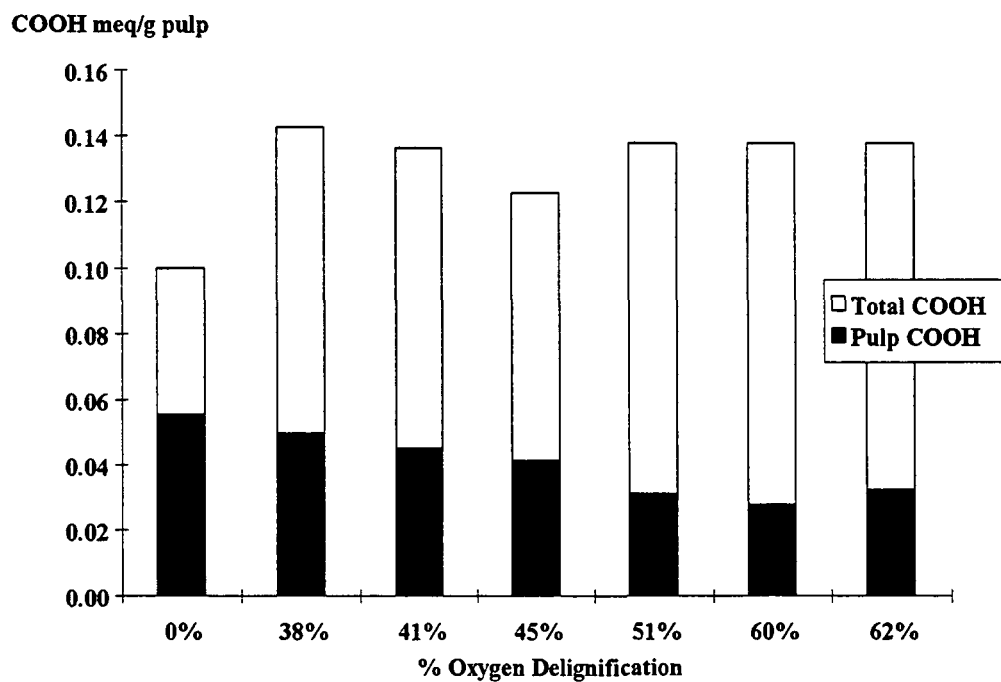


Figure 16. Total (pulp and dissolved) and pulp carboxylic acid concentrations for ozonated low lignin (K-22) kraft pulp.

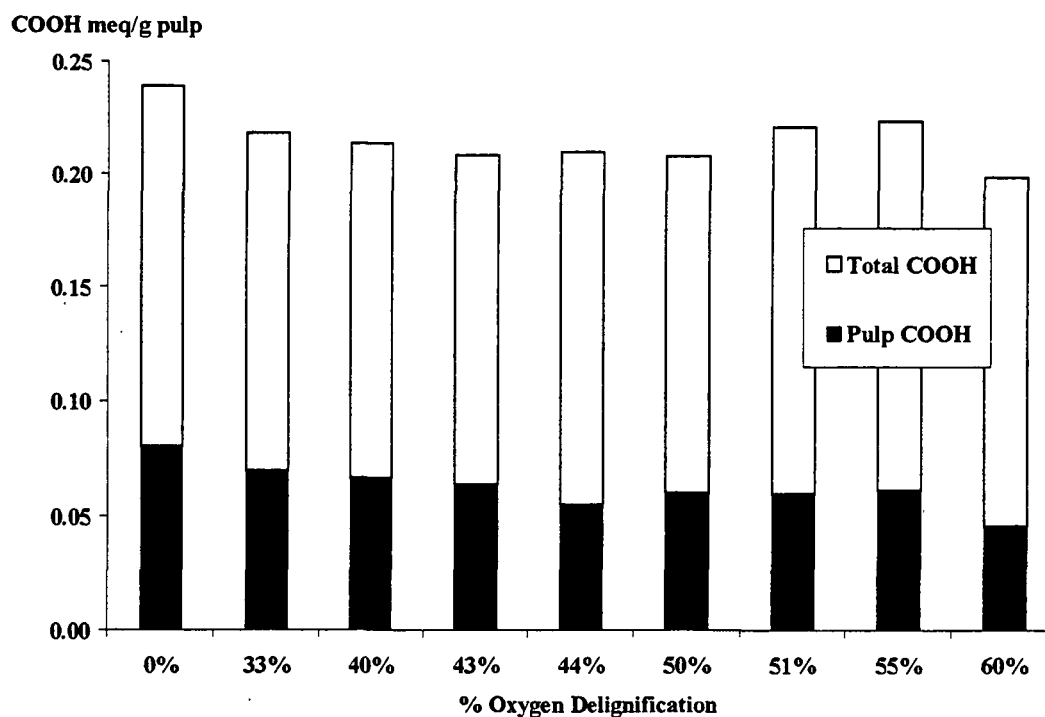


Figure 17. Total (pulp and dissolved) and pulp carboxylic acid concentrations for ozonated high lignin (K-31) kraft pulp.

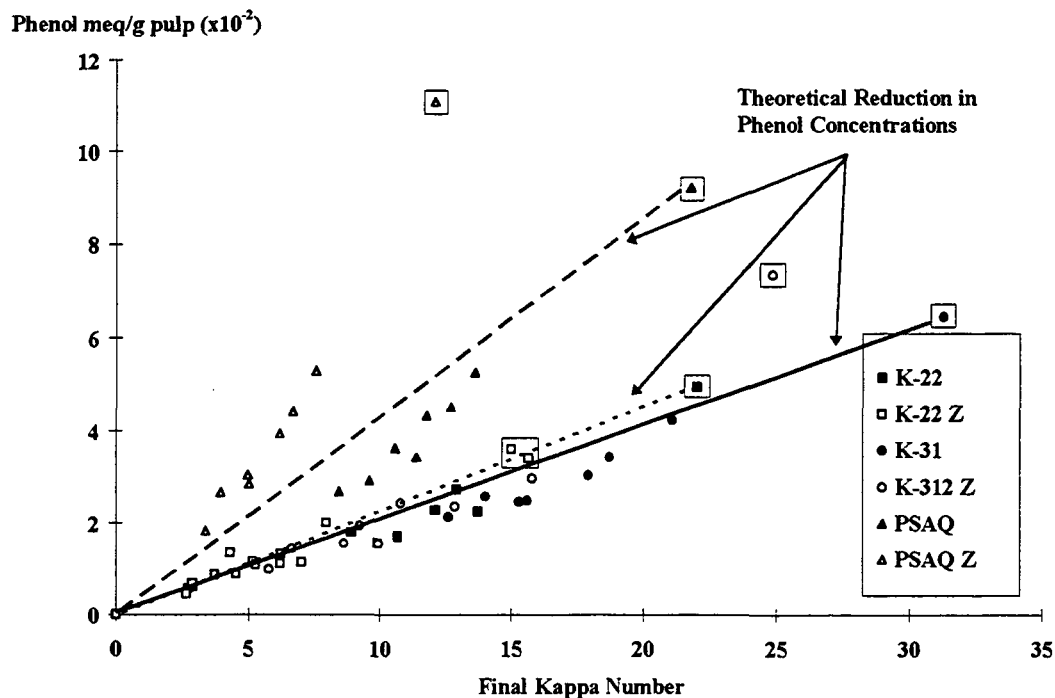


Figure 18. Phenol concentrations in pulp after oxygen and ozone. The Z suffix represents ozonated pulps (open symbols). Boxed points are pulps with no oxygen delignification.

