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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

ANNUAL RESEARCH REVIEW

CHEMICAL PULPING AND BLEACHING

MARCH 25, 1992
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TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE: FUNDAMENTALS OF BLEACHING CHEMISTRY
PROJECT STAFF: L.B. Sonnenberg, A.J. Ragauskas, D.R. Dimmel
BUDGET (FY 91-92): $175,000
REPORTING PERIOD: July 1991 - Feb. 1992
DIVISION: Chemical and Biological Sciences
PROJECT NUMBER: 3728

OBJECTIVE: Provide a fundamental understanding of the physical and chemical reactions that control lignin removal and residual structure. Understand the reasons for selectivity of reactions that occur in selected bleaching sequences.

IPST GOAL: Improved bleaching processes

SUMMARY:

The paper industry is seriously considering ozone as an alternative to chlorine-containing bleaching reagents. Information about major by-products from pulp ozonation, coupled with studies of the fundamental chemistry of lignin ozonolyses using lignin model compounds, can provide useful information about many aspects of this new bleaching technology. Results from both pulp ozonolysis studies and lignin model compound studies are reported. In addition, results from studies of a novel oxidant, dimethyl dioxirane, are presented.

Pulp ozonation produces basically two types of by-products. One type consists of small, gas chromatographable compounds which are primarily short-chain and long-chain aliphatic acids and diacids derived from ozonolysis of unsaturated fatty acids and aromatic rings. The other type is methanol-soluble and water-insoluble, and possibly consists of large, polar lignin fragments.

Few monomeric lignin compounds are produced or survive ozonation. Evidence of lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). These compounds appear to be major chromatographable components of ozonation mixtures. Glyoxylic acid is by far the most abundant aldehyde present, while glyoxal is another important carbonyl by-product.
It appears that at least some of the carbonyl compounds have polar precursors since pre-extraction of the pulp with methylene chloride does not reduce the formation of minor carbonyl compounds while alkaline washing does. Oxygen delignification prior to ozonation does not appear to greatly affect the distribution of carbonyl compounds.

Preliminary lignin model ozonations under different conditions suggest that the pathway of lignin ozonolysis is affected by the presence of carbohydrates. The reactivity of the lignin model is greater when dissolved or when adsorbed onto cotton linters than when it is suspended in water. The product distribution resulting from the ozonation of the adsorbed lignin model more closely resembles the product distribution found from ozonated pulp than from the dissolved or suspended model because small acids and aldehydes are detected.

It appears that a major reaction of ozone with the model in all of the systems is simply cleavage of the the most substituted ring of the lignin dimer. One of the major products found is a lactone arising from cleavage of an aryl double bond and subsequent cyclization.

Research efforts have been directed at exploring novel oxidative bleaching procedures for kraft pulps. Dimethyldioxirane has been shown to be an efficient reagent for delignifying and brightening kraft pulps. Preliminary bleaching studies have established practical methods of generating dimethyldioxirane and have explored process variables. The reactivity of dinitrogen pentoxide with kraft pulps was also examined; this reagent was not effective in bleaching.

Synthetic studies have been focused on preparing lignin model compounds which are to be employed in a series of fundamental bleaching studies. Recent efforts have been directed at attaching these model compounds onto carbohydrate structures so as to model lignin carbohydrate structures found in pulp.
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 is one such promising technique. Although the by-products from traditional bleaching practices are well characterized, less is known about the by-products from ozone bleaching. Information about major by-products from pulp ozonation can be invaluable in assessing potential toxicity of effluents, in evaluating treatment strategies for effluents, and in elucidating prevalent reaction pathways.

Studying the structures and reactions of pulp components with conventional bleaching agents and novel oxidants will provide insights into the fundamental chemistry which governs lignin removal during bleaching. Such information will aid in the development new bleaching strategies.

This report will discuss our research on (1) ozonolysis of pulps and lignin model compounds, with emphasis on product characterization, (2) model compound synthesis, (3) bleaching with dimethyldioxirane, and (4) bleaching with a combination of ozone and nitrogen dioxide. Each topic will be treated separately, meaning that each will have its own set of tables, figures, conclusions, and references.

FY 91-92 RESULTS TO DATE

Ozonolysis of Pulps and Lignin Model Compounds

The identities of low molecular weight pulp ozonolysis products can be determined by gas chromatography mass spectrometry. Small compounds produced from pulp ozonation are of particular environmental interest because they are believed to be more bioavailable than higher molecular weight material. Our analyses have paid particular emphasis on characterization aldehyde products, since they are produced by reactions of ozone with sites of unsaturation and because of the toxicity of some.¹

Information was sought about the precursors to the pulp by-products. Extracts from several different pulps were analyzed. These included extracts from an ozonated northwestern softwood kraft pulp that was prewashed with acid solution, prewashed with alkaline solution or pre-extracted with an organic solvent, and a southern softwood kraft pulp (with and without prior oxygen delignification). Derivatization of carbonyl compounds with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride selectively provided information about carbonyl by-products.

Lignin model compound studies reported here focus on changes in ozonolysis pathways as a function of the phase of the model (i.e., dissolved, solid, or adsorbed on cotton linters). Although 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 are conducted in water with a cosolvent such as acetone or ethanol. The effects of the phase of the model compounds and the influence of carbohydrates on the reaction pathways have been largely ignored. Results are reported from preliminary experiments in which a water-insoluble dimeric lignin model compound (Figure 1) was ozonated in the following ways: dissolved in acetone/water (neutral and acid pH), suspended in water (neutral and acid pH) and adsorbed onto cotton linters (acid pH, high consistency). The reaction products were identified and the extent of degradation of the model compound was evaluated.

**General Characteristics of Pulp Ozonolysis By-products**

Ozonations of several differently treated pulps yielded information about the general characteristics of the ozonation by-products, about the small compounds produced, and about the distribution of carbonyl compounds that are formed as a result of pulp ozonation.

In the initial investigations of ozonation by-products from a northwestern softwood pulp, the ozonated, high consistency pulp was washed with acidified water and filtered. The aqueous filtrate was extracted with ether as was the bleached pulp, producing two fractions: a water-soluble, ether-soluble fraction and a water-insoluble, ether-soluble fraction. A control sample underwent the same procedures except no ozone was applied to the pulp. Presumably, the products in the control extracts represent the adsorbed, weakly bound, or acid-labile pulp constituents. The gas chromatograms from these samples showed that the ozone shifted the distribution of ether-extractable, gas chromatographable compounds from higher molecular weight, water-insoluble compounds to smaller, water-soluble compounds. Therefore, some ozone is consumed in reactions with fairly small, gas chromatographable compounds associated with the pulp to produce even smaller, more polar compounds.

Solubility characteristics of the compounds associated with ozonated pulp were informative. Efforts to extract as much material as possible from ozonated pulp led to the use of methanol as the extraction solvent. A significant amount of the methanol-soluble material produced by pulp ozonation is not soluble in water. At least some of this water-insoluble portion is also insoluble in nonpolar solvents such as ether and hexane. This poorly solubilized fraction may contain polar, high molecular weight lignin fragments as well as lactones and other muconic acid derivatives. The water-soluble products appear to be mostly aliphatic, judging by gas chromatography (discussed below) and by $^1$H NMR spectra. In addition, while high pressure liquid chromatography of water-soluble products resulted in dozens of fairly well resolved peaks, the water-insoluble fraction was not chromatographable. These observations are consistent with ozone producing large, polar, nonchromatographable lignin fragments as well as producing some smaller, chromatographable compounds, possibly fragments of the aromatic ring. These results are consistent with results from ozonation of humic acid, a macromolecular material similar to lignin, in which ozone reduces the molecular weight, but generally only 5 to 30% of the original organic carbon is reduced below 1,000 daltons.
Composition of Ozonated Pulp Extracts

Aliphatic acids, ranging from six carbons to 24 carbons, were significant components in almost all of the extracts of ozonated pulp. The methyl esters of the acids, designated in Figure 2, have very characteristic mass spectra, including strong peaks at 74 and 87 amu. 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 signal identified as the methyl ester of octadecenoic acid suggests that complete cleavage of the unsaturated fatty acids does not occur at ozone doses used in this study (1%-2% on o.d. pulp). Several diacids were detected (Figure 2). The diacids probably also arose from cleavage of double bonds in fatty acids or, in the case of oxalic acid, from cleavage of the aromatic rings in lignin. 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 octadecenoic (oleic), hexadecenoic (palmitoleic), octadecadienoic (linoleic) and/or octadecatrienoic (linolenic) acids are cleaved by ozone.

Oxalic acid dimethyl ester and glyoxylic acid methyl ester signals were prominent in the chromatograms of the methanol extracts of ozonated pulp (Figure 2). The analytical method used does not distinguish between oxalic acid and its methyl esters or between glyoxylic acid and its methyl ester in the extracts. Glyoxal is another potential ozonolysis product from aromatics which is discussed more fully below. All of these compounds can form through muconic acid type intermediates upon ozonolysis of aromatics (Figure 3). Their presence may indicate the extent to which aromatic ring cleavage with subsequent secondary ozonolyses occur. Since the complete oxidation of the aromatic ring to these small fragments may be unnecessary for delignification, their presence in high concentrations may reflect inefficient ozone consumption.

Few monomeric lignin fragments were identified in any of the extracts. Vanillin and vanillic acid were the two most prevalent. The ozonation products contrast with chlorination effluents in which aromatics are important constituents. Another variation from chlorination effluents is the lack of catechols in the ozonation by-product mixtures. This reflects the fact that ozone does not demethylate aromatic methoxyl groups, while chlorine does. The scarcity of lignin monomers is consistent with ozone producing polar, high molecular weight material along with aromatic ring fragments from lignin.

General By-Products From Different Pulps

In order to characterize the precursors to the ozonolysis products, comparisons were made between pulps that were washed in acidic solution before ozonation, pulps that were washed in alkaline solution, and pulps that were pre-extracted with methylene chloride prior to ozonation. The distributions of products from two different softwood pulps were also compared. The total ion current (TIC) chromatograms are shown in Figure 4. There are few unique products in the different methanol extracts. The major differences lay in the relative amounts of the different classes of compounds.
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 more compounds in comparable amounts. The differences in the extractives contents of the two pulps 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.

The alkali wash was expected to remove nonbound polar constituents of the pulp. The chromatograms of the ozonated acid-washed and alkaline-washed southern softwood pulps had only minor differences in the relative distributions of their ozonation products. Although the absolute amounts of products appears to be less in the alkaline washes (samples were concentrated to exact volumes and exact volumes were injected in the gas chromatograph), these results can only be considered semi-quantitative and further verification is necessary. The similar product distributions suggest that no major class of precursors of the ozonation products are more alkali-labile than others. However, the alkaline wash may have affected the distribution of some carbonyl compounds present in small quantities, which is discussed below.

The methanol extracts of ozonated northwestern softwood pulp that was pre-extracted with methylene chloride consistently behaved differently than the other softwood extracts for unknown reasons. Upon methylation with diazomethane, there was significant precipitation of material, which did not occur with the other extracts. However, the chromatograms obtained from the pre-extracted pulp were somewhat similar to the unextracted pulp. Although there was a shift in the distribution of the compounds in the effluent away from fatty acids, there were clearly long chain aliphatic acids present, even after pre-extracting the pulp for 5 hours with methylene chloride (based on TAPPI Method T204 om-88 for extractives analysis). The same general trend was seen in the southern softwood pulp (data not shown). It is unlikely that ozone breaks covalent bonds to produce acids such as octa-decanoic (stearic) acid and hexadecanoic (palmitic) acid. Possibilities are that the methylene chloride extraction is inefficient in removing extractives compared to methanol and/or that ozonation causes a change in fiber morphology that allows more extractives to be removed by organic solvents.

A difference in the aliphatic components of the byprodut mixtures from the pre-extracted pulp and from the unextracted pulp was that the former contained little nonanedioic acid. This indicates that the dicarboxylic acid precursor(s) was effectively removed or reduced. Octadecenoic acid (oleic acid), a very likely precursor to nonanedioic acid, may have been effectively removed by the pre-extraction with methylene chloride.

The precursors of most of the ozonation products of pulps were not readily removed by methods expected to reduce the quantities of polar or nonpolar compounds. More thorough solvent pre-extraction and careful quantitation of the products will more fully address the interesting question of the role of extractives in ozonation by-product formation.
Carbonyl Compounds From Pulps

Ozone reacts with double bonds to produce aldehydes, which can frequently be autoxidized to carboxylic acids. Standard GC/MS analyses showed that significant numbers and quantities of carboxylated compounds, some of which were ozone-derived, were present in the extracts of the ozonated pulps. It is reasonable that the corresponding aldehydes of the ozone-derived acids may be present as well. Other carbonyl compounds may also be formed from ozone attack on activated hydrogens. One way to selectively look for these compounds is to derivatize them with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBOA). PFBOA reacts with aldehydes and, to some extent, ketones, to form the readily identifiable oximes.

Pentafluorobenzyl oxime derivatives have a signature mass spectrum consisting of a dominant base peak ($C_6F_5CH_2^+$). Comparing the TIC and the ion chromatogram for mass 181 of the derivatized extract of the southern softwood pulp shows that most of the compounds in the PFBOA-treated extracts are oxime derivatives. Vanillin, identified through standard GC/MS analyses of underivatized extracts, served as a monitor for the production of the oxime derivatives. This was important since the PFBOA derivatization methods used in this work were modified from literature methods. Figure 5 shows the chromatogram and mass spectrum of a derivatized vanillin standard and the vanillin oxime from an ozonated pulp sample.

Chromatograms from PFBOA-derivatized extracts of the pulps described in the previous sections are shown in Figure 6. The PFBOA derivatization technique was also used to analyze methanol extracts of the southern pulp which was treated in the following ways: oxygen delignified with a subsequent 0.6 % ozone charge, oxygen delignified with a subsequent 1.0 % ozone charge, and methylene chloride extracted and ozonated at a 1.1 % ozone charge (data not shown).

There is a remarkable similarity in all of the chromatograms. They are all dominated by one peak, the oxime derivative of glyoxylic acid methyl ester (Figure 7). [This compound was identified in the extracts without PFBOA treatment only after its oxime derivative was detected in this series of experiments]. Both PFBOA extracts and underivatized extracts indicate that glyoxylic acid and/or its methyl ester is the most prevalent carbonyl compound in the ozonation extracts. Its predominance in all of the extracts and its similar amount in the extracts (shown in Figure 6) suggest that its major precursor is lignin, since the lignin structures in the different pulps are likely to be similar.

The PFBOA samples show that glyoxal is another important carbonyl compound, although much less prevalent than glyoxalic acid (Figure 8). Glyoxal could arise from cleavage of unsubstituted double bonds of muconic acid derivatives (Figure 3). Identification of glyoxal in the underivatized samples is not possible because it elutes with methanol. Formaldehyde is another carbonyl compound of interest. Although it was detected in the PFBOA extracts, it was also present in the blanks in small amounts. In addition, the sample work-up was not conducive to good recovery of formaldehyde. Additional work is underway to confirm the presence of these two compounds in ozonation effluents.
Further examination of the smaller peaks reveals that, as in the underivatized samples, the peaks present are essentially the same in all of the chromatograms. However, there are some minor differences in their magnitude relative to the glyoxylic acid methyl ester derivative. Based on the chromatograms shown in Figure 7, it appears that there are fewer carbonyl precursors in the southern softwood pulp and the alkaline-washed northwestern softwood pulp than in the others. The derivatization technique revealed a small effect of the alkaline wash that was not apparent in the underivatized extracts. Interestingly, extracting the pulps with methylene chloride did not reduce the carbonyl compounds. These results suggest that some carbonyl precursors are alkali-labile or soluble but resistant to removal by organic solvents.

Oxygen treatment before ozonation does not appear to greatly affect the major reaction pathways that produce carbonyl compounds. This result was somewhat surprising since oxygen treatments tend to alter aromatic structures which seem to be a major source of the small carbonyl compounds.\textsuperscript{10}

The relatively strong molecular ion of the vanillin oxime, shown in Figure 6, is characteristic of aromatic derivatives.\textsuperscript{9} Few other oxime signals exhibited as strong a molecular ion, suggesting that vanillin is the major aromatic aldehyde produced by ozonation. These data are supported by the spectra from the underivatized extracts.

To simplify the task of identifying the oximes and their corresponding parent compounds, it is useful to compare an ion chromatogram for mass 59 which is strongly characteristic of methyl esters. The ion fragment that produces the mass peak at 59 amu is $-\text{COOCH}_3$. By comparing the 181 traces and the 59 traces, an idea of the number of compounds that are potentially bifunctional, i.e., contain an aldehyde and a carboxylic group, can be obtained. The ion chromatogram for mass 59 suggests that most of the carbonyl compounds have a carboxylic group, with a only few exceptions.

In this study, the PFBOA was added to the methanol extracts of the pulps and the reaction was quenched with acidic water. In literature methods\textsuperscript{8,9}, 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. In addition, glyoxylic acid becomes methylated upon acidification in methanol. 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.

**Lignin Model Compound Studies**

The degrees of degradation of the lignin model compound under different conditions are shown in Figure 9. Results are reported on the basis of moles of ozone consumed per mole of starting material. The data are approximate because of variability in ozone and lignin model compound measurements.
The lignin model reacted most readily when it was dissolved in acetone/water solutions and when it was adsorbed onto cotton linters. 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 its uniform access to the ozone. Another possibility is that the presence of the linters promoted the degradation of the undissolved, adsorbed model. Surprisingly, the pH of the solutions did not appear to affect the degree of degradation of the dissolved model.

Approximately the same amount of model degraded when similar amounts of ozone were applied to the adsorbed lignin model and to the dissolved model compound (see designated points in Figure 9). However, it appears that the adsorbed lignin model consumed more ozone than the dissolved model resulting in the same degree of degradation. Ozonation of linters blanks showed that direct consumption by the linters did not account for the higher ozone consumption. 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. Differences in product distributions of the two systems support this interpretation.

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 acid and the alcohol to form the lactone. These types of compounds have been frequently reported in dimeric lignin model ozonations conducted in solution. The major difference in chromatograms of products from ozonations of the dissolved model compound at low levels (9:1 molar ratio of applied ozone to dissolved lignin model) and high levels (30:1 ratio) is the relative sizes of the lignin model signal and the lactone signal. At the lower charge, the major chromatographic signal is from the model and a small signal representing the lactone is present; at the higher charge the relative amounts are reversed. It appears that a major reaction of ozone with the dissolved model is simply cleavage of the A ring. Other common products arise from cleavage of the side chain at various sites while the B ring remains intact. Initial tentative identifications indicate that many of these contain aldehyde functional groups.

The product distribution of the adsorbed model compound differs somewhat from the dissolved compound. The lactone and other aromatic fragments are present, however, small acids and aldehydes are detected from the adsorbed lignin model ozonations and they are not detected in the ozonation products of the dissolved model at similar ozone charges. It appears that the presence of the linters promotes ozonolyses at sites of unsaturation in the primary reaction products, thereby consuming more ozone and producing small, acidic and aldehydic fragments. In addition, although it is difficult to equate the ozone charges between the pulp and the lignin model systems, the presence of the small, acidic and aldehydic fragments is more similar to the pulp by-product distribution than a product mixture composed only of aromatic fragments.

The linters may affect the ozonation pathways of lignin either physically or chemically. The linters may play a physical role by limiting ozone accessibility to the adsorbed model compound so that primary reaction products can react with the ozone more readily. Alternatively, the linters may react with lignin intermediates and participate in the reaction pathways. Jacobson, et al. report that carbohydrates participate in lignin ozonolysis pathways during Z stages of
pulp bleaching and postulate that radical intermediates from lignin are the reactive species. Experiments in which the dissolved lignin model is ozonized in the presence of dissolved carbohydrates are planned and will indicate whether the latter compounds affect lignin reactions physically or chemically. In addition, viscosity measurements of linters ozonized in the presence and absence of the model compound will indicate whether carbohydrates are affected by ozonized lignin intermediates.

Conclusions

Pulp ozonation produces basically two types of by-products. One type consists of small, gas chromatographable compounds which are primarily fatty acids, short-chain and long-chain aliphatic acids and diacids. The other type is methanol-soluble and water-insoluble, and possibly contains large, polar lignin fragments.

The precursors of some of the aliphatic acids and diacids are unsaturated fatty acids. In particular, nonanedioic acid is an important product of fatty acid cleavage in ozonated pulps. Even though the contribution of aliphatic acids can be reduced by pre-extraction of the pulp with methylene chloride, complete removal of the fatty acids and their ozonolysis products cannot be effected by methods used in this study. Alkaline washes do not change the distribution of major products relative to one another.

Few monomeric lignin compounds are produced or survive ozonation. Evidence of lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). These compounds are major chromatographable components of ozonation by-product mixtures, based on relative signal sizes in TIC chromatograms. Glyoxylic acid is by far the most abundant aldehyde present. Derivatization by PFBOA indicates that glyoxal is another important carbonyl by-product.

Carbonyl compounds that are present in ozonated pulp in small quantities relative to glyoxylic acid (methyl ester) have precursors that resist extraction from pulp by methylene chloride. However, alkaline washing prior to ozonation reduces carbonyl compounds. These results suggest that the precursors are polar. In addition, northwestern pulp produces more carbonyl compounds than the southern pulp. Oxygen delignification prior to ozonation does not appear to greatly affect the distribution of carbonyl compounds. These differences in carbonyl content of the different pulps were discernible only in PFBOA-derivatized extracts, probably due to their small quantities relative to other detected compounds.

Preliminary lignin model ozonations under different conditions suggest that the pathway of lignin ozonolysis is affected by the presence of carbohydrates. The reactivity of the lignin model is greater when dissolved or when spiked onto cotton linters than when it is suspended in water. Better accessibility of the model to ozone may partially explain the greater degradation of the adsorbed model than the suspended model. However, the increased formation of small fragments of aromatic rings (oxalic acid dimethyl ester, glyoxylic acid methyl ester) in the
presence of the linters suggests that the linters' presence alters predominate chemical pathways. The product distribution with the small acids and aldehydes more closely resembles the product distribution found from pulp ozonations.

It appears that a major reaction of ozone with the model in all of the systems is simply cleavage of the the most substituted, free phenolic ring of the lignin dimer. One of the major products found in all systems is a lactone arising from cleavage followed by a condensation of the acid and the alcohol to form the lactone. Further or concurrent reaction produces several products arising from cleavage of the side chain at various sites while the least substituted ring remains intact.

Future Activity

Pulp ozonolysis products will be further identified and important products will be quantified. Changes in distribution of pulp ozonolysis products with different conditions will be investigated. Correlation of reaction products such as oxalic acid and glyoxylic acid methyl ester with pulp quality will be attempted in order to elucidate efficient ozonation conditions.

There will be further investigation into the role of carbohydrates in lignin ozonolyses. The course of the lignin reactions as well the effect on carbohydrate structure will be examined through the use of several lignin derivatives, including lignin-carbohydrate complexes. We will attempt to identify reactive lignin intermediates and determine any reactions they may have with carbohydrates.

References:


Figure 1. Lignin model compound used for fundamental ozonolysis studies. 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethan-1-ol
Figure 2. TIC chromatogram of a methanol extract of ozonated northwestern softwood pulp showing pulp ozonolysis by-products.
Figure 3. Potential pathways for the formation of carbonyl compounds from ozonation of lignin.
Figure 4. TIC chromatograms of methylated methanol extracts of ozonated pulp, a) southern softwood, prewashed with acid, b) northwestern softwood, prewashed with acid, c) northwestern softwood, pre-extracted with methylene chloride, and d) northwestern softwood prewashed with base.
Figure 5. Vanillin oxime derivatives; a) TIC chromatogram of a PFBOA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a vanillin standard derivatized in methanol.
Figure 6. Ion chromatograms (mass = 181) of PFBOA derivatized extracts of ozonated a) southern softwood, prewashed with acid, b) northwestern softwood, prewashed with acid, c) northwestern softwood, pre-extracted with methylene chloride, and d) northwestern softwood prewashed with base.
Figure 7. Glyoxylic acid methyl ester oxime derivatives; a) TIC chromatogram of a PFBGA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a glyoxylic acid methyl ester standard derivatized in methanol.
Figure 8. Glyoxal oxime derivatives; a) TIC chromatogram of a PFBOA derivatized extract of an ozonated northwestern softwood pulp, b) mass spectrum of the designated sample peak, and c) mass spectrum of a glyoxal standard derivatized in methanol.
Figure 9. The influence of the phase of the lignin model compound (LMC) on the extent of its degradation. Numerals in the graph are moles of ozone applied per mole of LMC degraded for the designated samples. (A = acid pH, N = neutral pH)
Research efforts have been directed at preparing lignin model compounds. The compounds currently being synthesized are to be employed to study the fundamental chemical reactions which contribute to bleaching. Initial synthetic efforts were directed at preparing 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethan-1-ol. The target compound was readily prepared following literature procedures; the results are summarized in Scheme 1. The removal of the benzyl group by hydrogenolysis could be accomplished employing routine synthetic procedures but the use of ammonium formate and Pd° was shown to be as efficient and more amenable for large scale reactions. The use of ammonium formate and Pd° to debenzylate protected lignin model compounds was shown to be very selective as this reagent could efficiently remove the benzyl group for 1-(4-O-benzyl-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethan-1-ol but did not debenzylate the corresponding the ketone.

Recent research endeavors have focused on preparing a series of lignin/carbohydrate complexes, as shown below. Several investigators have suggested these types of structures exist in kraft pulps and are of the principle reasons why the kraft pulping process yields a relatively high residual lignin content.

Current research efforts are directed at preparing compounds A and B, as summarized in Scheme 2. The experience acquired from preparing these compounds will then be employed to prepare C. These structures will then be used to study the fundamental chemical reactivity of lignin/carbohydrate bonds under bleaching conditions. The results of these studies will then be employed to devise new methods of chemically rupturing this structural unit.
Bleaching with Dimethyldioxirane

Introduction

Although no one reagent has been found to have all of the bleaching advantages of chlorine, significant advances have been achieved employing oxygen-based bleaching procedures.\(^1\) The use of oxygen, ozone, and hydrogen peroxide has been successfully incorporated into multi-stage bleaching sequences,\(^2\) and research is continuing to develop new bleaching alternatives to chlorine.

A variety of organic and inorganic peroxides have been examined with respect to their bleaching efficiency. Several recent papers have demonstrated that caroic acid (peroxymonosulfate) can be employed as a bleaching and/or delignification reagent for kraft pulp.\(^3\)\(^4\) The relative ease of preparing this reagent \textit{in-situ}, or the application of commercial sources of caroic acid as a triple salt of 2KHSO\(_5\)-KHSO\(_4\)-K\(_2\)SO\(_4\) ("Oxone" is the DuPont Co. commercial trade name), further enhances the utility of this inorganic peroxide for bleaching. The research efforts of Hammann et al.\(^5\) have illustrated that Caroic acid supports the bleaching effects of oxygen, ozone, and peroxide in a four-stage bleaching sequence of softwood kraft and ASAM pulps. Under optimized conditions, caroic acid appears to be as an efficient delignifying and brightening agent without overly affecting the technological properties of the pulp.

The principal bleaching reaction of Caroic acid has been proposed to be hydroxylation and oxidative rupture of the benzenic ring of lignin.\(^5\) The chemical literature indicates that peroxymonosulfate can oxidize a wide variety of compounds, although most frequently this reagent is employed in the presence of a ketone. The research efforts of Montgomery\(^6\) and Edwards\(^7\) demonstrated that certain ketones can catalyze the oxidative reactions of peroxymonosulfate through the intermediacy of dialkyl dioxiranes (see Scheme 1). In the presence of an oxidizable substrate (X) the dioxirane intermediate then becomes the effective oxidant. Recent studies have shown that these cyclic peroxides display impressive reactivity and efficient oxidizing capabilities.\(^8\) In light of these results and the potential applicability of Caroic acid for bleaching kraft pulps, we have initiated a research program directed at evaluating the use of dimethyldioxirane as a novel bleaching reagent. The results below describe our initial results of bleaching kraft pulps with dimethyldioxirane, generated from an aqueous solution of acetone, sodium bicarbonate, and Oxone.

Results and Discussion

Initial research efforts were focused on determining the intrinsic bleaching properties of dimethyl dioxirane without competing bleaching reactions from caroic acid. A 0.1 M solution of dimethyldioxirane in acetone was readily prepared by employing procedures developed by Adam.\(^9\) The oxidizing solution was prepared by adding Oxone to an aqueous acetone solution of sodium bicarbonate and vacuum distilling the dimethyldioxirane. The resulting dimethyl-
\[ R\text{-CO} + \text{H}_2\text{O-SO}_3^- \rightleftharpoons R\text{-CO-SO}_3^- \rightleftharpoons R\text{-CO} + H^+ + \text{SO}_4^{2-} \]

\[ \text{HO}^- + \text{H}_2\text{O} \]

\[ R\text{-CO} + \text{O}_3\text{SOO}^- \rightarrow R\text{-CO} + \text{O}_2 + \text{SO}_4^{2-} \]

Scheme 1

\( X = \text{oxidizable substrate} \)
A dioxirane-acetone solution was then applied to two different softwood kraft pulp samples. Treatment with dimethyldioxirane significantly reduced the Kappa number and raised the brightness for both pulp samples, as summarized in Table 1. Subsequent caustic extraction removed additional lignin and further raised the brightness of the resulting pulp (Table 1).

The bleaching residue from the 27.6 kappa pulp was concentrated and analyzed by $^1$H NMR (figure 1) and FT-IR spectroscopy. The proton NMR spectrum suggests that dimethyldioxirane extensively oxidized the aromatic portion of lignin since no signals were apparent in the 7.00-8.00 ppm range. In comparison, $^1$H NMR analysis of residue lignin isolated by acid hydrolysis of the 27.6 kappa pulp contained a broad multiplet centered at 7.33 ppm. The FT-IR spectrum of the bleach residue corroborated the NMR analysis since it contained only a very small aromatic CH signal at 1510 and 1470-1460 cm$^{-1}$. These results are consistent with the proposal that dimethyldioxirane can readily oxidize residual lignin found in kraft pulps.

The results of these preliminary studies clearly suggest that the strained cyclic structure of dimethyldioxirane yields an exceptionally reactive peroxide with unique bleaching properties. Although the bleaching efficiency of dimethyldioxirane was promising, the methods of preparation severely limited any practical application. To further explore the potential applicability of this reagent for bleaching chemical pulps, we examined alternative methods of generating dimethyldioxirane would yield an analogous bleaching response. The bleaching efficiency of in-situ generated dimethyldioxirane was explored through a series of bleaching studies employing aqueous acetone \ sodium bicarbonate \ Oxone solution. The bleaching reactions employed a volume ratio of acetone-to-water of 2:1; an equal weight basis of Oxone and sodium bicarbonate was added to a softwood kraft pulp, and the resulting mixture was stirred for 1 h. The bleaching efficiency of in-situ generated dimethyldioxirane was then evaluated through a series of control experiments employing Oxone \ sodium bicarbonate \ water as the bleaching system. For these latter experiments, the bleached pulp was washed with water, followed by an acetone wash and a final water wash. The results of these studies and control experiments are summarized in Table 2a. A comparison of the aqueous based reactions versus the acetone/water reactions demonstrates that the latter system is more efficient at removing lignin. These differences remain despite the fact that the aqueous pulp is washed with acetone after the bleaching reaction suggesting that the differences in kappa values were not solely due to solubility differences in oxidized lignin. Our results are consistent with a recent patent application by Lee Chung Li$^{10}$ titled "bleaching of lignocellulosic material with dioxiranes".

The changes in viscosity for bleaching with a 30% and 15% charge of oxone are summarized on Table 2b. This data also indicate that the use of acetone is advantageous with respect to changes in viscosity during bleaching. Although these results are suggestive of an enhanced bleaching effect due to the in-situ generation of dimethyldioxirane, it was difficult to fully attribute the differences in kappa numbers solely to changes in the bleaching oxidant.

Research efforts were next focused on developing an experimental procedure which minimized the acetone component and thus provide a more practical bleaching system. The bleaching of softwood kraft pulp was therefore investigated using an aqueous slurry of pulp and a premixed
Figure 1: Spectral Characterization of Bleach Effluents Isolated from DimethylDioxirane Oxidation of Softwood Kraft Pulp
mixture of the bleaching reagent. The bleaching solution employed an 8% charge of Na$_2$HCO$_3$ and Oxone and varying amounts of acetone and water. After vigorously stirring for 5 minutes, the bleaching solution was added to the pulp slurry. The resulting mixture was stirred for 1 h at room temperature and after washing was analyzed for lignin. The bleached pulp was then extracted with 1.5% NaOH at room temperature. The kappa values for the bleached and extracted pulps are summarized in Table 3. The results of these studies demonstrate that the bleaching response is sensitive to the premixing conditions and that small amounts of acetone enhance the overall delignification process. The premixing time was also shown to influence the extent of delignification and based upon current experimental data, the optimal time is within 5 minutes.

The increased delignification in the presence of acetone is attributed to the formation of the dimethyldioxirane and its enhanced bleaching efficiency. A comparison of the bleaching results using the optimal premixing conditions (Table 3, third entry) versus using an acetone/water solution (Table 2a, last entry) indicates that the final kappa values are virtually the same after caustic extraction. These results indicate that there is no need to employ acetone as a solvent during bleaching and that by pre-mixing the reagents it is possible to get an equally effective bleaching response.

