Quantitative Determination of Quinone Chromophore Changes During ECF Bleaching of Kraft Pulp

A Dissertation Submitted by
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August, 1999.
This Thesis is Dedicated to the Memory of my Father
Carl Zawadzki
1932–1998
All truth passes through three stages. First, it is ridiculed. Second, it is violently opposed. Third, it is accepted as being self-evident.

Arthur Schopenhauer (1788–1860).
Abstract

Benzoquinone–lignin substructures have often been cited as important contributors to the color of lignocellulosic materials. Previously, model compound studies have suggested that these lignin substructures may figure predominantly in the chemistry of industrially important pulp bleaching processes, particularly chlorine dioxide (D) and oxidative alkaline extraction (E*). Unfortunately, the practical significance of these structure toward brightness development during pulp bleaching cannot be known a priori from model compound studies.

This study was focused on the development of a quantitative analytical methodology for the determination of quinone structures in isolated lignins. Lignin–quinone quantification was achieved by the development and application of a novel $^{31}$P-NMR spectroscopy–based methodology. Benzoquinone structures in isolated lignins were derivatized by trimethylphosphite and yielded arylidimethylphosphate ester adducts after controlled hydrolysis. The lignin–arylidimethylphosphate ester could readily be quantified by solution $^{31}$P-NMR spectroscopy using a triarylphosphate internal standard.

The developed methodology was applied toward the analysis of lignin–quinone introduction and removal during chlorine dioxide bleaching of kraft pulp. Chlorine dioxide bleaching was found to dramatically increase the quinone content of residual lignin. Lignin–quinone contents of DE*DED pulps correlated well with pulp brightness and brightness ceiling values, indicating that these structures may negatively impact upon pulp brightness.

An isolated lignin treated in homogenous solution with chlorine dioxide revealed increased lignin–quinone formation with greater application of chlorine dioxide. The lignin–quinone content reached a maximum value of 0.30 mmol/g lignin and further chlorine dioxide application did not alter the amount. The results are consistent with previous studies which indicated that quinone compounds are relatively stable toward further oxidation by chlorine dioxide.
Industrially, oxidative alkaline extraction often follows chlorine dioxide delignification of pulp. Benzoquinone contents of a series of lignins isolated at the oxidative alkaline extraction stage reveal that alkali alone causes a significant reduction of lignin–quinone content. Hydrogen peroxide and oxygen reinforcement of the alkaline extraction stage resulted in enhanced degradation of lignin–quinone structures.

A series of peracetic acid pretreated and oxygen delignified pulps (PaO) were prepared using both aggressive and standard oxygen delignification conditions. Regardless of the delignification conditions, the quinone contents of these pulps were uniformly low. These results suggest that lignin–quinone structures may not be a major influence on brightness development of PaO pulps.

The fundamental chemistry of trimethylphosphite derivatization was explored on a series of ortho– and para–benzoquinone model compounds. Both ortho– and para–benzoquinones were found to give trimethylphosphate ester isomers of the analogous catechol or hydroquinone structures. The phosphorus chemical shift of the aryl-dimethylphosphate, quinone adduct, occurred in the δ-2 ppm region. Generally, derivatization yield was found to be high, although thermally unstable quinones likely underwent partial degradation before complete derivatization.

Non–benzoquinone model compounds representing additional lignin functional groups were also studied. Notably, 3,4-dimethoxybenzyl alcohol was found to undergo transesterification with trimethylphosphite giving, after hydrolysis, hydrogen–phosphate adducts with phosphorus NMR signals in the δ 12 ppm region. Derivatized lignin also gave products consistent with transesterification, although this side reaction did not interfere with quinone analysis.

This study presents a practical and robust methodology for studying previously poorly understood lignin–quinone structures. The present methodology may contribute to an understanding of how to optimize brightness response of modern ECF bleaching sequences by gaining a fundamental knowledge about the chemistry of lignin–quinone structures. Understanding the nature of chromophoric lignin substructures is important if we are to selectively brighten pulp with greater efficiency.
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Structure Numbering

All structure numbers refer only to the immediate section in which the structures are seen.

Abbreviations

BS = brownstock, unbleached pulp
Cr(acac)₃ = chromium–acetylacetonate
Dₐ, D = chlorine dioxide stage
DMF = dimethylformamide
DMSO = dimethylsulfoxide
E = alkaline extraction stage
E* = oxidative alkaline extraction stage
ECF = elemental chlorine–free
KF = kappa factor = % equivalent chlorine charge/ pulp kappa number = \( \frac{100(\text{g ClO}_2 / \text{g pulp}) \times 2.63}{\text{pulp kappa number}} \)
Me = methyl
MWw = weighted average molecular weight
NMR = nuclear magnetic resonance
O = oxygen delignification stage
ortho–benzoquinone = 1,2–benzoquinone
Pa = peracetic acid stage
para–benzoquinone = 1,4–benzoquinone
PVP = poly(4-vinylphenol)
T₁ = spin–lattice relaxation
TCF = totally chlorine–free
TMDP = 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane
TMP = trimethylphosphate
TTP = tri–meta–tolylphosphate
UV = ultraviolet
φ– = phenyl or aromatic
1. Introduction

Multistage bleaching of chemical pulp consists of delignification and brightening stages. In the delignification stages, bulk residual lignin is degraded and removed. The brightening stages are responsible for the elimination of residual chromophoric (colored) structures. The chromophoric structures may be both initially present in the pulp and/or formed during the preceding bleaching sequences. During the last stages of bleaching, the residual lignin concentration is low. Therefore, it is essential that the elimination of the chromophoric structures be highly selective, otherwise cellulose damage will occur.

Understanding the nature of chromophoric lignin substructures is important if we are to selectively brighten pulp with greater efficiency. Furthermore, monitoring the introduction and removal of chromophoric structures in lignin is useful for understanding and elucidating the chemical pathways that govern brightness development.

In the introduction of Gierer's comprehensive review of bleaching reactions, he stated one complicating factor that made the survey a challenge:

"... the structure of the substrate, i.e., residual lignin that has survived the cooking treatment and possibly treatments of previous bleaching steps, is virtually unknown." [1]

Similarly, in a review of chemical pulp bleaching chemistry, Dence stated:

"Any attempt to describe delignification and bleaching phenomena by a set of well-defined chemical reactions is of necessity limited by the meager amount of information available dealing with the structure of lignin in unbleached or partially delignified or bleached pulps." [2]

Although significant progress has been made toward the elucidation of bulk lignin structural features after pulp bleaching [3-9], the quantitative determination of chromophoric substructures are still relatively unexplored. In particular, this study addresses the broad problem areas encompassing: the nature of chromophoric substructures in lignin modified by chlorine dioxide and oxygen bleaching, and the relationship between lignin structure and brightness development.
The research focus is important for a number of critical reasons:

1) The problem area has been identified as a high-priority research need for the pulp and paper industry, as has been illustrated by the following statement by Baum:

"Basic research is needed to develop a better understanding of the chemical and physical nature of residual lignin, how it relates to bleachability, and how it might be modified to enhance bleachability." [10]

2) A greater understanding of the chemistry of lignin chromophores and brightness development is needed so that the efficiency of existing bleaching sequences can be optimized.

2. Literature Review

2.1. Kraft Lignin

Softwood lignin is formed through the coupling of coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol) radicals [11]. The numbering system for the basic phenyl-propane monomer of lignin is illustrated in Figure 1. Figure 2 illustrates structures and abundances of common linkages found in softwood lignin [11, 12]. Note, the dominant linkage is the β-O4 structure.

![Figure 1. Numbering system for the basic phenylpropane unit of softwood lignin.](image)

Recently, two-dimensional NMR studies have revealed dibenzodioxocin structures (Figure 2) as a major new linkage unit in softwood lignins [13, 14]. A representation
of the extended structure of softwood protolignin is given in Figure 3 and the abundances of lignin functional groups are given in Table 1.

![Chemical structures and functional groups](image)

**Figure 2.** Common linkage types in softwood lignin [11-14].

<table>
<thead>
<tr>
<th>Functional group</th>
<th>#/100 C₆C₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>methoxy (CH₃O−)</td>
<td>92–97</td>
</tr>
<tr>
<td>phenolic (φ−OH)</td>
<td>15–30</td>
</tr>
<tr>
<td>benzyl alcohol (φCH₂OH)</td>
<td>30–40</td>
</tr>
<tr>
<td>carbonyl (C=O)</td>
<td>10–15</td>
</tr>
</tbody>
</table>

C₆C₃ = lignin phenylpropane monomer.

---

3
The objective of kraft delignification is to modify the structure of protolignin to enhance its dissolution. Conventional kraft pulping involves the action of aqueous sodium hydroxide (NaOH) and sodium sulfide (Na₂S) on wood chips (~170°C for two
hours) [11]. The cook is terminated during the "residual delignification phase" to prevent significant loss of pulp strength. After cooking, the residual lignin content of a conventional kraft pulp is approximately 4.4% wt/wt (kappa number 30). The remaining residual lignin must be removed by other methods such as chlorine dioxide bleaching or oxygen delignification.

Three important categories of kraft delignification reactions can be delineated: fragmentation reactions, condensation reactions, and the formation of alkali stable structures. Fragmentation reactions assist with the dissolution of the protolignin. Phenolic aryl ether structures (β-O4 and α-O4, Figure 2) are labile under kraft pulping conditions. Base-induced (hydroxide, HO-) deprotonation of phenolic structures can result in the formation of a quinone methide at elevated temperatures. Quinone methide formation from α-OR structures occurs by the loss of an α-leaving group (A-O- > HO-). In the case of β-O4 quinone methide structures, the β-substituent can be eliminated as a result of nucleophilic attack of hydrosulfide (HS-) at the α-position and subsequent thirane formation [16]. Fragmentation can also occur via concerted and vinylogous elimination mechanisms.

Cleavage of β-aryl ether linkages in non-phenolic structures is a relatively slow reaction that is enhanced by the presence of an α-hydroxyl group. The α-hydroxyl group can be deprotonated under alkaline conditions, forming an alkoxide anion. Nucleophilic attack of the anion on the β-carbon allows for formation of an oxirane and elimination of the β-aroxyl substituent [16]. The abundance of α- and β-aryl ether linkages in softwood lignin (Figure 2) is important because cleavage of the ether linkages results in the formation of new reactive phenolic groups and increased aqueous solubility of the lignin.

Condensation reactions can occur during kraft pulping. The nucleophile HS- (or HO-) can compete with a phenolic carbon for attack on a quinone methide intermediate. Nucleophilic attack of a phenolic carbon on the α-position can lead to a diphenylmethane structure [17]. This reaction pathway is favored when the quinone methide possesses a poor leaving group at the β-position (such as aryl-) (Figure 4). Another condensation reaction involves the coupling of two phenolic precursors with formaldehyde as illustrated in Figure 5 [16].
Figure 4. Lignin fragmentation and diphenylmethane formation reactions [16].

Figure 5. Diphenylmethane formation by the phenol-formaldehyde reaction [16].