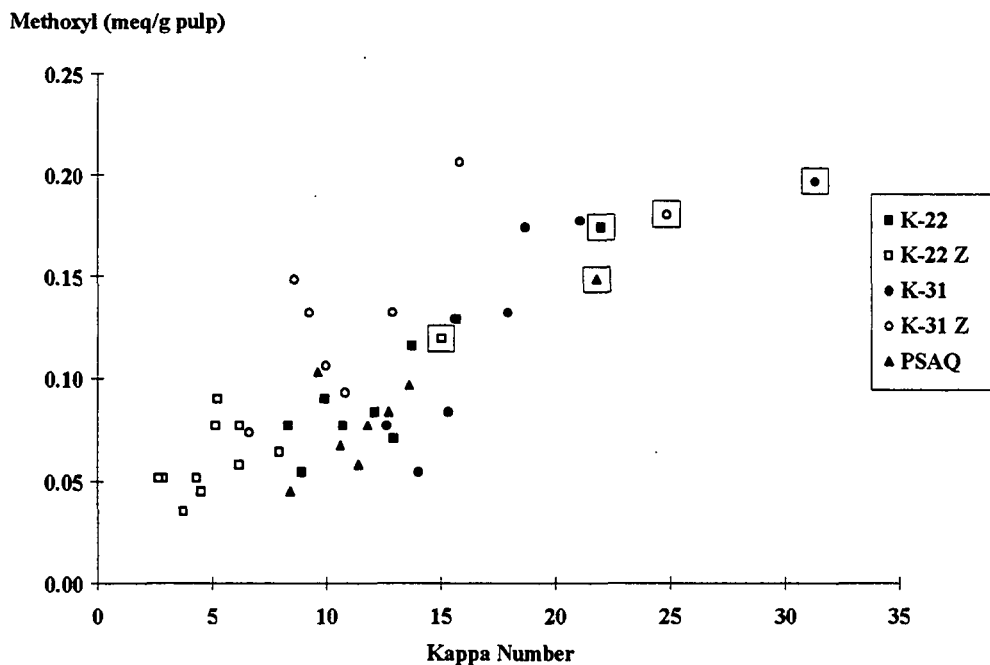


Figure 19. Methoxyl concentrations in pulp after oxygen and ozone. The Z suffix represents ozonated pulps (open symbols); boxed points are pulps with no oxygen delignification.

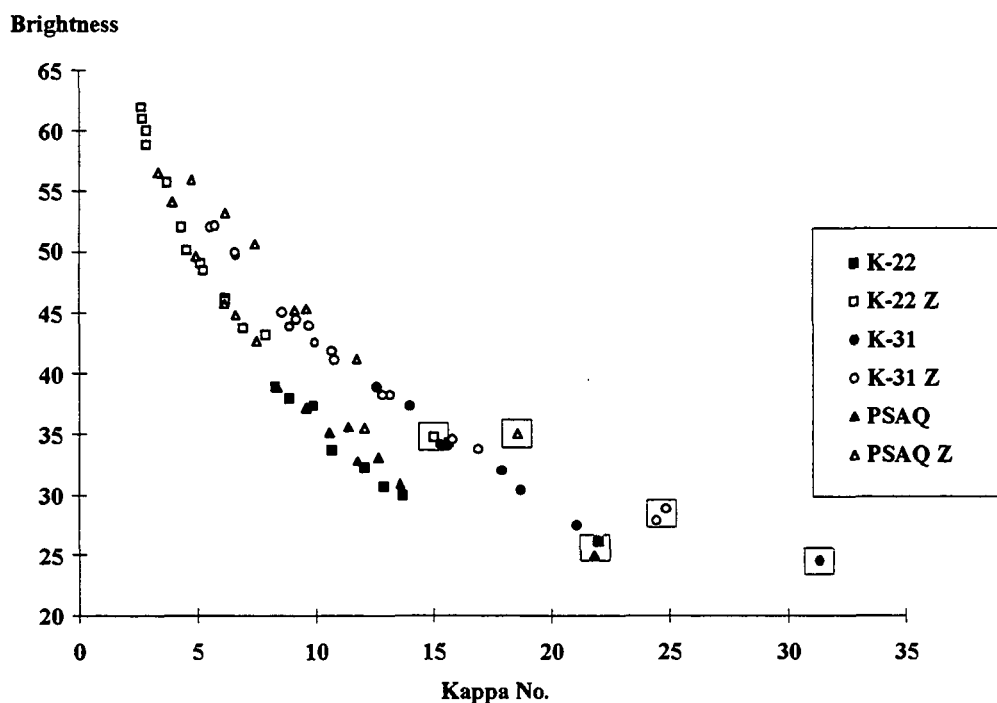


Figure 20. Brightness in oxygen delignified and ozone bleached pulps. The Z suffix represents ozonated pulps (open symbols); boxed points are pulps with no oxygen delignification.

**Table 1. Oxygen Delignification Methods**

Sample # <sup>a</sup>	o.d. g pulp	% NaOH	T (°C)	P (psi)	Time (min.)	Final pH	Kappa # <sup>b</sup>	% O <sub>2</sub> Delig.
K22-BS	-	-	110	100	-	-	22	-
K22-O38	140	1.0	110	100	30	9.4	14	38
K22-O41	140	1.3	110	100	30	9.5	13	41
K22-O45	140	1.5	110	100	30	9.8	12	45
K22-O47	140	1.7	110	100	40	9.5	12	46
K22-O51	140	2.0	116-117	100	60	9.8	11	51
K22-O55	100	1.7	110	100	40	9.2	10	55
K22-O59	140	2.5	110	100	60	9.4	9	60
K22-O62	140	2.0	110	100	60	9.8	8	62
K22-CN2	140	0.0	110	100	60	7.3	23	2
K22-CN2Alk	140	2.0	110	100	60	12.5	20	10
K22-CO2	140	-	110	100	60	6.6	20	7
K31-BS	-	-	110	100	-	-	31	-
K31O2-33	180	0.9	110	100	30	9.14	21	33
K31O2-40	180	1.3	110	100	30	9.37	19	40
K31O2-43	180	1.5	110	100	30	9.34	18	43
K31C-O2-44	180	2.0	110	100	30	9.54	18	44
K31O2-46	180	1.3	110	100	60	9.34	17	46
K31O2-50	180	2.0	110	100	30	9.62	16	50
K31O2-51	180	2.0	110	100	30	9.38	15	51
K31O2-55	180	2.5	110	100	40	9.66	14	55
K31O2-60	180	2.5	110	100	60	9.48	13	60
K31C-O2	180	-	110	100	30	7.77	28	10
K31C-N2	180	2.0	110	100	30	11.88	31	-
PSAQ22-BS	180	-	110	100	-	-	22	-
PSAQ22-O2-37	180	0.7	110	100	25	9.33	14	38
PSAQ22-O2-42	180	0.9	110	100	27	9.21	13	42
PSAQ22-O2-46	180	1.1	110	100	28	9.26	12	46
PSAQ22-O2-48	180	1.3	110	100	25	9.32	11	48
PSAQ22-O2-48	180	1.3	110	100	28	9.61	11	48
PSAQ22-O2-51	180	1.3	110	100	30	9.45	11	51
PSAQ22-O2-56	180	1.5	110	100	30	9.61	10	56
PSAQ22-O2-61	180	1.7	110	100	40	9.51	8	62
PSAQ22C-O2-	180	-	110	100	30	7.79	17	20
PSAQ22C-N2	180	1.3	110	100	30	11.4	17	22

<sup>a</sup> The samples names can be deciphered as follows: the prefix K refers to kraft pulps and PSAQ refers to polysulfide anthraquinone pulps. The second number refers to the initial kappa number, the suffix refers to the extent of oxygen delignification. The samples ending in O2 and N2 refer to oxygen and nitrogen control pulps.

<sup>b</sup> Average of duplicate kappa number measurements.

**Table 2. Ozone Bleaching Methods**

Sample # <sup>a</sup>	Weight Ozonated Pulp (o.d. g)		% Consistency		%Ozone Charge <sup>c</sup>		% Consumption	
	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Z1	Z2	Z1	Z2	Z1	Z2
K22-BS	40	40	35	-	0.40	0.40	93	93
K22-O38	40	40	37	-	-	-	-	-
K22-O41	40	40	36	-	0.41	0.44	84	87
K22-O45	40	40	37	-	0.45	0.44	90	91
K22-O47	40	40	-	-	0.51	0.52	83	83
K22-O51	40	40	36	-	0.43	0.35	84	83
K22-O55	40	40	36	-	0.41	-	82	-
K22-O59	40	40	37	-	0.39	0.41	79	83
K22-O62	40	40	38	-	0.40	0.41	79	80
K22-CN2	40	40	38	-	0.40	0.40	91	90
K22-CN2Alk	40	40	38	-	0.40	0.40	90	90
K22-CO2	40	40	38	-	0.38	0.39	88	91
K31-BS	50	50	32	32	0.39	0.35	92	97
K31O2-33	50	50	36	36	0.44	0.40	94	94
K31O2-40	50	50	33	33	0.41	0.38	89	86
K31O2-43	50	50	36	36	0.40	0.41	88	88
K31C-O2-44	50	50	37	37	0.40	0.45	94	95
K31O2-46	50	50	-	-	-	-	-	-
K31O2-50	50	50	36	36	0.40	0.42	90	91
K31O2-51	50	50	36	36	0.33	0.40	91	92
K31O2-55	50	50	37	37	0.38	0.43	89	93
K31O2-60	50	50	36	36	0.42	0.40	90	94
K31C-O2	50	50	35	35	0.41	0.40	91	90
K31C-N2	50	50	36	36	0.45	0.39	92	92
PSAQ22-BS	50	50	35	35	0.42	0.39	89	85
PSAQ22-O2-37	50	50	44	44	0.43	0.37	87	87
PSAQ22-O2-42	50	50	43	43	0.39	0.42	83	87
PSAQ22-O2-46	50	50	41	41	0.39	0.35	84	80
PSAQ22-O2-48	50	50	38	38	0.38	0.35	83	76
PSAQ22-O2-48	50	50	-	-	-	-	-	-
PSAQ22-O2-51	50	50	41	41	0.38	0.39	79	78
PSAQ22-O2-56	50	50	40	40	0.44	0.37	78	74
PSAQ22-O2-61	50	50	40	40	0.38	0.36	73	70
PSAQ22C-O2-	50	50	44	44	0.41	0.40	88	89
PSAQ22C-N2	50	50	44	44	0.40	0.42	89	89

<sup>a</sup> See footnote a in Table 1.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Ozone charge based on amount of ozone consumed.