With the premixing conditions optimized, the final phase of these initial studies focused on determining the optimal bleaching time, the charge response, and the effects of pH and temperature on the bleaching reaction. Samples of softwood kraft pulp were treated with 8% and 16% charges of Oxone, using the optimal conditions described in Table 3 for periods of 1/2, 1, and 14 h. As summarized in Table 4, it appears that the delignification reactions are virtually completed within 1 h at room temperature. Therefore, softwood and hardwood kraft pulp samples were bleached with varying charges of Oxone, and the results of these studies are summarized in Table 5. Although the efficiency of bleaching appears to be low, it must be remembered that the Oxone contains only 49% of potassium peroxymonosulfate per unit of charge. In terms of active oxygen, the bleach response data in Table 5 suggest that dimethyldioxirane is a reasonably effective bleaching reagent. The observed changes in viscosity with bleaching suggests that dimethyldioxirane does not extensively damage the carbohydrates present in the pulp.

The effect of pH on the delignification reaction was examined by repeating experiment 2 in Table 3 with an initial pH of either 5, 7, or 11 for the pulp slurry. As summarized in Table 6, to a first approximation bleaching with dimethyldioxirane is best preformed at a pH of 7. The experimental data indicates, however, that delignification occurs in both acidic and basic medium. The bleaching reaction was also shown to be most efficient at 80°C as summarized in Table 6. These results clearly demonstrate that dimethyldioxirane is a versatile reagent that could potentially be employed at various stages in a bleaching cycle without dramatic changes in the pH or temperature of the bleaching solution.
Conclusions

The bleaching of softwood kraft pulps with caroic acid can be significantly improved when employing minor amounts of acetone. The increased delignification and brightening of the pulps when Caroic acid and acetone is employed is attributed to the \textit{in-situ} generation of dimethyldioxirane. Preliminary bleaching studies have shown that the \textit{in-situ} generation of dimethyldioxirane can be achieved prior to addition to the pulp. There is no need to use an aqueous acetone slurry of pulp to enhance the bleach capabilities of peroxymonosulfate. These results suggest that the use of dimethyldioxirane generated from Oxone or alternative chemical procedures could be of potential use for bleaching kraft pulps in an oxygen-based bleaching sequence.

References


Table 1. Effects of a 5% Charge of DimethylDioxirane$^a$ on Softwood Kraft Pulp

<table>
<thead>
<tr>
<th></th>
<th>Initial Brightness</th>
<th>Direct$^b$ Kappa #</th>
<th>Brightness$^d$</th>
<th>Extracted$^e$ Kappa #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.5</td>
<td>23.1</td>
<td>12.5</td>
<td>31.4</td>
<td>11.9</td>
</tr>
<tr>
<td>27.6</td>
<td>20.5</td>
<td>11.1</td>
<td>30.2</td>
<td>8.5</td>
</tr>
</tbody>
</table>

$^a$ applied as a freshly distilled solution of 0.1 N dimethyldioxirane in acetone; $^b$ Kappa number of pulp treated with dimethyldioxirane; $^c$ Kappa number of treated pulp after extracting with an aqueous 1.5% NaOH solution; $^d$ Tappi standard.

Table 2a. Effects of Oxone Treatment on the Delignification of a Softwood Kraft Pulp$^a$

<table>
<thead>
<tr>
<th>Charge</th>
<th>Initial</th>
<th>Water$^b$ Direct$^d$</th>
<th>Water$^b$ Extracted$^e$</th>
<th>Water/Acetone$^c$ Direct</th>
<th>Water/Acetone$^c$ Extracted$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>145%</td>
<td>39.5</td>
<td>27.7</td>
<td>26.2</td>
<td>16.3</td>
<td>10.1</td>
</tr>
<tr>
<td>72%</td>
<td>39.5</td>
<td>31.6</td>
<td>30.1</td>
<td>17.8</td>
<td>10.8</td>
</tr>
<tr>
<td>30%</td>
<td>39.5</td>
<td>32.3</td>
<td>30.5</td>
<td>26.6</td>
<td>21.3</td>
</tr>
<tr>
<td>15%</td>
<td>39.5</td>
<td>--</td>
<td>--</td>
<td>28.5</td>
<td>23.9</td>
</tr>
<tr>
<td>3%</td>
<td>39.5</td>
<td>38.1</td>
<td>36.6</td>
<td>35.5</td>
<td>34.7</td>
</tr>
<tr>
<td>17%</td>
<td>27.6</td>
<td>--</td>
<td>--</td>
<td>16.9</td>
<td>14.0</td>
</tr>
</tbody>
</table>

$^a$ all bleaching reactions employed equal gram equivalents of Oxone and NaHCO₃; the high kappa pulp experiments employed 7.50 g of dry weight pulp and the low kappa pulp experiment employed 12 g dry weight pulp; $^b$ bleaching reactions employing only water (300 ml) as a solvent; $^c$ bleaching reactions employing a 2:1 mixture of acetone/water (300 ml) as a solvent; $^d$ kappa value after bleaching; $^e$ kappa value of pulp after bleaching and extracting with 1.5% NaOH solution.
Table 2b. Effects of Oxone Treatment on the Viscosity of a Softwood Kraft Pulp 38.7 cp Pulp*

<table>
<thead>
<tr>
<th>Charge</th>
<th>Viscosity (Cp)</th>
<th>Water</th>
<th>Extracted</th>
<th>Water/Acetone</th>
<th>Direct</th>
<th>Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Direct</td>
<td>Extracted</td>
<td>Direct</td>
<td></td>
<td>Extracted</td>
</tr>
<tr>
<td>30%</td>
<td></td>
<td>32.3</td>
<td>26.7</td>
<td>25.1</td>
<td>26.8</td>
<td>29.2</td>
</tr>
<tr>
<td>15%</td>
<td></td>
<td>--</td>
<td>--</td>
<td>29.2</td>
<td>28.4</td>
<td></td>
</tr>
</tbody>
</table>

* see Table 2a for experimental details

Table 3. Effects of Varying Premixing Conditions for an Oxonea / Water / Acetone / NaHCO3 Bleaching Mixture on Delignifying a 27.6 Kappa Softwood Kraft Pulp

<table>
<thead>
<tr>
<th>Premixture Solvent Volume/ml</th>
<th>Premixture Acetone:Water</th>
<th>Premixing Time/min</th>
<th>Consistency of Pulp During Bleaching</th>
<th>Kappa Number Directb</th>
<th>Extractc</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>3.0:1.0</td>
<td>5.0</td>
<td>1%</td>
<td>21.7</td>
<td>20.5</td>
</tr>
<tr>
<td>80</td>
<td>3.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>21.8</td>
<td>20.2</td>
</tr>
<tr>
<td>80</td>
<td>No Acetone</td>
<td>5.0</td>
<td>2%</td>
<td>24.4</td>
<td>23.1</td>
</tr>
<tr>
<td>80</td>
<td>1.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>24.1</td>
<td>20.8</td>
</tr>
<tr>
<td>80</td>
<td>1.0:1.8</td>
<td>5.0</td>
<td>2%</td>
<td>25.3</td>
<td>23.9</td>
</tr>
<tr>
<td>80</td>
<td>1.0:3.0</td>
<td>5.0</td>
<td>2%</td>
<td>23.9</td>
<td>21.2</td>
</tr>
<tr>
<td>80</td>
<td>1.0:7.0</td>
<td>5.0</td>
<td>2%</td>
<td>24.0</td>
<td>21.4</td>
</tr>
<tr>
<td>20</td>
<td>1.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>25.1</td>
<td>23.3</td>
</tr>
</tbody>
</table>

* bleaching reagent was premixed for a fixed period of time and was then added to an aqueous slurry of pulp and stirred for 1h; b kappa value after bleaching; c kappa value of pulp after bleaching and extracting with 1.5% NaOH solution.
Table 4. Effect of Varying Reaction Time on Delignification of a 27.6 Kappa Softwood Kraft Pulp

<table>
<thead>
<tr>
<th>Charge</th>
<th>Rxn Time/h</th>
<th>Direct</th>
<th>Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>8%</td>
<td>1/2</td>
<td>21.6</td>
<td>19.7</td>
</tr>
<tr>
<td>8%</td>
<td>1</td>
<td>21.8</td>
<td>20.2</td>
</tr>
<tr>
<td>8%</td>
<td>14</td>
<td>22.9</td>
<td>21.1</td>
</tr>
<tr>
<td>16%</td>
<td>1/2</td>
<td>20.6</td>
<td>17.2</td>
</tr>
<tr>
<td>16%</td>
<td>1</td>
<td>17.4</td>
<td>14.5</td>
</tr>
<tr>
<td>16%</td>
<td>14</td>
<td>18.4</td>
<td>14.8</td>
</tr>
</tbody>
</table>

*a bleaching solution was premixed employing 60 ml acetone, 20 ml water and an equal mass of oxone and NaHCO₃, after stirring for 5 min. the solution was added to a pulp slurry (2% consistency); b kappa value after bleaching; c kappa value of pulp after bleaching and extracting with 1.5% NaOH solution.

Table 5. Effect of Varying the Charge of Oxone on the Extent of Delignification and Viscosity For a Softwood and a Hardwood Kraft Pulp.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Charge</th>
<th>Direct</th>
<th>Extract</th>
<th>Initial/Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>8%</td>
<td>20.9</td>
<td>18.4</td>
<td>--</td>
</tr>
<tr>
<td>Softwood</td>
<td>4% (twice)</td>
<td>19.8</td>
<td>19.2</td>
<td>--</td>
</tr>
<tr>
<td>Softwood</td>
<td>4%</td>
<td>24.2</td>
<td>21.7</td>
<td>24.4/24.0</td>
</tr>
<tr>
<td>Softwood</td>
<td>2%</td>
<td>26.2</td>
<td>24.6</td>
<td>--</td>
</tr>
<tr>
<td>Hardwood</td>
<td>8%</td>
<td>5.9</td>
<td>5.2</td>
<td>--</td>
</tr>
<tr>
<td>Hardwood</td>
<td>2%</td>
<td>10.1</td>
<td>8.0</td>
<td>19.0/14.4</td>
</tr>
</tbody>
</table>

*a bleaching solution was premixed employing 60 ml acetone, 20 ml water and an equal mass of oxone and NaHCO₃, after stirring for 5 min. the solution was added to a pulp slurry (2% consistency) which was stirred for 1 h; b softwood pulp had a starting kappa of 27.6 and the hardwood pulp had a starting kappa of 11.5; c kappa value after bleaching; d kappa value of pulp after bleaching and extracting with 1.5% NaOH solution; e viscosity of pulp before bleaching.
Table 6. Effect of Varying Reaction pH and Temperature on Delignification of a 27.6 Kappa Softwood Kraft Pulp

<table>
<thead>
<tr>
<th>Charge</th>
<th>Rxn Temperature</th>
<th>Rxn pH</th>
<th>Kappa Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>8%</td>
<td>40°C</td>
<td>9</td>
<td>23.9</td>
</tr>
<tr>
<td>8%</td>
<td>50°C</td>
<td>9</td>
<td>23.1</td>
</tr>
<tr>
<td>8%</td>
<td>60°C</td>
<td>9</td>
<td>21.6</td>
</tr>
<tr>
<td>8%</td>
<td>80°C</td>
<td>9</td>
<td>18.9</td>
</tr>
<tr>
<td>8%</td>
<td>RT</td>
<td>5°</td>
<td>21.1</td>
</tr>
<tr>
<td>8%</td>
<td>RT</td>
<td>7°</td>
<td>18.8</td>
</tr>
<tr>
<td>8%</td>
<td>RT</td>
<td>13°</td>
<td>22.7</td>
</tr>
</tbody>
</table>

b bleaching solution was premixed employing 60 ml acetone, 20 ml water and an equal mass of oxone and NaHCO₃, after stirring for 5 min. the solution was added to a pulp slurry (2% consistency); b kappa value after bleaching; c kappa value of pulp after bleaching and extracting with 1.5% NaOH solution; d the initial pH (ca. 9) of the solution was lowered by adding 1.0 N H₂SO₄; e the initial pH of the solution was increased from 9 to 13 by the addition of 1.0 N NaOH solution.
Bleaching with NO₂/Ozone

Introduction

Recent research efforts by Suzuki and Shimizi have demonstrated that the dinitrogen pentoxide is a mild and efficient reagent for nitrating substituted aromatic compounds. Several other authors have also noted the enhanced ability of dinitrogen pentoxide to act as a nitrating reagent. Although dinitrogen pentoxide is an unstable reagent it can be readily prepared from ozone and nitrogen dioxide. Given the current interest in nitrogen dioxide as a pretreatment for oxygen bleaching and the potential application of ozone as a bleaching reagent, it was of some interest to determine if the simultaneous application of ozone/nitrogen dioxide to kraft pulps would have a synergistic effect. Based upon the literature results, it seemed reasonable to expect that dinitrogen pentoxide could nitrate the aromatic component of lignin, although the efficiency of this reaction would be countered by the known reaction of dinitrogen pentoxide with water.

The potential bleaching capabilities of nitrogen dioxide/ozone for kraft pulps were evaluated employing three bleaching experiments. The experimental design consisted of treating a fully characterized softwood kraft pulp with:

(i) ozone followed by caustic extraction;
(ii) nitrogen dioxide, followed by ozone followed by caustic extraction;
(iii) combined nitrogen dioxide, ozone treatment, followed by caustic extraction.

The bleached and extracted pulps were to be characterized by means of Kappa values and viscosities. This series of bleaching procedures should help identify any advantages to bleaching with dinitrogen pentoxide. An oxygen bleaching stage would be pursued if the initial studies appeared promising.

Results and Discussion

Following the usual ozonolysis conditions pulp samples for experiments i and iii were prepared by acidifying the pulp with acetic acid (pH = 2). For experiment ii the pulp was acidified after the nitrogen dioxide treatment. After preparation, each pulp sample was treated with an equal charge of ozone. The addition of nitrogen dioxide to ozone (experiment ii) yielded dinitrogen pentoxide which was visually confirmed (nitrogen dioxide is an off-brown colored gas while dinitrogen pentoxide is colorless). The amount of ozone consumed during bleached was also significantly increased for experiment ii, again suggesting that nitrogen dioxide had reacted with ozone. A complete summary of the experimental details is provide in Table 1.
The kappa determinations for the bleached and extracted pulps clearly indicated that the addition of nitrogen dioxide into an ozone stream was not advantageous for bleaching. The residual lignin remaining in the pulp was substantially higher for experiment ii than in either of the two other experiments. The ineffectiveness of dinitrogen pentoxide as a bleaching reagent was attributed to its reaction with water. The pH of the $O_3/NO_2$ (experiment iii) bleached pulp effluent was much more acidic (pH = 2) than for experiments i or ii (pH = 4). The differences in pH effluent support the proposal that dinitrogen pentoxide reacts quicker with water than with the lignin in the pulp. It was of interest to note that the pretreated nitrogen dioxide pulp after ozonolysis and caustic extraction was delignified to virtually the same Kappa value as the ozone treated pulp (experiment i) but without a large loss in viscosity. This result is consistent with literature results for oxygen bleaching.

Conclusion

In summary, treatment of kraft pulps with dinitrogen pentoxide, prepared \textit{in-situ} from ozone and nitrogen dioxide does not appear to have any advantages for bleaching chemical pulps.
**Table 1  Summary of Experimental Data for Bleaching Softwood Kraft Pulp**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/ Ozone</td>
<td>1/ Nitrogen Dioxide</td>
<td>1/ Ozone &amp; Nitrogen Dioxide</td>
</tr>
<tr>
<td>Pulp Consistency for Bleaching</td>
<td>29%</td>
<td>30%</td>
<td>29%</td>
</tr>
<tr>
<td>Charge of NO\textsubscript{x}</td>
<td>--</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>Charge of Ozone</td>
<td>1.16%</td>
<td>1.22%</td>
<td>1.14%</td>
</tr>
<tr>
<td>Ozone Consumed</td>
<td>79.2%</td>
<td>83.7%</td>
<td>89.1%</td>
</tr>
<tr>
<td>Kappa Value After Bleaching</td>
<td>17.9</td>
<td>15.6</td>
<td>20.1</td>
</tr>
<tr>
<td>Kappa Value After Extraction\textsuperscript{b}</td>
<td>12.6</td>
<td>11.9</td>
<td>19.3</td>
</tr>
<tr>
<td>Viscosity Value After Extraction\textsuperscript{b} (Cp)</td>
<td>11.1</td>
<td>14.4</td>
<td>----</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Initial Kappa value was 27.6 and initial viscosity was determined to be 24.4 Cp
\textsuperscript{b} For all three bleached pulp samples were extracted with 1.5% caustic solution after the initial Kappa values were determined.

**References**

Student Related Research

Characterization of Bleach Plant Effluents by $^1$H and $^{13}$C NMR
- B. Boyer

Characterization of Lignin Derived Extended Delignification Processes via $^1$H and $^{13}$C NMR
- P. Froass
PROJECT 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

RESEARCH REVIEW

MARCH 25, 1992

Arthur J. Ragauskas
OBJECTIVE: Research activities are directed at investigating the fundamental chemical reactions which are initiated when high yield-pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to stop or significantly retard the yellowing process will be pursued.

IPST GOAL: Increase the usefulness of high-yield fibers.

SUMMARY:
Advancements in the manufacturing and bleaching of high-yield mechanical pulps has resulted in the commercial preparation of pulps that have Tappi brightness levels of above 80%. To date, these pulps are used as furnishes for low-value or short-life paper products due to their tendency to undergo light-induced yellowing. It has been suggested that if the rate of brightness reversion was reduced from three to thirty six months, the potential market for bleached CTMP would be expanded by 0.6 to 2.2 million tonnes per year.

Clearly there is an increasing need to investigate the fundamental chemical reactions which are initiated when high-yield pulps are photolyzed and to apply this knowledge to halt or significantly retard the yellowing process. To accomplish this goal, research efforts have been focused on three important aspects of the brightness reversion phenomenon: the design of novel photostabilization techniques and reagents, the photo-formation of chromophoric structures, and the photo-reactivity of chromophoric structures.
Based upon the fundamental principal that brightness reversion of mechanical pulp is a photo-initiated oxidation of lignin, research efforts have been directed at examining the effectiveness of reagents which could be oxidized at rates comparable to lignin and yet remain colorless. Through an extensive survey of compounds, we have discovered three new structurally related sets of compounds which could retard relative rates of brightness reversion. All three sets of compounds are structurally related diene systems. The most successful reagent studied to date is trans,trans-2,4-hexadien-1-ol. Photo-reversion studies with BCTMP pulp samples treated with this alcohol have shown that this compound can photo-stabilize mechanical pulp as effectively as ascorbic acid. Although the application of this reagent has been shown to accelerate thermal reversion, several preliminary studies have suggested that this phenomenon can be halted.

The chemical mechanisms contributing to the photo-formation of chromophoric structures in mechanical pulp has also been explored in this research program. Research efforts over the past years have demonstrated that brightness reversion is initiated by the absorption of a photon of light by conjugated lignin structures. The excited state of these molecules then ultimately leads to the formation of radicals and the oxidation of lignin to highly colored material. The presence of α-carbonyl groups in lignin has been frequently cited as a principle component contributing to the formation of colored quinone-like structures in photo-yellowed mechanical pulp. The photo-reactivity of model lignin-like compounds has been studied by several groups and is believed to be a valid model for brightness reversion. Research efforts described in this report clearly demonstrate that current lignin model compounds employed in the literature fail to yield ortho-quinone like structures. Since ortho-quinones have been detected in mechanical pulp these results indicate that the exact chemical mechanisms involved in oxidizing phenolic structures in lignin to quinones is far from understood.

Finally, the photo-reactivity of chromophoric structures commonly believed to contribute to yellowing have also been studied. Employing a series of para- and ortho-quinone structures, we have determined that most quinone structures do not contribute to further photochemical yellowing of mechanical pulp. Research efforts have also demonstrated that hydroxy-para-quinones exhibit chemical behavior analogous to that of ortho-quinones. These results have important implications in the characterization of quinone structures found in mechanical pulp.
Brightness Stability

Project 3524

Photo-Stabilization of Mechanical Pulp

Introduction

Advances in mechanical pulping and bleaching have provided the means of manufacturing ultra high-yield pulps that have a Tappi brightness above 80%. At these levels of brightness, mechanical pulps could potentially be employed in high value paper products such as business forms, reprographic papers, and writing papers. However, the rapid light-induced yellowing of these brightened pulps restricts their use to short-life, low-value paper products. It has been suggested that if the relative rate of light-induced yellowing could be reduced from three months to thirty six months then the potential market for bleached CTMP would increase fourfold.

The principle component of mechanical pulps which contributes to photo-yellowing has been shown to be the lignin portion of the pulp. Although the photo-oxidation mechanisms have not been fully elucidated, significance advances have been made in understanding brightness reversion. It is now well recognized that extended conjugated structures present in lignin absorb near-UV light (\( \lambda = 300-400 \) nm) and that the excited state of these structures leads to the formation of radicals. Regardless of the exact mechanism responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of ortho- and para-quinones. The presence of quinoid-like structures in photo-aged mechanical pulp has been detected spectroscopically, and these structures are believed to be one of the principle components contributing to the yellowing of mechanical pulp. Clearly then, photo-stabilization of mechanical pulp requires that the photo-initiated oxidation of lignin be halted.

Research efforts over the past 45 years have identified three general methods by which mechanical pulps can be photo-stabilized. High-yield pulps can be stabilized by reducing the lignin chromophores with sodium borohydride followed by an alkylation. This two-step process removes most lignin chromophores and stabilizes the pulp with respect to photo-oxidation of phenolic groups. Alternatively, mechanical pulps can be stabilized with the addition of near-UV absorbing compounds such as dihydroxy or tetrahydroxybenzophenone. These latter reagents absorb harmful near-UV light and convert it to thermal energy thereby halting the photo-initiated oxidation of lignin. Although both of these processes are effective, the costs associated with these technologies has prevented their implementation.

A more-promising approach to stabilizing mechanical pulp has been to design inhibitors which are oxidized at rates greater than that of lignin itself. Early research efforts of Janson and Forsskahl demonstrated the efficiency of several mercaptans to retard brightness reversion of high-yield pulps. These observations have been further pursued by Sarkanen and Daneault. The results of their studies demonstrated that
reagents such as thioglycerol and 1-dodecanethiol can substantially improve the photo-stability of mechanical pulps. The use of ascorbic acid as an inhibitor of light reversion has also been explored. The effectiveness of this reagent and the proposed mechanism of photo-stabilization has been investigated by Heitner and others.

**Discussions of 1991 Results**

Based upon the results of these inhibitor studies and other reports, we initiated a survey study to identify novel methods of retarding brightness reversion. The three types of reagents considered in this study can be classified into one of three categories, novel alkylating reagents, reductive treatments, and antioxidant reagents. To date, the most successful results have been found from the latter category. Table 1 summarizes the types of alkylating reagents and reductive treatments which were examined and shown not to have a positive effect on reducing the rates photo-yellowing.

In contrast to these results a series of three new structurally related sets of compounds have been discovered which have been shown to reduce the relative rate of brightness reversion. As shown below, we have found that substituted cyclohexadienes; 1,4-pentadien-3-ol; and trans,trans-2,4-hexadien-1-ol are all effective at retarding brightness reversion of BCTMP pulp samples.

![Chemical structures](attachment:image.png)

Before examining the results of these studies, it is necessary to review the general experimental procedures employed and the means of reporting the photo-stabilization values. The experimental approach employed in our studies was to prepare a series of optical handsheets following Tappi procedures and then to wash these handsheets with methanol. The methanol wash was required to remove any extractives. Removal of the extractives was required so as to accurately determine the amounts of proposed inhibitor applied. A review of the literature indicates that extractives do not contribute to photo-yellowing of mechanical pulp, and their absence in these experiments does not invalidate...
the results. The handsheets were then air and vacuum dried; initial brightness values were recorded, and the pulp samples were then soaked in a methanolic solution containing the proposed inhibitor. After drying, the amounts of applied stabilizer were determined, and brightness values were measured. The photolysis experiments were preformed in either a Rayonet photochemical reactor with RPR-3500A lamps (λ = 300-400) or with the Oriel solar simulator. All photolysis experiments were carried out in the presence of a second set of reference handsheets which had been methanol washed but not treated with the proposed photo-yellowing inhibitor.

The rate of yellowing was monitored by measuring the changes in brightness. To evaluate the effect of a given reagent on stabilizing mechanical pulp, we have employed the % stabilization concept developed by Lamont\(^\text{11}\) (equation 1).

\[
\text{% Stabilization (PS)} = 100\% \times \left( \frac{\Delta \text{Brightness of treated sample} - \Delta \text{Brightness of reference sample}}{\Delta \text{Brightness of reference sample}} \right)
\]

Eq. 1

Our initial attempts at photo-stabilization of mechanical pulp employed 1-methoxy-1,3- cyclohexadiene (1,3-CHD); 1-methoxy-1,4-cyclohexadiene (1,4-CHD); and 1,2,4,5- tetramethyl-1,4-cyclohexadiene (TMCHD). Preliminary studies with 1,4-CHD indicated that the % stabilization was dependent upon the solvent the reagent was dissolved in. For example, handsheets treated with a solution of 1,4-CHD and dichloromethane yielded a negligible stabilization effect. Through a series of experiments with 1,4-CHD, it was determined that methanol was the best solvent to be employed. The stabilization effect for 1,4-CHD was also shown to be dependent upon the time of application. For example, handsheets treated with a 0.7 N 1,4-CHD/methanol solution for 15 min exhibited a maximum PS of 9%. In contrast, handsheets treated with methanolic 1,4-CHD for 2 h yielded a maximum PS of 21%. Based strictly upon experimental convenience, all handsheets were treated with methanolic solutions for 15 min.

Upon completing these preliminary experiments, research efforts were then focused on determining the efficiency of photo-stabilizing handsheets of TMP with 1,3-CHD; 1,4-CHD; and TMCHD. The results of these studies are summarized in Table 2, and the data clearly indicate that 1,3-CHD and 1,4-CHD can reduce the rate of brightness reversion. These studies were then repeated employing BCTMP hardwood pulp handsheets which had an ISO brightness of above 80%. The results of the photo-stabilization studies are tabulated in Table 2, and they demonstrate that the use of 1,3-CHD or 1,4-CHD can retard the relative rate of brightness reversion for low- and high-brightness pulps. The inefficiency of TMCHD to stabilize mechanical pulp was tentatively attributed to the hydrophilic nature of the molecule.
Although these results were promising, the use of 1-methoxy-1,3-cyclohexadiene or 1-methoxy-1,4-cyclohexadiene was difficult to study due to the volatility of these structures. The loss of inhibitor during reversion made studying the kinetics of this process virtually impossible. In an attempt to address these issues, handsheets of BCTMP were treated with 1,4-dihydro-2-methylbenzoic acid. It was anticipated that the carboxylate would prevent volatilization of the inhibitor and enhance the binding to the fibers. Furthermore, 1,4-dihydro-2-methylbenzoic acid retains the cyclic diene structure and so should act as a photo-stabilization reagent. Employing the usual experimental procedures doped handsheets were prepared and irradiated in the Solar Simulator. The results of these studies are summarized in Table 3, and the data indicate that 1,4-dihydro-2-methylbenzoic acid is a moderately effective stabilizing reagent. In comparison to the stabilization effects noted with 1-methoxy-1,4-cyclohexadiene the 1 and 2 h effects are comparable, but after 4 h of irradiation, the 1,4-dihydro-2-methylbenzoic acid treated handsheet continued to have a significant stabilization effect. The differences in stabilization were tentatively attributed to the differences in volatility of the compounds.

To investigate the possibility that the effectiveness of the above reagents was due to the conjugated olefinic ring structure, we surveyed a series of unsaturated cyclic compounds as potential photo-yellowing inhibitors. The potential use of 1,3-cycloheptadiene; cycloheptatriene; 1,3,5,7-cyclooctatetraene; abietic acid; 2-furoic acid; furfuryl; 2-thiophenecarboxylic acid; and 2-thiophenemethanol as photo-stabilization reagents was shown to be ineffective. Although these studies failed to identify alternative structural units which could stabilize mechanical pulp, they did contribute to our fundamental understanding of how the cyclic diene structures photo-stabilize high-yield pulps.

To determine if the photo-stabilization effect of 1,4-dihydro-2-methylbenzoic acid was due to its cyclic structure, we examined the stabilization effects for trans,trans-2,4-hexadienoic acid. This compound has been reported to be a "mild" photo-yellowing inhibitor. The % stabilization effects for trans,trans-2,4-hexadienoic acid applied to BCTMP handsheets are summarized in Table 3. Although it is difficult to compare the differences in stabilization between the cyclic and acyclic inhibitor due to the differences in the level of application, it was interesting to note such a strong stabilization effect for the acyclic compound.

The photo-stabilization effect of trans,trans-2,4-hexadienoic acid promoted our interest, and we initiated a study to determine what structural components of this compound were needed for photo-stabilization. Preliminary studies indicated that both acrylic and crotonic acid were ineffective at stabilizing BCTMP handsheets. Based upon these results, we concluded that both double bonds needed to be present in the inhibitor to retard brightness reversion. Furthermore, it was shown that the sodium salt of trans,trans-2,4-hexadienoic actually accelerated brightness reversion. Based upon these results the photo-stabilization effects of trans,trans-2,4-hexadien-1-ol and hexadienal were investigated. As anticipated BCTMP handsheets treated with the aldehyde yellowed
Brightness Stability

rapidly, as summarized in Table 3. It was therefore much to our surprise the alcohol was shown to be a very effective photo-stabilization compound, as reported in Table 3.

Due to the significant photo-stabilization effects of trans,trans-2,4-hexadien-1-ol on BCTMP, this reagent was further investigated. Photolysis of treated handsheets for prolonged periods of time indicated a continuing stabilization effect, as summarized in Table 4. A comparison of the % stabilization effect for 2,4-hexadien-1-ol with ascorbic acid indicated that both reagents were near equal in their ability to retard photo-yellowing. The application of ascorbic acid and 2,4-hexadien-1-ol onto BCTMP handsheets yielded a mild synergistic effect. In conclusion these results suggest that hexadien-1-ol is nearly as effective a photo-stabilization reagent as ascorbic acid.

The physical and chemical changes occurring with BCTMP handsheets treated with hexadien-1-ol were also investigated. Scattering coefficients for the treated and untreated handsheets were determined before and after photolysis, and these data indicated no differences within experimental error. Likewise, it was established that the opacity of all of the handsheets remained constant. These results clearly suggest that the changes in brightness reversion are due to differences in the relative rates of chromophore formation in the treated and untreated handsheets. The diffuse reflectance spectrum ($\lambda = 400 - 700$) for the treated and untreated BCTMP handsheets was recorded at 0, 1, 2, and 4 h of irradiation. These spectra, shown in Figure 1 serve to illustrate the pronounced effect that trans,trans-2,4-hexadien-1-ol has on the photo-yellowing of the handsheets. Although all treated and untreated handsheets have the same initial spectrum, after 1 h of irradiation, the treated handsheets exhibit higher % reflectance than the untreated handsheets. This trend is then continued throughout the photolysis experiment.

The successful commercial implementation of a photo-stabilization reagent for BCTMP and other ultra high-yield mechanical pulps is dependent upon several crucial issues, including cost, safety, and thermal stability of the reagent. The latter condition has imposed a serious challenge to the application of hexadien-1-ol for inhibition of photo-yellowing. A series of long-term experiments just recently completed have indicated that the unsaturated alcohol accelerates thermal reversion (see Table 5). It is our opinion that the thermal reversion process takes place due to a slow autoxidation of hexadien-1-ol to hexadienal. This aldehyde is known to have an "off-yellow" color, and its formation could readily lead to an apparent thermal reversion of the treated pulp samples. Currently, we are attempting to develop novel methods of halting this process. Preliminary data in Table 5 indicate that BCTMP handsheets treated with a mixture of ascorbic acid and hexadien-1-ol do not readily undergo thermal reversion. These experiments are long-term in nature and will require several additional months to confirm these initial trends.

An alternative means of halting the thermal reversion process is to chemically alter the hexadien-1-ol structure so that autoxidation can not readily occur. The principle method we are pursing in this field is to convert the alcohol into an ether or ester functional group. Clearly, for such an approach to be feasible the alcohol functional group must not be
involved in the chemical processes contributing to photo-stabilization. Recent reversion studies with the acetate of hexadien-1-ol have demonstrated that the acetate is an effective stabilization reagent, and thermal reversion studies have been initiated.

Finally, we have examined 1,4-pentadien-3-ol as a photo-stabilization reagent for BCTMP, and moderate stabilizing effects were noted (see Table 4). Presumably, this compound reduces reversion in much the same manner as the cyclohexadiene structures, by donating a hydrogen atom to phenoxy radicals generated during brightness reversion.

Conclusions and Recommendations

In summary, we have discovered several novel reagents which could retard brightness reversion. Based upon the results of these studies and the literature we believe that the use of inhibitors to stabilize mechanical pulp has great potential and is not fully developed. The thermal reversion issues associated with trans,trans-2,4-hexadien-1-ol need be resolved for future success of this reagent and we are optimistic that this hurdle will be overcome.

Finally, these studies have discovered a new set of structurally related compounds which are effective at retarding brightness reversion. It is our goal to pursue these findings so as to develop new and effective methods of stabilizing mechanical pulp.