Structures resistant to kraft pulping are the β-5, β-1, and 5-5 linkages (Figure 2). Lignin structures may be resistant to fragmentation under alkaline conditions due to their non-phenolic nature or the presence of a poor α-position leaving group. Carbon–carbon type structures (β-5, 5-5, and β-1) are present in protolignin (Figure 2) and these link-
ages are also alkali stable. Ligandin-carbohydrate complexes (LCCs) are alkali stable structures that may be formed during kraft pulping. LCCs may be formed from a non-phenolic β-O, oxide intermediate during the elimination of the β-aroyxy substituent when a cellulose hydroxyxyl acts as a nucleophile [18].

Enol ethers and stilbenes are formed by a mechanism involving base abstraction of a γ-hydroxyl proton which leads to formaldehyde elimination (Figure 6) [19]. Also, enol ether structures are thought to form from dibenzodioxin precursors [20]. These ring conjugated structures are important because of their chromophoric contribution to kraft pulp (Figure 8). Chromophoric ortho-benzoquinone structures are thought to arise from catechol structures formed during kraft pulping [16, 21]. During the kraft cook, hydrosulfide and methymercaptane anions are able to cleave methyl-aryl ethers to give catechols (Figure 7).

Figure 6. Formation of enol ether (R = O Aryl) and stilbene (R = Aryl) structures [16].

Figure 7. Quinone formation during kraft pulping [16].
2.1.1. Lignin Isolation

Lignin in bleached pulp is present in a solid matrix and usually at a concentration that makes structural elucidation studies difficult. Therefore, for bleached pulp, lignin isolation is a necessary step for subsequent structural elucidation studies. The purpose of the lignin isolation procedure is to collect a representative concentrated sample with minimal modification and contamination.

A widely used and convenient method for isolating carbohydrate-free residual lignin is by acidic dioxane–water extraction [22-25]. The method relies on the hydrolysis of lignin–carbohydrate linkages to liberate the residual lignin from pulp. Geierstedt and Lindfors reported that acidic dioxane treatment can also cleave enol ether and β-aryl ether linkages [19]. Froass studied the influence of acid concentration and reaction time on the isolated yield of residual lignin [25]. Essential observations were that much of the lignin capable of being extracted was removed during the first hour and the acid concentration has a minor influence on yield, until it is reduced to 0.05 N [25]. The acid concentration over the range 0.05–0.2 N had a small influence upon the yield of residual lignin (45–56% respectively for a 2 hour reflux time).

Argyropoulos and Bolker found a gradual increase in the molecular weight of residual lignin that was subjected to refluxing acidic dioxane–water for as long as 7 hours [22]. In a separate study, Solar and Kacik found that the change in molecular weight is dependent upon the concentration of the lignin solution, time and the temperature of the reaction [24]. Solar and Kacik reported a minor decrease in residual lignin molecular weight after 3 hours of refluxing in acidic dioxane–water. The results of both studies suggest that minor molecular weight changes and acid-catalyzed condensation reactions are limited if the total refluxing period is kept under 3 hours.

Potentially, acid hydrolysis conditions may lead to unwanted condensation reactions. Phenolic structures substituted at C6 have been suggested as probable condensation products under acidic conditions [16, 23, 26]. Batch acidic dioxane–water isolated residual lignin was compared with residual lignin isolated from continuous extraction of pulp and little difference was observed in many residual lignin structural features including:
carboxylic acid, aliphatic hydroxyl, phenolic hydroxyl, C5 substituted phenolic contents [27]. For one pulp sample, the batch extracted residual lignin was found to contain a slightly higher percentage of C6 substituted phenolics than the continuous extracted sample [23, 27]. Overall, the results of the study suggested that the acidic dioxane isolation technique has little influence on the structure of the isolated lignin.

Enzymatic liberation of lignin from pulp is potentially a good method to isolate lignin with minimal structural modification [28]. Unfortunately, the enzymatic liberation method suffers from a long isolation time required (>4 days) and the isolated samples are often contaminated with carbohydrates (3–7%) and proteins (~2%). These contaminants cannot be completely removed from the residual lignin [28] and interfere with subsequent structure elucidation studies. Conversely, the acidic dioxane-water isolation method is simple, controlled, and potential acid–catalyzed condensation reactions are minimized by using a short extraction time.

2.2. Chromophoric Lignin Structures

This section of the literature review is focused on an overview of the chromophoric structures thought to be present in lignins. Stability and formation of chromophoric structures during bleaching will be discussed in subsequent sections of the literature review.

Lignin contains a number of unsaturated functional groups that absorb light in the ultraviolet portion of the spectrum. These groups include carbonyl, aromatic rings, and carbon–carbon double bonds. When the unsaturated functional groups are conjugated with other unsaturated structures the absorption bands may shift into the visible region of the spectrum [29, 30]. Substituent effects and the local chemical environment may influence the absorption maximum. Simple prototypes for the chromophoric structures in mechanical pulp and lignin are given in Figure 8. Structures referred to as leucochromophores are potential chromophores that can be converted into chromophores upon oxidation [11, 31]. A number of structures have been implicated in causing the visible absorp-
tion spectra of mechanical pulps and kraft lignins: metal complexes [30, 32-34], conifer-
aldehyde [33, 35], ortho-quinone methide [36], stable radical [34], and benzoquinone
tostructures [32-34, 37-39]. A review of the literature has revealed that benzoquinone or
carbonyl structures may be major chromophoric contributors in mechanical pulp and kraft
lignins.

**Chromophoric structures:**

- Coniferaldehyde
  - Peak: ~340 nm
  - Wavelength: 420-460 nm

- p-Quinone
  - Peak: ~500-580 nm

- O-Quinone
  - Peak: ~310 nm

- p-Quinone Methide
  - Peak: ~400 nm

- O-Quinone Methide
  - Peak: ~478 nm

**Leuocromophoric structures:**

- Hydroquinone
  - Peak: ~330 nm

- Catechol
  - Peak: ~330 nm

- p-Hydroxy benzoic alcohol
  - Peak: ~330 nm

- Dihydroxy stilbene
  - Peak: ~330 nm

**Figure 8.** Lignin derived chromophoric and leuocromophoric structures (and associated absorbances) [31, 40, 41].

- Furman and Lonsky have identified phenolic-quinone charge-transfer complexes
  as major contributors to the color of kraft lignin [32, 34, 37]. Charge-transfer complexes
  are weak associations between electron donating (i.e., phenolic π-system) and accepting
  (i.e., quinone π-system) structures that can be highly colored [42, 43]. Local chemical
  environment and steric effects have an important influence on the charge-transfer com-
  plex absorption spectrum.
When Kraft lignin was amended with quinone model compounds or periodate oxidized (benzoquinone structures introduced) a charge-transfer absorption band was observed [37]. Acetylation or sodium borohydride reduction of Kraft lignin reduced the charge-transfer complex absorption band [37]. Acetylation derivatizes both phenolic (donor) and ortho-quinone (acceptor) structures [44, 45]. Sodium borohydride treatment reduces carbonyl (quinone) structures. Similarly, a model charge-transfer complex was prepared from 4-methylphenol and 3,5-di-tert-butyl-1,2-benzoquinone and the intensity of the charge-transfer absorption band was reduced after acetylation [37]. Sodium borohydride reduction of the Kraft lignin resulted in a 40% reduction of visible region absorption; two-thirds of the absorption decrease was attributed to removal of charge-transfer complexes [37]. Acetylation is also known to have a brightening effect on mechanical pulp, which is thought to arise from the removal of lignin ortho-benzoquinone structures [44].

Catechol structures are known to form colored metal chelates with transition metals [30, 32, 33]. The absorption spectra of ferric complexes of phenols and catechols generally have an absorption maximum centered around 500 nm [33]. Metal removal from Kraft lignin by EDTA treatment followed by electrodialysis was found to have little influence on the visible absorption spectrum [32, 34]. For bleached chemical pulps, the contribution of metal complexes to the absorption spectra is expected to be small.

Extended conjugated systems may be expected to contribute to the absorption spectrum of Kraft lignin. Hydrogenation of the carbon-carbon bonds in lignin was accomplished by diimide [32]. Interestingly, diimide hydrogenation resulted in a large decrease in the UV absorbance but no decrease in the visible region absorbance was detected [32]. Stilbene or hydroxy-stilbene structures were thought to be removed by the hydrogenation [32]. Conversely, for mechanical pulp, studies have suggested that less than 10% of the carbonyl fraction may account for much of the visible region absorption [29, 30]. The small carbonyl fraction is thought to be resistant to oxidative and reductive bleaching and may be conjugated [29, 30].

Quinone structures have been detected in milled-wood [33], mechanical pulp [46-51], Kraft lignin [52], and during residual lignin [53] and model compound bleaching.
studies [54-59]. Ortho- and para-benzoquinone structures in pulp have an absorption maximum at approximately 540 nm [33, 46] and 440 nm, respectively, [46] and these structures are often cited as chromophoric structures in lignin. Although the quinonoid structures are present at a low level (~0.7%) in milled-wood lignin, they may account for as much as 35-60% of absorption at 457 nm [33]. Quinone structures are formed during various bleaching reactions [1, 54, 60-62]. As a result of bleaching reactions, the benzoquinone structures may become conjugated, incorporated into polymeric structures [54, 63], or converted to hydroxy-quinone structures [33, 46, 64]. Studies have suggested that the modified quinone chromophoric structures are resistant towards further degradation [33, 38, 54, 60, 63, 65].

2.3. Kubelka-Munk Equation

The Kubelka-Munk equation (Equation 1) is a commonly used relationship describing the interaction of light with paper (a strong light-scattering material) [66]. The theory assumes diffuse illumination of the medium and that all light in the medium can be described by upward and downward fluxes. Also, the theory assumes that scattering centers are uniformly distributed throughout the medium. The theory has limitations, such as not directly accounting for the effect of fluorescence [67].

Brightness (B) is a measurement of the diffuse reflectance of visible blue light (λ = 457 nm region) from an "infinitely" thick paper sheet [68]. The bleaching reactions chemically reduce the quantity of chromophoric structures so that the resulting paper reflects more light. The Kubelka-Munk equation describes brightness of a sheet as a relationship between absorption and reflectance:

\[
\frac{B}{100} = 1 + \frac{k}{s} - \sqrt{\frac{2}{\pi} \left( \frac{k}{s} + \frac{2}{\pi} \right) ^2}
\]

(Equation 1)

\[ B = \text{brightness (}), B_{\text{ref}}/100 = R, \]
\[ k = \text{absorption coefficient} \]
\[ s = \text{scattering coefficient} \]
Generally, the bleaching sequences have little influence upon the scattering coefficient (s), which is a function of the fiber dimensions and interfiber bonding [68, 69]. Therefore, the absorption coefficient (k) is assumed to be proportional to the chromophore concentration (Equation 2). Figure 9 illustrates the relationship between sheet brightness value and chromophore removal. Notice that the change in chromophore concentration is not proportional to the change in brightness. Brightness increases rapidly as the last chromophoric remnants are removed.

\[
\frac{k}{s} = \left( \frac{q}{s} \right) c
\]

(Equation 2)

\( q \) = proportionality constant

\( c \) = chromophore concentration

Figure 9. Relationship between chromophore removal and brightness.