**Table 3. Ozone Filtrate Methods**

Sample # <sup>a</sup>	Filtrate Volume (mL)		Filtrate Initial pH		meq NaOH/L <sup>c</sup>		Filtrate Final pH	
	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Z1	Z2	Z1	Z2	Z1	Z2
K22-BS	1114	1140	3.08	3.10	4.3	4.3	-	-
K22-O38	1160	1160	-	3.00	5.1	4.7	6.7	6.6
K22-O41	1140	1140	3.01	2.89	4.7	4.8	7.5	6.8
K22-O45	1070	1070	2.98	3.04	4.6	4.6	6.3	6.4
K22-O47	1160	1160	3.04	2.98	4.8	4.8	-	-
K22-O51	1130	1140	2.94	3.02	4.9	4.8	6.4	6.4
K22-O55	1130	-	2.96	-	4.9	-	6.4	-
K22-O59	1150	1110	3.02	2.97	4.8	5.0	6.5	6.4
K22-O62	1140	1100	2.99	3.05	4.8	5.0	6.3	6.4
K22-CN2	1135	1120	2.90	2.92	4.2	4.2	6.1	6.4
K22-CN2Alk	1145	1145	2.89	3.13	4.1	4.1	6.5	6.5
K22-CO2	1135	1145	2.93	2.95	4.4	4.4	6.4	6.4
K31-BS	1080	1100	2.91	2.86	7.4	7.2	7.0	7.0
K31O2-33	1140	1150	2.90	2.91	6.4	6.6	7.0	7.0
K31O2-40	1140	1140	2.99	2.95	6.4	6.5	7.0	7.0
K31O2-43	1120	1120	3.01	3.01	6.4	6.5	7.0	7.1
K31C-O2-44	1140	1140	2.87	2.84	6.7	6.8	7.0	7.0
K31O2-46	-	-	-	-	-	-	-	-
K31O2-50	1120	1130	3.34	2.92	6.5	6.6	7.0	7.1
K31O2-51	1120	1140	3.14	2.92	7.2	7.1	7.0	7.0
K31O2-55	1140	1140	2.87	2.82	7.1	7.2	7.0	7.0
K31O2-60	1140	1150	2.93	2.83	6.9	6.5	7.0	7.0
K31C-O2	1120	1120	2.90	2.97	6.3	6.5	7.0	7.0
K31C-N2	1110	1130	2.95	2.95	6.4	6.3	7.0	7.0
PSAQ22-BS	1120	1140	2.87	2.86	5.8	5.7	7.0	7.0
PSAQ22-O2-37	1130	1140	2.98	2.93	5.1	5.0	7.1	7.0
PSAQ22-O2-42	1160	1120	2.94	2.96	5.1	5.3	7.0	7.0
PSAQ22-O2-46	1100	1100	2.78	2.80	5.5	5.5	7.0	7.0
PSAQ22-O2-48	1130	1140	2.40	2.44	9.0	8.9	7.0	7.0
PSAQ22-O2-48	-	-	-	-	-	-	-	-
PSAQ22-O2-51	1165	1160	2.98	2.96	5.2	5.3	7.0	7.0
PSAQ22-O2-56	1150	1140	3.00	2.96	5.5	5.5	7.0	7.0
PSAQ22-O2-61	1140	1140	2.91	2.90	5.4	5.4	7.0	7.0
PSAQ22C-O2-	1120	1120	2.99	2.97	5.5	5.8	7.0	7.1
PSAQ22C-N2	1120	1140	2.96	2.95	5.5	5.4	7.0	7.0

<sup>a</sup> See footnote a in Table 1.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Milliequivalents required to titrate pulp plus filtrate to final pH using 0.1 N NaOH.

**Table 4. Viscosity Data**

Sample # <sup>a</sup>	Average Viscosities <sup>c</sup>			Average Reduced Viscosities <sup>c,d</sup>		
	Unozonated	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Unozonated	Z1	Z2
K22-B5	24	19	18	21	20	19
K22-O38	18	14	14	18	16	-
K22-O41	17	13	13	18	15	15
K22-O45	16	12	12	16	14	14
K22-O47	-	-	-	-	-	-
K22-O51	15	11	12	16	14	14
K22-O55	15	10	-	15	-	-
K22-O59	14	10	10	14	12	12
K22-O62	16	10	10	15	12	12
K22-CN2	22	17	15	22	-	-
K22-CN2Alk	21	15	15	20	-	-
K22-CO2	20	16	16	21	18	-
K31-B5	29	26	26	30	28	-
K31O2-33	20	18	19	23	20	-
K31O2-40	19	18	18	21	20	-
K31O2-43	18	16	17	20	19	-
K31C-O2-44	-	14	14	-	-	-
K31O2-46	-	-	-	-	-	-
K31O2-50	17	15	15	18	18	-
K31O2-51(50b)	17	16	16	18	17	-
K31O2-55	15	14	14	17	16	-
K31O2-60	13	13	13	17	15	-
K31C-O2	25	23	24	28	-	-
K31C-N2	27	24	24	28	-	-
PSAQ22-B5	18	15	15	-	18	17
PSAQ22-O2-37	16	13	13	-	16	15
PSAQ22-O2-42	15	12	12	-	14	14
PSAQ22-O2-46	15	12	12	-	14	14
PSAQ22-O2-48	14	12	12	-	14	14
PSAQ22-O2-48		-	-	-	-	-
PSAQ22-O2-51	14	11	12	-	13	13
PSAQ22-O2-56	14	11	10	-	14	12
PSAQ22-O2-61	13	10	10	-	12	11
PSAQ22C-O2-	18	13	14	-	17	17
PSAQ22C-N2	18	14	14	-	16	16

<sup>a</sup> See footnote a in Table 1.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Averages of duplicate viscosity measurements for most samples.

<sup>d</sup> Reduced viscosities are viscosity measurements of pulps after sodium borohydride reduction.