Future Activity

Future research efforts will focus on investigating methods of retarding thermal reversion of BCTMP samples treated with trans,trans-2,4-hexadien-1-ol. Several structural variations of hexadienol will be investigated to optimize both thermal and photo-stabilization effects. Alternative methods of applying trans,trans-2,4-hexadien-1-ol and other inhibitors onto BCTMP pulp samples will be evaluated. The effectiveness of these reagents with conventional lighting sources such as, natural sunlight, photocopiers, and office fluorescent lamps will be examined.

Future advances in photo-stabilization of high-yield pulps with the reagents developed in our laboratories requires a rigorous understanding of the fundamental chemical processes that contribute to their efficiency. It is anticipated that as we develop a refined understanding of the chemical mechanisms contributing to photo-stabilization we will be able to optimize inhibition of photo-yellowing. Future research efforts in this are directed towards studying the chemical fate and reaction mechanisms of the inhibitors discovered in this program. All studies will executed with BCTMP pulp samples and the results should impact directly on retarding brightness reversion in mechanical pulp.
Brightness Stability

Finally, we plan to continue pursuing our survey study of novel brightness reversion stabilization techniques.

References


5. (a) Nolan, P.A. Paper Trade J. 1945, 121, 219


11. Personal communication.

Figure 1  Diffuse Reflectance Spectroscopy of Untreated BCTMP Handsheets and trans,trans-2,4-hexadien-1-ol Doped BCTMP Handsheets
Table 1  List of Reagents Which Were Shown to be Ineffective at Stabilizing Mechanical Pulp

<table>
<thead>
<tr>
<th>Phenoxy Blocking Reagents</th>
<th>Oxidizing Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl Isocynate</td>
<td>Dimethyl Dioxirane</td>
</tr>
<tr>
<td>Ethyl Isocynate</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Acetylenedicarboxylate</td>
<td></td>
</tr>
<tr>
<td>Thionyl Chloride</td>
<td></td>
</tr>
</tbody>
</table>

Table 2  Photo-Stabilization Effects for Mechanical Pulp Handsheets* Treated with Methanolic Solutions° of 1-methoxy-1,3-cyclohexadiene (1,3-CHD); 1-methoxy-1,4-cyclohexadiene (1,4-CHD); and 1,2,4,5-tetra-methyl-1,4-cyclohexadiene (TMCHD).

<table>
<thead>
<tr>
<th>Period of Irradiation(^d/h)</th>
<th>1,3-CHD(^*)</th>
<th>1,4-CHD(^*)</th>
<th>TMCHD(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TMP BCTMP</td>
<td>TMP BCTMP</td>
<td>TMP BCTMP</td>
</tr>
<tr>
<td>1</td>
<td>32 24</td>
<td>35 31</td>
<td>5 3</td>
</tr>
<tr>
<td>2</td>
<td>20 22</td>
<td>18 28</td>
<td>-5 2</td>
</tr>
<tr>
<td>4</td>
<td>3 7</td>
<td>-2 16</td>
<td>-3 2</td>
</tr>
</tbody>
</table>

Initial Brightness for Treated Handsheet°

<table>
<thead>
<tr>
<th>Mass of Inhibitor Applied (g/g handsheet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.052 0.035</td>
</tr>
</tbody>
</table>

\(^*\)optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; \(^°\)handsheets were soaked in a 10% by weight cyclohexadiene / methanol solution for 1/4 h and then air and high vacuum dried; \(^*\)see equation 1 for a definition of % stabilization; \(^d\)accelerated photo-aging was performed with a Oriel Solar Simulator and all experiments were performed in triplicate; \(^°\)TMP was prepared from juvenile pine; \(^f\) BCTMP was prepared from hardwood; \(^°\)ISO Brightness
Table 3  Photo-Stabilization Effects for BCTMP Handsheets* Treated with Methanolic Solutions* of 1,4-dihydro-2-methylbenzoic acid (1,4-DHBA); trans,trans-2,4-hexadienoic acid (2,4-HDA); trans,trans-2,4-hexadienal (2,4-HDAl); and trans,trans-2,4-hexadien-1-ol (2,4-HDol)

<table>
<thead>
<tr>
<th>Period of Irradiation(^d/h)</th>
<th>1,4-DHBA BCTMP(^*)</th>
<th>2,4-HDA BCTMP</th>
<th>2,4-HDAl BCTMP</th>
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<td>23</td>
<td>44</td>
<td>4</td>
<td>46</td>
<td>75</td>
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</tbody>
</table>

Initial Brightness for Treated Handsheet\(^f\)  

| Mass of Inhibitor applied (g/g handsheet) | 0.021 | 0.16 | 0.04 | 0.05 | 0.04 |

*optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; \(^*\)handsheets were soaked in a methanolic solution for 1/4 h and then air and high vacuum dried; \(^*\)see equation 1 for a definition of % stabilization; \(^*\)accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate; \(^*\)BCTMP was prepared from hardwood; \(^f\)Tappi and ISO Brightness measurements.
Brightness Stability

Table 4  Photo-Stabilization Effects for BCTMP Handsheets* Treated with Methanolic Solutionsb of trans,trans-2,4-hexadien-1-ol (2,4-HDol); Ascorbic Acid (AA); trans,trans-2,4-hexadienal (2,4-HDal); 1,4-pentadien-3-ol (1,4-PD); and the Acetate of trans,trans-2,4-hexadien-1-ol (A2,4-HDol).

<table>
<thead>
<tr>
<th>Period of Irradiationd/h</th>
<th>2,4-HDol</th>
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<th>2,4-HDol/AA</th>
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<th>A2,4-HDol</th>
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</thead>
<tbody>
<tr>
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<td></td>
<td>--</td>
<td>--</td>
<td>29</td>
</tr>
</tbody>
</table>

Initial Brightness for Treated Handsheetf:  

- 2,4-HDol: 85  
- AA: 88  
- 2,4-HDol/AA: 85  
- 1,4-PD: 88  
- A2,4-HDol: 88

Mass of Inhibitor applied (g/g handsheet):  

- 2,4-HDol: 0.028  
- AA: 0.032  
- 2,4-HDol/AA: 0.058  
- 1,4-PD: 0.021  
- A2,4-HDol: 0.042

*optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; bhandsheets were soaked in a methanolic solution for 1/4 h and then air and high-vacuum dried; csee equation 1 for a definition of % stabilization; daccelerated photo-aging was performed with a Oriel Solar Simulator, and all experiments were performed in triplicate; eBCTMP was prepared from hardwood; fTappi and ISO Brightness measurements.
Table 5  Thermal Reversion Effects for BCTMP Handsheets<sup>a</sup> Treated with Methanolic<sup>b</sup> Solutions of trans,trans-2,4-hexadien-1-ol (2,4-HDol); trans,trans-2,4-hexadien-1-ol/Ascorbic Acid (AA); and Acetate of trans,trans-2,4-hexadien-1-ol (A2,4-HDol).

<table>
<thead>
<tr>
<th>Days in Darkroom&lt;sup&gt;c&lt;/sup&gt;/h</th>
<th>2,4-HDol BCTMP&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Untreated BCTMP</th>
<th>2,4-HDol/AA BCTMP</th>
<th>A2,4-HDol BCTMP</th>
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<td>87</td>
<td>76</td>
<td>85</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Mass of Inhibitor applied (g/g handsheet) 0.151 0.032 0.021

<sup>a</sup>optical handsheets were prepared from a commercial BCTMP hardwood pulp following standard Tappi procedures; <sup>b</sup>handsheets were soaked in a methanolic solution for 1/4 h and then air and high-vacuum dried; <sup>c</sup>all handsheets were stored in a darkroom, and all experiments were preformed in triplicate; <sup>d</sup>BCTMP was prepared from hardwood.
Photo-Reactivity of Chromophoric Structures

Introduction

Although the exact chemical reactions by which mechanical pulp undergoes photo-initiated deterioration remain ambiguous, certain important aspects of this process have now been determined. The reaction is initiated by the absorption of a photon of light by extended conjugated structures present in lignin, such as \( \alpha \)-carbonyl groups or olefinic structures conjugated with a phenyl ring. It has been proposed that the excited state of these compounds then leads to the formation of radicals either directly by an intramolecular bond cleavage process (path a, see below) or intermolecularly via abstraction of a phenolic hydrogen (path b). Alternatively, it has been suggested that the excited state could lead to the generation of singlet oxygen. This reactive species could react further with lignin (path c), generating a variety of radical intermediates. Recent research efforts by several investigators have challenged the proposed role of singlet oxygen in photoyellowing.

Despite the results of model studies, the exact mechanism of photo-initiated oxidation of lignin in wood fibers remains uncertain. A recent paper by Francais et al. provided strong evidence for the intermediacy of hydroxyl radicals during brightness reversion of mechanical pulp. The authors therefore suggested that hydroxyl radicals (generated from...
either pathway a or b in Figure 1) were major contributors to the photoyellowing of mechanical pulps. In direct contrast to these results, Fisher has demonstrated that hydroxyl radicals and superoxide radicals can result in the bleaching of CTMP. The uncertainty about the reaction mechanisms contributing to the photo-aging of wood fibers was recently highlighted by Heitner in his 1991 ISWPC plenary lecture in which he concluded that "very little is known about the key oxidation step of phenoxy free radicals to quinones."

Regardless of the reaction mechanisms responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of ortho and para-quinones. The presence of quinoid-like structures in photo-aged mechanical pulp has been supported by studies employing diffuse reflectance FT-IR, NMR, and UV spectroscopy techniques.

Several recent publications have suggested that quinones formed during brightness reversion contribute to subsequent photochemical reactions which further darken irradiated mechanical pulp. If this suggestion were found to be generally true new mechanisms of photo-stabilizing mechanical could be designed. Research efforts from this laboratory have been directed at examining the photochemical behavior of ortho- and para-quinones believed to be present in photo-yellowed mechanical pulp handsheets.

Review of Past Project Activity

Previous research efforts in this area indicated that 2,6-dimethoxy-benzoquinone (DMBQ) was photo-stabile to the brightness reversion conditions. Samples of DMBQ applied to cotton linter handsheets and irradiated under the brightness reversion conditions did not undergo further photo-reversion. Furthermore, TMP handsheets treated with DMBQ and irradiated yellowed at a rates consistent with a reference handsheet. Both of these results suggested that DMBQ is not involved in subsequent photolysis reactions which could accelerate the rate of reversion. Applying the same experimental techniques with 2-methoxybenzoquinone (MMBQ) suggested that MMBQ is photo-reactive to the brightness reversion conditions.

Discussions of 1991 Results

The photochemical behavior of 2,6-dimethoxy-3-hydroxybenzoquinone, 3-methoxy-ortho-quinone, and 4-methyl-ortho-quinone under the brightness reversion conditions was examined. The initial photochemical studies employed cotton linter handsheets doped with the quinones and irradiated with the Oriel Solar Simulator. As summarized in Table 1 all three compounds failed to darken the handsheets upon photolysis and indeed a mild brightening effect was noted. Similar results were noted when the compounds were applied onto BCTMP handsheets and are summarized in Table 2. The results of these
studies clearly suggest that not all quinones formed during brightness reversion are photoreactive.

Further research efforts at determining the chemical mechanisms involved in darkening MMBQ doped cotton linter handsheets has inadvertently discovered a slow but significant thermal reversion process. Once this process was noted we pursued this observation by monitoring changes in brightness for MMBQ treated cotton linter and BCTMP handsheets. The results of these studies are summarized in Table 3. GC/MS analysis of the MMBQ spiked handsheets which have been "aged" for several days indicate the presence of dimeric MMBQ compounds. Analogous results have been noted by Forsskahl during photoreversion. This data is of importance in light of the fact that Forsskahl has proposed that the photo-reversion of MMBQ contributes to darkening of mechanical pulp handsheets. Although the rates of thermal reversion are not as significant as those reported for brightness reversion undoubtedly surface warming of MMBQ treated handsheets during the photolysis experiment would accelerate the thermal reversion phenomena. In conclusion the reported photo-yellowing of MMBQ spiked handsheets is most likely due to a complex series of thermal and photo-chemical reactions.

As discussed in the introduction to this section the detection of quinones in mechanical has been attempted with several spectroscopic techniques. Direct evidence for the presence of ortho-quinone structures in mechanical pulp was recently published by McDonough et al. Their research efforts demonstrated that ortho-quinones found in mechanical pulp could be reductively O-alklylated and that the resulting products yielded diagnostic chemical shifts in the $^{31}$P NMR, as summarized below.

![Chemical Structures](image)

The reactivity of trimethyl phosphite with ortho-quinones has now been employed by several researchers to characterize the types of chromophores generated during photo and thermal aging of mechanical pulp.

Our interest in this technique was focused on the potential reactivity of hydroxy para-quinones to also undergo an analogous type reaction with P(OCH$_3$)$_3$ to yield the reduced cyclic phosphate compound, as summarized below.
If this reaction were to occur then the diagnostic signals in the $^{31}$P NMR at ca -45 ppm could be attributed to either ortho-quinones or 2-hydroxy-para-quinones. Given the increasing use of P(OCH$_3$)$_3$ as a test for the presence of ortho-quinones it was of interest to characterize this potential reaction.

The addition of P(OCH$_3$)$_3$ to either 2,6-dimethoxy-3-hydroxybenzoquinone in CD$_2$Cl$_2$ (solution is a deep red color) or 2,5-dihydroxybenzoquinone in CD$_2$Cl$_2$ (solution is yellow colored) yielded a clear, colorless solution within a few minutes. The change in color suggested that the quinones had been reduced by the trimethyl phosphite but it was unclear if these substrates had reacted according to the ortho-quinone pathway or para-quinone pathway. The $^{31}$P NMR spectra of these reaction mixtures are shown in Figure 1. The NMR chemical shift data includes a strong signal at -45.2 ppm for 2,6-dimethoxy-3-hydroxybenzoquinone and -41.6 ppm for 2,5-dihydroxybenzoquinone. These results clearly demonstrate that hydroxy-para-benzoquinones can react in a manner similar to ortho-quinones. Hence the diagnostic signals in the $^{31}$P NMR spectrum of mechanical pulp samples photo-aged and treated with P(OCH$_3$)$_3$ could arise from either ortho-quinones or hydroxy-para-benzoquinones.

**Conclusions and Recommendations**

The research efforts described in this section have demonstrated that not all quinone structures which may be present in mechanical pulp contribute to further photo-yellowing of mechanical pulp. Experimental data for MMBQ suggests that this component could contribute both to thermal and photo-reversion. The thermal-reversion component of MMBQ has not been previously reported and these results add to the complexity of MMBQ and its role in brightness reversion.
Brightness Stability

The reaction of trimethoxy phosphite with hydroxy-para-benzoquinones has been shown to yield the reduced cyclic phosphate which has a diagnostic signal at ca -45 ppm. These results are of significance in regards to characterizing quinone like structures found in mechanical pulp samples.

Future Activity

Research efforts in this area are currently focused on completing several minor issues associated with the photolytic behaviour of ortho- and para-quinones. Once these research studies are completed the results will be summarized in a publication and no further research efforts are currently anticipated in this field as all of the original goals have been completed.

References

Brightness Stability


Brightness Stability

NMR Sample: \( P(OCH_3)_3/CD_2Cl_2/2,6\text{-dimethoxy-3-hydroxybenzoquinone} \)

Figure 1 \( ^{31}\text{P NMR Spectra} \)
**Table 1** Photolysis of Cotton Linter Handsheets (CLHS)\(^\text{a}\) Treated\(^\text{b}\) with 2,6-dimethoxy-3-hydroxybenzoquinone (DMBQ-3-OH); 3-methoxy-ortho-quinone (MMOQ); and 4-methyl-ortho-quinone (4-MOQ).

<table>
<thead>
<tr>
<th>Period of Irradiation(^\circ)/h</th>
<th>CLHS</th>
<th>DMBQ-3-OH/CLHS</th>
<th>MMOQ/CLHS</th>
<th>4-MOQ/CLHS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>85</td>
<td>68</td>
<td>54</td>
<td>64</td>
</tr>
<tr>
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<tr>
<td>4</td>
<td>85</td>
<td>81</td>
<td>60</td>
<td>69</td>
</tr>
</tbody>
</table>

\(^{\circ}\)optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with \(\text{CH}_2\text{Cl}_2, \text{CH}_3\text{OH}\); \(^{\circ}\)handsheets were soaked in a \(\text{CH}_2\text{Cl}_2\) solution for 1/4 h and then air and high vacuum dried; \(^{\circ}\) accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate.

**Table 2** Photolysis of Cotton Linter Handsheets (CLHS)\(^\text{a}\) Treated\(^\text{b}\) with 3-methoxy-ortho-quinone (MMOQ); and 4-methyl-ortho-quinone (4-MOQ).

<table>
<thead>
<tr>
<th>Period of Irradiation</th>
<th>Reference MMOQ</th>
<th>MMOQ/BCTMP</th>
<th>Reference 4-MOQ</th>
<th>4-MOQ/BCTMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>46</td>
<td>86</td>
<td>48</td>
</tr>
<tr>
<td>1</td>
<td>77</td>
<td>50</td>
<td>77</td>
<td>52</td>
</tr>
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<td>2</td>
<td>74</td>
<td>50</td>
<td>73</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>72</td>
<td>50</td>
<td>70</td>
<td>47</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\)optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with \(\text{CH}_2\text{Cl}_2, \text{CH}_3\text{OH}\); \(^{\text{b}}\)handsheets were soaked in a \(\text{CH}_2\text{Cl}_2\) solution for 1/4 h and then air and high vacuum dried; \(^{\text{c}}\) accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate.

---

"optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with \(\text{CH}_2\text{Cl}_2, \text{CH}_3\text{OH}\); handsheets were soaked in a \(\text{CH}_2\text{Cl}_2\) solution for 1/4 h and then air and high vacuum dried; accelerated photo-aging was preformed with a Oriel Solar Simulator and all experiments were preformed in triplicate."
Brightness Stability

Table 3  Thermal Reversion of 2-Methoxybenzoquinone (MMBQ) Applied onto Cotton Linter\textsuperscript{b} and BCTMP Handsheets

<table>
<thead>
<tr>
<th>Time in Dark Room\textsuperscript{c}/h</th>
<th>MMBQ/Cotton Linter Handsheets</th>
<th>MMBQ/BCTMP\textsuperscript{d} Handsheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>69</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>--</td>
<td>50</td>
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<td>24</td>
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<td>72</td>
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<td>144</td>
<td>--</td>
<td>45</td>
</tr>
<tr>
<td>192</td>
<td>49</td>
<td>--</td>
</tr>
<tr>
<td>240</td>
<td>--</td>
<td>44</td>
</tr>
</tbody>
</table>

Initial Brightness Prior Application of MMBQ

| Mass MMBQ/ g handsheet | 0.021 | 0.018 |

*optical handsheets were prepared from a commercial source of cotton linters, the linters were extracted with \textsuperscript{1}CH\textsubscript{2}Cl\textsubscript{2}, \textsuperscript{2}CH\textsubscript{3}OH; \textsuperscript{b}handsheets were soaked in a CH\textsubscript{2}Cl\textsubscript{2} solution for 1/4 h and then air and high vacuum dried; \textsuperscript{c}all handsheets were stored in a darkroom, and all experiments were preformed in triplicate; \textsuperscript{d}BCTMP was prepared from hardwood.
Brightness Stability

Photo-Formation of Chromophoric Structures

Introduction

Current theories of brightness reversion have been developed from extensive model compound work. The photo-reactivity of α-carbonyl groups has been extensively studied by several research groups. Grier and Lin\(^1\) demonstrated that several phenacyl-α-O-arylethers compounds were photo-labile and rapidly yellowed when irradiated with near-UV light. Castellan\(^2\) further explored the photo-reactivity of these compounds both in solution and absorbed onto cellulose fibers. Characterization of the products formed from photolysis are consistent with an initial homolytic rupture of the α-O-aryl ether bond and subsequent radical coupling and rearrangement reactions. In addition to these low-molecular-weight products, a larger oligomer component is always found in yields varying from 10% - 50%. Castellan\(^3\) has characterized this component and shown that peak molecular weight for the oligomer varies from 2667 to 4275 depending on the reaction medium employed (i.e. chemical fibers → benzene). Analysis of the photolysis product mixture indicates that the oligomer portion is the principal component contributing to the yellowing of the product mixture\(^4\). Furthermore, it has been postulated that the oligomers are formed from the reactive species generated during photolysis, such as radicals, phenols, and quinones\(^3\).

The photoreactivity of other chromophoric compounds\(^5\), such as biphenyl and stilbene derived lignin type structures, has also been shown to undergo rapid light-induced yellowing when exposed to UV light at wavelengths > 300 nm. These results clearly suggest that several structural subunits commonly found in lignin are prone to photo-chemical reactions under the conditions found to initiate photo-aging of wood. Regardless of the reaction mechanisms responsible for generating the proposed radicals, it is generally accepted that these intermediates lead to the oxidative formation of ortho-\(^6\) and para-quinones\(^7\).

Our principal research interest in this area was to determine if the photolysis (λ = 300 - 400 nm) of these types of compounds did indeed yield ortho-quinone like structures in the colored oligomeric product. Since these types of structures have been detected in photo-aged mechanical pulp, it was of concern to determine if current model studies also yield ortho-quinones. To date, the presence of these structures has not been detected in the photolysis of model compounds, although it has been proposed that these types of structures are incorporated into the colored oligomeric component generated during photolysis.
Review of Past Project Activity

Previous research efforts in this area have been focused principally on preparing a series of lignin dimeric and trimeric compounds. The photolytic behavior of these compounds has been explored and shown to be consistent with previously reported literature results.

Discussions of 1991 Results

Research efforts over the last year have been directed at determining if the photolysis of lignin model compounds I and II (see below) do indeed yield a oligomeric product which contains quinone-like structures.

The experimental approach that was employed consisted of photolyzing samples of A or B absorbed onto cotton linters. The products from photolysis were extracted with dichloromethane, concentrated, and treated with trimethyl phosphite. The total reaction mixture was then examined by $^{31}$P NMR. Employing this approach the presence of ortho-quinones should be readily detected (for an expanded discussion on the use of $^{31}$P NMR and trimethyl phosphite to detect ortho-quinones refer to the previous section).

It was therefore much to our surprise that when either I or II absorbed on cellulose was photolyzed, extracted, and treated with P(OCH$_3$)$_3$ the resulting $^{31}$P NMR spectrum, shown below, does not contain a signal at -45 ppm (see Figure 1). Although initially we attributed this to hydrolysis of the cyclic phosphorous compound, the addition of 3,5-di-t-butyl-1,2-benzoquinone yielded the diagnostic signal at -47.0 ppm. These results clearly suggest that if the photolysis experiment had yielded an ortho-quinone it would have been detected in the P(OCH$_3$)$_3$/$^{31}$P NMR experiment. To explore the potential that the ortho-quinones generated were unstable to subsequent photo-chemical and/or thermal reactions, we have photolyzed mixtures of I and 3-methoxy-1,2-benzoquinone. Following the same experimental procedure as above, the $^{31}$P NMR spectrum contained a signal at -44.2 ppm, as shown below (see Figure 1, NB: signals at 2.6 and 10.9 were shown not to be due to the lignin model compound or its photolysis products).
Initially, the deficiency of a signal in the NMR spectra for ortho-quinone-like structure was thought to be due to the fact the photolysis of I or II was preformed in the absence of lignin like structures. Therefore the photolysis reactions were repeated in the presence of 4-hydroxy-3-methoxybenzyl alcohol, 3-hydroxy-4-methoxybenzyl alcohol and 4-hydroxy-3-methoxy-methylbenzene. Analysis of these reaction mixtures employing the above procedures also failed to detect any signals which could be attributed to the ortho-quinone structure.

**Conclusions and Recommendations**

These results clearly demonstrate that the current model compounds employed to study brightness reversion fail to yield one of the most important chromophoric structures involved in brightness reversion. The results of these studies support Heitner's contention that the exact chemical mechanisms involved in oxidizing phenolic structures to quinones are far from understood. Due to the important role that quinones have in the brightness reversion phenomenon it is urgently needed that further studies be preformed so as to develop an understanding of their mechanisms of formation.

**Future Activity**

Future research efforts will examine the products formed from the photolysis of lignin trimers. Studies directed at understanding how the ultrastructure of wood fibers may influence the photo-reactivity of \( \alpha \)-carbonyl groups will also be examined.

Collectively, these investigations will provide fundamental investigations as to what is occurring in the chemically complex nature of mechanical pulp when it is irradiated. These studies will support our current efforts at designing novel methods of retarding the brightness reversion process.

**References**


$^{31}\text{P NMR}$ of the P(OME)$_3$ derivatives formed from photolysis of compound 1.

$^{31}\text{P NMR}$ of the P(OME)$_3$ derivatives formed from the photolysis of compound 1 and 3-methoxy-1,2-benzoquinone.

Figure 1  $^{31}\text{P NMR Spectra}$
PROJECT 3661

SULFUR-FREE SELECTIVE PULPING PROCESS

RESEARCH REVIEW

MARCH 25, 1992

Donald R. Dimmel
Xiaoqi Pan

and

Staff at the National Energy Renewable Laboratory
(Golden, CO)
Sulfur-free Pulping

TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE: SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT STAFF: Donald R. Dimmel and Xiaoqi Pan, and staff at the National Energy Renewable Laboratory (Golden, CO)

BUDGET (FY 91-92): $175,000

REPORTING PERIOD: Mar. 91 - Feb. 92

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3661

OBJECTIVE: The objective of this project is to develop the synthesis of a low-cost catalyst which, when used in pulping systems, will increase pulping rates and product yields, while reducing the dependence on sulfur additives. The process under investigation is based on conversion of an inexpensive pulping by-product, lignin, to a useful quinone-type pulping catalyst.

IPST GOAL: Improved pulping processes

SUMMARY:

A process is under development to provide low-cost anthraquinone pulping catalysts from lignin. Anthraquinone pulping offers the opportunity to reduce air emissions, simplify chemical recovery, improve productivity, conserve raw materials, and lower energy requirements.

The principal focus of the research has been to optimize the yields of catalyst synthesis from a low-molecular-weight lignin. The process involves treating
the lignin with an inexpensive oxidizing agent to give a mixture of methoxy- substituted benzoquinones and then converting the benzoquinones into anthraquinone precursors by treatment with a diene, using the well-known Diels-Alder reaction. The most important factor in the cost of anthraquinone catalysts prepared from lignin is the overall yield of the chemical processing steps.

A number of lignin oxidizing agents have been evaluated for generating benzoquinones. When used in a large excess, hydrogen peroxide oxidation gives 80-90% yields of benzohydroquinones from certain lignin models, but discouragingly low yields of either benzhydro- or benzoquinones from isolated lignins. However, the use hydrogen peroxide in the presence of transition metal catalysts has proven to be an effective oxidizing system with model compounds and somewhat effective with actual lignin for producing benzoquinones. Inexpensive oxygen in the presence of catalytic amounts of certain transition metal complexes gives benzoquinones yields as high as 85% from some lignin models; however, the metal complexes have generally not functioned well at low catalytic levels.

A room temperature methanol solution of nitrogen dioxide, in the presence of oxygen, effectively oxidizes many syringyl lignin models to dimethoxybenzoquinone (DMBQ) in 80-95% yields and low mol. wt. hardwood lignin in 15% yields. Pretreatment of higher mol. wt. lignin with Cu(OH)₂/NaOH degrades the lignin into smaller, oxidized fragments. With some lignins, the DMBQ yield (after NO₂/O₂ oxidation) triples with the Cu(OH)₂/NaOH pretreatment. The yields of monomethoxybenzoquinone (MMBQ) from oxidation of guaiacyl lignin or lignin models with NO₂/O₂ is low and limits the amount of useful benzoquinones that can be generated from most softwood species. Model experiments suggest a preference for addition of NO₂ to guaiacyl structures over oxidation to a quinone.

Placing bromo and hydroxymethyl groups into the 5-position of lignin guaiacyl units does not provide high benzoquinone yields after NO₂/O₂ oxidation. Peroxide/metal oxidations with model compounds and lignin do lead to MMBQ as a product. Consequently, there may be a way to directly convert the abundant guaiacyl rings of lignin into useful benzoquinones.
The yields for the second step in the chemical processing, addition of a diene to the benzoquinone mixture to give anthraquinone precursors, are good when the reaction is carried out in water. Alternatively, the use of catalysis to assist the diene addition provides respectable yields of anthraquinones, without isolation of non-aromatic precursors. A significant level of developmental work has gone into the optimization of the Diels-Alder yields; more needs to be done. For example, the suitability of different dienes in aqueous reactions with DMBQ has been studied; isoprene has proven to be the best. Both butadiene and cyclopentadiene, which are very low cost dienes, gave somewhat low adduct yields in water. A direct comparison of the aqueous reactions of isoprene with DMBQ and MMBQ, under identical conditions, showed that DMBQ produced adducts in much better yields.

A few simple ways have been examined to promote loss of methanol and hydrogen from the nonaromatic adducts to get the highly active aromatic catalysts. Several studies with alumina in organic solvents proved unsuccessful. An alternate approach to promote aromatization which worked, but gave low yields, was an alkaline aq. dioxane aeration of the adduct mixture.

Several large scale Diels-Alder reactions have been performed to obtain sufficient quantities of the NQ/AQ product mixture to test for catalytic pulping activity. The tests have been inconclusive due to inadvertent problems. Diels-Alder adducts from reactions of 2,3-dimethyl-1,3-butadiene with DMBQ were not very active in comparison to AQ.
INTRODUCTION

A process is under development to provide low-cost anthraquinone catalysts from lignin which will lead to improved chemical pulping. The research has been divided into two large stages, lignin processing and chemical processing. The lignin processing stage involves selectively isolating a low-molecular-weight fraction by supercritical fluid extraction of a pulping liquor after precipitation of the bulk lignin or simple organic solvent extraction of an organosolv lignin. The first displays good selectivity for low-molecular-weight lignin, but the yields are low; the second is less selective, but provides large amounts of low-molecular-weight material.

The chemical processing of the low-molecular-weight lignin involves: treating with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones (Fig. 1, structure 1) and converting the benzoquinones into nonaromatic anthraquinone precursors by treatment with a diene, using the well-known Diels-Alder reaction. Final conversion of these precursors to anthraquinone derivatives occurs by loss of methanol and hydrogen, either during reaction or in a separate step (Fig. 1). The aromatization step may be unnecessary; partially aromatic anthraquinone also functions as a pulping catalyst by in situ conversion to anthraquinone.

```
\begin{align*}
\text{CH}_2\text{OH} & \\
\text{CH} & \\
\text{CH} - X & \\
(\text{CH}_3\text{O}) & \\
\text{O} & \\
(\text{H}) & \\
\text{LIGNIN} & \\
\end{align*}
```

\[\text{Oxidation} \quad \text{DielsAlder} \quad -\text{CH}_3\text{OH} \]

```
\begin{align*}
1 & \\
2 & \\
\end{align*}
```

Figure 1. Chemical steps in the conversion of lignin to an anthraquinone.
REVIEW OF PAST PROJECT ACTIVITY

Oxidation Studies. The single most important determining factor in the final cost of anthraquinone catalysts prepared from lignin is the overall yield of the chemical processing steps. A number of lignin oxidizing agents have been evaluated for generating benzoquinones. Because of the structural complexity of lignin, the initial work was performed on compounds that model lignin's behavior.

When used in a large excess, hydrogen peroxide oxidation gives 80-90% yields of benzohydroquinones from certain lignin models, but discouragingly low yields of benzoquinones from isolated lignins. Inexpensive oxygen in the presence of catalytic amounts of certain transition metal complexes gives benzoquinones yields as high as 85% from some lignin models. Different transition metal complexes have been examined in an attempt to better understand key factors for promoting good benzoquinone yields. In general, the metal complexes have not functioned well at low catalytic levels.

Nitrogen dioxide, in the presence of oxygen, effectively oxidizes many syringyl lignin models to dimethoxybenzoquinone (DMBQ) in 80-95% yields at room temperature in methanol. The 15% yields of DMBQ obtained from oxidation of an extracted (low mol. wt.) hardwood lignin represented roughly a 60% conversion of the syringyl units to DMBQ. This yield is not an isolated yield. DMBQ is incorporated into the lignin macro-molecular structure during lignin precipitation; procedures for maximum isolation of lignin need to be established.

The yields of monomethoxybenzoquinone (MMBQ) from oxidation of guaiacyl lignin or lignin models with NO2/O2 is low and limits the amount of useful benzoquinones that can be generated from most wood species. Model experiments suggest a preference for addition of NO2 to guaiacyl structures over oxidation to a quinone.

Diels-Alder Studies. The yields for the second step in the chemical processing, addition of a diene to the benzoquinone mixture to give anthraquinone precursors, are high, especially for formation of one ring. However, the formation of two rings simultaneously (benzoquinone directly to an anthraquinone) is a more difficult task; the intermediate naphthaquinone structures react very slowly under standard conditions. The use of catalysis to assist the diene addition and a novel diene addi-
tion reaction carried out in water allow for a direct, reasonably high conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors.

\[
\text{benzoquinone (DMBQ)} \quad \text{diene} \quad \text{AQ analog (R_1, R_2 = H, CH}_3\text{)}
\]

Figure 2. Diels-Alder reaction to provide anthraquinone products.

The yields of naphthoquinone (NQ) and anthraquinone (AQ) adducts from the reaction of 5 equiv. of isoprene with DMBQ in water are typically 15 and 55%, respectively. The effects of co-solvents in the aqueous Diels-Alder reactions indicate that AQ and NQ adduct yields improve slightly with low concentrations of dioxane in water. A diene/DMBQ ratio of 5:1 appears best. In methanol, high yields of NQ adducts are observed, but AQ adduct yields are only about 4%. Yields are quite poor in the absence of a solvent, unless done on solid surfaces where 30-55% yields of anthraquinone have been observed. This result and the diene addition reactions carried out in water indicate that a direct conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors, is possible.