2.4. Brightness Ceiling

A brightness ceiling is the maximum brightness achievable in a given bleaching stage after which further application of a bleaching agent does not lead to an increase in brightness. Brightness ceilings have been observed during the bleaching of milled wood lignin (hydrogen peroxide [38]) and kraft pulps (elemental chlorine [70] and chlorine dioxide [7, 71-74]). The concept of pulp bleachable ability is closely related to that of the brightness ceil-
ing. Bleachability is the ease with which residual lignin can be removed from a pulp at a given kappa number [72, 73]. Bleachability is related to the chemical nature of the residual lignin in the fiber after pulping [72, 73].

Brightness ceiling development during elemental chlorine bleaching has been hypothesized to be due to the presence of oxidized lignin fragments [70]. These oxidized fragments or "blocking groups" may prevent further oxidative bleaching [70]. Extraction of the pulp with alkali "reactivates" the lignin toward the oxidative bleaching agent. Alternatively, steric constraints or diffusion limitations may contribute to the brightness ceiling. Pugliese and McDonough have proposed that the rapid elemental chlorine bleaching phase is followed by a slow phase because of cell wall structural changes brought about during bleaching [75]. These cell wall structural changes may cause a portion of the remaining lignin to be inaccessible to further bleaching [75].

Brightness ceiling development during ECF bleaching has been noted [7, 72-74]. EMCC® pulps can be bleached to a higher brightness ceiling than conventional kraft pulps produced at the same kappa number (Figure 11A, D₀(EO)₄D₂ED₂ sequence) [72, 73, 76]. Pulps produced at a lower unbleached kappa number can be bleached to a higher brightness ceiling (Figure 11B) [72, 73, 76]. Furthermore, brightness ceiling development during D₂ stage bleaching (of a D₀(EO)₄D₂ED₂ sequence) is dependent upon D₀ stage brightness (Figure 10) [72, 73, 76]. Senior et al. showed that the brightness ceiling of a DEDP sequence is greater than that of a DEPD sequence [7, 74]. The higher brightness ceiling of the DEDP (vs. DEPD) sequence may suggest that a portion of benzoquinone or carbonyl chromophores survive the DEP sequence only to be removed at the hydrogen peroxide stage [7, 74]. ECF bleaching studies suggest that the brightness ceiling and bleachability may all be dependent upon the residual lignin structural features.

Brightness ceiling development has been observed during homogeneous solution alkaline hydrogen peroxide bleaching of milled wood lignin [38]. Bleaching in homogeneous solution minimized physical inaccessibility of the lignin as a factor in brightness ceiling development [38]. The brightness ceiling was assigned to the presence of hydrogen peroxide resistant carbonyl chromophoric structures.
Figure 10. D$_1$ brightness ceiling is dependent upon D$_1$ stage brightness (conventional cook softwood, kappa number 28) [72].

Figure 11. A) Higher brightness ceiling observed for EMCC™ vs. conventional kraft softwood bleaching. B) Decreasing unbleached kappa number increases the brightness ceiling [72].

Observed brightness ceilings may be influenced by the multiple bleaching reaction pathways involving chromophore removal, chromophore formation, and unproductive degradative reactions. The relative importance of the individual reaction pathways are influenced by the structure of residual lignin. Potentially, a number of lignin structural features may influence brightness ceiling development: lignin–carbohydrate bonds, phenolic hydroxyl groups, carbonyl groups, condensed aromatic structures or ether linkages. Brightness ceiling development is a complex issue and residual lignin structural features may play an important role.
The observed brightness ceiling differences may also be related to the presence of chromophores. Table 2 contains data from recent brightness ceiling studies involving conventional and EMCC⁸ (extended modified kraft) pulps [73]. The relative concentration of chromophoric units was calculated at various stages of the bleaching process by using Equation 1, Equation 2, and their associated assumptions. Note that observed bleaching ceiling differences, between pulps of the same nominal kappa number, may be caused by significant chromophore content differences (Table 2).

### Table 2. Calculated chromophore contents for various pulps bleached to brightness ceilings.

<table>
<thead>
<tr>
<th>Brightness (%)</th>
<th>Chromophore content (Arbitrary units)</th>
<th>Pulp type and bleaching sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>6.43</td>
<td>CK28</td>
</tr>
<tr>
<td>76</td>
<td>5.79</td>
<td>MK29</td>
</tr>
<tr>
<td>72</td>
<td>5.44</td>
<td>CK19</td>
</tr>
<tr>
<td>81</td>
<td>2.23</td>
<td>MK19</td>
</tr>
<tr>
<td>87</td>
<td>0.97</td>
<td>CK28</td>
</tr>
<tr>
<td>88</td>
<td>0.82</td>
<td>MK29</td>
</tr>
<tr>
<td>87</td>
<td>0.97</td>
<td>CK19</td>
</tr>
<tr>
<td>89</td>
<td>0.68</td>
<td>MK19</td>
</tr>
</tbody>
</table>

1 Relative chromophore concentration calculated from the Kubelka-Munk equation (Equation 1, Equation 2, and constant as assumed).
2 CK = conventional kraft, MK = EMCC, CK# and MK# where # is the kappa number, data is taken from reference [73], Table 13, D, charge 0.8%.

### 2.5. Bleaching Chemistry

The bleaching stages investigated during this study involved chlorine dioxide (D), alkaline extraction (E), oxygen delignification (O), and peracetic acid (Pa). The alkaline extraction stage also included reinforcement with oxygen (E+O), peroxide (E+P), or oxygen...
and peroxide (E+O+P). Below, the major bleaching reactions will be reviewed with special reference to reactions with chromophoric structures.

2.5.1. Chlorine Dioxide

Chlorine dioxide (ClO₂) is a free radical electrophilic bleaching agent [1, 2]. Selected reactions of ClO₂ in aqueous solution are given in Equations 3–5. Chlorine dioxide gains five electrons upon reduction to chloride (whereas elemental chlorine gains two electrons). During delignification, ClO₂ is reduced to chlorous acid (HClO₂) and hypochlorous acid (HClO). Hypochlorous acid is in equilibrium with elemental chlorine (Cl₂) and both of these species can oxidize lignin. Hypochlorous acid and elemental chlorine are responsible for the formation of chlorine–substituted organic products during delignification [58]. During laboratory bleaching studies, chlorous acid salts (i.e. NaClO₂) may be added to ensure any Cl₂ present is converted to ClO₂. The reaction of chlorite (ClO₂⁻) with HClO (Equation 5) represents a loss of oxidative power of the ClO₂ solution because the product chlorate is an inactive bleaching species.

\[
\begin{align*}
\text{ClO}_2 + 2\text{H}_2\text{O} + 5e^- & \rightarrow \text{Cl}^- + 4\text{OH}^- \quad \text{(Equation 3)} \\
2\text{HClO}_2 + \text{HClO} & \rightarrow 2\text{ClO}_2 + 2\text{H}_2\text{O} + \text{H}^+ + \text{Cl}^- \quad \text{(Equation 4)} \\
\text{HClO} + \text{ClO}_2^- & \rightarrow \text{ClO}_3^- + \text{H}^+ + \text{Cl}^- \quad \text{(Equation 5)}
\end{align*}
\]

During delignification, ClO₂ preferentially attacks positions C1, C3, and C5 (Figure 1) of the lignin guaiacyl unit and the β-carbon of ring conjugated structures [1]. The reactions of ClO₂ with phenolic lignin structures are illustrated in Figure 12 [2, 3, 58]. Chlorine dioxide initially reacts with phenolic structures by hydrogen radical abstraction to give a phenoxy radical (I, Figure 12). The phenoxy radical is stabilized by delocalization of the electron in the π-orbital system. In model compound studies, a portion of the phenoxy radicals dimerize yielding biphenyl compounds, preferentially coupled at the C5 position (IV) [42, 77, 78].
Figure 12. Reactions of chlorine dioxide with phenolic structures [78-80].

The predominant reactions that occur between phenoxy radicals (I–III, Figure 12) and ClO₂ are the formation of chlorous acid ester intermediates [56, 78]. Chlorous acid esters subsequently decompose into muconic acid monomethyl ester (V), ortho–benzoquinone (VI), and para–benzoquinone (VII) products. Brage et al. noted that the muconic acid monomethyl ester (V) exists in equilibrium with its lactone form [78].

Model compound studies suggest that demethylation of chlorous acid ester VIII (Figure 12) leads to the formation of an ortho–benzoquinone structure (VI) [2, 56, 58, 78]. Ortho–benzoquinone (VI) formation is thought to be a major reaction pathway. The predominance of the reaction is suggested by the considerable amount of methanol
formed during the reaction of ClO₂ with model compounds [58] and found in chlorine dioxide stage bleaching effluents [81].

The formation of ortho-benzoquinone structures during the bleaching of lignin is significant because of their chromophoric properties. Vilén et al. found chlorine dioxide degradation of 4-methylcatechol gave mainly chlorinated cyclopentanone carboxylic acid as a product that likely formed from the action of hypochlorous acid on a para-benzoquinone product [82]. Qualitatively, others have suggested chlorine dioxide degradation of phenolic structures leads to low yield of benzoquinone products [56], but the low yield can possibly be accounted for by the instability of monomeric benzoquinones.

Similar to chlorine dioxide, elemental chlorine is known to rapidly oxidize cresol to chlorinated ortho-benzoquinones in very high yield (>90%) [83]. The red color of chlorine bleached pulp has been attributed to the presence of lignin ortho-benzoquinone structures [70]. Berry and Fleming suggested that chloro-ortho-benzoquinones and chlorouroconic acids may be partially responsible for the brightness ceiling observed during elemental chlorine bleaching of pulp because of their resistance to further oxidation [70]. Other studies, have also reported ortho-benzoquinone compounds are relatively stable toward elemental chlorine bleaching [70, 83, 84].

Few studies have attempted to qualitatively evaluate the stability of quinone structures toward chlorine dioxide. Further degradation of ortho-benzoquinone (VI, Figure 12) by ClO₂ can potentially occur from electrophilic attack on the ring carbon-carbon double bonds [2]. Although in practice, ClO₂ treatment of 4-methyl-ortho-benzoquinone did not yield the expected muconic acid degradation product [78]. Similarly, Dence et al. qualitatively reported that para-benzoquinone structures are stable toward chlorine dioxide oxidation [57].

Höigne and Bader studied the kinetics of chlorine dioxide degradation of a variety of compounds and 4-methylphenol was found to degrade 10⁶ times as rapidly as para-benzoquinone [85]. Brage et al. found that the predominant reaction of 4-methyl-1,2-benzoquinone during ClO₂ treatment was self dimerization and condensation reactions that occur in the absence of oxidant [78]. Marmor studied the reactivity of 1,4-
naphthoquinones and 2,5-diphenyl-1,4-benzoquinone with hypochlorous acid and chlorinated quinones were the major products of the reaction [86].

Additional chlorous acid ester degradation pathways can lead to the formation of muconic acid derivatives (V) and para-benzoquinone structures (VII) (Figure 12). The para-benzoquinone product is reported to form when an α-hydroxy group is present as a para (C6) substituent [58]. A muconic acid structure (V and cyclized lactone form [78]) may arise from the ortho-quinol chlorous ester via heterolytic fragmentation of the ring. An oxirane (IX) has also been noted as a product after the chlorine dioxide treatment of phenolic compounds [78, 87].