**Table 5. Papermaking Properties**

Sample # <sup>a</sup>	Brightness, dir. %			Z-Span (kN/m)			Breaking length (km)			Ozone % Yield	
	Unozone- ated	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Unozone- ated	Z1	Z2	Unozone- ated	Z1	Z2	Z1	Z2
K22-BS	26	35	34	7.9	7.5	7.6	12.5	11.7	11.9 <sup>c</sup>	-	-
K22-O38	30	43	44	6.4	6.2	6.8	10.1	9.7 <sup>c</sup>	10.6 <sup>c</sup>	96.2	96.5
K22-O41	31	46	46	6.3	6.2	6.3	9.9	9.6 <sup>c</sup>	9.8 <sup>c</sup>	97.1	97.4
K22-O45	32	49	49	5.8	6.0	5.9	9.2	9.3	9.2	97.1	96.9
K22-O47	-	-	-	-	-	-	-	-	-	-	-
K22-O51	34	52	50	5.8	5.4	5.4	9.2	8.7	8.6	98.9	98.3
K22-O55	37	56		7.0	5.6	-	-	9.2	-	98.2	-
K22-O59	38	59	60	6.0	5.3	5.3	9.5	8.3	8.4	99.4	98.5
K22-O62	39	61	62	5.9	5.6	5.7	9.4	8.8	8.8	96.8	96.5
K22-CN2	25	32	32	6.3	5.6	6.1	9.9	8.8 <sup>c</sup>	9.6 <sup>c</sup>	98.3	98.1
K22-CN2Alk	27	37	37	6.0	5.7	6.1	9.6	9.0 <sup>c</sup>	9.6 <sup>c</sup>	98.0	97.8
K22-CO2	27	35	35	6.1	5.7	5.3	9.6	8.9 <sup>c</sup>	8.2 <sup>c</sup>	96.7	97.1
K31-BS	25	29	28	7.5	8.3	8.0	11.9	13.5	12.9	99.3	100.9
K31O2-33	28	35	34	5.5	6.3	6.6	8.7	10.2	10.5	99.9	105.3
K31O2-40	30	38	38	5.5	6.6	7.2	8.7	10.5	11.2	98.7	96.2
K31O2-43	32	41	42	4.8	7.0	6.6	9.5	11.2	10.5	98.1	97.5
K31C-O2-44	-	45	44	6.7	6.5	5.6	10.6	10.5	9.4	100.0	104.3
K31O2-50	34	45	44	6.6	6.1	6.6	11.1	9.5	11.4	97.5	98.8
K31O2-51	34	43	45	6.3	6.2	6.4	10.4	9.8	10.6	100.3	102.5
K31O2-55	37	50	50	5.9	5.9	6.4	9.4	9.6	10.3	98.8	98.7
K31O2-60	39	52	52	5.2	6.4	6.5	8.6	10.4	10.7	99.5	99.5
K31C-O2	25	29	29	5.5	6.4	6.9	8.8	10.0	11.1	98.4	99.1
K31C-N2	24	29	28	5.8	6.1	6.7	9.2	10.0	11.0	99.4	100.2
PSAQ22-BS	25	36	35	6.4	6.3	6.5	10.3	10.2	10.6	98.5	99.0
PSAQ22-O2-37	31	43	41	5.1	5.4	5.5	8.1	8.5	8.6	97.9	97.7
PSAQ22-O2-42	33	45	45	5.4	4.9	4.9	8.6	7.8	7.8	98.5	98.4
PSAQ22-O2-46	33	46	45	5.2	5.2	5.4	8.2	8.2	8.4	97.4	97.4
PSAQ22-O2-48	36	50	50	5.3	5.0	5.2	8.4	8.0	8.1	98.7	99.0
PSAQ22-O2-48	-	-	-	-	-	-	-	-	-	-	-
PSAQ22-O2-51	35	50	51	5.0	5.2	4.9	8.0	8.2	7.9	98.6	99.2
PSAQ22-O2-56	37	54	53	5.1	5.3	4.8	8.0	8.3	7.7	98.7	98.8
PSAQ22-O2-61	39	57	56	5.0	4.7	4.8	7.9	7.3	7.5	99.0	97.8
PSAQ22C-O2-	28	36	37	5.1	5.6	5.4	8.0	8.9	8.6	97.5	96.6
PSAQ22C-N2	28	36	37	5.4	5.6	5.6	8.6	8.7	8.8	95.7	96.9

<sup>a</sup> See footnote a in Table 1.<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.<sup>c</sup> From basis weight estimates.

Table 6. Lignin Data

Sample # <sup>a</sup>	% Soluble Lignin			% Insoluble Lignin			Total % Lignin			Average Kappa Number <sup>c</sup>			mg lignin/g pulp, estimated <sup>d</sup>		
	Unozon.	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Unozon.	Z1	Z2	Unozon.	Z1	Z2	Unozon.	Z1	Z2	Unozon.	Z1	Z2
K22-BS	0.4	-	-	3.4	-	-	3.8	-	-	22.0	15.0	15.7	33.0	22.5	23.5
K22-O38	0.5	-	-	2.2	-	-	2.7	-	-	13.7	7.9	7.0	20.6	11.9	10.4
K22-O41	0.5	-	-	1.5	-	-	2.1	-	-	12.9	6.2	6.2	19.4	9.3	9.3
K22-O45	0.5	-	-	1.6	-	-	2.1	-	-	12.1	5.1	5.2	18.2	7.7	7.9
K22-O47	-	-	-	-	-	-	0.0	-	-	11.8	-	-	17.7	0.0	-
K22-O51	0.6	-	-	1.8	-	-	2.4	-	-	10.7	4.3	4.5	16.1	6.4	6.8
K22-O55	0.6	-	-	1.1	-	-	1.7	-	-	9.9	3.7	-	14.9	5.5	-
K22-O59	0.6	-	-	1.0	-	-	1.6	-	-	8.9	2.8	2.8	13.4	4.2	4.2
K22-O62	0.4	-	-	0.8	-	-	1.2	-	-	8.3	2.7	2.6	12.5	4.0	3.9
K22-CN2	0.6	-	-	6.2	-	-	6.8	-	-	22.5	15.1	15.0	33.8	22.6	22.5
K22-CN2Alk	0.6	-	-	6.5	-	-	7.1	-	-	19.9	12.0	11.8	29.9	17.9	17.7
K22-CO2	0.5	-	-	2.5	-	-	3.0	-	-	20.4	12.9	12.9	30.6	19.3	19.4
K31-BS	-	0.4	-	4.1	3.4	3.2	4.1	3.9	3.2	31.3	24.9	24.5	47.0	37.3	36.7
K31O2-33	-	0.5	-	2.8	2.0	1.7	2.8	2.5	1.7	21.1	15.8	16.9	31.7	23.7	25.4
K31O2-40	-	0.5	-	2.6	1.6	1.2	2.6	2.1	1.2	18.7	12.9	13.2	28.1	19.3	19.7
K31O2-43	-	0.5	-	2.3	1.3	0.9	2.3	1.8	0.9	17.9	10.8	10.7	26.9	16.2	16.1
K31C-O2-44	-	0.5	-	2.7	1.1	0.7	2.7	1.6	0.7	17.5	8.6	9.7	26.3	12.9	14.6
K31O2-50	-	0.5	-	1.9	0.9	0.3	1.9	1.4	0.3	15.6	9.2	8.9	23.4	13.8	13.4
K31O2-51	-	0.5	-	1.7	0.9	0.6	1.7	1.5	0.6	15.3	10.0	-	23.0	14.9	-
K31O2-55	-	0.5	-	1.7	0.4	-	1.7	0.9	-	14.0	6.6	6.7	21.0	9.9	10.0
K31O2-60	-	0.5	-	1.1	0.2	-	1.1	0.6	-	12.6	5.8	5.6	18.9	8.6	8.3
K31C-O2	-	-	-	-	-	-	-	-	-	28.1	21.7	21.5	42.2	32.6	32.3
K31C-N2	-	-	-	-	-	-	-	-	-	31.3	21.4	21.0	47.0	32.1	31.5
K31C-ClO2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

**Table 6 Continued. Lignin Data**

Sample # <sup>a</sup>	% Soluble Lignin			% Insoluble Lignin			Total % Lignin			Average Kappa Number <sup>c</sup>			mg lignin/g pulp, estimated <sup>d</sup>		
	Unozon.	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Unozon.	Z1	Z2	Unozon.	Z1	Z2	Unozon.	Z1	Z2	Unozon.	Z1	Z2
PSAQ22-BS	0.6	0.4	-	3.0	-	-	3.6	0.4	-	21.8	12.1	12.4	32.7	18.2	18.6
PSAQ22-O2-37	0.5	0.4	-	1.7	-	-	2.1	0.4	-	13.6	7.5	7.8	20.4	11.3	11.8
PSAQ22-O2-42	0.7	0.4	-	1.0	-	-	1.8	0.4	-	12.7	6.7	6.4	19.1	10.0	9.6
PSAQ22-O2-46	0.6	0.4	-	0.7	-	-	1.4	0.4	-	11.8	6.2	6.1	17.7	9.2	-
PSAQ22-O2-48	0.6	0.4	-	1.0	-	-	1.6	0.4	-	11.4	-	5.0	17.1	-	-
PSAQ22-O2-48	-	-	-	-	-	-	-	-	-	11.3	-	-	17.0	-	-
PSAQ22-O2-51	0.8	0.4	-	0.8	-	-	1.6	0.4	-	10.6	5.0	5.0	15.9	7.4	7.5
PSAQ22-O2-56	0.9	0.4	-	0.5	-	-	1.4	0.4	-	9.6	3.9	4.1	14.4	5.9	6.2
PSAQ22-O2-61	0.7	0.4	-	0.6	-	-	1.2	0.4	-	8.4	3.3	3.2	12.6	5.0	4.7
PSAQ22C-O2-	0.6	-	-	2.3	-	-	2.9	-	-	17.4	10.7	10.5	26.1	16.0	15.7
PSAQ22C-N2	0.8	-	-	1.1	-	-	2.0	-	-	17.1	10.6	10.6	25.7	15.9	15.9

<sup>a</sup> See footnote a in Table 1.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Averages of duplicate kappa number measurements.