Reactions of cyclopentadiene and DMBQ gave <15% NQ adducts and insignificant yields of AQ adducts. Cyclohexene was tested as an additive in the water reactions since it could possibly function as a hydrogen acceptor in disproportionation reactions and, thereby, promote adduct aromatization steps. However, it had no positive effects on yields and product distributions.

Several large scale Diels-Alder reactions have been performed to obtain sufficient quantities of the NQ/AQ product mixture to test for catalytic pulping activity. The tests have been inconclusive due to inadvertent problems. Diels-Alder adducts from reactions of 2,3-dimethyl-1,3-butadiene with DMBQ were not very active in comparison to AQ.
FY 91-92 RESULTS

Technoeconomic Evaluation. A key aspect of our research program is an ongoing technoeconomic evaluation of the various stages of the process. New methodology for AQ synthesis has been developed since our initial 1989 report. Our most recent evaluation describes three methods for the preparation of AQ; one based on organosolv lignin and the others based on the use of kraft lignin as a starting material. The primary difference between the cases is in the lignin processing stage. The organosolv case proceeds by separation and use of a low-molecular-weight (LMW) lignin fraction, produced directly in solvent recovery operations, followed by chemical conversion into AQ.

One of the kraft lignin cases assumes a conversion of the lignin into a mixture of vanillin and syringaldehyde as the lignin processing stage. The other case is a direct oxidation of kraft LMW lignin to benzoquinones. The parameters used to develop these three evaluations have been based on actual laboratory conditions and yields.

Some of the more important conclusions of the evaluation include:

1) If certain key assumptions are met, a lignin to AQ process still appears to be one of the most economic approaches yet developed.

2) The amortized manufacturing cost of AQ from organosolv lignin could be as low as $0.82/lb, while one based on kraft black liquor without an intermediate conversion to vanillin/syringaldehyde could be as low as $1.04/lb.

3) When compared to other known routes for AQ preparation, the process may have to meet a competitive cost performance target as low as $1.50/lb, but only if unproven technology becomes available. Otherwise, the target may not need to be lower than $3.00/lb.

Oxidation Studies. The oxidation of syringyl alcohol by NO\textsubscript{2}/O\textsubscript{2} in various solvent systems and reaction times has been extensively investigated. Methanol gives reproducible high DMBQ yields. Ethanol is poorer, as are water/alcohol mixtures and nonhydroxylic solvents. Yields of DMBQ from
the oxidation of syringyl alcohol by NO$_2$ were lowered by 5-10% when drying agents were used in an attempt to remove all water from the methanol solvent. The presence of a strong base, MeONa, in MeOH severely depressed DMBQ yields. Increasing the amount of air in the reaction vessel significantly increased DMBQ yields. Several experiments have been performed to determine the smallest ratio of NO$_2$ : substrate needed as part of an economic analysis of the current lignin-to-AQ process.

Degradation of lignin into smaller fragments before performing NO$_2$/O$_2$ oxidation should result in higher yields of benzoquinones. Several lignin pretreatments were examined: H$_2$O$_2$/NaOH oxidation, acidolysis, H$_2$O$_2$/NaOH oxidation after acidolysis, Cu(OH)$_2$/NaOH oxidation, Na$_2$S/NaOH, different sulfite treatments, NaBH$_4$ reduction, ozone, aqueous peracetic acid, trimethylsilyl iodide, sodium bisulfite, sodium dithionite, sodium hydroxide, and combinations of acidolysis/CuO/NaOH and acidolysis/NaBH$_4$ treatments. Of all these treatments, Cu(OH)$_2$/NaOH oxidation was the most effective; acidolysis was second best. The yields of monomethoxybenzoquinone were only a trace in all cases.

Extensive studies have been performed with the Cu(OH)$_2$/NaOH oxidation pretreatment. These studies include determining the best reaction conditions with lignin substrates, analyzing products from lignin and lignin model reactions, and applying the best conditions to more than 20 different lignin samples. With some lignins, the DMBQ yield triples with the Cu(OH)$_2$/NaOH oxidation pretreatment.

Lignin and oxidized lignin contain several lignin degradation products. The target quinone yield appears to depend on the level of syringaldehyde in the copper hydroxide treated lignin; the contributions of ketone and acid monomer products to the total DMBQ yield probably is insignificant. This statement is based on testing the response of syringaldehyde, acetosyringone, and syringic acid methyl ester to NO$_2$ oxidation; the DMBQ yields were 87, 31, and 0%, respectively. The differences in yields predicted on syringaldehyde content of the oxidized product mixture and actually observed can probably be attributed to condensation products, such as disyringylmethane, which also give good DMBQ yields (89%) upon NO$_2$ oxidation.
Substantial amounts of NO$_2$ are consumed in nitration of guaiacyl rings in the Cu(OH)$_2$/NaOH treated lignins, instead of oxidation to the desired quinone, MMBQ. The introduction of an appropriate group into the 5 position of lignin guaiacyl units may suppress nitration at this site and, thus, provide high benzoquinone yields after NO$_2$/O$_2$ oxidation (equation below). However, NO$_2$/O$_2$ oxidation of 5-bromovanillyl alcohol, 5-bromovanillin and 5-(hydroxymethyl)vanillyl alcohol (R = Br and CH$_2$OH, below) gave only small amounts of $p$-benzoquinones. The electron withdrawing nature of the bromo group may be suppressing oxidation; the ortho CH$_2$OH may itself be a site of oxidation, leading to undesirable side-products.

The research group at NREL has been testing peroxide/metal combinations with model compounds and lignin and are obtaining MMBQ as a product. Consequently, there may be a way to directly convert the abundant guaiacyl rings of lignin into useful benzoquinones.

One of the big questions which surrounds our research is whether or not an oxidizing agent, such as NO$_2$/$O_2$ or H$_2$O$_2$/metal, can progressively oxidize lignin units which are internal units in the polymer and not phenolic. In other words, if the first phenolic unit is oxidized to a benzoquinone, will the rest of the side chain be lost to produce another phenol for reaction? If the answer is "no," then it is important that we use very small lignin fragments as starting materials in the catalyst synthesis. Oxidation of the lignin model dimer shown below will help establish this point; production of two benzoquinones per dimer model upon oxidation would prove that the side chain breaks down to allow both the phenolic and nonphenolic aromatic rings to be oxidized. The synthesis of the compound is nearly complete; oxidation study will occur soon.
Diels-Alder Studies. The suitability of different dienes in aqueous Diels-Alder reactions with DMBQ has been studied. The two of greatest interest (because of their low cost) are butadiene and cyclopentadiene. However, the adduct yields in water were discouraging low. Additional experiments with cyclopentadiene in water and in organic solvents with \( p \)-benzoquinone, MMBQ, DMBQ, and 2-methoxynaphthaquinone, with different types of agitation and temperature ranges, led to the conclusion that cyclopentadiene will not add readily to benzoquinones having methoxyl substituents. It is obvious that isoprene is the best diene in aqueous Diels-Alder reactions.

A direct comparison of the aqueous reactions of isoprene with DMBQ and MMBQ, under identical conditions, showed that DMBQ produced adducts in much better yields. If an aqueous Diels-Alder reaction is the key way to accomplish the second step in our anthraquinone synthesis, isoprene and DMBQ are probably going to have to be the reactants.

The AQ adduct yield increased with isoprene and DMBQ concentration and with time. Of the several conditions studied, long reaction times at 155°C appeared to give the maximum adduct yields. Long reaction times favor the production of larger amounts of aromatic adducts. Addition of NaOH to the aqueous Diels-Alder reaction severely hurt adduct yields.

We have examined a few simple ways to promote loss of methanol and hydrogen from the nonaromatic adducts to get the highly active aromatic cat-
Sulfur-free Pulping

An example of the reaction that we are attempting to accomplish is shown below.

![Chemical Reaction](image)

Adduct Aromatization Reaction

Several studies with alumina in organic solvents proved to be a dead end. An alternate approach to promote aromatization, an alkaline aq. dioxane aeration of the adduct mixture was performed at both 55°C and room temperature. By 3 hours, everything but the aromatic AQ component had disappeared. The aromatic AQ yield increased by about 10% in each case from what was present in the original samples. However, destruction of nonaromatic adducts appeared to dominate over conversion reactions to aromatic adducts. Other solvents were also tested, including water, DMSO, isopropanol, and ethanol; all contained added NaOH. The conversion yields in isopropyl alcohol appeared to be the best.

Though the course of the aeration studies, we discovered that 2-methoxy-1,4-naphthaquinone, the internal standard for determining adduct yields, was unstable to NaOH. Since most the adduct analyses were done under neutral conditions, our reported yields are probably fairly accurate. Yet, it is apparent that we need to concentrate more on actual isolated yields.

We will continue to pursue efforts to understand the yield variations and to further increase the Diels-Alder yields. Any improvements in the Diels-Alder yields will compensate for deficiencies in the oxidation step leading to the benzoquinones.

Pulping Studies. Several large scale Diels-Alder reactions have been performed with isoprene/DMBQ (5:1) and water (152°C for 15 hr) to obtain sufficient quantities of the NQ/AQ adduct product mixture to test for catalytic
Sulfur-free Pulping

Pulping activity. Each of the samples were filtered through a silica gel column and collected in fractions. The weights of each fraction, and gas chromatograms for many, were determined. Some samples were "spiked" with naphthoquinone internal standard to determine their composition. The results showed a surprisingly low percentages of the desired products (about 5.6%), with the aromatic AQ present in less than 1% yield. However, NMR spectra appeared appropriate and we decided to proceed ahead with pulping studies.

The NQ/AQ adduct mixtures had catalytic pulping activity, but not as good as pure AQ. The mixture at a 0.2% on wood basis was less effective than AQ at 0.1%. This result conflicts with early findings. Addition work is needed to establish what is the true pulping activities of the NQ/AQ adduct mixtures; there are too many uncertainties with the recent sample preparations.

CONCLUSIONS

A process is under development to provide low-cost anthraquinone catalysts from lignin which will lead to improved chemical pulping. The principal focus of the research has been to optimize the yields of catalyst synthesis from a low-molecular-weight lignin. The process involves treating the lignin with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones and then converting the benzoquinones into anthraquinone precursors by treatment with a diene, using the well-known Diels-Alder reaction. The most important factor in the cost of anthraquinone catalysts prepared from lignin is the overall yield of the chemical processing steps.

A number of lignin oxidizing agents have been evaluated for generating benzoquinones. When used in a large excess, hydrogen peroxide oxidation gives 80-90% yields of benzohydroquinones from certain lignin models, but discouragingly low yields of either benzhydro- or benzoquinones from isolated lignins. However, the use hydrogen peroxide in the presence of transition metal catalysts has proven to be an effective oxidizing system with model compounds and somewhat effective with actual lignin for producing benzoquinones. Inexpensive oxygen in the presence of catalytic amounts of certain transition metal complexes gives benzoquinones yields as high as 85% from
some lignin models; however, the metal complexes have generally not functioned well at low catalytic levels.

A room temperature methanol solution of nitrogen dioxide, in the presence of oxygen, effectively oxidizes many syringyl lignin models to dimethoxybenzoquinone (DMBQ) in 80-95% yields and low mol. wt. hardwood lignin in 15% yields. Pretreatment of higher mol. wt. lignin with Cu(OH)$_2$/NaOH degrades the lignin into smaller, oxidized fragments. With some lignins, the DMBQ yield (after NO$_2$/O$_2$ oxidation) triples with the Cu(OH)$_2$/NaOH pre-treatment. The yields of monomethoxybenzoquinone (MMBQ) from oxidation of guaiacyl lignin or lignin models with NO$_2$/O$_2$ is low and limits the amount of useful benzoquinones that can be generated from most softwood species. Model experiments suggest a preference for addition of NO$_2$ to guaiacyl structures over oxidation to a quinone.

The introduction of bromo and hydroxymethyl groups into the 5 position of lignin guaiacyl units does not provide high benzoquinone yields after NO$_2$/O$_2$ oxidation. Peroxide/metal oxidations with model compounds and lignin do lead to MMBQ as a product. Consequently, there may be a way to directly convert the abundant guaiacyl rings of lignin into useful benzoquinones.

The yields for the second step in the chemical processing, addition of a diene to the benzoquinone mixture to give anthraquinone precursors, are good when the reaction is carried out in water. Alternatively, the use of catalysis to assist the diene addition provides respectable yields of anthraquinones, without isolation of non-aromatic precursors. A significant level of developmental work has gone into the optimization of the Diels-Alder yields; more needs to be done. For example, the suitability of different dienes in aqueous reactions with DMBQ has been studied; isoprene has proven to be the best. Both butadiene and cyclopentadiene, which are very low cost dienes, gave somewhat low adduct yields in water. A direct comparison of the aqueous reactions of isoprene with DMBQ and MMBQ, under identical conditions, showed that DMBQ produced adducts in much better yields.

A few simple ways have been examined to promote loss of methanol and
hydrogen from the nonaromatic adducts to get the highly active aromatic catalysts. Several studies with alumina in organic solvents proved unsuccessful. An alternate approach to promote aromatization which worked, but gave low yields, was an alkaline aq. dioxane aeration of the adduct mixture.

Several large scale Diels-Alder reactions have been performed to obtain sufficient quantities of the NQ/AQ product mixture to test for catalytic pulping activity. The tests have been inconclusive due to inadvertent problems. Diels-Alder adducts from reactions of 2,3-dimethyl-1,3-butadiene with DMBQ were not very active in comparison to AQ.

**FUTURE ACTIVITY**

The objective of our near future research is to develop and optimize our lignin extraction and chemical conversion efficiencies to further lower the cost of pulping catalysts from lignin. We will be looking at a new organosolv process being developed at NREL for its ability to produce low-molecular-weight lignins and continue to examine different lignin sources for their capacity to be oxidized to benzoquinones, ways to convert guaiacyl structures to monomethoxybenzoquinone, ways to degrade an isolated lignin into small pieces capable of conversion to quinones, and the best conditions for performing Diels-Alder reactions that give high yields of anthraquinones. The catalyst mixtures will be tested for activity. The successful laboratory research will be moved to larger scale in future years.
MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II:
CHLORINATION AND DIOXIN REACTIONS
(CHLORINE INSTITUTE FUNDED)

RESEARCH REVIEW

MARCH 25, 1992

Donald R. Dimmel
and
Battelle (Columbus, Ohio)
MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS (CHLORINE INST. FUNDED)

PROJECT STAFF: Donald R. Dimmel and Battelle (Columbus, Ohio)

BUDGET (FY 91-92): $55,000

REPORTING PERIOD: Mar. 91 - Feb. 92

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3685

OBJECTIVE:

To understand the mechanisms of formation of chlorinated dioxins and chlorinated furans, and to use this knowledge to eliminate or minimize their production in bleached pulp. The goal of this project is: (1) to develop a fundamental understanding of chemistry which leads to dioxins in bleached pulp, (2) study the reactions of dioxins with selected bleaching reagents, and (3) lay the foundations for developing new technologies for chlorinating pulps without dioxin production. Conditions will be sought that will (a) define the relative importance of different dioxin precursors, (b) determine the reactivity of chlorine with functionalized precursors, (c) selectively chlorinate lignin and not the dioxin precursors, and (d) destroy dioxins in partially bleached pulps.

IPST GOAL: Improved bleaching processes
SUMMARY:

Chlorination conditions have been established for observing the progressive development of ring chlorination of dibenzo-p-dioxane (DBD) and dibenzofuran (DBF), which have been adsorbed on cotton linters and are present in pulp. The experiments involving DBD and DBF adsorbed onto cotton linters employed simplified analytical procedures and provided fundamental information about reactivities without possible by-product problems. The experiments with pulp exhibited greater analytical problems. The sample work up involves a series of alumina chromatographies to remove interfering components. In general, the ability to accurately analyze for the mono-tetrachloro DBD and DBF has been accomplished. Because of the greater reactivity of DBD, the progressive development of mono-tetra-chloro-DBD was skewed towards the higher chlorinated products and few lower substituted compounds were observed with either spiked cotton linters or extracted pulp.

A comparison of the distribution of mono-, di-, tri-, and tetrachlorodioxins (DBD/F-Clₙ) as a function of chlorination time for the extracted unbleached pulp and DBD/F spiked cotton linters indicated that DBD and DBF are probably the major, if not only, dioxin precursors in pulp. It is possible that DBD and DBF related structures could be produced during chlorination, rather than being exclusively native materials in wood or contaminants introduced during the handling of wood and pulp.

Nitrogen dioxide pretreatment of a DBD/F spiked cotton linters effectively reduced dioxin levels observed after chlorination of the linters; in contrast, O₃ appeared ineffective. However, the O₃ treatment was performed on completely dry linters and may have been ineffective because solvent (water) may be required for efficient transportation of O₃ to reactive sites.

A pulp spiked with DBD/F was treated with NO₂ and O₃; both of the pre-treated pulps were then chlorinated. Ozone was much more effective than NO₂ in decreasing the levels of both TCDD (nondetect vs 1.5 ppt) and TCDF (4 vs 600 ppt). Based on this data, an ozone treatment in front of a chlorine bleaching stage may be quite effective at lowering dioxin levels in pulps.
Selected bleaching treatments were tested for their ability to reduce the dioxin content in pulp by presumably destroying the chlorinated materials. In terms of lowering TCDD/F levels in pulp, O$_2$/NaOH appeared more effective than H$_2$O$_2$ or O$_3$. In the O$_2$/NaOH case, fairly high levels of TCDD/F were found in the effluent; thus, it is uncertain whether the O$_2$/NaOH treatment destroyed materials or redistributed the dioxin components. Overall, the strategy of destroying most, if not all, of the dioxins in pulp samples does not appear to be very promising. The best approach would seem to be to destroy the dioxin precursors before chlorine bleaching of pulp.

Work on this project was completed in January 1992; a final report was prepared and submitted to the Chlorine Institute in February 1992.
INTRODUCTION

The chlorination of wood pulp to improve its brightness appears to lead to low levels of dioxins - substances which are extremely toxic to rats and may be harmful to humans. The chlorine and paper industries are concerned over the public's reaction to dioxins and meeting limits imposed by state and federal regulations. Consequently, ways to reduce the levels dioxins in paper products and mill discharges has been a recent major research thrust.

There is strong evidence suggesting that DBD/F are present in the pulp after pulping and that the chlorination of the DBD/F contaminant is responsible for a significant portion of the observed dioxins. The DBD/F compounds might be present in wood, be formed during pulping or bleaching, and/or be introduced from outside sources, such as oil-based defoamers. However, DBD/F may not be the only precursors to dioxins.

Further developments in dioxin control will be greatly aided with improved understanding of the fundamental chemistry of dioxin formation. Such information would provide a basis for making rational process changes. An important consideration is understanding the reactivity of dibenzodioxanes and dibenzofurans, in comparison to that of wood components.

Several questions have been raised relative to dioxin production during chlorine bleaching:

(1) Are DBD/F the principal dioxin precursors? Are other precursors significant enough to cause concern?
(2) How does DBD/F get in the pulp? Are they contained in the wood? Are they partially formed during pulping? Or do they solely come from outside sources?
(3) What are the mechanisms for DBD/F formation or destruction during pulping and bleaching, if such reactions exist?
(4) Can DBD/F components be selectively destroyed prior to chlorine bleaching? What are the reactivity differences of DBD/F and lignin towards typical pulp bleaching reagents?
(5) Can pulps be chlorinated without dioxin formation? At what stage in the chlorination are the tetrachloro dioxin isomers formed?

(6) Are there effective ways to destroy dioxins prior to effluent discharge to the environment and prior to manufacture of end products?

Answers to these questions will lead to more effective technologies to reduce dioxin production, while retaining low cost, effective chlorine bleaching. This investigation attempts to address several of these questions.

EXPERIMENTAL PLAN

Initially, experiments will be examined to define appropriate DBD/F spike levels and develop chlorination conditions which produce mixtures of mono- tetra chlorinated products and conditions for analytically quantifying such products. The first set of experiments address the issue of the source of the dioxin precursors. The distribution of mono-, di-, tri-, and tetrachlorodioxins (DBD/F-Cl_x) as a function of chlorination time will be compared for a DBD/F spiked cotton linters sample and an unspiked pulp sample. If the time development profile of the DBD/F-Cl_x components for the two substrates differ substantially, a precursors other than DBD/F will be indicated. The profile of tetrachloro isomers for the two samples will also indicate possible sources precursors. The dioxin isomer distribution in DBD/F spiked linters and unspiked pulp samples should be identical, if DBD/F are the only precursors in the pulp. Semiquantitative results would provide estimates of importance for different sets of precursors.

The reagents which prove effective in lowering the concentrations of DBD/F in spiked cotton linters (PART I of this research) will be tested for their ability to prevent dioxin formation when such treated DBD/F spiked cotton linters are chlorinated. The experiments are intended to show whether or not precursors which have been altered by selective treatments will still give rise to dioxins upon chlorination. For example, if nitrogen dioxide selectively attacks DBD/F to give a nitrogen derivatized product, what will the latter do upon chlorination? Those reactions that show promise with spiked cotton linters will be repeated with unbleached pulps to demonstrate their effectiveness in lowering dioxin levels in the presence of lignin.
Finally, bleached pulp which contains trace levels of dioxins will be treated with ozone, peroxide, oxygen, and other possible commercial electrophilic reagents to test the stability of dioxins to various post-chlorine bleaching stages.

PRIOR RESULTS:

Background levels of dioxin precursors, DBD and DBF, were determined for cotton linters and the solvent extraction procedure and appropriate DBD/F spike levels established. The experimental conditions for conducting chlorinations of DBD/F spiked cotton linters were also established. The initial chlorination experiments of DBD and DBF spiked cotton linters and various controls gave substantial quantities of a pale yellow residue which interfered with simple analysis for chlorinated DBD/F compounds. A combination of first extracting the linters with organic solvents and then employing chromatography through alumina provided clean samples with little interfering residue and excellent recovery of labeled internal standards. The reproducibility of the results with linter samples was good.

Analysis of the samples indicated that unchlorinated and mono - tetrachloro-DBD and DBF (DBD/F-Cl<sub>x</sub>, x=0-4) were present in both the linters and aqueous phases. Cotton linters which were spiked with unchlorinated and mono - tetrachloro-DBD and DBF (DBD/F-Cl<sub>x</sub>, x=0-4) gave spike recoveries of 120-180%, indicating that the analytical procedures effectively removed the DBD/F-Cl<sub>x</sub> components from linters. The DBD/F spiked levels were increased to 30 ppb and greater analytical precision was observed. The sample work up procedure and ability to accurately analyze for the mono-tetra chloro DBD and DBF looked appropriate.

SUMMARY OF RESULTS OF THE LAST YEAR

Chlorination of Spiked Cotton Linters and Spiked Pulp

A mild chlorination of spiked cotton linters was conducted over 10, 20, 40, 70, and 120 min. The appearance and disappearance of unchlorinated and mono
tetrachloro-DBD and DBF (DBD/F-Cl₅ x=0-4) for the combined linters and aqueous phases indicated that DBD is more reactive towards chlorine than is DBF. The conditions selected for the progressive development of mono-tetrachloro-DBF in spiked cotton linters was ideal. Because of the greater reactivity of DBD, the distribution of DBD products was skewed towards the higher chlorinated products.

The next step was to determine the distribution of mono-, di-, tri-, and tetrachlorodioxins and furans (DBD/F-Cl₅ₓ) as a function of chlorination time for an extracted (presumably DBD/F-free) unbleached pulp. The experiment required some developmental work to find the best chlorination conditions. The lignin in the pulp reacts rapidly with chlorine. Higher levels of chlorine and lower temperatures were employed. The conditions selected produced the desired effect: mono-tetrachloro-DBD/F analogs were observed at low levels.

Several samples in this data set had to be discarded because of interferences from (presumably) lignin by-products. Some interferences were decreased by additional clean up steps before GC-MS analysis. However, since the d₁₀-flourene (the internal standard recovery standard) had already been added and it probably is more volatile than the TCDD/F standards, internal standard recoveries were often high. This does not necessarily invalidate the data. While data at each chlorination time was available, we often did not have the back up duplicate to verify the observed results. Even with these shortcomings, several interesting conclusions could be drawn.

A comparison of the distribution of mono-, di-, tri-, and tetrachlorodioxins (DBD/F-Cl₅ₓ) as a function of chlorination time for the extracted unbleached pulp and DBD/F spiked cotton linters indicated that DBD and DBF are probably the major, if not only, dioxin precursors in pulp. This conclusion will be verified by studying the types of chlorinated products obtained from pulp and DBD/F spiked cotton linters.

The DBD and DBF products were expected to be in the low ppt level in the extracted pulp experiments. This was the case for the observed TCDD. However, the DBF products were present at nearly 1000 times higher
amounts, namely low ppb levels. This observation, together with the progression of mono- through tetrachloro-DBF, suggests that the sample still contained significant amounts of DBF or that DBF was formed during chlorination. The fact that ppb levels of DBF was observed in the process blank (which is another extraction of the pulp, but no subsequent chlorination) indicated that the thoroughly extracted pulp still contained DBF.

Pre-treatment Effects on Cotton Linters and Pulps

Samples of NO$_2$-treated and O$_3$-treated DBD/F spiked cotton linters were chlorination to see if the treatments inhibit dioxin formation. The NO$_2$ pretreatment effectively reduced dioxin levels, especially the TCDD type, while O$_3$ displayed only slight reductions. The latter could be a consequence of a change in the O$_3$ treatment from previous work done at IPST. The O$_3$ treatment was done on dry spiked cotton linters, the previous treatments employed wet samples.

A pulp which had been spiked with 0.2 ppb DBD and 10 ppb DBF was treated with ozone in one case and nitrogen dioxide in another case. The treated pulps were then chlorinated with chlorine water. The level of Cl$_2$ used was based on the residual lignin left in the pulp, employing common commercial practices. The results are given in Table 1. Good precision was obtained between duplicate samples. Internal standard and cleanup standard recoveries were greater than 50 percent in all cases indicating efficient removal of TCDD/TCDF from the sample matrix.

The data in the table indicate that O$_3$ is very effective in producing a pulp with low dioxin levels. The values observed for TCDF and TCDD (4 ppt and nondetect, respectively) were much lower (83 and 2 ppt, respectively) than the levels of dioxins found in a chlorinated spiked pulp which had not been pretreated. It should be kept in mind that the Cl$_2$ level was also much lower in the O$_3$-treated pulp, since this pulp contained less residual lignin.

The NO$_2$-pretreatment was much less effective at reducing dioxins levels. In fact, the 600 ppt TCDF is substantially above the level (83 ppt) observed with no pretreatment. This is a confusing result. The spike level of the pulp,
Mechanism of Dioxin Formation

10,000 ppt DBF, could account for 600 ppt TCDF in the product. Yet, the control chlorination gave only 83 ppt TCDF. It could be that the control value is in error (10,000 ppt DBF -> 83 ppt TCDF appears to be too low of a yield) or an outside DBF source contaminated the NO2-pretreatment experiment.

Table 1. Results for Pretreated Pulp Samples

<table>
<thead>
<tr>
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<th>O3-Cl2 Pulp</th>
<th>NO2-Cl2 Pulp</th>
<th>Spiked Control</th>
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<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>Avg</td>
<td>Avg</td>
</tr>
<tr>
<td>Concentration (pg/g)a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>3.0 3.0 3.0</td>
<td>399 409 404</td>
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<tr>
<td>Total TCDF</td>
<td>4.9 3.0 4.0</td>
<td>590 606 598</td>
<td>- - -</td>
</tr>
<tr>
<td>2378-TCDD</td>
<td>- - -</td>
<td>- 3.0 1.5</td>
<td>- - -</td>
</tr>
<tr>
<td>Total TCDD</td>
<td>- - -</td>
<td>- 3.0 1.5</td>
<td>- - -</td>
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</tbody>
</table>

Recoveries (%)

<table>
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<tr>
<th></th>
<th>2378-TCDD-13C12</th>
<th>2378-TCDF-13C12</th>
<th>2378-TCDD-37Cl4</th>
</tr>
</thead>
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<tr>
<td></td>
<td>69 66</td>
<td>62 64</td>
<td>98 89</td>
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<td>54 53</td>
<td>95 95</td>
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<td>86 84</td>
<td>72 80</td>
<td>97 99</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>70</td>
<td>93</td>
</tr>
</tbody>
</table>

a. "-" indicates analyte not detected.

Post-treatment Effects

A DBD/F spiked pulp has been chlorinated and extracted with base. The resulting pulp, which should contain enriched levels of dioxins, was then treated with three oxygen-based bleaching chemicals (O2/NaOH, H2O2, and O3). The chlorinated pulp and treated pulps were then analyzed for TCDD and TCDF to see if these commercial electrophilic reagents destroy dioxins adsorbed on pulps. Both H2O2, and O3 reduced dioxin levels by about 50%, while O2/NaOH brought about a 95% reduction. The results were surprising
in that the oxygen treatment appeared to be so much better than ozone.

The O₂/NaOH experiment was repeated; the results are given in Table 2. The internal standard recoveries for the pulp samples were above 50 percent, indicating efficient removal of the TCDD/TCDF from the pulp matrix. Precision between duplicate results was good. The internal standard recoveries for the effluent sample were low (ca. 10%), while recovery of the cleanup standard was 100 percent. These results suggest that TCDD/TCDF were not efficiently removed from the effluent sample prior to extract cleanup, since analyte losses did not occur in the extract cleanup. The analyte concentrations were corrected for these low recoveries.

Table 2. Dioxin Levels For Post-treatment of Chlorinated Pulp with O₂/NaOH (Repeat Experiment)

<table>
<thead>
<tr>
<th>Concentration (pg/g)a,b</th>
<th>Rep 1</th>
<th>Rep 2</th>
<th>Avg</th>
<th>Effluent</th>
<th>Blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDF</td>
<td>28</td>
<td>34</td>
<td>31</td>
<td>2400</td>
<td>--</td>
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<tr>
<td>Total TCDF</td>
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<td>49</td>
<td>45</td>
<td>3600</td>
<td>--</td>
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<tr>
<td>2378-TCDD</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>22</td>
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<tr>
<td>Total TCDD</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>22</td>
<td>--</td>
</tr>
</tbody>
</table>

Recoveries (%)

| 2378-TCDD-¹³C₁₂        | 73    | 71    | 6.4 | 86       |
| 2378-TCDF-¹³C₁₂        | 63    | 59    | 9.3 | 70       |
| 2378-TCDD-³⁷Cl₄        | 92    | 86    | 100 | 93       |

a values are on a wet weight basis  b "--" indicates analyte not detected.
The levels found in the repeat were about 45 ppt TCDF and nondetect for TCDD in the pulp. These values are similar to what was previously found for ozone and for peroxide. The effluent from the O₂-treatment was also analyzed; high levels of TCDF and moderate levels of TCDD were observed. Since this was the only effluent examined, it may be that the other treatments also had TCDF and TCDD in the effluent.

The data from this experimental set suggests that post-treatments of pulps containing dioxin can lower the TCDF and TCDD pulp contents by about 50% and 100%, respectively. However, the levels still may high in the effluents, suggesting that a post-treatment may not be effective in destroying dioxins.

CONCLUSIONS

Chlorination conditions have been established for observing the progressive development of ring chlorination of dibenzo-p-dioxane (DBD) and dibenzofuran (DBF), which have been adsorbed on cotton linters and are present in pulp. Because of the greater reactivity of DBD, the progressive development of mono-tetrachloro-DBD was skewed towards the higher chlorinated products and few lower substituted compounds were observed with either spiked cotton linters or extracted pulp.

A comparison of the distribution of mono-, di-, tri-, and tetrachlorodioxins as a function of chlorination time for the extracted unbleached pulp and DBD/F spiked cotton linters indicated that DBD and DBF are probably the major, if not only, dioxin precursors in pulp. It is possible that DBD and DBF related structures could be produced during chlorination.

Nitrogen dioxide pretreatment of a DBD/F spiked cotton linters effectively reduced dioxin levels observed after chlorination of the linters; in contrast, O₃ appeared ineffective. However, the O₃ treatment was performed on completely dry linters and may have been ineffective because solvent (water) may be required for efficient transportation of O₃ to reactive sites.

A pulp spiked with DBD/F was treated with NO₂ and O₃; both of the pre-treated pulps were then chlorinated. Ozone was much more effective than
NO\textsubscript{2} in decreasing the levels of both TCDD (nondetect vs 1.5 ppt) and TCDF (4 vs 600 ppt). Based on this data, an ozone treatment in front of a chlorine bleaching stage may be quite effective at lowering dioxin levels in pulps.

Selected bleaching treatments (O\textsubscript{2}/NaOH, H\textsubscript{2}O\textsubscript{2}, and O\textsubscript{3}) were tested for their ability to reduce the dioxin content in pulp by presumably destroying the chlorinated materials. Each treatment caused about a 50% lowering of the TCDD/F levels in the pulp. In the one case examined, O\textsubscript{2}/NaOH, fairly high levels of TCDD/F were found in the effluent; thus, it is uncertain whether the treatments destroy materials or redistribute the dioxin components. Overall, the strategy of destroying most, if not all, of the dioxins in pulp samples does not appear to be very promising.