Nonphenolic structures react with ClO₂ at slower rate than phenolic structures [58, 62, 88, 89]. From model compound studies it was found that, when both phenolic (4-hydroxy-3-methoxybenzyl alcohol) and non-phenolic (3,4-dimethoxybenzyl alcohol) model compounds were reacted together with ClO₂, the phenolic substrate reacts preferentially [58]. Figure 13 illustrates typical reactions of non-phenolic structures with ClO₂. Initially, radical cation structures (X-XIII) are formed by the reaction of ClO₂ with non-phenolic structures [1, 2, 89]. Addition of ClO₂ to radical cation X results in the formation of para-benzoquinone (XIV), muconic acid diester (XV), and α-carbonyl structures (XVI and XVII) after hydrolysis of the chlorous acid ester intermediate (Figure 13).

Ring conjugated structures are reactive with ClO₂ and can give a variety of products. One reaction pathway involves attack of ClO₂ on the carbon-carbon double bond to give an initial oxirane intermediate (Figure 14) [2, 62]. Under acidic conditions hydrolysis of the oxirane gives a diol. A second reaction pathway involves attack of hypochlorous acid on a carbon-carbon double bond to give a chlorohydrin product. Subsequently, the chlorohydrin is oxidized by ClO₂ to give an α-chloroketone (Figure 14). The reactions of ring conjugated structures with ClO₂ are important because chromophoric conferylaldehyde and stilbene structures (Figure 8) are eliminated, although other chromophoric structures such as ring conjugated carbonyl structures may be formed (Figure 14) [80].

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Figure 13. Reactions of chlorine dioxide with non-phenolic structures [2].

2.5.2. Alkaline Extraction

The primary function of the alkaline extraction stage is to solubilize the oxidized lignin fragments by conversion to ionized forms: carboxylate, phenolate, and enolate anions [2]. Hydroxide is a strong base and nucleophile which can react with chlorine substituted structures. Figure 15 shows the degradation of a chlorohydrin under alkaline conditions. Chloride is eliminated from the chlorohydrin via an intermediate oxirane to give a glycol.
Figure 14. Reactions of chlorine dioxide with ring conjugated structures [62].

Figure 15. Reactions of organochlorine compounds with hydroxide [62].

product. Chlorinated ortho-benzquinone structures may also react with hydroxide to eliminate chloride and give a resonance stabilized hydroxy-benzquinone structure (Figure 15) [62]. For kraft pulps it is estimated that 60–70% of the organically bound chlorine in the pulp is removed during alkaline extraction [2].

Nucleophilic addition of hydroxide may also take place on nonchlorinated structures [62]. The reaction of quinone structures with hydroxide is illustrated in Figure 16. Ortho-benzquinone structures may rearrange to an α-hydroxy-carboxylic acid cyclopentadiene structure via a benzylic acid type of rearrangement [62]. Also, hydroxide may add to quinone structures via nucleophilic addition to give hydroxy-substituted products (Figure 16). Hydroxy-benzquinone structures have been shown to be resistant
to hydrogen peroxide bleaching [46]. Hydroxy-benzoquinone structures are produced during the alkali-induced darkening of mechanical [46] and chemical pulps. Alkali-induced darkening also occurs with ozone bleached kraft pulp, but the resulting chromophores have not been identified [90].

Monomeric benzoquinone compounds are known to be unstable in alkaline solution. The quinones polymerize readily leading to dimers and higher condensed structures [77, 91]. Simmons et al. studied the self-condensation reactions of 4-methyl-1,2-benzoquinone over the pH range of 2–11 [91]. The rate of condensation was approximately 1000 times greater at pH 11 versus 2 [91] and series of oligomers were formed.

A general reaction for the anionic polymerization [92] of a para-benzoquinone is illustrated in Figure 17. The condensation reaction involves initial addition of hydroxide to the quinone ring. Carbon–carbon formation occurs via a Michael addition of carbanion XIX on the initial structure (XVIII). The polyphenolic dimer may be subsequently oxidized (Figure 17). Alternatively, quinones may form semiquinone radicals in alkaline solution which subsequently couple giving complex polymeric products [45].

2.5.3. Oxygen and Hydrogen Peroxide

Oxygen is a diradical electrophilic bleaching agent. During the bleaching process oxygen undergoes a number of one-electron reactions which involve the formation of superoxide
radical anion (O$_2^-$), hydroperoxide anion (HOO$^-$), and hydroxyl radical (HO$^-$)\cite{2,93}. Figure 18 illustrates the species formed during the reduction of oxygen. Also, transition metals ions, if present, can mediate in the formation of hydroxyl radicals.

\[
\begin{align*}
O_2 & \xrightarrow{\text{H}^+} \text{HOO}^- & \text{H}^+ + \text{O}^- & \text{HOO}^- + \text{H}^+ & \text{HO}^+ + \text{H}^+ & \text{O}^- + \text{H}^+ & 2\text{H}_2\text{O} \\
pK_a & 4.8 & 10.5 & 11.3 & 13.3 & \text{H}^+ + \text{O}^- & \text{H}^+ + \text{O}^- & \text{H}^+ + \text{O}^-
\end{align*}
\]

Figure 18. Species produced during the reduction of oxygen\cite{2}.

The main reactive structure towards oxygen bleaching is thought to be free phenolic groups. Pulp demethylation, via sodium ethanethiolate reaction, has been shown to increase the reactivity of the lignin to oxygen delignification\cite{94}. Also, the reactivity of model lignin phenolic compounds with oxygen under alkaline conditions has been dem-
ontrated [59, 95]. Interestingly, residual lignin analysis after oxygen delignification has demonstrated that less than 50% of the phenolic structures are eliminated [96]. Lai et al. hypothesized that diphenylmethane structures are resistant to the oxygen bleaching [96]. Model compound studies using diphenylmethane dimers have revealed that reactivity to oxygen is dependent on the aromatic substitution pattern [97]. Jiang and Argyropoulos reported that C5 and C6 condensed phenolics survive oxygen delignification reaction [23].

Figure 19 illustrates the many reactions possible between alkaline oxygen and phenolic structures. The initial step of oxygen bleaching is believed to involve the formation of a phenoxy radical via an electron transfer from phenolate anion to molecular oxygen with the formation of superoxide radical anion [2, 93]. Conjugated structures may also be an initial substrate for oxygen attack. Phenoxy radical formation is thought to be the rate limiting step of the sequence [93].

The resonance forms of the phenoxy radical can react with superoxide radical anion or molecular oxygen to give a hydroperoxide anion intermediate. Intramolecular attack of the hydroperoxide anion on a carbon–carbon double bond or carbonyl carbon can give a diol or a tetradecane (four-membered cyclic peroxide) structure [2, 93]. Rearrangement of the diol intermediates may give an oxirane, muconic acid derivatives, or α-carbonyl product [93].

Under alkaline conditions, superoxide radical anion is in equilibrium with hydrogen peroxide, hydroperoxide anion, hydroxyl radicals and other species as shown in Figure 18 [93]. Nucleophilic addition of hydroperoxide anion to carbonyl or conjugated carbonyl carbon can occur. Chromophoric ortho- and para-benzoquinone structures are degraded to muconic acid and carboxylic acid fragments by the nucleophilic addition of hydroperoxide anion [2, 18, 93, 98, 99] (Figure 20).

Hydroxyl radical is the strongest one electron oxidant in aqueous solution [93]. Hydroxyl radical is electrophilic and preferentially attacks aromatic and carbon–carbon double bonds but, also attacks aliphatic structures. Attack of hydroxyl radical on an aromatic ring gives a hydroxycyclohexadienyl radical which may undergo a number of reactions including: phenolic coupling and demethoxylation to give an ortho-
Dienoquinone structures. Non-phenolic substrates may undergo Cα-Cβ cleavage with formation of an α-carbonyl product [93].

Figure 19. Reaction of oxygen with phenolic structures [93].
2.5.4. Peracetic Acid

The delignifying and brightening effects of peracetic acid have been known since the 1950s. Recently, mill-scale trials results have been reported for the use of distilled peracetic acid [100, 101]. Peracetic acid has often been explored for its strong brightening ability; particularly in the later stages of TCF bleaching [102]. Simultaneous use of peracetic acid and chlorine dioxide has been reported to give increase brightness and lower the active chlorine charge required [100]. Percoids have been used as an activation stage prior to oxygen delignification or between oxygen stages. Industrially, peracetic acid is usually used either after oxygen delignification or in the brightening stages of a sequence [103].

Industrially, peracetic acid is prepared by the distillation of "equilibrium" peracetic acid [103]. Industrial distilled peracetic acid generally contains < 4% acetic acid, < 2% hydrogen peroxide, and ~ 38% peracetic acid [103]. The equilibrium peracetic acid contains ~ 25% acetic acid, ~ 5% hydrogen peroxide, and ~ 38% peracetic acid [103]. Distillation is beneficial for two reasons. Firstly, unreacted acetic acid, sulfuric acid catalyst and hydrogen peroxide may be recycled to lower the overall cost of the bleaching chemical. Secondly, the reduction in the content of acetic acid reduces the requirement for pH adjustment.
McDonough and Rapson [104] reported that peracetic acid under alkaline conditions degrades phenolic structures to a plethora of acid products. The reaction proceeds by electrophilic attack of peracetic acid on the phenolate, demethylation, and finally nucleophilic attack of peracetate on the ortho–benzoquinone intermediate (Figure 21). Additionally, alkaline peracetic acid may cause lignin side-chain oxidation, Baeyer–Villiger rearrangement to an aromatic ester, hydrolysis, and degradation to acid products [105].

![Figure 21. Peracetic acid (Pa) oxidation of creosol [104].](image)

### 2.6. Quinone Chemistry

#### 2.6.1. Quinone Synthesis

Benzoquinones can be synthesized either by oxidation of analogous catechol and hydroquinone compounds or by introduction of oxygen into aromatic substrates. Enzymatic oxidation has been used as a mild preparation of both ortho– and para–benzoquinone. For example, air oxidation of phenolic compounds can be accomplished under neutral conditions using tyrosinase [106]. In addition to bleaching agents previously discussed, dimethyldioxarane is also known to oxidize phenolic substrates to benzoquinone products [107]. In this study quinone synthesis was accomplished using the following reagents: periodic acid, Fremy's reagent, silver oxide and phenylglycin (III) diacetate.

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Ortho–benzoquinone structures may be formed by the oxidation of guaiacyl–lignin structures by periodic acid [108]. The mechanism of periodic oxidation involves nucleophilic attack of water on a periodate ester to give a hemiacetal then the ortho–quinone (Figure 22) [109]. Periodic acid also cleaves vicinal diols to give carbonyl products (Figure 23) [110, 111]. Oxidation of lignin by periodic acid should enrich the carbonyl content, [108] along with the ortho–benzoquinone content.

![Figure 22. Periodate oxidation of a guaiacyl structure [109].](image)

![Figure 23. Cleavage of vicinal diols by periodic acid [110, 111].](image)

Phenolic compounds can be oxidized to both ortho- and para–benzoquinones by the Teuber reaction which uses potassium nitrosodisulfonate (Fremy’s reagent) [109, 112-114]. The presence of a substituent on the aromatic ring para to the phenolic hydroxyl directs the oxidation towards the ortho–benzoquinone product [114]. When the para position is unsubstituted, oxidation may lead to the para–benzoquinone. Figure 24
Figure 24. Mechanism of phenolic compound oxidation by Freyny's reagent [109].

illustrates the reaction of a guaiacyl structure with Freyny's reagent leading to an ortho-
benzoquinone product. The reaction mechanism involves initial formation of a phenoxy
radical by proton abstraction with one equivalent of Freyny's reagent.