<sup>d</sup> Estimated lignin values = %lignin = kappa # x 0.15

**Table 7. Pulp Functional Groups**

Sample # <sup>a</sup>	COOH, meq/g pulp <sup>c</sup>			OCH <sub>3</sub> , meq/g pulp <sup>d</sup>			PhOH, meq/g pulp <sup>e</sup>		
	Unozonated	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Unozonated	Z1	Z2	Unozonated	Z1	Z2
K22-BS	0.06	0.06	0.06	0.17	0.12	0.13	4.96	3.60	3.40
K22-O38	0.06	0.05	0.05	0.12	0.06		2.26	2.02	1.15
K22-O41	0.07	0.05	0.04	0.07	0.08	0.06	2.73	1.34	1.13
K22-O45	0.06	0.05	0.04	0.08	0.08	0.09	2.29	1.16	1.08
K22-O47	-	-	-	-	-	-	-	-	-
K22-O51	0.06	0.03	0.03	0.08	0.05	0.05	1.71	1.36	0.89
K22-O55	0.06	0.03	-	0.09	0.04	-	1.57	0.87	-
K22-O59	0.05	0.03	0.03	0.05	0.05	0.05	1.80	0.61	0.67
K22-O62	0.06	0.03	0.03	0.08	0.05	0.05	3.53	0.57	0.46
K22-CN2	0.06	0.06	0.06	0.19	0.14	0.12	4.50	5.58	3.66
K22-CN2Alk	0.06	0.05	0.05	0.09	0.11	0.10	2.34	2.82	2.21
K22-CO2	0.06	0.05	0.06	0.15	0.13	0.09	2.74	3.03	3.14
K31-BS	0.08	0.08	0.08	0.20	0.18	-	6.47	7.36	-
K31O2-33	0.08	0.07	0.07	0.18	0.21	-	4.23	2.97	-
K31O2-40	0.09	0.07	0.07	0.17	0.13	-	3.43	2.38	-
K31O2-43	0.09	0.06	0.07	0.13	0.09	-	3.04	2.44	-
K31C-O2-44	-	0.05	0.06	-	0.15	-	-	1.56	-
K31O2-46	-	-	-	-	-	-	-	-	-
K31O2-50	0.08	0.06	0.06	0.13	0.13	-	2.49	1.95	-
K31O2-51	0.08	0.06	0.05	0.08	0.11	-	2.47	1.56	-
K31O2-55	0.08	0.06	0.07	0.05	0.07	-	2.60	1.45	-
K31O2-60	0.08	0.04	0.05	0.08	-	-	2.15	0.99	-
K31C-O2	0.08	0.08	0.08	0.19	-	-	6.76	4.68	-
K31C-N2	0.09	0.07	0.08	0.20	-	-	-	6.32	-
PSAQ22-BS	0.06	0.06	0.06	0.15	-	-	9.22	11.10	-
PSAQ22-O2-37	0.06	0.05	0.06	0.10	-	-	5.26	5.29	-
PSAQ22-O2-42	0.05	0.04	0.05	0.08	-	-	4.51	4.41	-
PSAQ22-O2-46	0.05	0.04	0.04	0.08	-	-	4.34	3.94	-
PSAQ22-O2-48	0.06	0.04	0.05	0.06	-	-	3.43	3.02	-
PSAQ22-O2-48	-	-	-	-	-	-	-	-	-
PSAQ22-O2-51	0.05	0.04	0.04	0.07	-	-	3.62	3.05	2.85
PSAQ22-O2-56	0.06	0.05	0.05	0.10	-	-	2.92	2.67	-
PSAQ22-O2-61	0.06	0.04	0.05	0.05	-	-	2.68	1.84	-
PSAQ22C-O2-	0.06	0.05	0.05	0.12	-	-	7.40	7.87	-
PSAQ22C-N2	0.06	0.05	0.05	0.13	-	-	7.79	7.61	-

<sup>a</sup> See footnote a in Table 1.      <sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Carboxylic acids      <sup>d</sup> Methoxyl groups      <sup>e</sup> Phenols

**Table 8. Ozone Filtrate Data**

Sample # <sup>a</sup>	Carboxylic Acids				Soluble TOC		Dissolved Glucose		Dissolved Lignin		Elemental Analysis <sup>d</sup>		
	Total meq/g pulp		Filtrate meq/g pulp <sup>c</sup>		mg C/g pulp		mg/L filtrate		(% pulp)				
	Z1 <sup>b</sup>	Z2 <sup>b</sup>	Z1	Z2	Z1	Z2	Z1	Z2	Z1	Z2	%C	%H	%O
K22-BS	0.10	0.10	0.04	0.04	2.3	0.0	220.1		1.11		38	3	44
K22-O38	0.15	0.14	0.10	0.09	4.6	4.6	51.9	52.7	0.16	0.2	33	3	45
K22-O41	0.14	0.14	0.09	0.09	4.6	4.8	57.3	50.2	0.19	0.2	-	-	-
K22-O45	0.12	0.12	0.09	0.09	3.5	3.7	46.2	44.2	0.18	0.2	-	-	-
K22-O47	0.12	0.12	-	-	-	-	-	-	-	-	-	-	-
K22-O51	0.14	0.14	0.11	0.11	3.5	3.6	45.6	43.2	0.18	0.2	32	3	44
K22-O55	0.14	-	-	-	3.5	-	43.7	-	0.19	-	-	-	-
K22-O59	0.14	0.14	0.11	0.11	4.2	4.0	47.8	49.7	0.17	0.2	-	-	-
K22-O62	0.14	0.14	0.11	0.11	2.5	4.1	58.2	38.6	0.18	0.2	-	-	-
K22-CN2	0.12	0.12	0.06	0.06	4.1	3.9	32.7	29.7	0.16	0.2	-	-	-
K22-CN2Alk	0.12	0.12	0.07	0.07	4.2	4.1	53.7	49.9	0.20	0.2	-	-	-
K22-CO2	0.13	0.13	0.07	0.07	4.4	4.8	45.4	45.1	0.15	0.2	-	-	-
K31-BS	0.16	0.16	0.08	0.08	3.6	3.3	52.7	60.7	0.15	0.2	36	3	42
K31O2-33	0.15	0.15	0.08	0.08	3.6	3.6	94.1	85.3	0.29	0.3	38	3	44
K31O2-40	0.15	0.15	0.08	0.08	4.7	4.8	54.4	55.7	0.18	0.2	-	-	-
K31O2-43	0.14	0.15	0.07	0.07	4.7	4.8	70.2	66.3	0.19	0.2	-	-	-
K31C-O2-44	0.15	0.16	0.10	0.10	4.1	3.7	90.1	85.2	0.21	0.2	-	-	-
K31O2-50	0.15	0.15	0.08	0.09	3.8	5.4	85.8	82.0	0.22	0.3	39	2	40
K31O2-51	0.16	0.16	0.11	0.11	4.4	5.4	60.6	77.2	0.13	0.2	-	-	-
K31O2-55	0.16	0.16	0.09	0.10	5.1	5.3	85.5	68.3	0.17	0.2	-	-	-
K31O2-60	0.16	0.15	0.11	0.10	5.5	5.3	107.5	94.7	0.24	0.2	-	-	-
K31C-O2	0.14	0.15	0.07	0.07	4.6	4.7	73.5	73.4	0.16	0.2	-	-	-
K31C-N2	0.14	0.14	0.06	0.06	4.8	4.7	80.2	70.7	0.15	0.2	-	-	-
PSAQ22-BS	0.13	0.13	0.07	0.07	3.8	2.9	54.2	53.0	0.14	0.2	36	3	43
PSAQ22-O2-37	0.12	0.12	0.06	0.06	2.7	2.7	72.7	69.3	0.15	0.2	35	3	46
PSAQ22-O2-42	0.12	0.12	0.06	0.06	2.3	2.5	40.1	51.1	0.13	0.1	-	-	-
PSAQ22-O2-46	0.12	0.12	0.08	0.08	2.4	2.7	61.1	71.6	0.13	0.1	-	-	-
PSAQ22-O2-48	0.20	0.20	0.15	0.15	2.4	2.5	50.6	60.9	0.15	0.1	-	-	-
PSAQ22-O2-51	0.12	0.12	0.09	0.09	2.8	3.0	72.9	84.7	0.20	0.2	36	3	45
PSAQ22-O2-56	0.13	0.13	0.08	0.08	3.0	3.0	91.6	93.7	0.18	0.2	-	-	-
PSAQ22-O2-61	0.12	0.12	0.08	0.08	2.6	2.7	77.3	75.7	0.14	0.1	-	-	-
PSAQ22C-O2-	0.12	0.13	0.08	0.08	2.7	3.1	38.1	52.3	0.19	0.2	-	-	-
PSAQ22C-N2	0.12	0.12	0.07	0.07	2.6	2.8	41.9	61.3	0.16	0.2	-	-	-

<sup>a</sup> See footnote a in Table 1.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Calculated as total COOH content minus pulp COOH content.