**FUTURE ACTIVITY**

Work on this project was completed in January 1992; a final report was prepared and submitted to the Chlorine Institute in February 1992.
PROJECT 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

RESEARCH REVIEW

MARCH 25, 1992

Thomas J. McDonough
TECHNICAL PROGRAM REVIEW REPORT

Project Title: Environmentally Compatible Production of Bleached Chemical Pulp


Budget (FY 91-92): $500,000

Reporting Period: March 1991 - February 1992

Division: Chemical and Biological Sciences

Project Code: BLECH

Project Number: 3474

OBJECTIVE:

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

GOALS:

A. Elimination of AOX

1. Identify residual lignin structural features likely to be of importance in defining bleachability.

2. Assess the role of carboxyl group introduction in the mechanism by which chemical pretreatments improve the selectivity of a subsequent oxygen delignification stage.

3. Define effects of phenolic hydroxyl groups, alpha carbonyl groups and other lignin structural features on ease of lignin removal by oxygen, ozone and hydrogen peroxide, in comparison with the corresponding effects on ease of lignin removal by chlorine and chlorine dioxide.
4. Assess the importance of lignin-carbohydrate bonds as a factor determining ease of lignin removal by oxygen and alkali, in comparison with the corresponding effects on ease of lignin removal by chlorine and chlorine dioxide.

5. Determine the rate law governing the kinetics of cellulose degradation by ozone.

6. Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.

7. Determine effects of degree of oxygen dispersion on medium consistency oxygen bleaching.

8. Establish experimental techniques for measuring selectivity of catalyzed hydrogen peroxide delignification in a model system.


B. Reduction of AOX

1. Quantify the effect of mixing on AOX formation over a wide range of kappa factors.

2. Develop techniques for characterizing the AOX in CE and DE partial bleach sequences.

SUMMARY:

Work on this project during the past year has encompassed a wide range of research activity by both staff and students. It has been divided between investigations of chlorine compound free systems on one hand and chlorine and chlorine dioxide based ones on the other. Effects of residual lignin structure on bleachability comprise the focus of one set of project goals.

Effects of Carboxyl Groups in Residual Lignin (Goal A2) The influence of carboxyl content on oxygen stage selectivity was studied by conductometric titration of pulp samples which had been subjected to a variety of selectivity-improving pretreatments (NO₂, O₃, Cl₂ and Na₂SO₃ at several levels of application), followed by oxygen bleaching of the same samples. No single correlation between acid group content and oxygen stage selectivity could be identified. On the other hand, selectivity generally increased within each group of samples as the acid group content was increased. It was concluded that acid groups contribute only modestly to the ease of lignin removal by oxygen and alkali, and therefore to its selectivity.
Lignin-Carbohydrate Linkages and Bleachability (Goal A4) A second study is aimed at determining the importance of lignin-carbohydrate linkages as a factor contributing to difficulty of lignin removal during bleaching. Kraft pulp samples were subjected to the selectivity-improving pretreatments listed above. We then measured the ease with which carbohydrate could be removed from these samples by a cellulolytic enzyme. Unexpectedly, no positive correlation between carbohydrate release rate and bleachability was observed. This indicates either that lignin-carbohydrate linkages are not an important factor in determining bleachability, or that the rate of enzymatic carbohydrate removal from preoxidized pulp samples is not controlled by the frequency of such linkages. An as yet unexplained observation is that the residues from enzymatic treatment had high carbohydrate contents, suggesting that much lignin had gone into solution with the carbohydrate during the enzymatic digestion.

Additional experiments were carried out to determine whether xylanase pretreatment significantly improved oxygen bleachability, to provide further information on the possible importance of lignin-carbohydrate bonds. The results showed a modest improvement could be associated with the pretreatment. The cellulase results described above suggest that it was due to some phenomenon other than disruption of lignin carbohydrate linkages, perhaps decreased resistance to diffusion of lignin fragments.

Identification of Lignin Structural Features (Goal A1) It was expected that an additional product of the cellulolytic enzyme treatments would be lignin samples sufficiently freed of carbohydrate to be soluble in organic solvents. This would facilitate spectroscopic determination of lignin structural changes that had occurred as a result of the pretreatments. In fact, however, the resulting samples had high carbohydrate contents and were insoluble in organic solvents. Structural information was nevertheless obtained by FTIR examination of some of the unhydrolyzed, pretreated pulp samples. The analysis verified the introduction of carboxyl groups and some loss of aromaticity as the major structural changes resulting from NO2 treatment.

Ozone-Cellulose Kinetics (Goal A5) Ozone bleaching has been the subject of studies aimed at obtaining a better understanding of factors affecting the rate and extent of cellulose degradation. A kinetic study of ozone depolymerization of cotton linters has shown that the process exhibits two distinct rate phases. The initial phase is rapid and has a rate that depends on both the ozone concentration and the extent of depolymerization; the second phase is slower and depends only on ozone concentration, showing no tendency to slow down with increasing extent of depolymerization. The significance of these results derives from the fact that the rapid phase, complete in just a few minutes, may account for a substantial fraction of the total viscosity loss during ozone bleaching. Further study of this phase promises to uncover reasons for its existence and to point the way to methods of controlling it, thereby making ozone delignification a more commercially viable process.

Ozone Delignification and Pulp Properties (Goal A6) Another route to increased viability of ozone delignification is to gain an improved understanding of its effect on pulp properties and
refining behavior. We have initiated a study toward this end, with the initial objectives of characterizing the changes and comparing low and high consistency processes. Preliminary data are available, but are too few to allow any conclusions to be drawn yet.

Gas Dispersion in Oxygen Delignification (Goal A7) Processes for delignification with oxygen, although well established, still suffer from an incomplete knowledge of the interplay between physical and chemical factors controlling the extent of delignification. One such factor is the degree of mixing, or dispersion, of oxygen into the pulp in medium consistency systems. The study of this phenomenon is complicated by the difficulty of measuring bubble size distribution. We have approached the problem by first establishing the relationship between mass transfer and the operating parameters of a particular mixer. This has been done by determining the amount of carbon dioxide absorbed by an alkaline medium consistency pulp suspension under systematically varied conditions of mixer operation. The resulting relationships have been mathematically described by regression equations, which may be considered as predictors of the amount of interfacial area developed for given operating conditions. The next step will be to repeat the experiments with oxygen instead of carbon dioxide, and with degree of delignification as a dependent variable instead of amount of carbon dioxide absorbed. This will allow relationships to be established between interfacial area and degree of delignification that will, in turn, allow mixing requirements to be established for oxygen delignification under various sets of circumstances.

Hydrogen Peroxide Delignification (Goal A8) Hydrogen peroxide delignification is one process that appears to have the potential, with further research, to become a useful alternative or complement to delignification with ozone or oxygen. Another is delignification with lignin degrading enzymes. The latter process, however, appears to be further in the future. A third possibility is that ways may be found to mimic the action of enzymes in catalyzing hydrogen peroxide delignification by using simpler, synthetic substitutes. This is the subject of a current Ph.D. thesis (Ms. C. Walker). A lignosulfonate and hydroxyethylcellulose are being used as soluble polymeric models for lignin and cellulose, respectively. High pressure size exclusion liquid chromatography and solution viscosity are being used to determine extent of degradation of the models, and concentrations of hydroxyl radicals are being determined by a chemiluminescence method. Methods have been developed for all three procedures.

Evaluation of Novel Bleaching Agents (Goal A9) This activity has been pursued jointly between Projects 3728 and 3474, principally the former. The effort has focussed on the potential of dimethyldioxirane (DMD) as a delignifying agent. DMD has been generated in situ from peroxymonosulfuric acid and acetone and shown to be capable of extensively delignifying kraft pulp. A brief summary of this work can be found in the present report, and a more detailed account under Project 3728.

Mixing in Chlorination and Effluent Quality (Goal B1) The effect of mixing on chlorination effluent quality has been the subject of continued investigation. Research reported at the 1991
annual review had suggested the possibility of different relationships between AOX and chlorine charge for poorly mixed and well mixed chlorinations of kraft pulp. Additional work has confirmed this and the effect has been quantified. When mixing was poor, AOX increased linearly with kappa factor. In contrast, chlorination under conditions of extremely good mixing gave very low levels of AOX at kappa factors of 0.1 or below, and rapidly increasing levels thereafter. At low kappa factors, in other words, very good mixing sharply reduced the rate of AOX generation. This effect was even more apparent when it was evaluated at fixed CE kappa number rather than at fixed kappa factor, because of the effect of mixing on delignification. At a CE kappa number of 7, the effluent AOX reduction attributable to improved mixing was approximately 60%.

Characterization of AOX (Goal B2) It is generally recognized within the industry that adsorbable organic halides (AOX) is an unsatisfactory criterion by which to judge the environmental compatibility of any bleaching process. There is a need for more information on the characteristics, and methods of characterizing, the mixtures of chlorinated organic materials that constitute AOX. In addition, there is a need for the effects on effluent quality of various AOX-reducing measures (chlorine dioxide substitution, oxygen predelignification, etc.) to be understood in terms, not just of their AOX, but of the composition and likely potential for environmental effect of that AOX. Meeting both needs is among the objectives of a current IPST Ph.D. thesis research project (T. Schwantes). Techniques have been established for fractionating the effluents and characterizing the fractions in terms of molecular weight distribution, total organic carbon (TOC), and chlorine-to-carbon ratio.

Because early experiments have focussed on technique development, no attempt was made to ensure that the effluents analyzed were well defined or otherwise characterized. Nevertheless, the results have demonstrated that, for the chlorination effluents analyzed, 30-40% of the TOC was volatile, and that about half of the nonvolatile material was ether extractable. The chlorine-to-carbon ratio was lowest in the volatiles, and much higher in the ether extractable than in the nonextractable fraction. About 85% of the extractable fraction was acidic, 9% was phenolic and 6% neutral. For the extraction effluent analyzed, 10% was volatile, and 60% of the remainder was ether extractable. About 83% of the extractable fraction was acidic, less than 2% was phenolic, and 15% was neutral.
ENVIROMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

INTRODUCTION

The use of chlorine and chlorine-containing compounds to bleach kraft pulp has come under increasing scrutiny in recent years. As a result, there is growing pressure on the industry to (a) demonstrate that its bleaching processes are without harmful effect on the environment, (b) modify existing processes, or (c) find alternative processes. The goals of this project may be categorized under all three headings. We are studying:

- effects of residual lignin structure on bleachability, to allow optimization of pulping and pretreatment processes for both nonchlorine and chlorine-compound-based bleaching,
- fundamental aspects of ozone bleaching that determine its selectivity,
- physical factors governing the extent of oxygen delignification processes,
- catalyzed hydrogen peroxide delignification,
- novel nonchlorine bleaching agents,
- effects of delignifying agents on pulp properties,
- effects of mixing on chlorination effluent quality, and
- fundamental characteristics of mixtures of chlorinated organic compounds produced during bleaching with chlorine dioxide and chlorine.

Progress in each of these areas is reported in the following sections.
SECTION 1

EFFECTS OF RESIDUAL LIGNIN STRUCTURE ON BLEACHABILITY

Kyle R. Reed

Thomas J. McDonough
SUMMARY

In the kraft process, the selectivity between lignin removal and carbohydrate degradation changes when about 8% of the original lignin remains. Extending the cook to remove residual lignin compromises pulp quality and the cook must be interrupted and supplemented with a series of alternating oxidative steps for further delignification and bleaching. Selectivity for lignin removal over carbohydrate degradation determines the effectiveness of an oxidative step and should be determined by structural features of the residual lignin. A major focus of our research has been the determination of residual lignin structure and the chemistry which determines selectivity for bleaching of kraft pulp with oxygen under alkaline conditions. Unbleached kraft pulp was subjected to various types of pretreatments, each of which has been previously demonstrated to have a beneficial effect on oxygen stage selectivity. Theses consisted of nitrogen dioxide, chlorine, sodium sulfite, and ozone. Experiments were performed to assess the importance of the content of carboxylic and other acid groups in the treated pulps. Carboxyl groups were introduced by all treatments except sodium sulfite. The sulfite treatment introduced some strongly acidic groups, which may be assumed to be sulfonic acid groups. An attempt to correlate the selectivity of a subsequent oxygen stage with the sum of the contents of the carboxylic and strongly acidic groups showed no single correlation exists for all pretreatments, but selectivity generally increases within each as acid group content increases. It was concluded that acid groups contribute modestly to the ease of lignin removal during oxygen delignification and, therefore, to the selectivity of that process. There is, however, no dominating influence of such groups on lignin removal from pretreated pulps by oxygen and alkali. Additional experiments were conducted to support the above conclusions. If introduction of acid groups to lignin is not the main determinant of oxygen stage selectivity, the role of lignin-carbohydrate linkages may be an important factor. Recent experiments using xylanase enzymes as a pretreatment to the oxygen stage may clarify the importance of lignin-carbohydrate linkages to selectivity.

INTRODUCTION

Modern kraft mills increasingly employ oxygen delignification before chlorination to decrease requirements for chlorine and chlorine-containing bleaching chemicals. This trend has recently intensified, owing to a growing desire to reduce the formation of chlorinated organic byproducts in both the bleaching effluent and the bleached pulp.

Conventional application of oxygen predelignification leads to a reduction in unbleached lignin content, and a corresponding reduction in chlorine demand, of 40-50%. More extensive delignification is normally precluded by the limited selectivity of the oxygen stage, which results in losses of pulp viscosity and strength at high degrees of delignification. On the other hand, laboratory studies have demonstrated that certain chemical pretreatments of the unbleached pulp increase the selectivity of a subsequent oxygen stage. They include nitrogen oxides, chlorine, chlorine dioxide, ozone, hydrogen peroxide and sodium sulfite. Their use allows the upper limit on oxygen delignification to be substantially increased from its normal level of about 50%.
Application of any of these pretreatments, followed by oxygen delignification under a fixed set of conditions, has two major effects on the properties of the pulp emerging from the oxygen stage. These are a decrease in kappa number and an increase in viscosity. The kappa number decrease demonstrates the existence of an accelerating effect of the pretreatments on the delignification reactions. The viscosity increase may be due to a protective effect of the pretreatment agent or its reaction products on cellulose. On the other hand, it may simply be due to a reduction in average alkalinity due to more rapid consumption of alkali by sensitized residual lignin. We favor the latter interpretation, in view of an earlier observation that addition of NO2-treated lignin to cotton linters had no effect on linters viscosity after treatment under simulated oxygen delignification conditions. This interpretation implies that, to understand the mechanism of action of the pretreatments, studies should be focussed on their acceleration of delignification reactions.

The mechanism by which any pretreatment accelerates subsequent oxygen delignification may involve one or more of the following component mechanisms: a decrease in the molecular mass of the lignin, an increase in its hydrophilicity, an increase in its sensitivity to depolymerization and solubilization under the conditions of oxygen delignification, cleavage or sensitization of lignin-carbohydrate linkages, and blocking of lignin condensation reactions.

The actual mechanisms, for the most part, remain unknown. They have received most attention in the case of treatment with NO2. Andersson, Samuelson and Mansson, for example, have demonstrated the occurrence of the following changes in kraft lignin during NO2 treatment: demethylation, loss of phenolic hydroxyl groups, increase in titratable acid groups and nitration. In a similar, more recent study, Larsson, Samuelson and Ojteg showed increases in acid groups and hydrophilic properties and the formation of ester groups. Ester formation was associated with an increase in the molecular mass of the lignin, which was, in turn, attributed to the hot acidic conditions of the pretreatment. Hot alkali treatment of the modified lignins resulted in a rapid reversion of molecular mass to its untreated level. This was attributed to cleavage of intermolecular ester linkages. In some samples the alkali reduced the molecular size to levels below that of the original pulp, suggesting that ether linkages may have been rendered sensitive to alkali by the treatment. In others, however, the molecular size of the alkali treated lignin remained higher than that of the untreated sample. These observations suggest that rendering the lignin hydrophilic may be important, but that depolymerizing the lignin or rendering it sensitive to depolymerization may not be.

Lindeberg and Walding speculated that nitration of nonphenolic units makes residual lignin more susceptible to depolymerization by facilitating alkaline hydrolysis of alkyl-aryl ether bonds. A more recent study by Ohi and McDonough, however, shows that nonphenolic model compounds are not nitrated under conditions of the pretreatment, rendering the Lindeberg-Walding mechanism unlikely.

It is apparent from the above review that much remains to be done in gaining an understanding of selectivity-improving pretreatments for oxygen. In fact, this objective can be usefully generalized to include effects of all processes to which the pulp is subjected before it enters an oxygen delignification stage, including the pulping process. Stated in this way, the objective
becomes that of identifying structural features of residual lignin that enhance the response of pulp to oxygen delignification.

The purpose of the study described here was to assess the importance of one such structural feature, the content of carboxylic acid groups in kraft residual lignin. The likelihood that carboxyl groups and the hydrophilicity they impart to lignin are important contributors to ease of lignin removal has been suggested by several studies. Samuelson and co-workers, in the studies already referred to, have shown that NO2 treated pulps consume more alkali in titrations to pH 9 than untreated pulps. Gellerstedt and Lindfors have emphasized the importance of carboxyl introduction during bleaching, and have shown that the carboxyl content of dissolved and isolated residual lignins correlates with the relative efficiencies of bleaching stage types. None of these studies, however, has addressed the degree to which carboxyl group introduction can account for the efficacy of pretreatments for oxygen bleaching.

The general approach we adopted was to subject kraft pulp to various types of pretreatments, each of which has been previously demonstrated to have a beneficial effect on oxygen stage selectivity. These consisted of nitrogen dioxide, chlorine, sodium sulfite, and ozone. Each pretreating chemical was applied at several different charge levels, under otherwise similar conditions. The pretreated pulps were then analyzed for carboxyl group content prior to being subjected to oxygen delignification.

The method chosen for determination of carboxyl groups was that of Katz, Beatson and Scallan. It consists essentially of conductometric titrations of pulp samples previously equilibrated with dilute acid and subsequently washed. Sodium chloride was added to suppress Donnan equilibrium effects.

RESULTS AND DISCUSSION

Analysis of Pretreated Pulps

The results of conductometric titrations of the untreated pulp and samples of the same pulp after treatment with 2 and 8% NO2 are shown in Figure 1. Before each titration was begun, 1.5 mL of 0.1N HCl was added. The descending portion of each curve is due to neutralization of conductive hydrogen ions originating with the added acid and any strongly acidic functional groups in the pulp. The flat portion at the bottom corresponds to neutralization of the titrant's hydroxyl ions by carboxyl groups bound to the pulp, the majority of which may be assumed to reside within the lignin component (see additional experiments section). Since these are weakly acidic, they do not contribute appreciably to the conductivity of the pulp suspension, and their conversion to the salt form results in no change in conductivity. When all the carboxyl hydrogen ions have been consumed, continued addition of titrant contributes excess conductive hydroxyl ions, accounting for the ascending portion. The carboxyl content may be estimated from the consumption of titrant during the period characterized by constant conductivity. This is determined by drawing straight lines through the descending, ascending and flat portions of the curve and measuring the distance between intersections on the flat portion. Consumption of titrant up to the point of the first intersection should be exactly equivalent to the amount of HCl.
added before beginning the titration, unless strongly acidic groups (such as sulfonic acid groups) are present in the pulp. The amount of such groups present can thus be estimated from the position of this intersection along the titrant volume axis.

The results of Figure 1 confirm that carboxyl groups are introduced by NO2 treatment. The calculated carboxyl contents for the three samples shown were 100, 144 and 150 meq/kg, respectively. Small contents of strongly acidic groups are also indicated: 11, 14 and 14 meq/kg, respectively. Determinations of the kappa numbers of these three pulps gave values of 39.5, 39.0 and 38.4, showing that little delignification had occurred during the pretreatment. Methoxyl contents were 353, 303 and 271 meq/kg. The reasonable agreement between the increases in carboxyl and reductions in methoxyl shows that the carboxyl groups were introduced into the lignin component of the pulp. Figure 2 shows the corresponding titration curves for ozone treated pulps. In this case, the width of the titration interval corresponding to carboxyl group neutralization decreased with increasing treatment level. This was due to delignification, rather than to removal of carboxyl groups from lignin, and resulted from the large decreases in kappa number that accompanied ozone treatment. The kappa numbers of pulps treated with 0, 0.5, 1 and 2% ozone were 39.5, 34.5, 30.1 and 21.9 respectively. The carboxyl group contents of the lignin were 1.68, 1.83, 1.97 and 2.33 meq/g. The latter determinations were made by combining the conductometric titration and kappa number data, and assuming that the lignin content (as % of o.d. pulp wt.) of a treated pulp is equal to 0.15 times its kappa number.

The results of conductometric titrations of the remaining pretreated pulps are presented in Table 1, together with the results of determinations of their kappa numbers and methoxyl contents. Carboxyl groups were introduced by all treatments except that with sulfite. The sulfite treatment introduced some strongly acidic groups, which may be assumed to be sulfonic acid groups. Total acid group content is shown in Figure 3 as a function of the type and amount of pretreating chemical applied. Nearly all of the acid groups introduced were carboxyl groups, except in the case of the sulfite treatment.

When calculated as a percentage of the lignin component (as estimated from kappa number), methoxyl contents generally decreased, as shown in Figure 4. This is to be expected when carboxyl groups are introduced into lignin by demethylation and ring oxidation with the formation of products such as substituted muconic acids. An apparent exception to the trend of decreasing lignin methoxyl content was the pulp treated with 2% ozone. The highly oxidized lignin in this pulp may have reduced permanganate demand in the kappa number test, leading to underestimation of the lignin content and overestimation of the methoxyl content of the lignin. In addition, ozone is capable of cleaving the aromatic ring of lignin model compounds without disrupting the linkage between the ring and the methoxyl group.

**Oxygen Bleaching**

To be effective, a pretreatment must possess two characteristics. The first is that it must be selective in itself; it must be able to extensively modify the residual lignin in a kraft pulp without simultaneously depolymerizing cellulose. The second is that it must confer selectivity upon an ensuing oxygen stage. The first characteristic can be measured by determination of viscosity
Table 1: Experimental Pretreatment Data

<table>
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<th>Pretreatment</th>
<th>Kappa No.</th>
<th>Functional Groups, meq/g lignin&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Viscosity After Pretreatment, cp.</th>
<th>Oxygen Stage Selectivity&lt;sup&gt;e&lt;/sup&gt; ΔK/ΔV</th>
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<th>Post-Oxygen Viscosity at 50% Delignification, cp.&lt;sup&gt;f&lt;/sup&gt;</th>
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<td>40.0</td>
<td>5.38 1.37 0.26 1.63</td>
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<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt; 16</td>
<td>37.7</td>
<td>4.82 1.47 0.57 2.03</td>
<td>28.5</td>
<td>1.56</td>
<td>0.15</td>
<td>17.5</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; 0.5</td>
<td>34.5</td>
<td>5.42 1.83 0.15 1.98</td>
<td>23.7</td>
<td>2.50</td>
<td>0.29</td>
<td>18.2</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; 1</td>
<td>30.1</td>
<td>5.72 1.97 0.20 2.17</td>
<td>20.1</td>
<td>2.90</td>
<td>0.46</td>
<td>17.2</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; 2</td>
<td>21.9</td>
<td>6.14 2.33 0.17 2.50</td>
<td>14.1</td>
<td>4.80</td>
<td>0.66</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Notes:

a. After estimating lignin content from: % lignin (o.d. pulp basis) = 0.15 x Kappa no.
b. Viscosity not measured after NO<sub>2</sub> pretreatment; it was assumed that viscosity was unaffected by the pretreatment.
c. Viscosity of 4% Cl<sub>2</sub>-treated pulp increased during oxygen stage.
d. Not measured. May be assumed to be high.
e. For 50% removal of the lignin in the pretreated pulp.
f. After 50% removal of the lignin in the unpretreated pulp.
before and after the pretreatment. The second is reflected by the relative changes in viscosity and kappa number that occur during the oxygen stage, relative to their values after the pretreatment. It may be quantitatively expressed as the inverse of the slope of the viscosity-kappa number relationship, averaged over the duration of the oxygen stage.

The emphasis in the present study was on the latter of these two characteristics, and whether it depends on the introduction of carboxyl groups. Accordingly, the main objective of our oxygen bleaching experiments was to establish the degree of selectivity conferred by each pretreatment.

Subsamples of each pretreated pulp were oxygen bleached at 25% consistency and approximately 100 deg. C with 1, 2 and 4% NaOH addition, based on the dry weight of the pulp sample. To avoid pretreatments of large amounts of pulp, microscale bleaching reactors were used and microanalytical procedures were used to evaluate the resulting bleached pulps. Since the bleaching procedure was newly developed and of unproven precision, all bleaching runs, with one exception, were done in duplicate.

In addition, untreated controls were included with each batch of samples.

Figure 5 shows the kappa number and viscosity data for all of the unpretreated control samples, except for two outlying points, which were discarded. The line drawn through these points is included in Figures 6-9 for reference.

The results of oxygen bleaching of nitrogen dioxide pretreated pulps are shown in Figure 6. As expected, treatment with 2% NO2 brought about a significant improvement in selectivity, while larger additions had relatively small additional effect.

Figure 7 contains the corresponding results of chlorine pretreatments. For this pretreatment, the selectivity improvement was strongly dependent on post-oxygen kappa number. As the chlorine charge was increased, the maximum selectivity improvement became larger and occurred at lower kappa numbers.

During the first of the two replicate runs shown in Figure 7, some difficulty was encountered with reactor temperature control, with the result that this run was conducted at significantly lower temperature than the second one. The temperature decrease resulted in improved selectivity for the pretreated pulps, but not for the controls. A final observation of interest is that the highest chlorine application resulted in an apparent viscosity increase during oxygen bleaching. This may be due to removal of low molecular weight material, or may reflect improved stability of the oxygen bleached pulps toward depolymerization by the solvent used in the viscosity determination.

Treatment with ozone before oxygen bleaching gave the results shown in Figure 8. The pretreatment itself was less selective than oxygen, but it did confer relatively high selectivity on the oxygen stage, as evidenced by the low slope of the curves shown.
Treatment with sodium sulfite, as shown in Figure 9, also reduced the slope of the viscosity-kappa number relationship, but not by a sufficient amount to offset a viscosity loss incurred during the pretreatment itself.

**Acid Groups and Selectivity**

For each of the curves shown in Figures 6-9, selectivity during the oxygen stage was measured as the decrease in kappa number divided by the decrease in viscosity in reducing the lignin content of the pretreated pulp by 50%. Averaging the results for both replicates gave the oxygen stage selectivity values shown in Table 1. Figure 10 shows the results of an attempt to correlate these with the sum of the contents of carboxylic and strongly acidic groups. It is apparent that no single correlation exists for all pretreatments, but that within each, selectivity generally increases as acid group content increases. This suggests that, although a strong cause-effect relationship does not exist, the hydrophilicity conferred on lignin by acidic groups contributes to the ease of lignin removal during oxygen bleaching.

To reiterate one of our introductory remarks, selectivity during the oxygen stage is only one of two necessary characteristics of a good pretreatment-oxygen sequence. It combines with the selectivity of the pretreatment itself to determine the selectivity of the sequence. One measure of the latter quantity is the viscosity after the oxygen stage at a given overall degree of delignification, as shown in Table 1. The superiority of nitrogen dioxide and chlorine over the other two pretreatments, not apparent from Figure 10, can be traced to the selectivity of the pretreatment itself.

**Additional Experiments**

A number of additional experiments were performed to test the above observations. On such experiment was FTIR analysis of the nitrogen dioxide and chlorinated pulp samples. Figure 11 shows FTIR analysis of the series of nitrogen dioxide treated pulps. There appears to be a loss of aromatic character accompanied by an increase in carbonyl content. If the carbonyl content is associated with introduction of carboxylate into the pulp, the absorption peak should be shifted by conversion to the salt form to lower wavenumbers. Figures 12 and 13 are difference spectra between pulp equilibrated with acid and base. A shift in the carbonyl absorption is observed for both nitrogen dioxide and chlorine treated pulp.

A key assumption of our work is that the residual lignin of the pulp is oxidized to a far greater degree than the carbohydrate phase. Various oxidants are known to oxidize carbohydrate; for example, nitrogen dioxide is able to oxidize the C6 carbon of carbohydrates to carboxylate. To determine if carboxylate was introduced preferentially to the lignin phase, untreated pulp and pulp treated with 6% nitrogen dioxide was extensively delignified using chlorine dioxide. The delignified pulps were then analyzed for carboxylate as shown in Figure 14. There was no significant difference in carboxylate content for the delignified pulps. It appears that the oxidation is highly selective in introducing carboxylate into the lignin in accord with our initial assumption.
Another assumption of our work was that the method used to determine carboxylate is not influenced by phenolic hydroxyl groups. Since the pH during the titration rises to about 10 at the end of the titration, it is possible that ionization of phenolic groups is contributing to the carboxylate determination. To determine if phenolic groups were contributing to the values determined for carboxylate, untreated pulp was extensively methylated with diazomethane. This should block phenolic groups and convert carboxylic acid groups to methyl esters. Methoxyl groups should be very stable at high pH while methyl esters are easily hydrolysed. If phenolic hydroxyls were contributing to previously determined carboxyl results, a lower value should be obtained after methylation and saponification. The methylated untreated pulp was titrated as is shown in Figure 15. Initially there is very little carboxylate detected (Figure 15 A). The pulp suspension was then heated to 50 deg. C for 11 hours at a pH of 11 and the titration repeated as shown in Figure 15 B). This titration curve gives a carboxylate value of about 105 meq/kg. Since the carboxylate content of the unmethylated pulp was 100 meq/kg, there is apparently no contribution from phenolic hydroxyl groups to the carboxylate value for the untreated pulps. Further exposure to heat and alkali showed that the carboxylate value was very stable.

A difficulty in determining lignin content arises from the nature of the kappa number test which involves oxidation with permanganate. For a highly oxidized pulp, the reaction with permanganate may be slowed thereby resulting in an erroneously low kappa number. Slow reaction rates with permanganate were observed with methylated pulp samples, but in this case, the reaction rate is slowed by methylation of the free phenolic groups of the lignin. To investigate if the extent of oxidation influenced the kappa number results, hypo number tests (TAPPI 253) were performed on the pretreated pulps. The hypo number results were then plotted against the kappa number results as shown in Figure 16. Since both hypo number and kappa number are directly proportional to lignin content, pulps over a range of lignin content should fall along a line on this plot. For a line drawn through the ozone delignified pulps, the methylated pulp and the pulp treated with 4% chlorine show large deviations. The highly chlorinated pulp seems to give a low hypo number result while the methylated pulp gives a low kappa number result. Since hypo numbers are determined by consumption of chlorine in the test, the highly chlorinated pulp may be limited in uptake of chlorine thus giving a low result. However, if the line is drawn through the chlorinated pulps, the methylated pulp and the pulps treated with ozone depart from the line; the ozone pulps giving low kappa numbers. It is clear that a larger number of pulps delignified through various means is required to determine which line better represents lignin content.

Having supported some of the key assumptions of our work on acid groups, our attention was turned to other possible mechanisms for selectivity. To investigate the structure of residual lignin in more detail, it was desirable to enzymatically isolate lignins for dissolution in a solvent suitable for NMR spectroscopy. In addition, the carbohydrate content of an enzymatically isolated lignin could be associated with the degree of linkage between the lignin and carbohydrate in the original pulp. Lignin-carbohydrate linkages have been suggested as an important factor controlling the dissolution of residual lignin from fibers\(^{13}\).
Enzyme Experiments

A large number of pulp samples were treated with cellulase enzymes from *Trichoderma reesei* (Sigma C-8546) and glucosidase from almonds (Sigma G-0395). To follow the hydrolysis of the pulp samples, the amount of reducing sugar in the enzyme supernatant was determined using 3,5-dinitrosalicylic acid with glucose standards. From the concentration of sugar and the total volume of the suspension, the mass hydrolyzed was estimated. Figure 17 shows the progress of the hydrolysis for 31 pulp samples over the course of several enzyme treatments. All samples except those treated with 8% NO₂ were originally 1.500 o.d. grams of air dry pulp. One of the 8% NO₂ samples was only 484.8 mg and the other was an oven-dried sample. This was required because of the limited amount of pulp left over from past testing and experiments. The following observations are noted: 1) For the first hydrolysis, chlorination seems to slow the rate of enzymatic hydrolysis. 2) NO₂ treatment slows the rate of hydrolysis only a small amount. 3) Ozone and sodium sulfite treatments do not effect the rate of hydrolysis. 4) Oven drying leads to very slow rates of hydrolysis. Insoluble material was isolated from 7 of the samples by centrifugation and washed extensively with distilled water by resuspension and centrifugation. These samples included two untreated samples, two samples treated with 4% NO₂, one treated with 4% chlorine, one treated with 2% ozone, and one treated with 16% sodium sulfite. One of the untreated samples was acetylated with acetic anhydride/pyridine for NMR analysis. Only a small amount of the resulting solid was dissolved by DMSO-D6 and the NMR obtained showed few peaks assignable to lignin. The remaining samples were analyzed for carbohydrate content using the method of alditol acetates. As shown in Figure 18, all of the samples had carbohydrate contents of over 80%. This result was much higher than expected and implies that much of the lignin was solubilized by the cellulase enzymes.

Figure 19 is obtained by converting the weight percent of each sugar to a mole percent. This emphasizes how the ratios of the various sugars have been changed.

As expected, the glucose ratio is high for the samples as there is still a large amount of cellulosic material left. There is a depletion in the xylan content for all of the pretreated samples.