Freyny's reagent can also be used for the synthesis of para-benzoquinones from
phenolics containing substituents in the para position (Figure 25) [108, 114, 115]. The
reaction is thought to involve attack of Freyny's radical at the para position of the phe-
noxy radical substrate leading to a cyclic intermediate and the para-benzoquinone prod-
uct. Also, biphenolic compounds have been reported to be oxidized to the di-para-
benzoquinone product by Freyny's reagent (Figure 25) [108].

Figure 25. Additional reactions involving Freyny's reagent [108].
2.6.2. Diels–Alder Cycloaddition

Both ortho- and para–benzoquinones dimerization by the Diels–Alder reaction (2π + 4π cycloaddition) [116]. Figure 26 illustrates the cycloaddition product of the self dimerization of 3-methoxy–1,2-benzoquinone. One equivalent of benzoquinone can act as a diene and another equivalent can act as the dienophile. A variety of products including heterocyclic adducts can be formed [116]. Benzoquinones can also be used as precursors of anthraquinone derivatives by reaction with substituted dienes [117].

![Figure 26](image)

Figure 26. One possible Diels–Alder product from the self dimerization of 3-methoxy–1,2-benzoquinone [116].

2.6.3. Methods of Quinone Determination

Although lignin–quinones are widely acknowledged to be important chromophores, until recently few reliable methodologies were available for the quantitative analysis of these structures in lignocellulosic materials [118]. Visible absorption spectroscopy is not directly effective for lignin–quinone quantification because of the broad featureless nature of lignin absorption spectra [119]. Classical colorimetry–based [118] and hydrazine oxidation [118] methods of quinone measurement are difficult to apply. Ortho–phenylenediamine derivatization and fluorescence spectroscopy has been used for the determination of ortho–benzoquinone structures in mechanical pulps [120, 121]. Unfortunately, the technique is not applicable for the analysis of important para–benzoquinone structures.
Recently, $^{19}$F–NMR–based spectroscopic techniques have been developed for the analysis of quinone structures in isolated lignins. 4-Trifluoromethylphenylhydrazine derivatization and $^{19}$F–NMR spectroscopy have been applied for quinone analysis on a range of isolated lignins [122, 123]. Alternatively, Argyropoulos et al. reported that Ruppert's reagent can be used for trifluoromethylation of carbonyl structures in lignin [124, 125]. Although Argyropoulos et al. [124, 125] claimed high yield for the derivatization of two quinone model compounds, other reports have indicated that the derivatization yield is variable [126]. Also, model compound studies have revealed overlap between para-benzoquinone and aldehyde trifluoromethyl derivatives [125].

The ability of trimethylphosphite to form adducts with carbonyl groups has been developed into a technique to allow for the specific determination of ortho-benzoquinone structures [47-51, 127, 128]. Lebo et al. were first in applying trimethylphosphite derivatization, phosphorus microanalysis, and 31P–NMR spectroscopy for ortho–benzoquinone quantification during a mechanical pulp photoyellowing study [47, 49]. Similarly, Konya and Scalaio employed a trialkylphosphite–based derivatization procedure to detect ortho–benzoquinones by fluorescence spectroscopy [129].

Based on the studies by Lebo et al. [47, 49], Argyropoulos et al. employed solid-state 31P–NMR spectroscopy and trimethylphosphite derivatization to qualitatively monitor ortho–benzoquinone levels in a range of mechanical pulps [50]. Lignin-derived ortho–benzoquinone structures were monitored as cyclic phosphate esters at δ 12 ppm. Argyropoulos et al. reported that carbonylic acids may form 1:1 (uncharacterized) adducts with trimethylphosphite, also giving a 31P–NMR signal in the δ 12 ppm region [51, 128, 130]. The carboxylic acid group interference was thought to be eliminated by ensuring that acid groups were in the sodium salt form [51, 128]. Figure 27A illustrates solid-state 31P–NMR spectra of trimethylphosphite treated mechanical pulp, suggesting that the presence of carboxylic acid groups in pulp can cause an overestimation of the ortho–benzoquinone content.

The solid-state trimethylphosphite 31P–NMR technique has been used to follow chromophore formation during the light induced yellowing of mechanical pulp [48, 50]. Upon exposure of mechanical pulp to light ortho–benzoquinone structures are initially

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formed. Subsequently, α,β-unsaturated carbonyl structures are thought to be formed, as indicated by the increase in the downfield signals in the δ 20 to 40 ppm region (Figure 27B, and Figure 27C) [50]. The introduction of ortho–benzoquinone structures via Fremy’s salt oxidation was also monitored by the technique (Figure 27B). Furthermore, the destruction of both ortho–benzoquinone and α,β-unsaturated carbonyl structures by alkaline hydrogen peroxide bleaching is illustrated in Figure 27B.

3. **Dissertation Objectives**

Initially, the major purpose of this study was to understand the chemistry of brightness ceiling development during ECF bleaching of kraft pulps. The objective was to be achieved by bleaching a series of pulps to full market brightness and then extracting the residual lignin. Lignin structural features were then to be determined by standard NMR spectroscopic techniques and possibly new methods to be developed.
The majority of the visible light absorption coefficient of pulp is thought to arise from lignin. Therefore, bleachability and brightness ceiling differences between pulps may possibly arise from the lignin component. Studies by McDonough have suggested that structural features of lignin may play an important role in brightness development. The anticipated result of the study was that observed brightness ceiling values may correlate with residual lignin structural features as determined by standard analytical techniques.

During a preliminary study, residual lignin was isolated from a fully bleached (O/E/O+P)D industrial softwood kraft pulp. The lignin isolation was found to be difficult and required a large amount of pulp (~1 kg) and extraction solvent. More importantly, analytical studies revealed that the lignin was contaminated with process additives from the pulp. Additionally, recent studies were beginning to reveal that structural differences between lignins isolated from bleached pulps are minor and difficult to detect by standard analytical techniques [3, 131]. As a result of the difficulty of lignin isolation and likely limited use of current analytical methods, the objective of this dissertation was altered to focus on the development of a new analytical tool that could be used to quantify important chromophoric substructures in lignins.

A review of the literature reveals that lignin–quinone substructures have often been cited as important contributors to the color of lignocellulosic materials. Previously, model compound studies have suggested that these lignin substructures may figure pre-dominantly in the chemistry of industrially important ECF pulp bleaching processes, particularly chlorine dioxide and oxidative alkaline extraction. Unfortunately, the practical significance of these structure toward brightness development during pulp bleaching cannot be known a priori from model compound studies.

The new objective of this study was to develop a quantitative analytical methodology for the determination of quinone structures in isolated lignins. Furthermore, the goal was to use the analytical method to monitor the introduction and removal of lignin–quinone structures during chlorine dioxide bleaching, oxidative alkaline extraction, and oxygen delignification. Specifically, the study investigated the correlation of lignin–quinone contents with pulp brightness development. The practical context of this study
was to contribute to an understanding of how to optimize the brightness response of modern ECF bleaching sequences, by gaining fundamental knowledge about the chemistry of lignin–quinone structures.

The four primary objectives of this research were as follows:

1) Develop a quantitative analytical method for the determination of quinone structures in isolated lignins.

2) Verify the developed method by studying model compounds and chemically modified lignin.

3) Determine the lignin–quinone contents of a series of DE*DED and PaO bleached softwood kraft pulps.

4) Correlate the presence of lignin–quinone structures with experimentally determined brightness values.

4. Thesis Format

The Results and Discussion section of this thesis is composed of four articles that have been published and presented in a variety of forums. Supporting documentation and additional research results are located in the Appendices of this thesis. The four publications comprising the main body of this dissertation are entitled:


4) Quantitative Determination of Quinone Chromophores in Isolated Lignins, submitted to Industrial Engineering and Chemical Research.

Publication one describes the development and application of trimethylphosphite derivatization for the analysis of ortho- and para-benzoquinone structures in residual lignins. Specifically, a series of residual lignins were isolated from DE*D (E* = oxidative
alkaline extraction) pulps. This paper describes the first report of a practical technique for the quantitative determination of benzoquinone structures in isolated lignins. Also, the paper discusses lignin—quinone introduction and removal in light of known chlorine dioxide and oxidative alkaline extraction chemistry.

An addendum for publication one extends lignin—quinone analysis to DE* effluent lignins collected during the bleaching study. Quinone contents of both effluent and residual lignins were similar in value suggesting that quinone structures in the lignin macromolecule are relatively resistant toward chemical degradation. The addendum continues with an analysis of lignin—quinone derivatization kinetics and the influence of the derivatization solvent. Finally, the requirements for quantitative NMR spectroscopic acquisition are discussed.

Publication two describes application of the technique toward the analysis of chemically modified residual lignins and two benzoquinone model compounds. The purpose of this study was to verify the specificity of trimethylphosphite derivatization. Chemically modified lignins likely containing a wide range of potential lignin–quinone contents were studied. In particular, a Fremy's reagent oxidized lignin was studied because of the well-known ability of Fremy's reagent to produce lignin–quinone structures. A dithionite reduced chlorine dioxide residual lignin was also studied because such a lignin was expected to contain minimal lignin–quinone content.

Publication three focused on the application of trimethylphosphite derivatization toward the analysis of residual lignins isolated from DE*DED pulps, in particular D1 stage lignins. A good correlation between the content of benzoquinone structures and the brightness at the corresponding stage was found. Additionally, the content of benzoquinone structures was found to correlate well with the final achievable brightness ceiling value for the pulp suggesting that benzoquinone structures may contribute to brightness ceiling development.

Publication four documents a fundamental study of trimethylphosphite derivatization chemistry. The derivatization technique was used on a series of synthesized ortho- and para-benzoquinone compounds including a polymeric ortho-benzoquinone compound. Model compound derivatization yield was monitored and in many cases was
found to be high. Cases of less than complete derivatization were attributed to thermal instability of the model compounds.

Major degradation products of the reagent, trimethylphosphite, were identified. The chemistry of trimethylphosphite degradation was discussed along with the interferences observed, specific procedures for the removal of degradation products, and NMR parameters necessary to minimize their influence.

Potential side reactions of trimethylphosphite with non-benzoquinone lignin functional groups were explored. Secondary lignin–trimethylphosphite reactions were interpreted and found not to interfere with lignin–quinone analysis. An addendum for publication four further explored additional secondary lignin–trimethylphosphite reactions.

The last chapter of the Results and Discussion section documents a study of lignin treated in homogeneous solution with a series of chlorine dioxide charges. The lignin–quinone formation trends were similar to those observed during pulp bleaching. Additionally, lignin–quinone introduction displayed a logarithmic profile very similar to that of a pulp brightness development curve. A series of residual lignins isolated from both high and low kappa pulp treated with peracetic acid and oxygen were studied. The quinone contents of these lignins were uniformly low. A $^{31}$P–NMR technique was modified from the literature and used to verify the quinone contents determined by trimethylphosphite derivatization and $^{31}$P–NMR spectroscopy.
5. Experimental

5.1. Chemicals

Chemicals and reagents used for this study were purchased at analytical grade. Unless otherwise noted, chemicals were used without further purification. For routine use, dioxane was purified by distillation from sodium borohydride (NaBH₄). Deionized water was used in all procedures which required water. Both diethylether and chloroform were supplied with 1% ethanol as a stabilizer and were used as received.