<sup>d</sup> Dry weight basis; uncorrected for ash.

**Table 9. Molar Ratios of Dissolved Solids in Ozone Filtrates**

Sample # <sup>a,b</sup>	Mole H / Mole C <sup>c</sup>	Mole O / Mole C <sup>c</sup>
	0.88	0.87
K22-BS-Z1		
K22-O2-38-Z1	1.21	1.02
K22-O2-51-Z1	1.14	1.02
K31-BS-Z1	1.04	0.88
K31-O2-38-Z1	1.10	0.88
K31-O2-51-Z1	0.76	0.78
PSAQ-BS-Z1	1.11	0.9
PSAQ-O2-38-Z1	1.12	0.96
PSAQ-O2-51-Z1	1.11	0.95

<sup>a</sup> The samples names can be deciphered as follows: the prefix K refers to kraft pulps and PSAQ refers to polysulfide anthraquinone pulps. The second number refers to the initial kappa number; the suffix refers to the extent of oxygen delignification. The samples ending in O2 and N2 refer to oxygen and nitrogen control pulps.

<sup>b</sup> Z1 and Z2 refer to duplicate ozonations.

<sup>c</sup> Dry weight basis; uncorrected for ash.

## APPENDIX I. SELECT PROCEDURES

### Ozonation

The standard operating procedure developed for IPST was used with slight modification.

The reaction system employed a modified Buchi rotary evaporator (rotovap) and a Welsbach Model T816 ozone generator. Ozone from the ozone outlet of the generator was introduced to the sample through the center inlet tube of the rotovap and, after coming in contact with the sample, exited through the vacuum outlet of the rotovap to a double trap system. The primary trap consisted of a gas washing bottle containing a known volume of 10% potassium iodide (KI) solution. The secondary trap was a 500 mL graduated cylinder equipped with a gas dispersion tube. This trap contained "Killer" solution (prepared from 125 g  $\text{Na}_2\text{SO}_3$ , 5 g KI, 2 L water, and 1 drop 4N  $\text{H}_2\text{SO}_4$ ). A similar system of traps was setup for a second ozone line as a blank to be run simultaneously with the sample.

First, the cold water and  $\text{O}_2$  was turned on (2 psig) for the ozonator and the instrument was set to flow rates of 1 and 0.2 L/min for  $\text{O}_3$  and sample flow, respectively. The pulp to be bleached was prepared by first creating a pulp slurry and lowering its pH to 2 by addition of  $\text{H}_2\text{SO}_4$ . The pulp was centrifuged for 10 min and water removed to achieve a consistency of approximately 35%. After fluffing, the pulp (50 g o.d.) was then placed into a 5 L round bottom flask and spun on the rotovap. The system was then checked for leaks. The  $\text{O}_3$  and sample rates were increased to 4 and 1 L/min. The  $\text{O}_2$  pressure was increased to 8 psig. The pulp was tumbled at an appropriate rate of about 1 spin/sec. The ozonator was turned on for a predetermined amount of time by flipping the switch on the generator and switching the flow from the cylinders to the traps. When the time was up, the stopcocks were switched to put the flow back through the cylinders and the ozonator was turned off. A stream of  $\text{N}_2$  was purged through the system for 15 minutes to remove excess  $\text{O}_3$ . The traps were removed from the system and 100 mL aliquats of each were titrated with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ , after adding 50 mL 4N  $\text{H}_2\text{SO}_4$  and starch indicator. The pulp was diluted with 1 L water and neutralized with a measured amount of NaOH. This slurry was soaked overnight to be titrated further the following day; upon sitting, the slurry's pH would drop. The slurry was then filtered and the collected pulp was washed with 200 mL of water and set to dry. The effluent volume amount was measured and then the effluent was stored in a cold room for future analysis.

Calculations:

$$\text{O}_3 \text{ produced} = (\text{total KI vol./aliquat})(\text{mL Na}_2\text{S}_2\text{O}_3 \text{ to sample})(0.1\text{N Na}_2\text{S}_2\text{O}_3)(0.024 \text{ g/eq})$$

$$\text{O}_3 \text{ applied} = (\text{ozone/sample split ratio}) (\text{O}_3 \text{ produced})$$

$$\text{O}_3 \text{ excess} = (\text{total KI vol./aliquat}) (\text{mL Na}_2\text{S}_2\text{O}_3 \text{ to ozone})(0.1\text{N Na}_2\text{S}_2\text{O}_3)(0.024 \text{ g/eq})$$

$$\text{O}_3 \text{ consumed} = \text{g applied} - \text{g excess}$$

$$\% \text{ O}_3 \text{ consumption} = (\text{g O}_3 \text{ consumed/g applied}) \times 100\%$$

$$\text{O}_3 \text{ charge} = [(\text{g applied} - \text{g excess})/\text{g o.d. pulp}] \times 100\%$$

### Kappa # and Viscosities

Tappi procedure T236 cm-85 was used for kappa analyses. T230 om-89 was used for viscosity measurements.

### Colorimetric Lignin Quantitation

Procedures T222 om-88 and UM 250 published by Tappi were adapted.

Each effluent sample was first filtered (5  $\mu$ m filters) and then combined with  $\text{H}_2\text{SO}_4$  to prepare a 3% sulfuric solution. The samples were allowed to sit for 1 hour and then filtered onto dry, weighed paper. A sample of filtrate was removed for UV analysis at 205 nm. Sample dilution and blanks were performed with 3%  $\text{H}_2\text{SO}_4$ . The filter containing the insoluble lignin was washed repeatedly with warm water and then dried for 1 hour at 132°C before re-weighing. When a cross-section of the samples showed no significant acid-insoluble lignin content, the weighing of the filter paper was eliminated. Samples were performed in duplicate in the beginning but, due to good reproducibility, the bulk of them were run singularly. Note: A sample of D-mannose was tested for absorbance (conc. = 62.5 g/L) to see if sugars in the sample might interfere. No absorbance was detected.

Calculations:

$$\text{g acid soluble lignin/L} = AD/110$$

A = Absorbance, D = Dilution factor, 110 = extinction coefficient adopted in the Tappi procedure.

$$\% \text{ lignin} = [(\text{g soluble lignin})(\text{total volume O}_3 \text{ effluent recovered})]/\text{g pulp ozonated}] \times 100\%$$

### Colorimetric Sugar Analysis

The following procedure was modified from that of Michel Dubois, Anal. Chem., 28 (3), 350-356 (1956).

Solutions containing 1 mL sugar solution, 1 mL 5% phenol, and 5 mL concentrated  $\text{H}_2\text{SO}_4$  were analyzed by UV absorption at 490 nm. Water was replaced for phenol in the reference solution. A linear calibration curve was first prepared using glucose, operating on the assumption that glucose would be representative of the filtrates to be analyzed. Each sample was then evaluated in duplicate to determine its sugar concentration. Concentrations were calculated by using the equation for the calibration curve.

### Molecular Weight Determination

Each effluent sample was filtered and LiCl added to achieve a concentration of 0.1 M. The pH was lowered to 5.5 with phosphoric acid. The sample was purged with  $\text{N}_2$  for 15 minutes to remove any carbonates. Calibrations were not performed due to time constraints. A curve for the gel permeation chromatography (GPC) calibration derived 2 weeks previous was used for the columns. Total organic carbon (TOC) calibrations from 2 months previous were used for TOC detection. A 5.00 mL sample was injected using a flow rate of 0.6 mL/min. and 0.1 M LiCl as eluent. A check on the calibration was neglected before the samples were determined. A mixture of four different polyethylene glycol standards was put through the column after all analyses to gauge the shift in calibration. Note: the GPC column had compacted itself while determining the last few samples. The first solution to this column compacting was merely to tighten the column's end cap to eliminate volume above the gel. At this point, however, the cap was fully extended so that when the column compacted further, it was necessary to carry on injecting the samples even though the volume above the gel would likely cause spreading of the resultant peaks.