We obtained a source of xylanase from Jan L. Yang at the University of Georgia, Department of Biochemistry for bleaching studies at this time. To determine to what degree xylanase causes release of lignin-carbohydrate complexes (LCCs), a series of softwood samples were treated with xylanase in increasing dosages. The samples were treated with xylanase in an 0.05 M acetate buffer pH 5.0 and a consistency of about 10% for 90 minutes at 50 deg. C. The increase in absorbance at 280 nm was determined in the enzyme solution after this time and is plotted in Figure 20. There is a slowly increasing release of LCCs from the pulp with increasing xylanase dosage. Figure 21 shows that the release of reducing sugar increases in a linear fashion as xylanase dosage increases.

When kappa number and viscosity tests were performed on all of the treated samples, no statistically significant difference could be determined between the samples. Choosing the highest level of dosage from the preceeding experiment, a sample of softwood kraft pulp was treated with xylanase at 10 units/g. This pulp was oxygen bleached in a manner identical to the chemical
pretreatment experiments. Samples of hardwood pulp supplied by Dr. Yang were also oxygen bleached. Control samples for these experiments consisted of pulp which had been incubated in acetate buffer but without enzyme present. Figure 22 shows the resulting viscosity versus kappa number plots for the two experiments conducted on softwood pulps and Figure 23 shows the two experiments conducted on the hardwood pulps. A modest improvement in selectivity is observed for both softwood and hardwood pulp.

CONCLUSIONS

Acid groups in unbleached kraft pulps, believed to reside in the residual lignin component, contribute modestly to the ease of lignin removal during oxygen delignification, and therefore to the selectivity of that process. There is, however, no single relationship between acid group content and selectivity for different pretreatments, and therefore no dominating influence of such groups on lignin removal from pretreated pulps by oxygen and alkali. Recent experiments using xylanase as a pretreatment suggest that breakage of lignin-carbohydrate linkages may play a complementary role in determining selectivity during oxygen delignification.

EXPERIMENTAL

Material

Never-dried industrial southern pine kraft pulp with a kappa number of 39.5 and a CED viscosity of 40.6 cP was used in all experiments involving softwood pulp. For oxygen bleaching experiments involving hardwood pulps, both the control pulp and xylanase treated pulp were supplied by Jan L. Yang from the University of Georgia, Department of Biochemistry. The hardwood pulp was a mixture of white oak and sweet gum. All pulps were stored at 4°C and 33% consistency. After the initial softwood experiments on nitrogen dioxide pretreatment, it was determined that shives in the pulp caused poor repeatability in the kappa number and viscosity tests after oxygen bleaching. The pulp was therefore screened and stored at 4°C and 34% consistency for use in the remaining experiments. Kappa number and viscosity tests on the screened pulp were within experimental error of the results obtained for the unscreened pulp.

The xylanase enzyme preparation was supplied by Jan L. Yang from the University of Georgia, Department of Biochemistry. A strain of *Aureobasidium pullulans* was used to produce the enzyme fraction using oat-spelt xylan as the only carbon source in a 2 liter continuous fermenter. The enzyme preparation was supplied as a brownish liquid with the following activities as determined by Dr. Yang: xylanase 480 U/ml, glucosidase 5 U/ml, xylosidase 5 U/ml, and galactosidase 13 U/ml. No mannanase activity was detected in the preparation. The molecular weight distribution of the preparation was determined to be 5-100 kD.
The kraft pulps was pretreated with the chemicals and conditions given in Table 2.

Table 2. Pretreatment conditions.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Consistency %</th>
<th>Temp. °C</th>
<th>Time minutes</th>
<th>Application level % on o.d. pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>33</td>
<td>25</td>
<td>15</td>
<td>2%, 4%, 8% as NO₂</td>
</tr>
<tr>
<td>Cl₂</td>
<td>3</td>
<td>25</td>
<td>30</td>
<td>1%, 2%, 4% as active Cl</td>
</tr>
<tr>
<td>O₃</td>
<td>30</td>
<td>25</td>
<td>10</td>
<td>0.5%, 1%, 2%, as O₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.1% acetic acid</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>20</td>
<td>140</td>
<td>30</td>
<td>1%, 4%, 16% as SO₂</td>
</tr>
<tr>
<td>Xylanase</td>
<td>10</td>
<td>50</td>
<td>90</td>
<td>2 U/g softwood, 10 U/g hardwood</td>
</tr>
</tbody>
</table>
Sodium Sulfite Treatment
Sodium sulfite was mixed with 20 o.d. grams of pulp in a Hobart mixer at 20% consistency. Treatments of pulp with sodium sulfite were performed in 500 ml stainless steel vessels heated in an oil bath with a temperature ramp from ambient to 140 °C in 30 minutes. Because of the small size of the reaction vessels, the treatments were performed in duplicate for each application level and the pulps then combined. The combined pulps were fluffed and air dried in preparation for oxygen bleaching.

Xylanase Treatment
Before enzyme treatment, softwood pulp was disintegrated for 10,000 revolutions in a disintegrator, filtered on a large coarse fritted funnel and dewatered to a consistency of about 20%. Enzyme solution equivalent to 500 units of xylanase activity was added to 300 ml of 0.05 M pH 5.0 acetate buffer. After stirring, the enzyme solution was added to 50 o.d. grams of the softwood pulp in a kapak bag giving a final consistency of 10%. The bag was sealed and the pulp kneaded for about 5 minutes to thoroughly disperse the enzyme solution. The bag was incubated at 50 deg. C in a thermostatted water bath for 90 minutes. Every 30 minutes the pulp mixture was again kneaded. After incubation, the pulp was filtered on a large coarse fritted funnel. A sample of the filtrate was collected for analysis of reducing sugar and absorbance at 280 nm. The pulp was then washed several times with distilled water until the conductance of the filtrate reached a constant value. The pulp was allowed to partially air dry and fluffed for oxygen bleaching. The control pulp went through a identical procedure except for the addition of enzyme solution.

Oxygen Delignification
To prepare samples for alkaline oxygen bleaching, the pulp samples were partially air dried and fluffed. To ensure a homogeneous sample for both nitrogen dioxide and ozone treated pulps, the pulps were gently disintegrated in a blender prior to air drying. The time between pretreatment varied from 4 days in the case of chlorinated pulps to several weeks for nitrogen dioxide treated pulps. Bleach trials were performed in a stainless steel pressure vessel of 2.2 liter capacity which could accommodate 12 samples of pulp of 3 o.d. grams each. The 12 samples were composed of the three application levels of each pretreatment and three untreated control samples with NaOH charge levels of 1%, 2%, and 4%. For the xylanase experiments, the hardwood and softwood samples were combined for each bleaching run. In these experiments, 3 of the samples were the hardwood control samples, 3 were the hardwood xylanase treated samples, 3 were the softwood control samples, and 3 were the softwood xylanase treated samples. The 3 samples of each pulp corresponded to three levels of NaOH application: 1%, 2%, and 3% for the first experiment and 1%, 2%, and 4% for the second experiment. All samples were treated with 0.1% MgSO₄ as Mg²⁺. To apply caustic/MgSO₄ solution at a consistency of 26%, 3 o.d. gram pulp samples were tared in 100 ml plastic beakers and the impregnation solution was dispersed in the pulp by compressing the pulp several times so that the solution was released and reabsorbed by the sample. The samples were then taken in random order, fluffed by hand, and placed in perforated pvc cups.
which were then stacked in the pressure vessel. After charging with 70 psig oxygen at room temperature, the vessel was heated in an oil bath for 70 minutes with the average temperature over the last 30 minutes ranging from 87-104 °C. After bleaching, samples were washed with 200 ml of distilled water at which time a pH reading was taken. The sample was filtered, disintegrated in 1 liter of distilled water and filtered again on a coarse fritted funnel. The pulp pad was allowed to air dry for later testing of kappa number and CED viscosity.

**Conductometric Titrations**

Initially, conductometric titrations were performed using the procedure reported by Pu and Sarkanne. It was found that this procedure could be modified in two principal ways and still produce reproducible results. The tests could be scaled down so that only 1.5 o.d. grams of pulp was used in each determination of acid group content. In addition, the rate of addition of titrant could be increased substantially without changing the result by a significant amount. After being stirred in 300ml of 0.1 M HCl for about one hour, the pulp was filtered on a small fritted funnel and washed exhaustively with distilled water. The pulp was then dispersed in 250 ml of 0.001 M NaCl and 1.5 ml of 0.1 M HCl added to the solution. The conductivity of this solution generally was about 385 uS/cm except for Na₂SO₄ treated pulps which had a conductivity of over 400 uS/cm. Additional 0.001 M NaCl was then added dropwise to the solution thereby reducing the conductivity to a common point for all titrations performed. The solution was titrated with freshly prepared 0.05 M NaOH solution. The alkali was added in units of 0.25 ml from a 10 ml buret while bubbling nitrogen through the solution to eliminate effects from CO₂ absorption. Since volume changes during titrations were only about 4%, volume corrections were not necessary. A Markson Electromark Analyzer was used for conductivity measurements and NIST traceable standardized acid and base solutions were obtained from commercial sources.

A disadvantage of the conductometric method is that it requires acid washing of the pulp which could lead to a reduction in carboxylic acid content by lactone formation. Slow addition of titrant would seem to be necessary in order that lactones formed during acid washing are hydrolyzed during the titration. It was found that speeding up the rate of the titration to less than one hour gave results only a few percent lower than titrations performed over several hours. In addition, extending the length of time in which the pulp was soaked in acid did not affect the results.

Conductometric titration curves of pulp suspensions are characterized by three linear regions. Initially, excess acid is neutralized by titrant and the conductivity descends in a linear fashion. The first transition at a pH of about 4 occurs when the pulp begins to be ionized. While the pulp is in an intermediate state of ionization, the conductivity remains constant as the pulp consumes titrant. The length of this linear region is a measure of the carboxylate content of the pulp. The end of the titration is then characterized by a linear region where the conductivity increases due to excess titrant. To calculate values from the titration curves, lines were drawn through each of the aforementioned linear regions thereby obtaining two endpoints where the line intersect. The value for strong acid content in the pulp was obtained by subtracting the equivalents of strong acid added before the titration from the equivalents.
corresponding to the first endpoint. The value for carboxylate content was obtained by subtracting the equivalents corresponding to the first endpoint from the number of equivalents corresponding to the second endpoint. The average repeatability was 5%.

**Methoxyl Determinations**

Methoxyl analysis was done by Chem-Lig International Industries, Inc. (320 Ross Avenue, Schofield, WI 54476, USA) by reacting the test samples with HI and determining the resultant methyl iodide liberated by the sample. The average repeatability was 9%.

**Kappa, Hypo Number and Viscosity Tests**

Kappa number tests were at 1/10 the scale of the TAPPI test method T236 cm-85 with an average repeatability of about 1.7%. Hypo number tests were at 1/2 the scale of the TAPPI test method T253 om-86 with an average repeatability of about 5%. CED viscosity tests were by TAPPI test method T230 om-89 with repeatability generally less than 4%.

**FTIR Analysis**

Spectra were collected (500 scans/spectrum) in duplicate in the DRIFT mode at 4 cm⁻¹ resolution on a Nicolet 7199 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and a Harrick Praying Mantis diffuse reflectance cell. Disks were cut from air-dried pulp sheets and pressed flat with a Noble and Wood sheet press at 200 psi for 5 minutes. Spectra were manipulated using LabCalc (Galactic Industries) software routines.

**Determination of Reducing Sugars**

Reducing sugars were determined using 3,5-dinitrosalicylic acid¹° (DNS). Depending on the concentration of reducing sugar, either 0.10 ml or 1.00 ml samples were added to 3.00 ml of the DNS reagent in a test tube. For 0.10 ml samples, an additional 0.90 ml of distilled water was added to the test tube. The tube was placed in a boiling water bath for 5 minutes. After cooling to room temperature, the absorbance of the solution was determined at 540 nm with a water blank in a Beckman Lambda 20 spectrometer. Standards of several sugars produced highly linear plots in absorbance versus concentration. The limit of detection for the technique was about 50 ppm.

**Carbohydrate Analysis**

Carbohydrate analysis was performed according to TAPPI method T 249 cm-85. Because of the limited amount of material for testing, samples were dried over P₂O₅ and assumed to be 100% solids.
ACKNOWLEDGMENTS

The gift of the xylanase enzyme preparation by Jan L. Yang from the University of Georgia, Department of Biochemistry is gratefully acknowledged.
LITERATURE CITED

1. Yethon, A.E., Canadian Patents 1,045,759 (1974) and 1,070,909 (1976).


**Figure 1.** Conductometric titration curves for untreated pulp and pulps pretreated with 2 and 8% NO$_2$. 
Figure 2. Conductometric titration curves for untreated pulp and pulps pretreated with 1 and 2% O₃.
Figure 3. Total acid groups (sum of carboxyl and strongly acidic groups) as a function of chemical application for all pretreatments.

Figure 4. Methoxyl group content as a function of chemical application for all pretreatments.
Figure 5. Viscosity as a function of kappa number after oxygen bleaching for unpretreated pulps.
Figure 6. Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with nitrogen dioxide. Data for two complete replicates, (A) and (B), are shown.
Figure 7. Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with chlorine. Data for two complete replicates, (A) and (B), are shown.
Figure 8. Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with ozone.
Figure 9. Viscosity as a function of kappa number after oxygen bleaching for pulps pretreated with sodium sulfite. Data for two complete replicates, (A) and (B), are shown.
Figure 10. Oxygen stage selectivity vs total acid group content for all pretreatments.
DRIFT Spectra of Unbleached Loblolly Pine Pulp Following Treatment with 0, 2, 4, 6, 8, and 10% NO₂

Note appearance of a new peak at 1720, tentatively identified as a carbonyl vibration.

Figure 11. FTIR analysis of pulps treated with increasing amounts of nitrogen dioxide.
8% Nitrogen Dioxide Treated – Na Salt

Absorbance

Wavenumbers

Figure 2: Difference spectrum for nitrogen dioxide treated.
Figure 13. Difference spectrum for chlorine treated pulp.
Figure 14. Conductometric titrations of pulps delignified with chlorine dioxide.
Figure 15. Conductometric titrations of untreated pulp methylated with diazomethane: A) Initial titration shows no free carboxylate; B) After exposure to alkaline conditions for 11 hours, methyl esters are hydrolysed freeing carboxylate groups. Carboxylate value for methylated and saponified sample is 105 meq/kg compared to 100 meq/kg for unmethylated pulp.
Figure 16. Comparison between hypo number and kappa number for treated pulps.
Figure 17. Mass balance for the hydrolysis of pulp samples by cellulase.
Figure 18. Carbohydrate analysis of enzymatic preparations shown on a weigh percent basis.

Figure 19. Carbohydrate analysis of enzymatic preparations shown on a mole percent basis.
Figure 20. Release of lignin-carbohydrate complexes from softwood kraft pulp by xylanase.

Figure 21. Release of reducing sugar from softwood kraft pulp by xylanase.
Figure 22. Viscosity as a function of kappa number for softwood kraft pulp treated with xylanase at 10 units/g. A) NaOH levels of 1%, 2%, and 3%; B) NaOH level of 1%, 2%, and 4%.
Figure 23. Viscosity as a function of kappa number for softwood kraft pulp treated with xylanase at 10 units/g. A) NaOH levels of 1%, 2%, and 3%; B) NaOH level of 1%, 2%, and 4%.
SECTION 2

KINETICS OF CELLULOSE DEGRADATION

BY OZONE

Barbara I. Johnson

Thomas J. McDonough
INTRODUCTION

The purpose of this work is to gain a better understanding of the factors affecting the rate of degradation of cellulose by ozone. There is little data in the literature on the kinetics of this process, especially under conditions where the concentrations of both ozone and glycosidic bonds can be monitored and controlled. Consequently, there is no accepted rate law available for this reaction. The need for such a rate law is obvious in view of the corresponding need to improve the selectivity of commercial ozone bleaching.

EXPERIMENTAL APPROACH

The experiments were done at low consistency in a semibatch flow reactor continuously fed with a stream of ozone dissolved in a buffer solution. Both the concentration and flow of ozone to the reactor were held constant throughout the experiment. The reactor was fitted with a fine mesh screen at the liquid outlet, to prevent the escape of fibers. The reaction was begun by adding a weighed sample of solvent extracted cotton linters to the reactor. Figure 1 is a diagram of the apparatus.

At frequent intervals during the experiment, samples of the effluent stream from the reactor were collected, and their ozone concentration was determined by measurement of ultraviolet absorbance at 260 nm.

RESULTS AND DISCUSSION

Figure 2 shows data from runs at two different influent concentrations. The sudden drop in ozone concentration corresponds to a rapid initial reaction; the failure of the ozone concentration to recover within the time span of the experiment corresponds to a slower, but sustained, consumption of ozone by the linters. These observations are confirmed by the corresponding plots of ozone uptake versus time in Figure 3. Upon termination of any given run, the linters sample was collected and its viscosity (TAPPI T-230) was measured, both with and without prior borohydride reduction of the sample. The data obtained from numerous runs are shown in Figures 4 and 5.

It can be shown mathematically that the number of cellulose macromolecules (chains) present is proportional to the reciprocal of the degree of polymerization (DP, number of anhydroglucose units per chain). Also, every time a chain is broken, the number of chains present increases by one. It follows that the number of chain scission events is proportional to the increase in the reciprocal of the DP. The increase in this quantity is thus analogous to the increase in product concentration that occurs in a simple chemical reaction.

Figure 6 is a plot of the change in reciprocal DP (as calculated from viscosity) for borohydride-treated and untreated samples from "Run 1" (really a series of 9 runs). Two conclusions may be drawn: (a) the extent of carbonyl group introduction, measured as the vertical distance between the two lines, proceeds at a rate that is roughly half as great as the rate of direct chain
cleavage and (b) both reactions have a slow second phase that is zero-order with respect to the concentration of glycosidic bonds remaining. Comparison with Figure 7, at a lower ozone concentration, allows the additional conclusion that the rates of of the slow phase of both reactions decrease when the ozone concentration is decreased, or, in other words, that they exhibit a positive order in ozone.

Analysis of the data from the initial phase must take into account the fact that the ozone concentration cannot be considered constant during this part of the reaction. An ozone mass balance around the reactor showed that the rate in this phase is not a function only of ozone concentration, but also depends on some property of the solid phase. This lends credence to the hypothesis that the two rate phases correspond to the presence in the cellulose of two different kinds of glycosidic linkages which, in the absence of any additional information, may be labeled "accessible" and "inaccessible" (after Chandra and Gratzi, 1985 International Pulp Bleaching Conference). The number of accessible bonds is limited and their exhaustion corresponds to the changeover to the slow phase.

We analyzed the rapid initial phase data, with this picture in mind, estimating \( b_o \), the number of accessible bonds initially present, by extrapolating the slow phase straight-line plot of \( 1/DP \) vs time back to zero time. This number was then subtracted from the observed values to calculate the number of accessible bonds remaining at any time.

The rate laws so far derived by proceeding as outlined above are:

(a) for the slow phase,

\[-d[\text{bonds}]/dt = k_2[O_3]^{0.8}\]

and (b) for the initial phase,

\[-d[O_3]/dt = k_1[O_3][b_{\text{acc}}]^{0.1} + k_2\nu[O_3]^{0.8}\]

where \( \nu \) is the stoichiometric coefficient, \([O_3]/[\text{bonds}]\).

Further analysis of the data, perhaps supplemented by further experiments, will allow estimation of the above rate constants and stoichiometric coefficient, as well as the corresponding quantities for the carbonyl introduction reaction.

These results are significant from several points of view. They provide a framework for assessing the effects of bleaching process variable changes on selectivity by allowing the results of experiments to be expressed as rate constants which, because they are fundamental quantities, will greatly facilitate data interpretation. Secondly, they suggest a new line of experimentation, aimed at controlling the proportion of glycosidic bonds that are accessible and therefore vulnerable to attack by ozone.
FUTURE ACTIVITY


2. Additional experiments on cotton linters to allow final rate laws to be derived. Determination of stoichiometric coefficients and purchase of a flow cell to greatly speed up data acquisition. Continuous measurement of ozone concentration will serve to provide a continuous indication of cellulose degradation, assuming that the stoichiometric coefficient proves to be constant.

3. Investigation of methods of decreasing the proportion of accessible bonds, vulnerable to ozone degradation. Determination of effect of cellulose crystallinity and pretreatments. Determination of effects of chlorine dioxide as pretreatment or cotreatment.

CONCLUSIONS

1. Ozone degradation of cellulose proceeds in two phases: an initial fast phase followed by a slow phase.

2. The rate of the slow phase is constant and therefore independent of the degree of ozonation of the substrate, i.e., zero order in glycosidic bonds remaining.

3. The rate of the slow phase is approximately of order 0.8 in ozone.

4. The rate of the initial phase depends on the degree of ozonation of the substrate as well as on the ozone concentration. This was interpreted as a dependence on the concentration of accessible bonds remaining. The order in such bonds is approximately 0.1.

5. The rate of the initial phase is first-order in ozone.

6. The increase in viscosity of oxidized pulps upon subsequent borohydride reduction is consistent with the hypothesis that the rate of carbonyl group introduction during ozonation is approximately half as great as the rate of direct chain cleavage.
Figure 2.
Figure 3.

**OZONE CONSUMPTION**

**OZONE UPTAKE vs TIME**

- Ozone Uptake (mg)
- Ozone Consumption

<table>
<thead>
<tr>
<th>Ozonation Time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>RUN #1</td>
</tr>
<tr>
<td>RUN #2</td>
</tr>
</tbody>
</table>

- Figure 3.
Figure 4.
VISCOSITY vs REACTION TIME

RUN #2. W & W/O BOROHYDRIDE REDUCTION

Figure 5.
Figure 6.
CHAIN SCISSIONS vs OXONATION TIME

RUN #2. (1/DP-1/DP₀) VS TIME

Figure 7.
SECTION 3

GAS DISPERSION
IN OXYGEN DELIGNIFICATION

Edouard Benroubi

Thomas J. McDonough
GAS DISPERSION IN OXYGEN DELIGNIFICATION

Oxygen delignification of kraft pulp at medium consistency is a complex process, involving transfer of oxygen across gas-liquid and liquid-solid interfaces, as well as chemical reactions with fiber wall components. Gas-liquid transfer can become rate limiting, as shown by the increased effectiveness of commercial two-stage oxygen delignification systems in which doing nothing more than redispersing unreacted oxygen significantly increases the extent of delignification. On the other hand, oxygen enhancement of caustic extraction stages has sometimes been observed to be rather insensitive to the degree of mixing of oxygen with the pulp.

The purpose of the work described here is to determine the relationship between gas-liquid mass transfer and oxygen delignification. This will allow mixing requirements to be better defined in commercial systems, and will allow situations where mixing is especially critical to be identified and distinguished from those where other factors dictate the effectiveness of lignin removal.

The approach we have adopted is to (a) experimentally determine the relationship between the operating variables of a flow-through laboratory mixer and the amount of interfacial area generated, as measured by carbon dioxide absorption into an alkaline pulp suspension and (b) observe the effect of the same variables on extent of delignification with oxygen. This will allow the relationship between interfacial area and extent of delignification to be inferred and its dependence on process variables (pH, temperature, extent of delignification, pretreatment, etc.) to be defined.

RESULTS AND DISCUSSION

To date, we have nearly completed step (a). The flow-through mixer we used is represented in Figure 1. A factorial experiment was designed in four variables, as follows:

<table>
<thead>
<tr>
<th>Variable</th>
<th>LOW LEVEL</th>
<th>HIGH LEVEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consistency, %</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>Rotor Speed, RPM</td>
<td>750</td>
<td>3250</td>
</tr>
<tr>
<td>Piston Speed, in/sec</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>CO₂ Charge, % o.d. pulp</td>
<td>0.5</td>
<td>2</td>
</tr>
</tbody>
</table>

In practice, the maximum gas flow allowed by the equipment allowed a maximum charge of only 1% when the piston speed was high. With this one deviation, a half-replicate of the factorial experiment was completed in duplicate. The results were subjected to stepwise regression analysis with a result that can be approximated by the
Flow-through Fluidizing Mixer

from hydraulic system

Piston

"Reactor"

Mixing Chamber

Control Panel

Rotor & Pump

Clutch

Valve

Wheel

Gas

Pressure gauge

Rotameter

Outlet

Samples collector

Gas Tank

Belt

Engine

Figure 1.
following equation:

mmol CO₂ absorbed = 2X₂ - 0.5X₃ + 3X₄ + X₂X₃ + X₂X₄ + X₃X₄

in which X₂ = scaled rotor speed, X₃ = scaled piston speed and X₄ = scaled CO₂ charge.

CONCLUSIONS

Consistency has no effect over the range investigated, and the effect of rotor speed is positive, intensified by increased piston speed, increased gas charge, or both. The effect of piston speed is negative, especially at low rotor speed and low gas charge. The effect of gas charge is positive, especially at high rotor speed and high piston speed.

FURTHER RESEARCH

Additional experiments with CO₂ will be conducted to resolve possible ambiguities inherent in the half-replicate factorial design used, and the results reanalyzed, both empirically, by regression and by constructing a model based on the physical phenomena involved. The latter model will be tested and refined in a final set of experiments, and then used to predict the effects of mixer variables on oxygen delignification. The predictions will be tested by experiments with oxygen.
SECTION 4

BIOMIMETIC HYDROGEN PEROXIDE

DELIGNIFICATION

Colleen C. Walker
R.J. Dinus
K.-E. Eriksson
Thomas J. McDonough
DEVELOPMENT OF A BIOMIMETIC APPROACH TO PULP BLEACHING

Colleen C. Walker, PhD Candidate
Thesis Committee: Dr. Ronald Dinus
Dr. Karl-Erik Eriksson (Univ. of Ga., Athens)
Dr. Thomas McDonough

SCOPE OF THESIS

In the presence of hydrogen peroxide the enzyme ligninase, isolated from white-rot fungi, has been used to bleach softwood kraft pulp. Unfortunately, mill process temperatures often exceed those necessary to maintain high enzymatic activity. The macroscopic structure of ligninase has been elucidated; it is similar to that of porphyrins. Preliminary research efforts have shown that porphyrin-like substances, i.e. hemoglobin, in the presence of hydrogen peroxide mimics the action of ligninase. Laboratory experiments using this "biomimetic" approach to pulp bleaching have produced promising results; Pettersson, et al. (1) found that reductions in Kappa number and viscosity for a biomimetically bleached pulp were equal to that of an oxygen bleached pulp.

Researchers have established that hydroxyl radicals do not participate in the enzymatic mechanism of lignin degradation, but it is not known if this also applies to biomimetic systems. The objective of this thesis is to examine three biomimetic systems for their selectivity for lignin over carbohydrate. It is hypothesized that hydroxyl radicals play a significant role in the bleaching chemistry of these systems; consequently, biomimetic systems are not likely to be highly selective for lignin. The second segment of this thesis will be to modify the most selective catalyst to increase its affinity for lignin-like structures.

The experimental plan requires the selection of lignin and carbohydrate model compounds. Three different types of biomimetic compounds, Fe (II), EDTA-Fe(II) and a ferrous porphyrin, will be evaluated for their preference for the lignin model over the carbohydrate model. Hydrogen peroxide will be used as the oxidant for all experiments. Development of an assay for detecting the production of hydroxyl radicals in these biomimetic systems is also required to evaluate selectivity.

PROGRESS TO DATE

Lignosulfonate has been chosen as the lignin model compound. It is soluble in slightly acidic aqueous solutions and changes in its molecular weight distribution can easily be evaluated using High Performance Liquid Size-Exclusion Chromatography (HPLSEC).
Hydroxyethyl cellulose (HEC) has been chosen as the carbohydrate model compound. HEC maintains a constant viscosity for pH 2 - 10, an ideal quality for experiments in which pH is a variable. The molecular weight change of HEC can be determined from capillary viscometer measurements and published correlations between molecular weight of HEC and intrinsic viscosity (2). Additional information about the effect of reaction conditions can be obtained by using HPLSEC to observe changes in HEC molecular weight distributions.

The reactor system used for these experiments has been designed so that the amount of hydrogen peroxide consumed by chemical reaction as well as catalytic decomposition can be measured. As hydrogen peroxide decomposes into oxygen, the evolved gas can be measured without pressurizing the reaction vessel. Residual hydrogen peroxide is determined by iodiometric titration. The amount of hydrogen peroxide consumed by reaction is determined by subtracting the residual and decomposed hydrogen peroxide from the original amount. Rates of hydrogen peroxide decomposition and reaction with substrate can then be calculated from these measurements.

The preliminary selection of reaction pH was 3.0, the optimum for ligninase activity; 45°C has been chosen as the reaction temperature. Size-exclusion chromatography profiles of reacted lignosulfonate indicated that no polymerization occurred in the presence of hydrogen peroxide alone or when catalytic amounts of ferrous sulfate were added. Figure 1 shows an HPLSEC profile of lignosulfonate before and after reaction with hydrogen peroxide; a reduction in average molecular weight is evident from the decreased retention time.

Preliminary experiments with HEC have shown that a decrease in viscosity average molecular weight can be measured with the proposed viscometric technique. Figure 2 shows the change in intrinsic viscosity in the presence of hydrogen peroxide at pH 3.0 and 45°C. The Mark-Houwink equation was used to determine viscosity average molecular weights. Future experiments will examine the effect of ferrous sulfate on viscosity change.

Hydroxyl radicals are believed to be the reactive species in this system; therefore, it is imperative that they be detected if present. Many analytical techniques are available for quantitatively measuring *OH, but these techniques often require synthesis of the active substrate or involve significant capital expenditure. Gierer of STFI and Reitberger from the Royal Institute in Sweden have developed a practical method for detecting hydroxyl radicals which utilizes a commercially available chemical and a simple, relatively inexpensive apparatus (3).

This method involves adding a substrate, phthalic hydrazide, to reaction mixtures in which the aromatic portion of this substrate reacts with hydroxyl radicals. Samples are then removed and
placed in a photometer where subsequent oxidation emits light that is detected by the instrument. Figure 3 shows a light intensity curve produced upon oxidation; the area under the curve is proportional to the hydroxyl radical content. Gierer and Reitberger have used this method to qualitatively measure the production of hydroxyl radicals during oxygen and hydrogen peroxide bleaching of pulp.

The Gierer and Reitberger chemiluminescence assay has been used to study the decomposition of hydrogen peroxide in alkaline aqueous solutions. In these experiments only a very small amount of hydroxyl radicals were detected, even in the presence of small amounts of ferrous sulfate (Figure 4).

To verify that radicals could be detected with the photometer, the decomposition of hydrogen peroxide under highly catalyzed conditions was studied by varying the molar ratios of hydrogen peroxide : catalyst : phthalic hydrazide. During these experiments a significant increase in the area under light intensity curves indicated an increase in the production of hydroxyl radicals (see Figure 5).

FUTURE WORK

The carbohydrate and lignin model systems need to be fully understood in order to accurately measure decomposition of each substance before the selectivity of biomimetic compounds can be studied. After this has been accomplished, three selected biomimetic compounds will be tested for their preference of carbohydrate versus lignin. The next segment of the thesis will be to modify the biomimetic compound which shows the most affinity for lignin. The final phase of this project will be to optimize reaction conditions for biomimetic bleaching of a softwood kraft pulp.

REFERENCES


Figure 1. Reaction Conditions: 150 mM H2O2, 0.04 mg/mL Lignosulfonate, pH 3.0, 45°C
(A) Unreacted lignosulfonate
(B) Lignosulfonate after 3.0 hours

Figure 2. Change in intrinsic viscosity and viscosity average molecular weight during uncatalyzed decomposition of hydrogen peroxide. Reaction Conditions: 150 mM H2O2, pH 3.0, 45°C.
Sample #10 (t=60 minutes)

Figure 3. Light intensity curves for three separate injections of a sample into the photometer.
Figure 4. Area under the light intensity curve for the catalyzed alkaline decomposition of hydrogen peroxide. Reaction Conditions: 150 mM H2O2, 0.3 mM FeSO4, 5 mM phthalic hydrazide, pH 11.0, 45°C.

Figure 5. Area under the light intensity curve for the catalyzed decomposition of hydrogen peroxide. Reaction Conditions: 100 mM H2O2, 10 mM Fe-EDTA, 20 mM phthalic hydrazide, pH 8.5, 45°C.
SECTION 5

INVESTIGATION OF NOVEL BLEACHING AGENTS

Arthur J. Ragauskas
Investigation of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulps

Dimethyldioxirane is a three member cyclic peroxide which possesses unique oxidizing capabilities. Preliminary bleaching studies employing 0.1 M solutions of dimethyldioxirane in acetone suggested that the dimethyldioxirane yields an exceptionally reactive peroxide with unique bleaching properties. Although the bleaching efficiency of dimethyldioxirane was promising the methods of preparation severely limited any practical application. To further explore the potential applicability of this reagent for bleaching chemical pulps, it was necessary to determine if alternative methods of generating dimethyldioxirane would yield an analogous bleaching response. The bleaching efficiency of \textit{in-situ} generated dimethyldioxirane from acetone/water/sodium bicarbonate/Oxone was therefore explored. The results of these studies and control experiments, in which all the acetone was replaced with water are summarized in Figure 1.

![Diagram](image)

**Figure 1**

- **BI Water**: Pulp was bleached in an Oxone/Water/Sodium Bicarbonate Solution;
- **BI/Ext Water**: Pulp after being bleached under BI Water conditions and then extracted with 1.5% caustic;
- **BI Water/Acetone**: Pulp was bleached in an Oxone/Water/Acetone/Sodium Bicarbonate Solution;
- **BI/Ext Water/Acetone**: Pulp after being bleached under BI Water/Acetone conditions and then extracted with 1.5% caustic.
Although these results suggest that the *in-situ* generation of dimethyldioxirane is advantageous, practical applications would be limited due to the need to use an acetone/water solvent system for bleaching. Research efforts were next focused on developing an experimental procedure which minimized the acetone component and these results are summarized in Table 1.