5.1.1. Synthesis and Purification of Quinone Compounds

3-Methoxy-1,2-benzoquinone was prepared by silver oxide oxidation [132] of 3-methoxy-catechol (Lancaster Synthesis Incorporated). Catechol (2.01 g), 13 g of MgSO₄, and 11 g of AgO were combined in 150 mL diethyl ether, stirred for 1.5 minutes, and then filtered into a round bottom flask. The volume of the solution was reduced by using a rotary evaporator (without a water bath) until dark red needles formed and the product was collected by filtration, washed with cold pentane, and stored in the freezer. The material was dried overnight, under slight vacuum, over P₂O₅. The recovered yield was 325 mg (16.8%).

4-Methyl-1,2-benzoquinone was prepared by silver oxide oxidation [132] of 4-methyl-catechol (2.45 g, Lancaster Synthesis Incorporated, 98%, beige powder) using 15 g of MgSO₄ and 11 g of AgO in 150 mL diethyl ether. The mixture was stirred for 1.5 minutes and then filtered into a round bottom flask. The volume of the solution was reduced to approximately 75 mL by using a rotary evaporator (no water bath). Red needles formed as the solvent volume was reduced and the flask cooled. Pentane, 40 mL, was added to the flask and the solution volume was reduced to approximately 30 mL by a rotary evaporator (without a water bath). Then the product was collected by filtration and washed with cold pentane. The material was dried overnight, under slight vacuum, over
P₂O₅. Note, the ortho–quinone was found to sublime and decompose when dried under high vacuum. The recovered yield was 1.26 g (53.2%).

4–tert–Butyl–1,2–benzoquinone was prepared by silver oxide oxidation [132] of 4–tert–butyl–catechol (3.93 g, Lancaster Synthesis Incorporated, beige/brown powder) using 15 g of MgSO₄ and 10 g of AgO in 150 mL diethyl ether. The mixture was stirred for 2 minutes and then filtered into a round bottom flask. Pentane, 200 mL, was added to the flask and the flask was transferred to the freezer (−20°C). Fire brown/purple needles were formed after cooling. The volume of the solution was reduced by a rotary evaporator (without a water bath) to give a large crop of crystals. The collected crystals were washed with cold pentane and dried under vacuum, over P₂O₅, for 8 hours. The recovered yield was 2.02 g (53.5%).

2–Methoxy–1,4–benzoquinone was prepared by phenylidione (III) diacetate oxidation of 2–methoxyhydroquinone (Lancaster Synthesis Incorporated) using a procedure similar to Takada and others [115, 133]. 2–Methoxyhydroquinone (2.10 g) was dissolved in 150 mL chloroform and 10 g of phenylidione (III) diacetate was added. The solution was stirred for 30 minutes and then the solvent volume was reduced to 30 mL by using a rotary evaporator with a water bath temperature of 40°C. The solution was cooled (−20°C) overnight and yellow crystals formed. The material was recrystallized from 5 mL acetone, collected by filtration and dried under vacuum, over P₂O₅, for 8 hours. The recovered yield was 385 mg (19.0%).

2–tert–Butyl–1,4–benzoquinone was prepared by silver oxide oxidation [132] of 2–tert–butyl–hydroquinone (Acros). Hydroquinone (1.92 g), 15 g of MgSO₄ and 13 g of AgO were combined in 150 mL diethyl ether. The mixture was stirred for 2 minutes and then filtered into a round bottom flask. The volume of the solution was reduced to 5 mL by using a rotary evaporator (without a water bath). The fine golden yellow crystals were collected by filtration, recrystallized from pentane, and dried under vacuum, over P₂O₅, for 8 hours. The recovered yield was 601 mg (32.6%).

Poly(4–vinylphenol) was oxidized with Fremy's reagent [112, 113] to give a polymer containing ortho–quinone structures. Approximately 2 g of poly(4–vinylphenol) (MW ~22,000, Polysciences Incorporated) was dissolved, with stirring, in 100 mL diox-
ane. Water, 50 mL (pH = 11), and 2 g potassium nitrosodisulfonate (Fremy’s reagent) were added. A few drops of 1.0 N sodium hydroxide solution were added to the reaction and the resulting solution was stirred vigorously for 30 minutes under an argon atmosphere. The reaction was terminated by adding 50 mL 1.0N HCl. Then 300 mL of water was added, with agitation, to precipitate the polymer. The solution was filtered and the solid was taken up in methanol. Methanol was removed under vacuum to give a brown/red solid (373 mg).

Additional quinone compounds were purchased and used as received:
- 3,5-di-tert-Butyl-1,2-benzoquinone (Aldrich Chemical Company)
- 2,6-Dimethoxy-1,4-benzoquinone (Lancaster Synthesis Incorporated)
- 2,5-Dihydroxy-1,4-benzoquinone (Lancaster Synthesis Incorporated)
- 2,3,5,6-Tetrahydroxy-1,4-benzoquinone (Sigma Chemical Company)
- 1,4-Benzooquinone (Aldrich Chemical Company)

5.1.2. Ultraviolet and Visible Spectroscopy

The visible absorbance spectra of selected quinone compounds were measured in 90% (v/v) dioxane/water and DMF. Spectra were acquired in a quartz cuvette at room temperature. The spectra were acquired using either a Perkin–Elmer Lambda 900 spectrometer or a Shimadzu UV160 ultraviolet/visible spectrometer. The Perkin–Elmer spectrometer was controlled by Perkin–Elmer UV Winlab, version 2.9, software operating under Windows–95.

5.2. Pulp Source

A series of residual lignins isolated from chlorine dioxide bleached and oxidative alkaline extracted pulps were prepared and characterized by Runge [131]. The pulping and bleaching conditions used during the preparation of those pulps was previous described
For this investigation, the residual lignins donated by Runge were analyzed for ortho- and para-quinone contents and the results are discussed in publications one through three (see Thesis Format section). Additional residual lignins isolated by Froass [25, 134] (chlorine dioxide bleached pulps) and Moe [135] (peracetic acid/oxygen delignified pulps) were analyzed in publication four (see Thesis Format section).

A series of peracetic acid/oxygen delignified pulps were prepared during this study. An industrial source of wood chips was used, and the major wood species was Douglas Fir (Pseudotsuga menziesii). The chips were classified and the chip distribution data is given in Appendix 3. The wood chips were cooked in a laboratory digester and used to prepare three separate Kraft pulps. The cooking parameters and resulting pulp kappa numbers are listed in Appendix 3.

5.3. Safety

Chlorine dioxide decomposes, with a minor pressure pulse, into elemental chlorine and oxygen at a partial pressure above 100 mm Hg [136]. Above a partial pressure of 300 mm Hg ClO₂ decomposes explosively [136]. Chlorine dioxide can be safely stored in the dark as an aqueous solution provided no headspace exists above the solution. The solubility of chlorine dioxide in water is ~10 g/L [136].

Dioxane is a highly flammable solvent. A considerable amount of this solvent was used for the extraction of lignin from pulp samples. Dioxane is listed as a possible human carcinogen [137]. Although the acute toxicity of dioxane is low, repeated exposure may cause liver and kidney injury [137]. Proper protective clothing and manipulations in the fume hood were employed when this solvent was used.

Arylphosphates are known to cause paralytic action in many mammals [138]. The toxic influence is both species and compound specific. For example, tri-ortho-tolylphosphate, is reported to be very potent in causing paralysis in hens [138]. Triphenylphosphate and tri-meta-tolylphosphate are reported to be considerably less toxic than tri-ortho-tolylphosphate. Trimethylphosphite was also used in this
investigation and the compound is volatile, a suspected cancer causing agent, and dis-
plays an unpleasant odor. Samples containing any organic phosphates or phosphites were
assumed to be toxic, handled with caution, and disposed of in properly labeled containers.

All other chemicals and equipment were handled in accordance with MSDS in-
formation, the IPST safety manual, the IPST Chemical Hygiene Plan, Bleaching group
and Ragauskas' group safety policies.

5.4. Bleaching Methods

5.4.1. Peracetic Acid Treatment

Pulps were treated with a 4% charge of distilled peracetic acid at 6% consistency in
sealed polyethylene bags. Pulps were not chelated before peracetic acid treatment.
Peracetic acid preparation and analysis is described in Appendix 3. The pH of the
medium was adjusted to 8 with 1.0N NaOH solution. The pulp was treated at 70°C for
one hour and the final pH was ~5. After treatment, pulps were thickened by dewatering
using a Büchner funnel and not washed before oxygen delignification.

5.4.2. Oxygen Delignification and Bleaching Sequence Nomenclature

A series of oxygen delignified (O) pulps was prepared from the peracetic acid pretreated
pulps. In a modified M&K digester, the following basic oxygen delignification conditions
were used: ~100 g pulp, 5.5% consistency, final pH >10.5, 75 psig oxygen, and 60-
minute reaction. Specific details of the peracetic acid/oxygen delignification experiments
and bleaching sequence abbreviations are given in Table 3. After oxygen delignification,
pulps were immediately washed with 50°C deionized water, dewatered, fluffed and stored
at 5°C until needed. Effluents were collected and the exit pH was noted.
5.4.3. Pulp Analysis

Pulps were characterized by micro-kappa (tenth scale) number (TAPPI 236 om–85), cupriethylenediamine viscosity (TAPPI 230 om–94), and brightness (TAPPI 205 sp–95).

5.4.4. Bleaching Isolated Lignins

Chlorine dioxide bleaching of isolated residual lignin was performed similar to the procedure developed by Froass [25]. A solution containing 20 mg lignin/mL dioxane/water (90:10 v/v) was prepared. The lignin used in the investigation was isolated by the acidic dioxane/water procedure from a softwood, conventional kraft, brownstock kappa number 28 pulp (Appendix 3).

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Bleaching conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS(47)</td>
<td>brownstock, kappa = 47</td>
</tr>
<tr>
<td>BS(47)O*</td>
<td>oxygen delig.: 2.3% alkali charge, 90°C</td>
</tr>
<tr>
<td>BS(47)O*</td>
<td>oxygen delig.: 4.2% alkali charge, 105°C</td>
</tr>
<tr>
<td>BS(47)PaO</td>
<td>peracetic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C</td>
</tr>
<tr>
<td>BS(47)PaO*</td>
<td>peracetic acid: 4% charge, oxygen delig.: 4.2% alkali charge, 105°C</td>
</tr>
<tr>
<td>BS(47)OO</td>
<td>double oxygen delig.: 2.3% alkali charge, 90°C each stage</td>
</tr>
<tr>
<td>BS(47)OPaO</td>
<td>oxygen delig.: 2.3% alkali charge, 90°C, peracetic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C</td>
</tr>
<tr>
<td>BS(24)</td>
<td>brownstock, kappa = 24</td>
</tr>
<tr>
<td>BS(24)O</td>
<td>oxygen delig.: 1.3% alkali charge, 90°C</td>
</tr>
<tr>
<td>BS(24)O*</td>
<td>oxygen delig.: 2.2% alkali charge, 105°C</td>
</tr>
<tr>
<td>BS(24)PaO</td>
<td>peracetic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 90°C</td>
</tr>
<tr>
<td>BS(24)PaO*</td>
<td>peracetic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 105°C</td>
</tr>
</tbody>
</table>

* for additional conditions see experimental text, * = aggressive conditions.