### Moisture/ Ash Content of Freeze Dried O<sub>3</sub> Effluents

First, crucibles to be used were dried in an 105°C oven to a constant weight. A known amount of effluent sample was then added to each. These were placed in a 105°C oven and dried to a constant weight. The o.d. weighed samples were then placed into a 300°C high temperature oven. The temperature was ramped to 600°C, and maintained for 1 hour. The samples were then cooled in a dessicator overnight and re-weighed to determine their ash content.



## APPENDIX II. CARBONYL QUANTITATION

### Introduction:

An important aspect of Project F-015 was to examine how different percentages of oxygen followed by ozonation affected the functionality and selectivity. One functionality of particular interest was carbonyls. Quantitation of the carbonyl content of pulp both before and after ozonation provides a better understanding of this group's role in the depolymerization of both lignin and carbohydrates.

### Objective:

The objective of this investigation was to develop a method, based on examples in literature, which would be applicable in quantifying the carbonyl concentrations in the pulps of interest.

### Approach:

Two quantification reactions were evaluated: oxime and cyanohydrin formation. The former may be achieved by exposing a carbonyl containing compound to hydroxylamine hydrochloride. The amount of acid liberated is quantified by titration. Two methods for performing this were considered.

Cyanohydrin formation is initiated by combining the carbonyl compound with an excess of sodium cyanide. The unreacted cyanide is then quantified by titration with silver nitrate. Both methods have been cited as useful in quantitation at the levels at which this study is operating (1-3).

### Experimental and Results:

#### I. Oxime Formation

The first procedure attempted was suggested by J. W. Green (4). A 0.720M hydroxylamine solution was combined with cellulose under  $N_2$ . After a 50°C, 5 hour reaction with continuous  $N_2$  flow, an aliquat was back titrated with 0.1N HCl to a pH=3.2. Results from this method proved highly erratic and irreproducible. Klimova and Zabrodina (5) proposed that the presence of triethanolamine will drive the reaction by neutralizing the acid liberated in the oxime formation. The excess TEA is then titrated. A series of these reactions were performed by changing five reaction parameters. These parameter changes and selections of results follow.

#### 1. Time/Temperature (5 Hour and 50°C vs. 24 Hour and Room Temperature)

1.00 g pulp, 0.36 M $NH_2OH \cdot HCl$ , 0.017M TEA, 5 hr, 50°C, One $N_2$ Purge					
Sample #	mL 0.1N HCl to Blank	Final pH	Volume 0.1N HCl to Sample	Final pH	mmol C=O/g Sample
1	2.72	3.31	2.64	3.30	0.027
1	2.72	3.31	2.63	3.29	0.030
2	2.74	3.30	2.64	3.30	0.030
2	2.72	3.28	2.63	3.30	0.033
3	2.74	3.29	2.60	3.31	0.048
3	2.75	3.31	2.64	3.31	0.035

Mean = 0.034 mmol C=O, s = 0.0077, Coefficient of Variation (CV) = 22.63%

1.00 g Pulp, 0.36M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 hr, RT, One N <sub>2</sub> Purge					
Sample #	mL 0.1N HCl to	Final pH	Volume 0.1N HCl to	Final pH	mmol C=O/g
	Blank		Sample		Sample
1	2.76	3.29	2.64	3.31	0.038
1	2.75	3.28	2.64	3.28	0.038
2	2.73	3.31	2.64	3.28	0.032
2	2.74	3.30	2.63	3.30	0.035
3	2.75	3.31	2.63	3.31	0.040
3	2.75	3.31	2.64	3.30	0.037
Mean = 0.037 mmol C=O, s = 0.0030, CV = 8.11%					

*Conclusion:* A 24 hour, room temperature reaction was chosen based on its increased precision (increased CV%), as well as its ease in use, especially in the case of the non-aqueous solutions.

## 2. TEA Presence.

0.01mmol Cyclohexanone, 0.36M NH <sub>2</sub> OHHCl, 24 Hr, RT, 1 N <sub>2</sub> Purge				
mL 0.1N HCl to Blank	Final pH	mL 0.1N HCl to Sample	Final pH	mmol C=O
9.18	3.29	8.93	3.31	0.090
9.21	3.28	8.99	3.31	0.070
9.20	3.30	8.95	3.29	0.077
9.15	3.29	9.02	3.28	0.053
Mean = 0.072 mmol C=O, s = 0.016, CV = 21.51%				

0.01 mmol Cyclohexanone, 0.36M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge				
mL 0.1N HCl to Blank	Final pH	mL 0.1N HCl to Sample	Final pH	mmol C=O
11.74*	3.28	11.51*	3.29	0.075
11.72	3.29	11.45	3.30	0.095
11.70	3.28	11.45	3.30	0.087
11.71	3.28	11.45	3.29	0.087
Mean = 0.086, s = 0.0068, CV = 7.90%				

\*Note: Volumes necessary to titrate increased due to an increase in aliquat amounts. Throughout comparisons within this report, titration volumes may or may not be comparable between tables.

*Conclusion:* An increase in precision, although not accuracy, was observed with the use of TEA. In another set of runs which follow, however, the use of TEA seemed detrimental.

1.00 g Pulp, 0.36 M NH <sub>2</sub> OHHCl, 24 Hr, RT, 1 N <sub>2</sub> Purge				
mL 0.1N HCl To Blank	Final pH	mL 0.1N HCl to Sample	Final pH	mmol C=O/g Sample
9.11	3.30	9.05	3.29	0.027
9.15	3.31	9.05	3.28	0.027
9.13	3.28	9.06	3.29	0.027
9.15	3.30	9.06	3.30	0.027
Mean = 0.027 mmol C=O, s = 0, CV = 0%				

1.00 g Pulp, 0.36 M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge				
<u>mL 0.1N HCl to Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to Sample</u>	<u>Final pH</u>	<u>mmol C=O/g Sample</u>
11.67	3.30	11.62	3.28	0.013
11.65	3.28	11.60	3.29	0.020
11.63	3.27	11.57	3.29	0.020
11.63	3.29	11.54	3.29	0.030

Mean = 0.021 mmol C=O, s = 0.0069, CV = 33.1%

### 3. Aqueous vs. Non-Aqueous Reaction Solution.

1.00 g Pulp, 0.36M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge, Non-Aqueous					
<u>Sample #</u>	<u>mL 0.1N HCl to</u> <u>Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to</u> <u>Sample</u>	<u>Final pH</u>	<u>mmol C=O/g</u> <u>Sample</u>
1	2.76	3.29	2.64	3.31	0.038
1	2.75	3.28	2.64	3.28	0.038
2	2.73	3.31	2.64	3.28	0.032
2	2.74	3.30	2.63	3.30	0.035
3	2.75	3.31	2.63	3.31	0.040
3	2.75	3.31	2.64	3.30	0.037

Mean = 0.037 mmol C=O, s = 0.0030, CV = 8.11%

1.00 g Pulp, 0.36 M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge, Aqueous				
<u>mL 0.1N HCl to Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to Sample</u>	<u>Final pH</u>	<u>mmol C=O/g Sample</u>
11.67	3.30	11.62	3.28	0.013
11.65	3.28	11.60	3.29	0.020
11.63	3.27	11.57	3.29	0.020
11.63	3.29	11.54	3.29	0.030

Mean = 0.021 mmol C=O, s = 0.0069, CV = 33.1%

*Conclusion:* The non-aqueous case seemed more precise; it had a higher CV.

### 4. Hydroxylamine Concentration.

0.01 mmol Cyclohexanone, 0.36M NH <sub>2</sub> OHHCl, 24 Hr, RT, 1 N <sub>2</sub> Purge				
<u>mL 0.1N HCl to Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to Sample</u>	<u>Final pH</u>	<u>mmol C=O</u>
9.18	3.29	8.93	3.31	0.090
9.21	3.28	8.99	3.31	0.070
9.20	3.30	8.95	3.29	0.077
9.15	3.29	9.02	3.28	0.053

Mean = 0.072, s = 0.016, CV = 21.5%

0.01 mmol Cyclohexanone, 0.72 M NH <sub>2</sub> OHHCl, 24 Hr, RT, 1 N <sub>2</sub> Purge				
<u>mL 0.1N HCl to Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to Sample</u>	<u>Final pH</u>	<u>mmol C=O</u>
19.28	3.30	18.77	3.29	0.163
19.22	3.30	18.78	3.31	0.160
19.22	3.29	18.80	3.30	0.148
19.25	3.30	18.84	3.28	0.134

Mean = 0.151, s = 0.013, CV = 8.66%

*Conclusion:* An increase in hydroxylamine concentration seems to have increased the precision of the reaction, but decreased the accuracy (from bad to worse). Below, doubling the concentration in the presence of TEA did not raise the precision by as great of an amount as without the TEA; but again, it lowered the accuracy.