### Table 1. Effects of Varying Premixing Conditions for an Oxonea / Water / Acetone / NaHCO₃ Bleaching Mixture on Delignifying a 27.6 Kappa Softwood Kraft Pulp

<table>
<thead>
<tr>
<th>Premixture Solvent Volume/ml</th>
<th>Premixture Acetone:Water</th>
<th>Premixing Time/min</th>
<th>Consistency of Pulp During Bleaching</th>
<th>Kappa Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>3.0:1.0</td>
<td>5.0</td>
<td>1%</td>
<td>21.7</td>
</tr>
<tr>
<td>80</td>
<td>3.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>21.8</td>
</tr>
<tr>
<td>80</td>
<td>No Acetone</td>
<td>5.0</td>
<td>2%</td>
<td>24.4</td>
</tr>
<tr>
<td>80</td>
<td>1.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>24.1</td>
</tr>
<tr>
<td>80</td>
<td>1.0:1.8</td>
<td>5.0</td>
<td>2%</td>
<td>25.3</td>
</tr>
<tr>
<td>80</td>
<td>1.0:3.0</td>
<td>5.0</td>
<td>2%</td>
<td>23.9</td>
</tr>
<tr>
<td>80</td>
<td>1.0:7.0</td>
<td>5.0</td>
<td>2%</td>
<td>24.0</td>
</tr>
<tr>
<td>20</td>
<td>1.0:1.0</td>
<td>5.0</td>
<td>2%</td>
<td>25.1</td>
</tr>
</tbody>
</table>

*a* bleaching reagent was premixed for a fixed period of time and was then added to an aqueous slurry of pulp and stirred for 1h; b kappa value after bleaching; c kappa value of pulp after bleaching and extracting with 1.5% NaOH solution.

The results of our preliminary studies in this field suggest that the total amount of acetone needed for bleaching can be reduced to at least 10% of the solution volume. Further studies employing the optimal conditions discovered in Table 1 indicate that delignification occurs both in an acidic or basic medium, but the optimal pH is near neutral. The bleaching reaction was also shown to be most efficient at 80°C. These results clearly demonstrate that dimethyldioxirane is a versatile reagent that could potentially be employed at various stages in a bleaching cycle without dramatic changes in the pH or temperature of the bleaching solution.
SECTION 6

MIXING IN CHLORINATION
AND EFFLUENT QUALITY

Amy R. Malcolm

Thomas J. McDonough
EFFECT OF MIXING IN CHLORINATION ON EFFLUENT QUALITY

MIXING IN PULP BLEACHING

The residual lignin in kraft pulp reacts very rapidly with chlorine, as shown by the fact that it can be extensively chlorinated in just a few seconds. Objectionable components of AOX, such as dioxins and polychlorinated phenolics (PCP), are probably formed at a slightly slower rate. Evidence for this is provided by the observations that neither class of compound is formed in appreciable amounts when the amounts of chlorine applied are low and that the amounts of both formed rise nonlinearly when the amount of chlorine applied is above some threshold value. These observations suggest that lignin preferentially consumes chlorine except when excess chlorine is present. The PCP- and dioxin-forming reactions are nevertheless probably also fairly fast, given the known high rates of chlorination of model compounds.

It follows from the above analysis of relative reaction rates that poor mixing will lead to increased levels of formation of such compounds as PCP's and dioxins. This is because, in areas of locally high chlorine concentration, excess chlorine will generate disproportionately large amounts of these compounds.

An analysis by Bennington and coworkers shows that mixing chlorine with pulp in conventional mixers, although it leads to a good final mixture, has an effect on pulp quality similar to that of a poor final mixture. This occurs because of the rapidity of pulp chlorination reactions and the slowness with which conventional mixers distribute chlorine throughout the pulp. It suggests that highly efficient mixers, such as high-shear mixers, may be expected to generate less of these undesirable classes of compounds. Since few chlorination stages are equipped with high shear mixers, there is clearly a need to investigate and quantify the environmental benefits of good mixing during chlorination.

RESULTS AND DISCUSSION

In a few preliminary experiments, reported at the 1991 Annual Research Review, an apparent effect of mixing quality on AOX formation was observed. Experiments were first conducted in a laboratory high shear mixer using a dye tracer technique to establish conditions giving definable degrees of mixing. Southern pine kraft pulp was then chlorinated and caustic extracted, under conditions of both poor and extremely good mixing, at several different kappa factors. The results suggested a beneficial effect of mixing on AOX at low kappa factors. Since then, additional work has been done to confirm the existence of this effect and to
quantify it to a greater degree. The results are shown in Tables 1 and 2 and Figure 1.

When mixing was poor, AOX increased linearly with kappa factor. In contrast, chlorination under conditions of extremely good mixing gave extremely low levels of AOX at kappa factors of 0.1 or below, and rapidly increasing levels thereafter. At low kappa factors, in other words, very good mixing sharply reduced the rate of AOX generation. This effect was even more apparent when it was evaluated at fixed CE kappa number rather than at fixed kappa factor, because of the effect of mixing on delignification. At a CE kappa number of 7, the effluent AOX reduction attributable to improved mixing was approximately 60%.

FURTHER RESEARCH

Further research is needed to determine the dependence of the mixing effect on important operating variables, including reaction time, pH, ClO₂ substitution and order of addition of Cl₂ and ClO₂. In addition, potential beneficial effects on AOX composition and characteristics need to be evaluated. This might be accomplished by adopting two parallel approaches: effluent fractionation followed by fraction characterization, and detailed analysis for specific components. A third area in need of investigation concerns the effects of the experimental variables on the amount and fate of chlorine that remains covalently bound to the pulp emerging from the chlorination stage. A final research goal should be the incorporation of the findings from the above research into a process that uses a substantial proportion of chlorine while producing acceptably low amounts of AOX. An attempt is underway to obtain funding for this work by the Chlorine Institute. If the funding is not obtained a subset of the above work is planned.

EXPERIMENTAL

Chlorination Stage

Softwood kraft pulp was received from Boise Cascade, Washington, with kappa number 27.9 and viscosity 36.2 cp.

All chlorinations were performed in the Quantum Technologies high shear mixer. Conditions were as shown below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Good Mixing</th>
<th>Poor Mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, minutes</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>oven dried grams</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Consistency, %</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>kappa factor</td>
<td>varied</td>
<td></td>
</tr>
</tbody>
</table>

-188-
Rotor speed (hertz)  
30.0  

1.0  

Total Injection and Mix Time (seconds)  
180  

13  

The chemical was added to the injection cylinder by using a vacuum to pull the chlorine water under a piston within the cylinder. The concentration of the chlorine water in the cylinder was determined by removing a sample with a syringe through the side valve of the injection cylinder.

An additional 30 ml of chlorine water was charged to the injector to allow for holdup in the line leading to the reactor bowl. Following chlorination, the pulp was thickened to 20 % consistency and the resulting effluent collected for AOX analysis.

**Extraction Stage**

Extraction stages were carried out in sealed Kapak bags in a heated water bath. Caustic addition was adjusted in all extraction stages in order to accommodate the lower kappa factors. The following formula was developed: $(0.55 \times TAC) + 1 = \% NaOH$. Conditions were as shown below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, minutes</td>
<td>60</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>70</td>
</tr>
<tr>
<td>Oven dried grams</td>
<td>40</td>
</tr>
<tr>
<td>Consistency, %</td>
<td>10</td>
</tr>
</tbody>
</table>

After the extraction stage, the pulp was diluted to 4% consistency, and stirred for approximately 5 minutes. It was then thickened to 20 % consistency and the resulting effluent collected for AOX analysis.

The combined AOX sample consisted of 20 ml of C-stage effluent and 24 ml of E-stage effluent in order to simulate combined mill effluent. Separate C-stage and E-stage samples were collected and set aside but not analyzed for AOX. The collected samples were adjusted to a pH of 2.0 with 4N H$_2$SO$_4$ and stored at approximately 45 °F. AOX testing was performed by S. Van Travis according to EPA method 9020. Kappa number and viscosity determinations were run on all E-stage pulps.
SECTION 7

CHARACTERIZATION

OF AOX

Todd Schwantes
Thomas J. McDonough
A FUNDAMENTAL CHARACTERIZATION OF PULP BLEACHING EFFLUENTS PRODUCED UNDER VARIOUS LOW AOX PROCESS CONDITIONS

A-490 Thesis Research

Todd Schwantes
INTRODUCTION

The effects that bleach plant effluents may have on the environment is a major concern of environmentalists and the public in general. Chlorinated organic material (measured as AOX) is currently of considerable interest.

The result of environmental concern is impending government regulation of AOX in effluents and pressure by consumers who want to buy "environmentally friendly" products. These considerations have led many pulp mills to implement AOX reduction strategies, including AOX reducing process changes such as oxygen delignification, ClO₂ substitution, and oxidative extraction.

Although these strategies do reduce AOX, it is uncertain what effect these, and other AOX reducing changes, actually have on the environment, since AOX reduction does not necessarily mean environmental impact is reduced. This is because certain fractions of the effluent may be more troublesome than others.

Most effluent characterization studies have measured sum parameters (AOX¹,² etc.) or quantified individual compounds of special interest (chlorophenols¹,²,³,⁴ TCDD²,⁵ chloroform¹,⁶ etc.). Although all this work is valuable, it alone tells only a very small part of the story. AOX sums all organic chlorine into one category and does not distinguish between that which may be the most harmful and that which may be less harmful. Analysis of individual compounds considers only a tiny fraction of the total effluent and ignores the rest.

No study has completely characterized effluents produced under several different low AOX processes. This research strives to determine what effects different low AOX process changes have on the nature of the entire effluent. The characterization may help demonstrate the unsuitability of AOX as a measure of environmental effect, by showing low potential harmfulness for effluents containing measurable levels of AOX. Such a characterization of effluents must be done before millions
of dollars are invested in process changes which may or may not eliminate a problem.

RESEARCH OBJECTIVE

It is the objective of this research to completely characterize the effluents produced by bleaching of Kraft pulp under various conditions known to reduce AOX. Total organic carbon (TOC) and AOX will be measured on the whole effluent and fractions of the effluent based on ether extractability, volatility, and acidity. This will allow determination of carbon to chlorine ratios for the whole effluent and for the fractions, and will provide information on how AOX and TOC is distributed among the effluent fractions. Molecular weight distributions will also be determined, by gel permeation.

A variety of pulp bleaching conditions which are known to reduce AOX will be studied, including the following:

I) Oxygen Delignification

II) C/D Stage Conditions
   A) Reaction Time
   B) Reaction Temperature
   C) ClO₂ Substitution Level
   D) Mill vs. Lab

III) E₁ Stage Conditions
   A) Temperature
   B) Presence of O₂ and/or H₂O₂

The C/D stage reaction time will be considered in some detail, using a specially designed batch reactor which will allow very short reaction times. Characterization of effluents produced at such short times may provide valuable information about how the process kinetics can be changed to produce the most acceptable effluent.
PRELIMINARY WORK

Preliminary work has been done on a lab produced effluent sample and mill produced samples. The purpose has been to develop methods and procedures to use on the lab effluents produced by this research.

Effluent Fractionation:

The ether extract of an effluent contains the majority of the effluent's toxicity as well as a considerable fraction of its mutagenicity, and therefore is an important fraction to consider when characterizing effluents. Furthermore, since ether extraction removes 4-6 times as much AOX from effluent samples as extraction with other solvents (as done in EOX methods), it will more readily allow further fractionation.

A lab produced chlorination effluent was initially used for fractionation work. The effluent was divided into several fractions including volatiles, a non-volatile whole effluent sample (NVW), a non-volatile ether extract (NVEE), and a non-volatile non-ether extractable fraction (NVNEE). Volatiles were removed by vacuum and calculated by difference between a whole effluent sample and the NVW sample. Ether extraction was carried out for 48 hours in a continuous liquid-liquid extractor. The separation scheme for this sample is given in figure 1.

TOC and AOX balances were performed around the fractionation, and carbon to chlorine ratios calculated for these fractions. This data is shown in Table I. As shown by the data, the balances are complete, indicating all material is accounted for in the fractions. The carbon to chlorine ratios show that the ether extractable material contains the highest concentration of chlorine. This is consistent with the high potential environmental impact of this fraction. The volatiles contain the lowest concentration of chlorine which is consistent with the expected high methanol content of this fraction.
Figure 1: Effluent separation scheme used on a lab produced effluent.

Table I: Carbon and chlorine balance data for a lab produced effluent.

<table>
<thead>
<tr>
<th></th>
<th>TOC (mg C)</th>
<th>AOX (mg Cl)</th>
<th>C/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Whole</td>
<td>307</td>
<td>66.0</td>
</tr>
<tr>
<td>B</td>
<td>NVW</td>
<td>178</td>
<td>52.8</td>
</tr>
<tr>
<td>C</td>
<td>Volatiles (A - B)</td>
<td>129</td>
<td>13.2</td>
</tr>
<tr>
<td>D</td>
<td>NVEE</td>
<td>82.8</td>
<td>32.7</td>
</tr>
<tr>
<td>E</td>
<td>NVNEE</td>
<td>95.7</td>
<td>16.7</td>
</tr>
<tr>
<td>F</td>
<td>(D + E)</td>
<td>179</td>
<td>49.4</td>
</tr>
</tbody>
</table>

Further studies were done on mill produced C/D and E₁ stage effluents. In this case effluents were fractionated into volatiles, NVW, three non-volatile ether extracts (NVEE I, NVEE II, NVEE III), three subfractions of the first ether extract (non-volatile ether extractable acids--NVEEA, non-volatile ether extractable phenolics--NVEEP, non-
Figure 2: Effluent separation scheme used on mill produced effluents.

<table>
<thead>
<tr>
<th></th>
<th>C/D</th>
<th>E₁</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOC (mg C)</td>
<td>% Of Whole</td>
</tr>
<tr>
<td>A Whole</td>
<td>645</td>
<td>---</td>
</tr>
<tr>
<td>B NVW</td>
<td>473</td>
<td>73.3</td>
</tr>
<tr>
<td>C Volatiles (A - B)</td>
<td>172</td>
<td>26.7</td>
</tr>
<tr>
<td>D NVEE I</td>
<td>212</td>
<td>32.9</td>
</tr>
<tr>
<td>E NVEE II</td>
<td>37.6</td>
<td>5.83</td>
</tr>
<tr>
<td>F NVEE III</td>
<td>19.6</td>
<td>3.04</td>
</tr>
<tr>
<td>G NVNNE</td>
<td>214</td>
<td>33.2</td>
</tr>
<tr>
<td>H (D+E+F+G)</td>
<td>483</td>
<td>---</td>
</tr>
<tr>
<td>I NVVEA</td>
<td>183</td>
<td>28.4</td>
</tr>
<tr>
<td>J NVVEP</td>
<td>19.5</td>
<td>3.02</td>
</tr>
<tr>
<td>K NVVEEN</td>
<td>13.6</td>
<td>2.11</td>
</tr>
<tr>
<td>L (I+J+K)</td>
<td>216</td>
<td>---</td>
</tr>
</tbody>
</table>

Table II: TOC balance data for mill produced effluents.
volatile ether extractable neutrals--NVEEN), and a non-extractable portion (NVNEE). The three consecutive ether extracts were done to determine how ether extractability proceeds over time and how the carbon to chlorine ratios vary for these extracts. The first extract was done for 50 hours, the extract removed and replaced with fresh ether which was used to extract the effluent for another 200 hours. This ether was removed and replaced with fresh ether which extracted the effluent for a final 72 hours. The first ether extract (NVEE I) was fractionated into acids (by extraction with 0.5 M NaHCO$_3$), phenolics (by extraction with 0.5 M NaOH), and neutrals (which remained in the ether). The separation scheme is given in figure 2.

TOC balances around this fractionation for both a C/D and an E$_1$ effluent are shown in Table II. Also included is the percentage of the whole effluent TOC in each fraction. Distinct differences can be seen between the effluent types. For example, the C/D contains a higher percentage of volatiles, ether extractable material, and ether extractable phenolics, while the E$_1$ contains a noticeably higher percentage of neutrals. Once AOX analysis is done for these samples, carbon to chlorine ratios will be determined for each fraction.

Gel Permeation Of Effluents:

Gel permeation was chosen as a method to determine the molecular weight distributions of effluents and effluent fractions because it offers the possibility of continuous distributions and has been widely applied to lignin materials. It was chosen over ultrafiltration mainly because ultrafiltration allows separation only into broad molecular weight ranges.

Initial work was done using 0.5 M NaOH as the gel permeation eluent with a Sephadex G-50 column and UV detection, as done by Sagfors and Starck$^{10}$. This system is known to break up molecular associations in lignins and thus give an accurate molecular weight distribution.$^{11}$ Successful molecular weight distributions, similar to those at
tained by previous work,\textsuperscript{10} were obtained (figure 3) but the stability of the C/D effluent to 0.5 M NaOH was questioned. Figure 3 also shows approximate molecular weights of several standards.

![MW distributions for mill effluents (single column, 0.5 M NaOH).](image)

Since C/D effluent obviously contains considerable amounts of low molecular weight material, and since G-50 gel only separates to a molecular weight of 1,500, a dual column system was devised to improve separation before the stability of C/D effluent was checked. The system consists of a G-50 column followed by a G-15 column which separates compounds with molecular weights of less than 1,500.

Various eluents were compared on the dual column system. Since LiCl is also known to break associations\textsuperscript{11} and is unlikely to degrade effluents, 0.1 M aqueous LiCl was compared to 0.5 M NaOH. A 0.1 M
LiCl/0.1 M NaHCO\textsubscript{3} eluent was also studied. The resulting chromatograms for the three different solvent systems are shown in figures 4 and 5 for the E\textsubscript{1} and C/D effluents respectively. All three systems give similar distributions for the E\textsubscript{1} effluent, however major differences occur with the C/D effluent. The 0.1 N LiCl and 0.1 N LiCl/NaHCO\textsubscript{3} give similar distributions above relative retention volumes of about 0.7 yet are different below. Apparently increased pH is needed in the higher molecular weight effluent material to make it absorb UV, and be detected. The 0.5 M NaOH does not appear to break down the C/D effluent since its apparent molecular weight distribution increases. However, some changes are caused by NaOH which results in unexplained differences from the other two systems. We therefore believe this system gives falsely high molecular weight distributions and is unacceptable.

![Relative Retention Volume](image)

**Figure 4:** Comparison of E\textsubscript{1} effluent MW distributions with different eluents (dual columns).
Figure 5: Comparison of C/D effluent MW distributions with different eluents (dual columns).

This dual column GPC system gives much more distinctive distributions compared to the one column system. An example of the molecular weight distributions using the dual column system and 0.1 N LiCl/NaHCO₃ eluent is given in figure 6. A comparison of figures 3 and 6 illustrates the increased separation achieved on the dual column system, particularly for the C/D effluent. The dual column system will be used in future work since it may allow distinguishing features of different effluent molecular weight distributions to be seen, unlike the single column system.¹⁰
Figure 6: MW distributions for mill produced effluents (dual columns).

LITERATURE CITED


PROJECT 3699/3741

EVALUATION OF COMMERCIALY AVAILABLE CONDUCTIVITY SENSORS

RESEARCH REVIEW

MARCH 25, 1992

Charles E. Courchene
Tanya Kubicar
Blair Carter
Technical Program Review Report

PROJECT TITLE: EVALUATION OF COMMERCIALY AVAILABLE CONDUCTIVITY SENSORS

PROJECT STAFF: Charles Courchene, Tanya Kubicar, Blair Carter

FY 91-92 BUDGET: $55,000-3699, $38,000-3741

REPORTING PERIOD: Feb.'91-Feb.'92

DIVISION: Chemical and Biological Sciences

FUNDING SOURCE: AMERICAN PAPER INSTITUTE - MEASUREMENT TECHNOLOGY COMMITTEE (API-MTC)

PROJECT NUMBER: 3699/3741

OBJECTIVE:

To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams.

FY 91-92 Goals:

1. Establish a relationship between conductivity for three sensor-transmitter types and chemical concentration of white liquor.
2. Evaluate the effect of velocity and temperature on conductivity.
3. Write report of findings for white liquor testing.
4. Establish test plan and identify appropriate black liquor samples for testing.
5. Conduct testing with black liquor and write report of results.
6. Prepare proposal for testing green liquor applications.
SUMMARY:

Testing of conductivity sensor-transmitters on white liquor was completed and a report issued as API-MTC Report No. 71 and IPST Project 3699 Report One. Some of the results and conclusions are discussed here.

Three types of conductivity sensors were evaluated for their response to changes in flow, temperature, and concentration of laboratory white liquors.

The three sensor types were:

- Four-electrode
- Flow-Through Electrodeless
- Insertion Electrodeless

The sensors, along with the appropriate transmitters, were supplied by three different suppliers. The sensor-transmitters were installed and used according to the supplier’s recommendations.

Initial testing was done with NaOH solutions from 57 g/l to 124 g/l as Na$_2$O and temperatures from 30°C to 100°C. This was done to check or calibrate the instruments and the data acquisition system. The conductivity readings were found to correlate very well with the alkali concentration for all three sensor-transmitters. The four-electrode sensor measurements were found to increase with increasing temperature. This sensor had an integral temperature compensation to 25°C.

Testing was done with white liquor made from reagent grade salts. The temperature was varied from 80 to 100°C. The flow was varied from 4-28 gpm, which is a velocity range of 1.5 to 10.4 fps in the 1" line used for testing. The white liquor concentration was varied from 55 to 135 g/l as active alkali and 13% to 35.5% sulfidity. Sodium carbonate, sodium sulfate, and calcium carbonate were also added in concentrations up to 9 g/l.

There were no differences among the three sensor types with respect to chemical concentration. All three responded equally to any changes. The insertion electrodeless sensor compensated to 100°C and the flow-through electrodeless sensor compensated to 25°C did not vary with temperature in the range 80-100°C. These sensors utilized external RTD’s for temperature measurement. The four-electrode sensor with an integral thermocompensator did show a consistent variation with temperature.

There was no effect from flow variations in the range used for this study.

Regression analysis showed that NaOH, Na$_2$S, and Na$_2$CO$_3$ had a significant effect on the conductivity. The regression equations were solved for effective alkali in terms of the conductivity. The total titratable alkali and % sulfidity were determined to have an effect on
the EA determination from conductivity.

There was no effect on the conductivity readings from fibers or black liquor solids added at levels of 2300 ppm and 1000 ppm, respectively.

While the sensors did not show any differences in response to chemical concentrations, different suppliers have transmitters with different options. There are also differences in the temperature compensation functions used by the suppliers.

The long-term response and fouling of the sensors was not evaluated in this part of the study.

A proposal was written and accepted for further testing of the conductivity sensor-transmitters on black liquor and this work has begun as Project 3741.
INTRODUCTION

Conductivity is the measurement of the ability of a solution to conduct electric current. This ability is primarily determined by the concentration and species of electrolytes in the solution. The current that can be passed through the solution is measured at a known constant voltage. Conductance is then calculated based on cell dimensions and electrolyte concentration. The common unit of measure has been mhos/cm or micromhos/cm derived from the reciprocal of ohms or resistivity. The accepted unit of measure is now microSiemens/cm. One microSiemen is equal to one micromho.

Conductivity measurements are affected greatly by temperature. Increasing temperature will increase ionic mobility resulting in higher conductivity. Conductivity measurements must be corrected to a standard reference temperature.

Electrical conductivity measurements are particularly useful for kraft mill process streams because of the large concentration of strong electrolytes. The hydroxide ion in particular has a specific conductivity that is three - four times that of other ions.

The major areas where conductivity is used in a kraft pulp mill include:

1. White Liquor Alkalinity
2. Black Liquor Residual Alkali
3. Caustic Dilution and Hypochlorite Manufacture
4. Pulp Washing Efficiency
5. Evaporator Condensate Carry-over
6. Black Liquor Spill Reclamation
7. Steam Condensate Quality
8. Slaker/Caucisticizer Control
9. Chlorine Dioxide Stage Control

The determination of alkali concentration by conductivity measurements is not always straightforward, particularly in kraft liquors with the presence of a number of other ionic species. A number of studies have been done investigating the use of conductivity as a measure of alkali strength.

Previous Studies

A comprehensive literature review on the use of conductivity measurements in pulp mills was summarized in the project report. Both direct conductivity measurements and conductometric titration methods have been tried previously with varying degrees of success. Conductivity can be an excellent indicator of hydroxide ion concentration but in pulp mill applications the
measurement is greatly affected by other process ions, temperature changes, and dissolved matter. Conductometric titration methods were developed to overcome some of these problems but such analyzers require frequent maintenance for cleaning and replacement of chemicals.

A method for direct measurement of alkali strength with minimum maintenance would yield enough benefits for a pulp mill that development and testing continues on improving conductivity sensors and transmitters for this application. Some of the major sources of error have been identified and newer sensor and transmitter designs are being developed that are less prone to fouling and instrument drift.

The Measurement Technology Committee (MTC) of the American Paper Institute (API) established a project to evaluate currently available conductivity sensors for pulp mill applications.

**Review of Past Project Activity**

During the last reporting period the appropriate sensors and transmitters were acquired on loan from suppliers and installed in a test stand consisting of a recirculation loop on the Institute’s 1.8 cu. ft. digester as shown in Figure 1.
**Sensor-Transmitters**

COND1 (CT1) in this report is a four-electrode type with an integral thermistor and electronics for temperature compensation to a 25°C standard. The sensor was installed according to the manufacturer’s recommendations in a pipe line "t" with the direction of flow into the face of the sensor. The transmitter is a two wire model with digital display and 4-20 mA output.

The sensor-transmitter referred to as COND2 (CT2) is a flow-through electrodeless type mounted on the outside of a 1" diameter Teflon-lined, carbon steel pipe. A separate RTD is furnished for measuring the process temperature for compensation to a standard of 25°C. The transmitter is a microprocessor-based unit with factory preset values for cell constant, range, and temperature coefficient. The cell constant and temperature coefficient were changed based on initial testing with NaOH solutions as described in the previous report.

COND3 (CT3) is an insertion type electrodeless sensor. The operating principle is the same as the COND2 sensor. COND3 has the toroids mounted on the end of a stem. The total length is about 6". To accommodate this, a pipe expansion was built and installed in the test loop. The pipe expansion was 6" in diameter with a flanged face. The sensor was screwed into the flange from the inside. An O-ring supplied with the unit provided a seal. The transmitter for COND3 is a microprocessor-based unit and comes supplied with several measurement and compensation curves in the microprocessor. These are selected by a code on the keypad. Three curves are standard and supplied with the transmitter. These were 0-15% NaOH at 25°C, 0-20% NaOH at 100°C, and black liquor at 160°C. The module used for the testing was the 0-20% NaOH at 100°C. An external RTD was used for temperature measurement and compensation.

Other instrumentation included a mag flow meter, pressure transducers, RTD temperature sensors, and a level transmitter. A circulating pump with a variable speed drive was used for all testing.

Data acquisition was done with a 386-20 mHz computer and a process control software package.

**NaOH Testing**

As described in the previous report, initial testing was done with solutions of NaOH to check the calibration of the sensors and temperature compensation functions.

COND1 and COND3 were operated with the standard temperature compensation supplied with the unit since the respective suppliers indicated there was no need for adjustment.
COND2 comes with a preset coefficient value for temperature compensation, but the manufacturer recommends testing in the process, if possible, to more accurately calculate a coefficient. For this testing then, COND2 was operated with the temperature compensation turned off to get data to calculate a temperature compensation coefficient.

NaOH concentrations ranged from 57 to 124 g/l as Na₂O. The concentration was determined by titration with 0.5N HCl. The temperature was slowly raised to 100°C and readings from each transmitter taken every minute.

COND1 exhibited a consistent rise in the conductivity readings with increasing temperature with the factory supplied temperature compensation function. The supplier's response was that the original sensor tip may not be the optimum for this application so a new tip was supplied and used for the subsequent white liquor testing.

It should be noted that the temperature sensor for COND1 was a built-in thermistor in the tip while both COND2 and COND3 used external RTD's for more accurate response. In an installation where temperature may vary, a COND1 type sensor could use an external RTD for greater sensitivity, or an uncompensated signal could be used with correction by a compensation algorithm determined by testing in the particular process according to the supplier.

The COND2 sensor-transmitter comes with a factory preset temperature compensation coefficient of 2%/°C and cell constant of 3.0. It is recommended that calibration testing be done, if possible, under process conditions to more accurately determine a coefficient. For the NaOH testing, the temperature compensation was turned off so that the recorded values were uncompensated. It was also found that, at 25°C, the conductivity on the transmitter was considerably higher than published values for the particular NaOH concentration. The cell constant was adjusted until the transmitter value agreed with the expected conductivity. The constant in this case was 6.36 and was used for all subsequent testing. A temperature compensation coefficient was also calculated from the data as 2.11% and this value was used for the white liquor testing.

The conductivity vs. temperature relationship for COND3 showed a positive increase for a given alkali strength up to a temperature around 64°C then the conductivity readings remained very constant as the temperature was increased to 100°C. According to the supplier, the results are expected since the 100°C is specified for use above 64°C. For process temperatures below this, a temperature compensation curve in the microprocessor for 25°C should be used.

For each sensor, the conductivity readings obtained at 100°C vs. alkalinity were compared and good linear agreement was obtained for all three. There were no distinct differences obtained in the responses between sensors. The slope of COND3 compensated to 100°C is nearly twice that of COND1 compensated to 25°C, indicating that, for an instrument compensated to 100°C, the response range of conductivity is twice that of an instrument...
compensated at 25°C over a given alkali concentration range.

Discussion of 1991 Results

White Liquor Testing

White liquor was made by dissolving the appropriate reagent grade salts in deionized water in the digester. The concentrations of NaOH, Na₂S, and Na₂CO₃ were determined by the "ABC" test with an automatic titrator.

The range of concentrations was determined by several references on the typical makeup of kraft white liquors. Initially, a 2⁵ factorial design was planned with a half replicate to be tested. The five variables were the concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium sulfate, and calcium carbonate. A "-" and "+" level were defined for each chemical. In practice, as the liquor was made up, it was not possible to duplicate the defined levels every time and the "-" and "+" levels became a range of concentrations.

The active alkali ranged from 55 to 134.6 g/l. The sulfidity was varied from 13% to 35.5%. Sodium carbonate ranged from 1.9 to 8.9 g/l. Sodium sulfate ranged from 0 to 5.6 g/l. Calcium carbonate ranged from 0 to 5.6 g/l.

Conductivities were recorded at three temperature levels of 80, 90, and 100°C.

Flow

The effect of flow on the conductivity readings was investigated for the first eleven tests on white liquor. The flow was varied from 4-5 gpm to 28-29 gpm by the variable speed circulating pump.

The velocity in the 1" line at the maximum flow of 29 gpm was 10.5 fps. The velocity at the maximum flow in the 6" expansion used for COND1 was 0.35 fps.

As shown in Figure 2 it was evident from these tests that there was no effect of flow on the conductivity in the range tested.
Temperature Compensation

A major consideration in the use of the sensor-transmitters is the temperature compensation function used. Both COND1 and COND2 are supplied with integral temperature compensation to a standard of 25°C. COND3 has three preprogrammed curves for compensation at 25°C, 100°C, or 160°C.

For the white liquor testing, measurement with COND1 for a given liquor strength showed a consistent increase in conductivity as the temperature increased from 80 to 100°C. Over this range, both COND2 and COND3 had no change in conductivity readings for a given liquor concentration.

Alkali Correlation

Simple linear correlations were done for each sensor versus active alkali (AA), effective alkali (EA), and total titratable alkali (TTA). The results for EA vs. conductivity at the three temperatures for each sensor are shown in Figures 3-5. The regression lines and the equations at each temperature are also shown. The graph for COND1 shows the effect of the temperature on the conductivity reading.
Conductivity Sensors

Figure 3

COND1 vs EFFECTIVE ALKALI
For White Liquor @ 80, 90, 100 °C

Figure 4

COND2 vs EFFECTIVE ALKALI
For White Liquor @ 80, 90, 100 °C
Stepwise linear multiple regression analysis was done to determine the significant variables on the conductivity at 100°C.

As expected, NaOH and Na$_2$S contribute significantly to the conductivity. Na$_2$CO$_3$ contributes only slightly to the fit of the data, but it is significant enough to be included in the model.

All cross product terms were investigated in the regression, but these were not found to contribute significantly to the fit of the data. Also, in the interest of keeping the model as simple as possible, only linear regressions were considered.

The regression equation determined from the data for COND1 at 100°C is:

$$\text{COND1}(100\degree C) = 217.1 + 2.013(\text{NaOH}) + 1.843(\text{Na}_2\text{S}) - 3.59(\text{Na}_2\text{CO}_3)$$

$$R^2 = 0.910$$

where COND = conductivity, mS/cm
NaOH, Na$_2$S, Na$_2$CO$_3$, as g/l Na$_2$O

At 80°C the regression equation determined by the same analysis is:

$$\text{COND1}(80\degree C) = 205.3 + 1.808(\text{NaOH}) + 1.594(\text{Na}_2\text{S}) - 3.429(\text{Na}_2\text{CO}_3)$$

$$R^2 = 0.907$$
The contribution from \( \text{Na}_2\text{CO}_3 \) is negative, presumably because the low ionic mobility of the carbonate ion can hinder the mobility of the faster hydroxide ions. The negative effect of sodium carbonate has been described in some of the previous studies, particularly those of Dorris.