A quantity of the lignin/dioxane/water solution was mixed with 100 mL dioxane/water (90:10 v/v). Then the resulting solution was treated with the desired ClO₂.
charge (Equation 6, Note: Froass [25] used \( g \text{ ClO}_2 \) = kappa factor (g lignin) / 0.394) corresponding to a kappa factor range of 0.004 to 2.0. After 30 minutes a 1.0 mL aliquot of solution was titrated for residual chlorine dioxide and the reaction was terminated by removing chlorine dioxide under vacuum. At the end of the reaction the solution pH was approximately 2.4. An additional 100 mL water was added to the solution and dioxide was removed by using a rotary evaporator with a water bath temperature of 45°C. The volume of the solution was reduced to approximately 80 mL. Then the solution was transferred to a centrifuge bottle, frozen, freeze-dried and used for further analysis.

Sodium hydrosulfite (dithionite) was used as a reducing agent to eliminate quinone structures in an isolated lignin sample. Reduction conditions were selected to ensure that aldehyde and ketone carbonyl groups were nonreactive [139]. A 100 mg sample of residual lignin \( (D_m \text{ KF} = 0.2, [131]) \) was dissolved in 50 mL of 0.1 N NaOH containing 100 mg sodium dithionite. The solution was stirred for 12 hours in the dark, at room temperature, under argon. The reduced lignin was recovered by: acid precipitation at pH = 2.0, sample freezing, thawing, centrifugation, and then decanting. The recovered lignin was freeze-dried and used for analysis.

\[
\text{kappa factor} = \frac{\% \text{ equivalent chlorine}}{\text{kappa number}} = 100 \left( \frac{g \text{ ClO}_2}{g \text{ pulp}} \right) \left( \frac{2.63}{0.0015 \frac{g}{g}} \right) = 0.395 \frac{g \text{ ClO}_2}{g \text{ lignin}} \Rightarrow g \text{ ClO}_2 = \text{kappa factor (g lignin)} / 0.395
\]

(Equation 6)

5.4.5. Chemical Modification of Isolated Lignins

Sodium periodate was used to introduce ortho–quinone structures into a residual lignin sample (softwood brownstock, conventional kraft, kappa = 28, Appendix 3). The procedure used was a slight modification of ones previously reported [140, 141]. A 517 mg sample of lignin dissolved in 25 mL 90% (v/v) dioxane/water was added to 670 mg so-
dium periodate dissolved in 10 mL water and the solution was stirred in the dark, at room temperature. After 30 minutes, 100 mL water was added and dioxane solvent was removed by using a rotary evaporator with a water bath temperature of 45°C. The treated lignin was recovered by: acid precipitation at pH = 2.0, sample freezing, thawing, centrifugation, and then decanting. The recovered lignin was freeze-dried and used for analysis.

Fremy's reagent (potassium nitrosodisulfonate) was used to introduce ortho-quinone structures into a residual lignin sample (softwood brownstock, conventional kraft, kappa = 30.5, [131]). Brownstock residual lignin was oxidized using a procedure modified from the literature [113]. Residual lignin (100 mg) was dissolved in 15 mL of 50% (v/v) 1,4-dioxane/water adjusted to pH = 8.0 with 0.1 N sodium hydroxide. To the solution was added 450 mg of Fremy's reagent (Aldrich Chemical Company). The resulting mixture was stirred vigorously under an argon atmosphere for 1.5 hours. Excess Fremy's reagent in the reaction mixture was decomposed by adding 5 mL of 1.0 N HCl. The 1,4-dioxane solvent was removed from the reaction mixture by vacuum evaporation at a temperature of 45°C. The modified lignin was recovered by: sample freezing, thawing, and then centrifugation. The recovered lignin was washed once with water (pH = 2.0), freeze-dried and used for analysis.

5.5. Lignin Analysis
5.5.1. Residual Lignin Isolation

Residual lignin was extracted from the pulp samples by a mild acidic-dioxane isolation method [8, 26, 142, 143]. Prior to lignin isolation, pulps were Soxhlet extracted for 24 hours with acetone, washed with water and air-dried. A 10% consistency solution of pulp and solvent (90% dioxane and 10% 0.1M HCl) was refluxed under an argon atmosphere for 2 hours. The pulp solution was cooled, filtered, and the pH was adjusted to 6 with saturated aqueous sodium bicarbonate. The solution was then filtered through a layer of Celite™ and the resulting cake was washed with several portions of dioxane to elute entrained lignin.

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The dioxane solvent was removed under reduced pressure using a rotary evaporator (45°C). The solution was diluted with water and trace dioxane was removed with a rotary evaporator (35°C). The resulting aqueous lignin solution was transferred to centrifuge bottles and acidified (to pH = 2.5 with 36% HCl) to precipitate the lignin. Then, this mixture was taken through three cycles of a freeze–thaw–centrifuge–decant sequence to purify the isolated lignin. Briefly, the cycle involves freezing the aqueous lignin sample (-20°C), slow thawing, centrifugation, decanting and washing the solid with water. Between each cycle the pH of the solution was adjusted to 2.5. After freeze drying, the lignin sample was used for further analysis. The average yield of residual lignins relative to pulp kappa was found to be 47.8% and individual values are listed in Table 4.

<table>
<thead>
<tr>
<th>Bleaching sequence *</th>
<th>Yield (%)</th>
</tr>
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<tr>
<td>BS(24)</td>
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</tr>
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<td>BS(24)O</td>
<td>47.54</td>
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<td>BS(24)O*</td>
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<td>44.69</td>
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<tr>
<td>BS(47)O</td>
<td>47.31</td>
</tr>
<tr>
<td>BS(47)O*</td>
<td>44.08</td>
</tr>
<tr>
<td>BS(47)PaO</td>
<td>44.71</td>
</tr>
<tr>
<td>BS(47)PaO*</td>
<td>54.39</td>
</tr>
<tr>
<td>BS(47)OO</td>
<td>53.14</td>
</tr>
<tr>
<td>BS(47)OPaO</td>
<td>57.38</td>
</tr>
</tbody>
</table>

* bleaching sequence nomenclature see Table 3.

5.5.2. NMR Spectroscopy

NMR spectroscopic techniques were used to elucidate the structural features of isolated residual lignins: ¹H-, ¹³C-, ¹⁹F-, and ³¹P-NMR. All NMR spectra were recorded on IPST's Bruker 400 MHz DMX NMR spectrometer. The spectrometer was controlled by
Xwinmr 2.1 (Bruker Instruments Incorporated) software running on a Silicon Graphics Indigo server using the Irix 7.0 operating system. A review of $^1$H-, $^{13}$C-, and $^{31}$P-NMR spectroscopy for lignin analysis is given in Appendix 1. The procedures followed for $^1$H-, $^{13}$C-, and $^{31}$P-NMR (hydroxyl group) lignin analyses are given in Appendix 2.

For new NMR methods, pulse calibration was performed both manually and using the Xwinmr PAROPT utility. Spin–lattice (T1) relaxation parameters were determined by using the inverse–recovery pulse sequence [144]. NMR data analysis was performed with either Windows–95 based NUTS–NMR Utility Transform Software (Acorn NMR Incorporated) or Xwinmr 2.1 (Bruker Analytik GmbH) software. Simulation of NMR spectra was accomplished with ACD Labs (ACD Incorporated) Windows–95 based software.

5.5.3. Fluorine(19)–NMR

Carbonyl functional groups in lignin were determined by using a modification of the $^{19}$F–NMR procedure developed by Sevillano et al. [145]. Approximately 60 mg of lignin was dissolved in 500 $\mu$L DMF, then 1 mL of 50% DMF/water (v/v) containing 110 mg 4–trifluoromethylphenylhydrazine (Aldrich Chemical Company, recrystallized from pentane) was added. The mixture was kept at room temperature, in the dark, for 12 hours. The derivatized lignin was precipitated by the addition of ~20 mL of water (pH = 2.0 adjusted with 36% HCl). The aqueous layer was discarded and the lignin was freeze–dried. The resulting lignin was Soxhlet extracted with dichloromethane for 2 hours, then dried under vacuum over P$_2$O$_5$.

Approximately 25 mg of derivatized lignin was dissolved in 450 $\mu$L DMSO–d$_6$, containing 3–trifluoromethoxybenzonic acid (0.5 mg/mL, δ -57.19 ppm, Lancaster Synthesis Incorporated) as an internal standard. Quantitative NMR parameters used were: 90° pulse without proton decoupling, 10–second pulse delay, and approximately 400 acquisition transients. Chemical shifts were adjusted to CCl$_4$ (δ 0.00 ppm) used as an external standard. Integration was accomplished by lineshape analysis using NUTS–NMR Transform Utility Software (Acorn NMR Incorporated).
5.5.4. Phosphorus(31)–NMR

5.5.4.1. Ortho– and Para–Quinone Content

A procedure was developed to measure the combined ortho– and para–quinone contents of isolated lignins. Dry residual lignin (30 mg) was derivatized with 250 µL trimethylphosphite and 250 µL anhydrous DMF under an argon atmosphere at room temperature for 2 days. Lignin samples were previously dried under vacuum at 40°C for 24 hours. NMR grade trimethylphosphite (Aldrich Chemical Company) was either used from a freshly opened bottle or purified by distillation from solution containing sodium metal.

Derivatized lignin samples were prepared for analysis by removing excess trimethylphosphite under vacuum at 40°C for 3 hours. The treated lignins were dissolved in 450 µL of solvent consisting of 60% DMSO–d₆/pyridine (v/v) containing tri–meta–tolylphosphate (0.7 mg/mL) and chromium–acetylacetone (0.9 mg/mL). Derivatized lignin–quinone structures were hydrolyzed to the open–chain phosphate ester by the addition of 5 µL water (0.3 mmol per 30 mg lignin). After 12 hours, the ³¹P–NMR spectrum of the resulting solution was acquired with a Bruker 400 MHz NMR spectrometer.

Phosphorus–NMR spectra were acquired under quantitative conditions at 305°K. A 90° pulse was utilized with a 5–second pulse delay along with inverse–gated broadband proton decoupling. A line–broadening factor of 5 Hz was used and the time domain (TD) size was 64K. For each spectrum ~1500 scans were collected. The internal standard tri–m–tolylphosphate (δ -16.3 ppm) was used both for quantification and as a shift reference. The ³¹P–NMR chemical shift of tri–meta–tolylphosphate in DMSO–d₆ was determined with the aid of 85% H₃PO₄ as an external shift reference. Previously, the chemical shift of tri–meta–tolylphosphate was reported as δ -17.3 ppm (CDCl₃ solvent) [146]. Quantification of lignin–quinone content was achieved by integrating the areas of the internal standard, δ -15.3 to -17.1 ppm, and the phosphate–ester (quinone adduct) resonance at δ -0.3 to -6.0 ppm (Figure 28).
A $^{31}$P–$^1$H heterocorrelation experiment was performed using the COLOC (Correlation via Long–Range Couplings) pulse sequence [144]. The following acquisition parameters were used: selected $^{31}$P–$^1$H coupling constant ($J_{31P,1H}$) of 11.0 Hz, $^1$H sweep width of 16.92 ppm, center of $^1$H channel at 6.18 ppm, $^{31}$P sweep width of 29.91 ppm, center of $^{31}$P channel at -9.89 ppm, Waltz–16 $^1$H decoupling, 1.0 second pulse delay, 160 scans acquired, 16 dummy scans, and 64 experiments.