0.01 mmol Cyclohexanone, 0.36 M NH <sub>2</sub> OHHCl, 24 Hr, RT, 1 N <sub>2</sub> Purge				
<u>mL 0.1N HCl to</u>	<u>Final pH</u>	<u>mL 0.1N HCl to</u>	<u>Final pH</u>	<u>mmol C=O</u>
<u>Blank</u>		<u>Sample</u>		
11.74	3.28	11.51	3.29	0.075
11.72	3.29	11.45	3.30	0.095
11.70	3.28	11.45	3.30	0.087
11.71	3.28	11.45	3.29	0.087
Mean = 0.086 mmol C=O, s = 0.007, CV = 7.9%				

0.01 mmol Cyclohexanone, 0.72 M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge				
<u>mL 0.1N HCl to</u>	<u>Final pH</u>	<u>mL 0.1N HCl to</u>	<u>Final pH</u>	<u>mmol C=O</u>
<u>Blank</u>		<u>Sample</u>		
21.71	3.31	21.35	3.29	0.126
21.73	3.31	21.30	3.29	0.143
21.71	3.31	21.34	3.29	0.117
21.66	3.29	21.28	3.28	0.138
Mean = 0.1309, s = 0.012, CV = 8.81%				

#### 5. Nitrogen Purge (Continuous vs. One Purge at Reaction Start)

1.00 g Pulp, 0.36 M NH <sub>2</sub> OHHCl, 0.017M TEA, 24 Hr, RT, Contin. N <sub>2</sub> Purge (with loss of rx. volume)					
<u>Sample #</u>	<u>mL 0.1N HCl to Blank</u>	<u>Final pH</u>	<u>mL 0.1N HCl to</u>	<u>Final pH</u>	<u>mmol C=O/g</u>
			<u>Sample</u>		<u>Sample</u>
1	2.47	3.31	2.20	3.36	0.085
1	2.43	3.34	2.23	3.38	0.075
2	2.78	3.38	2.40	3.30	0.132
2	2.80	3.47	2.38	3.47	0.138
Mean = 0.107 mmol C=O/g sample, s = 0.032, CV = 30.1%					

1.00 g Pulp, 0.36 M NH <sub>2</sub> OHHCl, 0.017 M TEA, 24 Hr, RT, 1 N <sub>2</sub> Purge					
<u>Sample #</u>	<u>mL 0.1N HCl</u>	<u>Final pH</u>	<u>mL 0.1N HCl</u>	<u>Final pH</u>	<u>mmol C=O/g</u>
	<u>to Blank</u>		<u>to Sample</u>		<u>Sample</u>
1	3.02	3.14	2.72	3.24	0.098
1	3.00	3.16	2.75	3.19	0.088
2	3.00	3.16	2.80	3.26	0.071
2	3.02	3.17	2.74	3.32	0.092
Mean = 0.087, s = 0.011, CV = 13.11%					

*Conclusion:* A decision was made in favor of the single purge towards the beginning of the experimental design due to the loss of reaction solution [this was only a problem if the reaction solution was aqueous], and also because this extra time-consuming and cost-consuming factor did not seem necessary. The oxime reaction investigation was discontinued due to an inability to achieve reproducible, accurate, or precise results.

## II. Cyanohydrin

The method used was proposed by M. Lewin (6) and consisted of combining the carbonyl compound with a sodium cyanide/buffered solution for at least 24 hours at room temperature. To an aliquot of this solution was added KI and NaOH. This was then titrated with  $\text{AgNO}_3$  to a turbidimetric end point using a colorimetric probe, potentiograph, and auto buret. It was determined that:

- a. Precise, accurate, and reproducible determinations of  $[\text{CN}]$  are possible.

Method Analysis				
Sample #	mL 0.014M <u><math>\text{AgNO}_3</math></u>	mmol CN (u = 0.25 mmol)	mL 0.014M <u><math>\text{AgNO}_3</math></u>	mmol CN (u = 0.025 mmol)
1	8.988	0.2517	0.950	0.0266
2	8.912	0.2495	0.972	0.0272
3	9.090	0.2545	0.984	0.0276
4	8.764	0.2454	0.968	0.0271
5	9.104	0.2549	0.972	0.0272
6	9.078	0.2542	0.980	0.0274

Mean = 0.2517	Mean = 0.0272
s = 0.0037	s = 0.0004
CV = 1.47%	CV = 1.24%
x-u = 0.0017	x-u = 0.0022
ts/(N) <sup>1/2</sup> = 0.004 (95% CL)	ts/(N) <sup>1/2</sup> = 0.0012 (99% CL)
x-u < 0.004, therefore, x = u	x-u > 0.0022, therefore, although the precision is high, x = u is not true.

- b. Reproducible and somewhat precise carbonyl quantitation for pulps seem achievable.  
(Judging from the first two runs performed.)

3.00 g Pulp Determination, Visual End Point Detection		
<u>mL <math>\text{AgNO}_3</math> to Blank</u>	<u>mL <math>\text{AgNO}_3</math> to Sample</u>	<u>mmol C=O/g pulp</u>
11.3	9.1	0.031
11.3	9.6	0.024
11.3	9.0	0.032
11.2		
Ave. = 11.275		

Mean = 0.474 mmol C=O, s = 0.005, CV = 15.7%
--

1.50 g Pulp Determination, Instrumental End Point Determination		
<u>mL <math>\text{AgNO}_3</math> to Blank</u>	<u>mL <math>\text{AgNO}_3</math> to Sample</u>	<u>mmol C=O/g pulp</u>
5.424	4.540	0.0256
<u>5.488</u>	4.674	0.0219
5.456	4.424	0.0289

Mean = 0.0255 mmol C=O, s = 0.0035, CV = 13.7%
--

These results indicated that a more in-depth analysis of the pulp determinations could lead to establishing an internal standard. A more investigative analysis of the same pulp used in all previous experiments yielded poor results, however. Even consistency within each run could not be established. This unexpected result has not been explained.

Varying Amounts of Pulp/ Internal Standard Experiment			
Grams of Pulp	mL AgNO <sub>3</sub> to Sample	mmol C=O/g Pulp	
0.5	5.312	0.049	Mean = 0.050
0.5	5.004	0.075	s = 0.025
0.5	5.606	0.024	CV = 51.1%
1.0	5.728	0.007	Mean = 0.008
1.0	5.602	0.012	s = 0.004
1.0	5.764	0.006	CV = 42.5%
1.5	5.538	0.010	Mean = 0.022
1.5	4.656	0.035	s = 0.012
1.5	5.130	0.022	CV = 55.7%
2.0	5.502	0.008	Mean = 0.017
2.0	4.900	0.021	s = 0.007
2.0	4.912	0.021	CV = 43.5%

\*Blank runs used 5.840mL and 5.954 mL of AgNO<sub>3</sub> in titration. The average = 5.897 was used in calculations.

- c. The model compounds chosen do not show cyanohydrin formation at the carbonyl concentrations attempted.

Model Compound Determination (10 days), (u = 0.0225 mmol C=O)			
Model	mL AgNO <sub>3</sub>	mmol C=O	
Cyclohexanone	5.200	0	s = 0.0025
	5.252	0	CV > 100%
	5.076	0.005	
2,4-Hexadienal	5.148	0.002	s = 0.001
	5.144	0.002	CV = 100%
	5.244	0	
4-Methyl-2-pentanone	5.420	0	s = 0
	5.332	0	
	5.346	0	
Syringaldehyde	4.254	0.044	s = 0.022
	5.014	0.008	CV > 100%
	5.098	0.004	
3,4-Dimethoxyacetophenone	5.264	0	s = 0
	5.272	0	
	5.240	0	

#### Statistical Analysis of Titration Volumes:

Cyclohexanone: s = 0.09, CV = 1.75%

2,4-Hexadienal: s = 0.05, CV = 1.1%

4-Methyl-2-pentanone: s = 0.05, CV = 0.9%

Syringaldehyde: s = 0.46, CV = 9.7%

3,4-Dimethoxyacetophenone: s = 0.02, CV = 0.3%

**Conclusion:** The model compounds are either not forming the cyanohydrin or, if they are, the levels of formation are below the limit of detection of the method.

**Overall Summary:** Both methods have produced very confounding results. Reproducibility has not been established for either. Further plans for experiments are on hold.

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