Solving the regression equation at 100°C for EA in terms of the conductivity yields the following:

\[
\text{EA} = (\text{COND}(100°C)-217.1+3.59(\text{TTA}))(200-\%S)/(1121-0.34(\%S))
\]

where \( \text{EA} = \) Effective Alkali, g/l \( \text{Na}_2\text{O} \)

\( \text{COND} = \) conductivity, Ms/cm

\( \text{TTA} = \) Total Titratable Alkali, g/l \( \text{Na}_2\text{O} \)

\( \%S = \) % Sulfidity

The linear regression equation determined for \( \text{COND2} \) at 100°C is:

\[
\text{COND2}(100°C) = 196.0 + 1.642(\text{NaOH}) + 1.748(\text{Na}_2\text{S}) - 2.785(\text{Na}_2\text{CO}_3)
\]

\( R^2 = 0.926 \)

where \( \text{COND} = \) conductivity, mS/cm

\( \text{NaOH}, \text{Na}_2\text{S}, \text{Na}_2\text{CO}_3 \) as g/l \( \text{Na}_2\text{O} \)

At 80°C the regression equation is:

\[
\text{COND2}(80°C) = 198.6 + 1.673(\text{NaOH}) + 1.626(\text{Na}_2\text{S}) - 2.619(\text{Na}_2\text{CO}_3)
\]

\( R^2 = 0.914 \)

Solving the regression equation at 100°C for EA in terms of \( \text{COND2} \) results in the following equation.

\[
\text{EA} = (\text{COND2}(100°C)-196+2.785(\text{TTA}))(200-\%S)/(885.4+0.212(\%S))
\]

where \( \text{EA} = \) Effective Alkali, g/l \( \text{Na}_2\text{O} \)

\( \text{COND2} = \) conductivity, mS/cm

\( \text{TTA} = \) Total Titratable Alkali, g/l \( \text{Na}_2\text{O} \)

\( \%S = \) % Sulfidity

The regression equation for \( \text{COND3} \) at 100°C is:

\[
\text{COND3}(100°C) = 467.99 + 4.597(\text{NaOH}) + 4.173(\text{Na}_2\text{S}) - 8.418(\text{Na}_2\text{CO}_3)
\]

\( R^2 = 0.911 \)

where \( \text{COND} = \) conductivity, mS/cm

\( \text{NaOH}, \text{Na}_2\text{S}, \text{Na}_2\text{CO}_3 \) as g/l \( \text{Na}_2\text{O} \)
At 80°C the regression equation is:

\[
COND3(100°C) = 474.3 + 4.537(\text{NaOH}) + 4.141(\text{NaS}) - 9.059(\text{Na}_2\text{CO}_3) \\
R^2 = 0.904
\]

For COND3 the equation for EA in terms of conductivity at 100°C is:

\[
EA = \frac{(COND3(100°C)-468+8.418(rTA)(200-%S))/(2603-0.848(%S))}{(COND3(100°C)-468+8.418(rTA)(200-%S))/(2603-0.848(%S))}
\]

At the conclusion of the white liquor testing, the sensors were removed from the test loop. There was some fine black powder, most likely sulfide compounds, on the sensors, but there was no obvious scaling or fouling.

Effect of Fibers and Black Liquor Solids

Several runs were done to determine the effect of fiber and black liquor solids on the conductivity reading. Unbleached softwood kraft fiber at an approximate concentration of 0.23% or 2300 ppm was added to one liquor sample. Black liquor solids from a softwood kraft cook were added at an approximate concentration of 0.1% and 0.2%.

While there were some slight differences in the conductivity values, there was not a significant change due to the fibers or the black liquor solids for any sensor. The black liquor solids level used was not significant enough to affect the liquor analysis. This testing was not pursued at higher levels of fiber and black liquor solids because it is expected to be evaluated in continued testing.

Conclusions

There were no significant differences between the responses of the sensors to changes in chemical concentration. When the response of each sensor was regressed against the other two and each chemical component, only the sensor response was significant with an $R^2$ of 0.997. None of the sensors responds any differently to changes in the concentration.

COND1 did exhibit a variation with temperature both for the NaOH testing and white liquor testing. Two different tips were used with this sensor, and both showed a positive variation. This unit comes with an integral thermocompensator built into the tip. It should be noted that this sensor was the only one employing a built-in temperature sensor. The other two used external RTD’s and the signal from these was used in the respective transmitter for temperature compensation. For a process with varying temperature it would be recommended to have an external RTD for measurement and compensation with any of the three sensor types tested. An alternative would be to use an uncompensated signal and develop an algorithm for temperature compensation by testing in the actual process. The
uncompensated signal could be compensated by the algorithm in a DCS or computer-based process control system.

While the temperature standard for conductivity measurement has been 25°C, many processes in a pulp mill operate at temperatures well in excess of this. Compensation to 25°C then becomes a lengthy extrapolation. While no differences were seen in the relative responses of the sensors, COND3 compensated to a standard of 100°C had over twice the response range of the other two compensated to a standard of 25°C. According to one supplier of an instrument commonly supplied with a 25°C compensation, use of compensation to 100°C will give a larger range of conductivity readings, but the noise will be amplified accordingly. Also, liquor titrations done to check an instrument's response would normally be done at temperatures closer to 25°C than 100°C.

The testing with NaOH for COND3 showed that the 100°C compensation function should not be used for process temperatures less than 64°C. This agrees with the manufacturer's specifications.

Each of the sensors showed a good correlation of alkali strength and conductivity for pure NaOH solutions. The correlation for white liquor was not as good but still can provide a good indication of alkali strength. Linear multiple regression analysis determined that NaOH and Na₂S contributed significantly to the conductivity in nearly equal amounts. Na₂CO₃ was just significant enough to be included in the model. The other components did not have a statistically significant affect, but it is likely they had enough of an affect to contribute to some of the scatter in the data.

The addition of fibers up to 2300 ppm and of black liquor solids up to 1000 ppm did not have any significant effect on the sensor readings.

As was described in previous studies, other ions in solution will have an effect on the conductivity. However, a correlation of conductivity versus AA or EA was accepted as a viable measurement for a mill, provided the effects of interfering substances remains constant.

In any installation of direct conductivity in a kraft mill, the liquor should be characterized as to its composition and checked periodically to see if this composition is changing. In particular the presence of potassium ions, sulfate ions, and solids should be noted. If these remain relatively constant, then the conductivity should be useful as a measure of alkali content.

Conductivity does not, of course, distinguish between the sources of conducting ions, so a separate indication of sulfidity at a given alkali strength would have to be arrived at if this information is required.
This study did not look at the long-term response of conductivity sensors in this phase. This has been a major concern with the use of direct conductivity measurements. Fouling can affect the measurement, so frequent cleaning may be required. Electrodeless and four-electrode sensors are less sensitive to fouling than the older two electrode types. The electrodeless sensors use a non-contacting measurement technique, while four-electrode sensors use two potential sensing electrodes to compensate for any scaling. An alarm can be included with the four-electrode sensors to monitor the voltage drop-off as an indication of the degree of fouling.

Future Work

Future work will include the use of conductivity to measure alkalinity of black liquor. This is now under way as Project 3741. Activity beyond this phase could include the measurement of green liquor, which is really where the white liquor makeup is determined. Also, the long-term response of the sensors is a major consideration. This type of study may well be better conducted in a mill environment.
PROJECT 3716

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMICHEMICAL PULPING

RESEARCH REVIEW

MARCH 25, 1992

Clark P. Woitkovich

and

Thomas J. McDonough
OBJECTIVE:

To identify or develop an analytical test method for the estimation of yield in semichemical pulping and to develop empirical correlations between the analytical test data, estimated yield, and specific end-use properties.

GOAL:

To develop a technology that can be used to improve the control of industrial semichemical pulping processes.
SUMMARY

In the middle- to high-yield range of semichemical pulping, there currently exists no reasonably quick, reliable way of obtaining a quantitative estimate of pulp yield. This project is designed to evaluate several analytical methods that have been determined to be good candidates for this type of application. Several spectroscopic techniques are the most promising of the candidate methods because they possess the greatest potential for on-line application. This report summarizes the progress that has been made in applying these spectroscopic techniques to the analysis of semichemical pulp and liquor samples that have been prepared in the laboratory.

The three spectroscopic methods being investigated are near-infrared (NIR), ultraviolet (UV), and ultraviolet-visible (UV-VIS) fluorescence. To date two of these methods have been applied to lab-generated semichemical liquors and both have exhibited significant yield sensitivity. Sophisticated data analysis approaches have been employed to generate calibrations that can accurately predict yield based on spectral information.

Unfortunately, the value of having a liquor-based yield estimate becomes questionable in light of the fact that many semichemical pulping processes recycle brownstock wash water back to the digester. This complicates the makeup of any given liquor sample and introduces difficulty in attempting to relate that liquor sample to a specific pulp sample. Consequently, it is recommended that liquor analysis be abandoned as a potential yield estimation method and that all future efforts focus exclusively on the analysis of pulp.

The NIR spectroscopic technique is the only pulp analysis method that has exhibited yield sensitivity in the laboratory. However, the small size of our laboratory sample set has not allowed for a rigorous test of the predictive capability of this method. Future work will focus on the development of more robust calibrations and then testing the performance of these calibrations in actual mill environments.
INTRODUCTION

Knowledge of the yield associated with a chemical reaction is critical if raw materials are to be utilized with maximum efficiency. In the pulping of wood, yield is defined as:

\[
\% \text{ Yield} = \frac{\text{pulp weight} \times \text{pulp consistency}}{\text{wood weight} \times \text{wood consistency}} \times 100
\]

In industry, the pulping process is generally conducted on such a large scale that it is nearly impossible to accurately measure the parameters that determine yield. Consequently, yield becomes an elusive quantity that can only be estimated through some indirect approach.

Typically, such an approach is based on an analysis of pulp lignin content (e.g. "Klason" lignin or kappa number). Lignin content analyses, however, generally suffer several drawbacks. They are destructive, time-consuming, wet-chemical tests that require skilled laboratory personnel. Another problem is that these analyses ignore the carbohydrate fraction in pulp and its contribution to a yield estimation. Furthermore, kappa number, the most routinely used lignin content test, is limited in its range of applicability and becomes virtually useless when lignin content is high, as is the case with semi-chemical pulps.

Consequently, in the middle- to high-yield range of semichemical pulping there exists no reasonably quick, reliable way of obtaining a quantitative estimate of yield. If such a capability were to be achieved it would become possible to monitor yield regularly, or perhaps even continuously. Yield could thus be used as a process control parameter, making it possible to more effectively control the pulping reaction, and thereby, the development of pulp properties.

Several analytical methods have been determined to be good candidates for this type of application and are being applied to pulps and/or liquors as indicated in Table 1. A brief background on the spectroscopic techniques is presented as follows; for a more detailed discussion of these methods, the reader is referred to the preceding report (1).
Table 1: Candidate Yield Estimation Techniques

<table>
<thead>
<tr>
<th>SPECTROSCOPIC METHODS</th>
<th>PULP</th>
<th>LIQUOR</th>
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<tbody>
<tr>
<td></td>
<td>Near-Infrared Reflectance</td>
<td>Near-Infrared Transmittance</td>
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<tr>
<td></td>
<td>Ultraviolet-Visible Luminescence</td>
<td>Ultraviolet-Visible Transmittance</td>
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<td>Ultraviolet-Visible Reflectance</td>
<td>Ultraviolet-Visible Transmittance</td>
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<td></td>
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<td>Total Organic Carbon</td>
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<tr>
<td></td>
<td>-</td>
<td>Total Dissolved Solids</td>
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<td></td>
<td>Hypo Number</td>
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</table>

Near-infrared Absorbance Spectroscopy

The near-infrared (NIR) absorption characteristics of pulp samples are readily measured by monitoring the intensity of reflected radiation as incident wavelength is varied. In the case of liquor samples, the measurement is based on transmitted rather than reflected radiation. The resultant data is a plot of absorbance as a function of wavelength and is called an absorbance spectrum.

NIR spectra consist primarily of overlapping bands that result in broad spectral features from which it is difficult to derive structural information. The spectra, however, have been found to be empirically useful in a variety of quantitative analysis applications. The appeal of NIR spectroscopy (NIRS) lies in its fast analysis time, its minimal sample preparation requirement, its relatively compact and rugged design, and its recently emerged compatibility with fiber optic technologies. These attributes have rendered NIRS an ideal candidate for several on-line applications in the pulp and paper industry.
Ultraviolet-Visible Fluorescence Spectroscopy

The fluorescence phenomenon is observed when a substance, excited by incident light radiation, dissipates some of its excitation energy in the form of emitted light. With suitable instrumentation three distinctly different records of fluorescence behavior can be acquired; excitation spectra, emission spectra and synchronous spectra. Excitation spectra arise when the intensity of the fluorescence is monitored, at a specific emission frequency, while continuously varying the excitation frequency. Conversely, the excitation frequency can be held constant while the intensity of the fluorescence is monitored over a wide range of emission wavelengths. This results in what is known as a fluorescence emission spectrum. Finally, there is the capability of simultaneously varying both excitation and emission wavelength settings, at a fixed wavelength separation, to generate a synchronously scanned, or "fingerprint" fluorescence spectrum.

As in the case of NIR spectra, fluorescence spectra exhibit primarily broad spectral features that tend to confine data interpretation to an empirical level. On the other hand, all of the same attributes that have rendered NIRS an ideal candidate for potential on-line applicability also hold true for fluorescence spectroscopy. Although the method does not seem to share the increasingly widespread industrial acceptance enjoyed by NIRS, its attributes warrant that it be included in this study.

Ultraviolet-Visible Absorbance Spectroscopy

The measurement of UV-VIS absorbance involves essentially the same approach as that used in the measurement of NIR absorbance; the only difference is in the wavelength range that is used. The technique, as applied to liquid samples, is a commonplace analytical tool that has proven useful in the routine measurement of solution concentration. As applied to non-homogeneous solids, the method is far less developed.

In this study, a somewhat novel approach was taken to the measurement of the UV-VIS absorbance characteristics of pulp. Spectra were recorded by operating the scanning UV-VIS fluorescence spectrometer in a mode that had the excitation wavelength and the emission wavelength set to the same value.
Sample Preparation

The set of samples used throughout this portion of the project was prepared in the laboratory by cooking chestnut oak chips, under neutral sulfite semichemical (NSSC) conditions, to eight different yield levels that varied over the range of 74.7% to 84.0%. Cooked chips exiting the digester were extensively washed and then fiberized for 15 minutes in a Waring blender. Following the fiberization step, the pulp underwent further washing and was then pressed to a common consistency before being mechanically fluffed. Liquor samples received no treatment other than a dilution (1:100) prior to the UV-VIS fluorescence and UV-VIS absorbance measurements.

REVIEW OF PAST PROJECT ACTIVITY

In the previous progress report presented to this body, we reported our earliest observations of spectroscopic differences that were apparently yield-related (1). Specifically, significant differences were shown to exist in the transformed NIR absorbance spectra recorded from a subset of the laboratory pulps that had been cooked under semichemical conditions to different yields. This early work included experiments designed to study the effect of sample form on spectral data. It was found that the above-mentioned spectral differences were consistently exhibited to varying degrees, in all three of the investigated sample forms: moist fluff, dry fluff, and dried sheet. The most pronounced differences were observed in the case of the dried sheets. If samples were presented in a fluffed form that still contained an appreciable amount of moisture, spectral differences were reduced. The differences remained significant, however, and were thought to justify the elimination of a drying step in the sample preparation procedure, thereby simplifying the NIRS analysis.

Spectral differences were also evident in the UV-VIS fluorescence excitation spectra acquired from the same pulp samples. At that time, the fluorescence technique had been applied only to fluffed pulp and no conclusions could be made regarding the effect of sample form on these measurements. There was an indication, however, that the technique might not be suitable for wet pulp analysis.

Since these findings, our research efforts have continued to focus exclusively on the spectroscopic techniques. Using an expanded sample set, we set out to explore factors that were critical to the development of yield sensitivity in a given method. Specifically, there was a need to further understand the effects of not only yield, and sample form, but also moisture content, and sample presentation on the spectral data.
acquired by the various methods. In addition, in the case of the fluorescence work, it was necessary to investigate a variety of data acquisition and data analysis options. This report addresses the progress that has been made in these key areas.

DISCUSSION OF 1991 RESULTS:

NIR Spectroscopy as Applied to NSSC Pulps

Since pulp NIR spectra exhibited apparent yield-related differences even when the pulps were wet, it was decided to work exclusively with wet pulps. Wet pulp is, after all, what is likely to be encountered in an eventual on-line implementation of this technology.

Our efforts in this area were divided into essentially two sets of experiments. The first set of experiments focused on only two pulp samples from our original eight-sample set so that the method could be further optimized before analyzing the entire number of samples. The two samples, representing the extremes of our known yield range, were first brought to a consistency of 30-35% and then analyzed repeatedly in fluffed and unfluffed form using two different types of sample presentation cell. The objective was to quantify the effects of sample form and sample cell type on the discriminatory power of the method. The discriminatory power can be thought of as an indicator of yield sensitivity and is dictated by the relationship between the magnitude of the observed spectral differences and the magnitude of the measurement variability.

Figure 1 shows raw NIR spectra acquired from the two different high yield pulp samples. One sample was a pulp that was cooked to a yield of 82.7% and the other was a pulp cooked to a 74.7% yield. These two representative absorbance spectra illustrate the types of differences that are observed in the raw data acquired from wet samples that differ significantly in yield. One noticeable difference resides in the intensities at the two very strong absorption bands centered at approximately 1490 and 1950 nm. These bands are water absorption bands and their intensity differences probably arise from slight differences in consistency between the two samples. Although potentially useful for the estimations of pulp consistency, the regions of the spectrum where these bands appear must be avoided when developing correlations between spectral features and yield.
Figure 1. Raw NIR absorbance spectra acquired from two different high yield pulp samples at a consistency of approximately 30-35%.

The other important difference between the spectra in Figure 1 is the vertical offset or base line shift that is observed throughout most of the acquisition range. Base line shift is primarily a surface scattering effect. It can be caused, at least in part, by a variety of sampling-related factors, such as particle size distribution, packing density, and other sample surface properties. In order to focus on spectral differences that are not influenced by surface related effects, it is essential to compensate for base line differences. A convenient way of accomplishing this is to mathematically transform raw spectral data into second derivative spectra. The conversion of spectra to their second derivatives compensates for these factors by combining displaced or sloping base lines into a common, horizontal base line.
Second derivative spectra were calculated using raw data acquired from wet, fluffed and unfluffed pulps that were presented for analysis in the two different sample cells. A select region of the derivative spectra, known to be devoid of water absorption bands (1580-1750 nm), is shown in Figure 2. In each of the four separate plots, four spectra representing four different reloads, are shown for each sample. The most prominent difference between samples occurs at approximately 1638 nm, a region where lignin is known to absorb. The yield sensitivity or discriminatory power, of each presentation condition was quantified by performing a two sample t-test on the measured intensity at 1638 nm (Table 2).

Table 2. t-values representing the relative discriminatory power of indicated presentation conditions. Values were calculated on measured intensities at 1638 nm.

<table>
<thead>
<tr>
<th></th>
<th>CUP</th>
<th>TRANSPORT</th>
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<tbody>
<tr>
<td>UNFLUFFED</td>
<td>4.1</td>
<td>11.0</td>
</tr>
<tr>
<td>FLUFFED</td>
<td>5.7</td>
<td>38.1</td>
</tr>
</tbody>
</table>

Note: A t-value greater than 2.8 indicates that the two pulps can be said to differ in yield with a 95% probability of being correct. The higher the t-value, the greater is the probability of correctness of this statement, and the greater is the ability of the measurement method to detect a yield difference of any given magnitude.
Figure 2. Low frequency region of second derivative NIR absorbance spectra acquired from fluffed and unfluffed pulps in two different sample cells.
The results summarized in Table 2 indicate that, at 1638 nm, the highest discriminatory power (or lowest reload variability) is achieved when pulps are presented in fluffed form using the transportable cell. This finding is not surprising because, under these conditions, both analyzed surface area and surface homogeneity are maximized. What is surprising is the magnitude of the improvement that can be made by optimizing sample presentation.

In summary, two important findings have emerged from this set of NIRS experiments:

1) the transportable sample cell is the superior sample presentation device for the NIRS reflectance analysis of pulp, and

2) excellent yield discriminatory power is achievable without the necessity of sample drying.

The NIRS method appears to be relatively unconstrained by elaborate sample preparation requirements, thus enhancing its potential applicability to on-line analysis.

The second set of NIRS experiments mentioned above focused on acquiring a series of spectra from the entire pulp sample set. In this case, the analyses were performed at a pulp consistency of approximately 16.5% to more closely simulate the type of analysis that would be done in the mill on pulp exiting a brownstock washer. Figure 3 shows representative raw NIR spectra acquired from two high-yield pulps (74.7 and 84.0%) at 16.5% consistency. The spectra illustrate the dominance of water absorption bands and the apparent subtlety of yield-related differences, if they even exist. A comparison of Figures 1 and 3 reveals the effect that a significantly higher moisture content has on raw spectral data.

After second derivative transformation and expansion on the wavelength axis, the set of spectra is seen to exhibit significant differences that correlate closely with gravimetric yield values (Figure 4). The overall appearance of these spectral differences, however, when compared to those observed in Figure 2, seems to be significantly affected by the changed pulp moisture content. The yield-related differences appear to be reduced in magnitude and confined to a smaller wavelength range.
Figure 3. Raw NIR spectra acquired from two different high-yield pulp samples at a consistency of approximately 16.5%.

Figure 4. Selected region of NIR spectra acquired from wet (16.5% consistency) pulps obtained by cooking chestnut oak, under NSSC conditions, to a variety of yields ranging between 74.7% and 84.0%. Spectral data is shown after second derivative transformation and wavelength scale expansion.
A plot of gravimetric yield vs. predicted yield is shown in Figure 5. Predicted yield values were generated using a Partial Least-Squares cross validation (PLS-CV) algorithm (2,3) that is resident in the NIRS software.

![NSSC YIELD PREDICTIONS
BASED ON PLS-CV ANALYSIS OF NIR SPECTRA ACQUIRED FROM WET PULPS](image)

**Figure 5.** Plot of measured vs. predicted yield. Predicted yield values were generated using the calibration developed by PLS-CV analysis of spectra acquired from the eight wet pulp samples that varied in yield from 74.7% to 84.0%.

The conclusions drawn from this second set of NIRS experiments are:

1) Decreasing pulp consistency (to a level that might be encountered on a brownstock washer) results in a significant reduction in the magnitude of yield-related spectral differences, and

2) Yet, sophisticated calibration algorithms are still capable of generating accurate yield predictions based on the NIR spectral data acquired from low consistency (16.5%) pulps.
UV-VIS Fluorescence Spectroscopy as Applied to NSSC Liquor

At the outset, it was not known which, if any, of the three possible fluorescence acquisition modes would prove to be most informative. Therefore, it seemed wise to investigate all three of these capabilities in an effort to develop a complete characterization of liquor fluorescence behavior. Unfortunately, for each acquisition mode, there were literally dozens of possible wavelength settings. Consequently, a fairly exhaustive preliminary investigation was required in order to identify those wavelength settings that were optimal for subsequent quantitative analysis.

By analyzing a single liquor sample in all of the different acquisition modes, it was found that the choice of wavelength settings significantly influenced either the overall signal intensity, the shape of prominent spectral features, or both. This information was used to identify what appeared to be the most informative settings in each mode before beginning the analysis of liquor samples that represented different pulp yield levels.

Additional preliminary spectra were acquired, using the selected settings, in an effort to ascertain: a) whether liquors associated with widely different yield levels would generate significant spectral differences, and b) whether the magnitude of measurement variability was sufficiently small relative to observed yield-related spectral differences. Unless both these conditions were met, it would not be possible to develop correlations between pulp yield and liquor fluorescence. What was concluded was that, under all of the selected acquisition conditions, significant yield-related differences were evident. Specifically, in the case of both the excitation and synchronous spectra, yield-related differences appeared in the form of dramatic changes in the relative intensities of prominent spectral features.

Ultimately, the entire laboratory series of eight different NSSC liquors was analyzed using six selected acquisition conditions (i.e., two different wavelength settings for each of the three acquisition modes). Two of the six complete data sets, comprised of eight spectra each, are shown in Figure 6. Each spectrum displayed represents a computed average spectrum derived from duplicate acquisitions.
The representative data shown in Figure 6 consists of two series of spectra acquired in the excitation mode, one set (6a) was recorded with the emission wavelength set to 470 nm, and the other (6b) with it set to 530 nm. For display purposes, each spectrum in Figures 6a and 6b was multiplied, over its entire range, by a factor chosen to give a constant intensity at approximately 395 nm. One observation that is immediately apparent in Figure 6 is that fluorescence spectroscopy, as applied to NSSC liquors, is evidently highly sensitive to variations in liquor composition that are associated with pulp yield differences (74.7-84.0%). Spectral features appear to vary in a regular fashion.

The apparent abundance of information in full-range fluorescence spectra, including the observed yield sensitivity, is presumed to reflect the overall chemical characteristics of the liquor samples. The implication is that both dissolved carbohydrate fragments and dissolved lignin fragments contribute to the measured fluorescence. This is important from the standpoint of our objective because no yield-estimation method can be considered reliable unless it is based on an analysis that reflects information related to both the lignin and carbohydrate fractions of the analyte.

Identification of an optimum quantitative analysis approach required an intensive investigation of several different normalization and calibration methods. The simplest normalization approach was a base line subtraction procedure. Performing this type of normalization and measuring the ratioed intensities of prominent spectral features generated a strong linear correlation between the spectral data and known gravimetric yield ($R^2 = 0.896$). The use of more sophisticated normalization and calibration procedures, i.e. Multiplicative Scattering Correction (4) and PLS-CV, demonstrated that the fluorescence data can be used to accurately predict yield, as seen in Figure 7.

One early indication to come out of this fluorescence work was that the shape of a fluorescence spectrum did not appear to be affected by changes in sample concentration. Spectral information believed pertinent to yield prediction was reported to be retained up to a point where dilution becomes excessively high (resulting in an unacceptable signal-to-noise ratio). It turns out, however, that after more careful scrutiny, this conclusion proved not to be entirely correct. Spectral features
Figure 6. Fluorescence excitation spectra acquired from diluted (1:100) spent semi-chemical pulping liquor obtained by cooking chestnut oak under NSSC conditions, to a variety of yields ranging between 74.7% and 84.0%. Spectra in 6a were recorded at Emₐ = 470 nm; in 6b Emₐ = 530 nm.
Semichemical Pulping

NSSC YIELD PREDICTIONS
BASED ON PLS-CV ANALYSIS OF FLUORESCENCE SPECTRA ACQUIRED FROM LIQUORS

Figure 7. Plot of measured vs. predicted yield values. Pretreated yield values were generated by performing a PCS-CV analysis of fluorescence excitation spectra acquired from the eight liquor samples representing a pulp yield range of 74.7 to 84.0%.

are indeed affected by liquor concentration levels in a way that will interfere with fluorescence-based yield estimation. The magnitude of the interference is fairly subtle, however, which is why it escaped detection earlier. Current efforts are exploring the development of potential correction methods designed to compensate for these unwanted concentration effects. Some measurable success has already been achieved.
UV-VIS Fluorescence Spectroscopy as Applied to NSSC Pulps

The characteristic fluorescence behavior of one particular semichemical pulp sample (82.7% yield) was recorded in the excitation, emission, and synchronous scan acquisition modes over a wide range of wavelength settings. The wavelength settings that produced the most dramatic spectral features were adopted in subsequent fluorescence experiments that focused on detecting possible yield-related spectral differences.

Although apparently significant differences were found, the potential usefulness of the observed differences was ultimately undermined by the degree of variability associated with the acquisition of each spectrum (i.e. reload variability). Such variability is shown in Figure 8, along with the effect of moisture content on overall spectral features. Reload variability appears to be substantial, approaching, in several cases, the magnitude of the differences that are apparently related to yield. It is also obvious that increasing moisture content causes a drastic reduction in the overall intensity of the detected fluorescence. For these reasons, it was decided to abandon further pursuit of the UV-VIS fluorescence method as applied to pulp, especially in light of the relative success achieved with the NIRS method.

Perhaps the most significant reason behind the failure of fluorescence spectroscopy, as applied to pulp, is that there is no sample presentation accessory that allows for the averaging of spectral information from a large sample area. As seen with the NIRS data, this capability is crucial when analyzing the optical phenomena of non-homogeneous materials, such as pulp.
Figure 8. Fluorescence excitation spectra showing the effect of consistency and a comparison of reload variability vs. the magnitude of apparent yield-related differences.
UV-VIS Absorbance Spectroscopy as Applied to NSSC Pulp

Raw UV-VIS reflectance spectra were acquired from two air-dried, fluffed pulp samples that possessed different yield levels. Figure 9 shows the reflectance spectra obtained when excitation and emission wavelength settings were synchronously scanned over the ranges 230-350 nm and 350-650 nm. It was necessary to scan the overall wavelength range in two separate parts because a reduction in signal attenuation was required in order to detect the extremely low reflectance in the UV region.

In the UV and UV-VIS reflectance plots, each yield level is represented by six individual spectra acquired from six different sample reloads. It is readily apparent from Figure 9 that, in both wavelength regions, there is considerable overlap of the ranges of reload variability for each sample. Apparently, it is not possible to obtain acceptable measurement reproducibility with our present capabilities. Since the UV-VIS absorbance of pulps was measured using the fluorescence spectrometer, the explanation for this finding can be traced back to the above-mentioned instrumental drawback.

UV Absorbance Spectroscopy as Applied to NSSC Liquor

Figure 10 shows UV absorbance spectra acquired from the eight NSSC liquor samples described earlier. As in the case of the fluorescence spectra, UV absorbance spectra appear to be sensitive to apparent variations in liquor composition that are associated with yield differences. Two prominent absorption bands are immediately evident: one appears in the 255 to 260 nm range; the other at approximately 275 to 280 nm.

Difficulties in data downloading with this instrument prohibited us from employing the more sophisticated PLS-CV approach to the development of a yield correlation. Thus, we opted for a simple linear regression analysis using a single peak intensity ($I_{275}$) or ratio of intensities ($I_{275}/I_{255}$). These values are tabulated with the gravimetric yields in Table 7. The $R^2$ values indicate the existence of moderately strong correlations between the UV absorbance data and known yield levels. Further work is necessary, however, to assess the reproducibility of these measurements and to examine the impact of liquor concentration on the appearance of pertinent spectral features.
Figure 9. Raw UV-VIS reflectance spectra acquired from two air-dried, fluffed pulp samples having different yield levels. Each sample was reloaded and reanalyzed six times.
Figure 10. Ultraviolet absorption spectra acquired from diluted (1:100) spent semi-chemical pulping liquor attained by cooking chestnut oak, under NSSC condition, to a variety of yield levels ranging between 74.7 and 84.0%.

Table 7. Intensities and ratioed intensities of selected ultraviolet absorption bands.

<table>
<thead>
<tr>
<th>Yield, %</th>
<th>$I_{274}$</th>
<th>$I_{274}/I_{254-258}$</th>
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<tr>
<td>84.0</td>
<td>10.85</td>
<td>0.977</td>
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<td>82.7</td>
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<td>80.7</td>
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<td>78.0</td>
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<td>76.9</td>
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<tr>
<td>76.6</td>
<td>15.47</td>
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<td>76.1</td>
<td>17.12</td>
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</tr>
<tr>
<td>74.7</td>
<td>20.45</td>
<td>1.082</td>
</tr>
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</table>

$R^2 = 0.830$  $R^2 = 0.832$
CONCLUSIONS AND RECOMMENDATIONS

The two spectroscopic methods that have been applied to the analysis of lab-generated semichemical liquors have both exhibited significant yield sensitivity. Sophisticated data analysis approaches have generated calibrations that can accurately predict yield based on spectral information.

The value of having a liquor-based yield estimate becomes questionable, however, in light of the fact that many semichemical pulping processes recycle brownstock wash water back to the digester. This complicates the makeup of any given liquor sample and introduces difficulty in attempting to relate that liquor sample to a specific pulp sample. Consequently, it is recommended that liquor analysis be abandoned as a potential yield estimation method and that all future efforts focus exclusively on the analysis of pulp.

Investigations of the various spectroscopic methods, as applied to pulps, has shown that the NIR technique is the only pulp analysis method that has exhibited yield sensitivity in the laboratory.

FUTURE WORK

As recommended, all future work on this project will focus exclusively on the NIR spectroscopic analysis of pulp. The technique will undergo mill evaluations that are designed to test its performance under the daily rigors of plant operation. Prior to the initiation of any mill trial, further laboratory work will be conducted to develop a statistically sound, workable calibration to be used for yield prediction while on-site. To enhance the applicability of the laboratory calibration to mill data, considerable attention will be devoted to the careful simulation of mill pulping conditions.

A wet chemical laboratory analysis designed to quantify the major chemical constituents of pulp, i.e. cellulose, hemicellulose, and lignin, will be used as a backup analytical test to verify that spectral measurements in the mill actually reflect real yield variations. Such an analysis will also add to our knowledge concerning the fundamental reasons behind the observation of yield-related spectroscopic differences.
REFERENCES