5.5.5. NMR Repeatability Study

Calculated functional group contents of replicate lignin samples were used to determine a least significant difference (LSD, Equation 7) value. The calculated LSD value was then used to determine if differences in the measured functional group values were statistically significant. The trimethylphosphite/$^{31}$P–NMR method for quinone analysis was repeated in triplicate on a D$_6$ residual lignin (KF = 0.2) to give an average quinone content of 0.302 mmol/g lignin, standard deviation of 0.004, and LSD of 0.02.

\[
LSD = 2(T)(SD)
\]

(Equation 7)

$T =$ Student's $t$ value at a % confidence interval and degrees of freedom

$SD =$ standard deviation

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6. Results and Discussion


Abstract

The chromophoric properties of a series of residual lignins were studied in order to understand brightness development during pulp bleaching. This study focused upon lignins isolated from kraft softwood brownstock, chlorine dioxide delignified brownstock, and a series of oxidative alkaline extracted pulps. The chromophoric properties of the isolated lignins were assessed by both visible absorbance and 31P–NMR spectroscopy. A 31P–NMR spectroscopic method was employed for the quantification of the combined ortho– and para–quinone content in the isolated lignins. The 31P–NMR method, modified from the literature, utilized the derivatization of lignin quinone structures by trimethylphosphite. The results suggest that chromophores, such as ortho– and para–quinones, may be important contributors to brightness ceiling development during chemical pulp bleaching.
Introduction
A number of structures have been implicated as chromophores in mechanical and chemical pulps, including: catechol–metal complexes [29, 33, 147, 148], coniferaldehyde [33, 35, 147], quinone methides [147], stable radicals [147] and quinones [32, 33, 37, 38, 141, 147, 148]. Of the various possible chromophores, quinones have been suggested to be major contributors to the color of kraft lignin [30, 32, 37, 141]. This study employed visible absorbance spectroscopy and a \(^{31}\text{P}-\text{NMR}\)-based procedure to investigate the presence of quinone chromophores in residual lignin isolated from bleached kraft pulps. The generation of quinone structures during chlorin dioxide bleaching and their fate during oxidative alkaline extraction were explored.

Chemical Pulp Bleaching. Multistage bleaching consists of delignification and brightening stages. In the delignification bleaching stage, bulk residual lignin is degraded and removed. Chlorine dioxide (D), as a delignification agent, is replacing chlorine (C) or chlorine/chlorine dioxide (C/D) because of environmental pressures to reduce adsorbable organic halide (AOX) formation.

Contemporary bleaching sequences use alkaline extraction (E) after a chlorine dioxide (D) stage to remove oxidized lignin and increase the efficiency of a subsequent chlorine dioxide stage. The primary function of the alkaline extraction stage is thought to involve solubilization of oxidized lignin fragments by conversion of various functional groups to their ionized forms: carboxylate, phenolate, and enolate anions [2]. Oxidants, such as hydrogen peroxide (P) and oxygen (O), are often applied in the alkaline extraction stage to further assist with delignification and increase pulp brightness.

The final brightening stages are responsible for the elimination of residual chromophoric structures. The chromophoric structures may be present initially both in the pulp and/or formed during the preceding bleaching sequences. During the final brightening stages of bleaching, the residual lignin concentration is low. Therefore, during brightening, the elimination of the chromophoric structures must be highly selective or else cellulose damage will take place.
Quinone Chemistry. Lignin quinone structures are important because of their chromophoric properties and because they may be formed and destroyed concurrently during bleaching. For example, chlorine dioxide has been shown by several investigators [56, 58, 78, 79, 149-151] to react with phenolic lignin structures giving ortho- and para-quinone structures among its products. Conversely, hydroperoxide anion, generated during hydrogen peroxide bleaching, specifically removes conjugated carbonyl structures such as quinones [18, 98, 99]. Quinones may also be formed by the Dakin reaction of hydrogen peroxide with para-hydroxy carbonyl structures [54, 62].

During alkaline oxygen bleaching, hydroxyl radicals may generate lignin-hydroxycyclohexadienyl radicals which lead to quinone formation via disproportionation or demethoxylation [93]. Alternatively, given the presence of superoxide anion, the hydroxycyclohexadienyl radical may be degraded to muconic acid structures.

Lignin model compound studies have also shown ortho-quinones to be susceptible to nucleophilic attack by hydroxide anions. Ortho-quinone structures may rearrange to an α-hydroxy-carboxylic acid cyclopentadiene structure by a benzylic acid type of rearrangement [62]. Also, hydroxide may add to quinone structures by nucleophilic addition to give precursors of chromophoric hydroxy-substituted quinones [62, 64].

Materials and Methods

Chemicals. All chemicals, except 1,4-dioxane, were purchased and used as received. Before use, 1,4-dioxane was purified by distillation over sodium borohydride.

Pulp. Conventional kraft pulp was obtained from a single, 30-year-old, disease-free Loblolly pine (Pinus taeda) tree. Brownstock pulp (kappa number 30.5) was bleached in a D₈ stage under the following conditions: 2.3% chlorine dioxide charge, 10% consistency, 45°C, final pH = 2.0, and 45-minute reaction. The bleached pulp was then washed with water and characterized for kappa number, Klason lignin content, and viscosity.
Alkaline Extraction. Chlorine dioxide (D₃) delignified pulp was alkaline extracted in a stirred pressure reactor under the following general conditions: 10% consistency, 70°C, and 75-minute reaction. Table 5 summarizes the specific conditions used for the oxidative alkaline extraction study. Washed alkaline extracted pulps were characterized in terms of kappa number, Klason lignin content, and pulp viscosity.

Table 5. Alkaline extraction stage conditions.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Bleaching Conditions¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>2.0% NaOH; atmospheric pressure air.</td>
</tr>
<tr>
<td>E+O</td>
<td>2.5% NaOH; 60 psig O₂ decreased by 12 psig/5 minutes.</td>
</tr>
<tr>
<td>E+P</td>
<td>2.5% NaOH; 0.5% H₂O₂.</td>
</tr>
<tr>
<td>E+O+P</td>
<td>2.5% NaOH; 0.5% H₂O₂; 60 psig O₂ decreased by 12 psig/5 minutes.</td>
</tr>
<tr>
<td>E+Ar</td>
<td>Air removed by a freeze-thaw cycle; 2.0% NaOH; 10 psig argon.</td>
</tr>
</tbody>
</table>

¹ final pH > 10.5

Brightness Ceiling Determination. The alkaline extracted pulps were further bleached with a D₈ED₇ sequence. The D₈ stage conditions were as follows: 0.75% chlorine dioxide charge, 10% consistency, 70°C, and 3-hour reaction. E₇ stage conditions were as follows: 1.0% sodium hydroxide charge, 10% consistency, 70°C, and 60-minute reaction. Washed E₇ stage pulps were bleached in a D₈ stage. Chlorine dioxide charge in the D₈ stage was varied from 0.2% to 0.8% charge in a series of separate experiments. A small amount of sodium hydroxide (25% of chlorine dioxide charge added) was added at the D₈ stage for pH adjustment.

Isolation of Residual Lignin. Residual lignin was isolated from the pulps by a mild acidic dioxane hydrolysis procedure modified from the literature [8, 26, 142, 143]. Pulp was extracted using 90% 1,4-dioxane/0.1 N HCl (v/v) solution (8% consistency) by refluxing for 2 hours under an argon atmosphere. The extract was filtered, neutralized, and

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1,4-dioxane was removed under reduced pressure at 40°C. The resulting aqueous lignin solution was acidified (pH 2.5) to precipitate the lignin. The precipitated lignin was purified by three cycles of a freeze–thaw–centrifuge–decant sequence. The purification sequence involved freezing the aqueous lignin sample (-20°C), slow thawing, centrifugation, decanting, and washing the lignin with water. Between each cycle the pH of the solution was adjusted to 2.5. After freeze drying, the yield of residual lignin, relative to Klasson lignin, was 45–65%.

Visible Spectrum of Lignin. The visible absorbance spectra of isolated lignins were measured in 90% 1,4-dioxane/water (v/v) solvent. The visible absorbance spectra were acquired with a Shimadzu UV160U ultraviolet/visible spectrophotometer.

Pulp Characterization. The lignin contents were measured by both a kappa number test (¼ modification of TAPPI method T 236 om–85) and a modified standard Klasson lignin content test (TAPPI method T 222 om–88). The modified Klasson lignin content test used an autoclave to speed up the time required for pulp digestion. Viscosity of cupriethylenediamine (CED) dissolved pulp was measured by TAPPI method T 230 om–94. Standard TAPPI handsheets were prepared from D2 stage pulp (basis weight of 150 g/m²) and used to measure ISO brightness (TAPPI method T 205 sp–95).

Quinone Determination. Dry residual lignin (30 mg) was derivatized with 500 μL 50% trimethylphosphite/DMSO (v/v) under an argon atmosphere at room temperature for seven days. Lignin samples were previously dried under vacuum at 40°C for 24 hours.

Derivatized lignin samples were prepared for analysis by removing excess trimethylphosphite under vacuum at 40°C for 3 hours. The treated lignins were dissolved in 400 μL of solvent consisting of DMSO–d6, tri-methy–tolylphosphate (2.5 mg/mL) and chromium–acetylacetonate (1.0 mg/mL). Derivatized lignin quinone structures were hydrolyzed to the open-chain phosphate ester by the addition of 5 μL water (0.3 mmol per 30 mg lignin). After 12 hours, the 31P-NMR spectrum of the resulting solution was acquired with a Bruker 400 MHz NMR spectrometer.
Phosphorus-NMR spectra were acquired under quantitative conditions at 305°C. A 90° pulse was utilized with a 5-second pulse delay along with inverse-gated broadband proton decoupling. A line-broadening factor of 15 Hz was used and the time domain (TD) size was 64K. For each spectrum 1000 – 3000 scans were collected. The internal standard tri-meta-tolylphosphate (δ -16.3 ppm) was used both for quantification and as a shift reference. The 31P-NMR chemical shift of tri-meta-tolylphosphate in DMSO-d6 was determined with the aid of 85% H3PO4 as an external shift reference. Quantification of lignin-quinone content was achieved by integrating the areas of the internal standard and the phosphate-ester (quinone adduct) resonance centered at δ -2.5 ppm.

Chromium-acetylacetonate was used to reduce the T1 (spin-lattice) relaxation of the components of interest including the internal standard. The T1 value for the open-chain phosphate ester (quinone adduct) in trimethylphosphate treated lignin was found to be 0.7 seconds. The T1 relaxation time constant for the internal standard, tri-meta-tolylphosphate, was found to be 0.9 seconds. A standard inversion-recovery experiment [144] was used to determine the T1 parameters.

Results and Discussion

Pulp Characterization. Lignin contents of the bleached pulps were determined by both Klasson lignin and kappa number tests and are shown in Table 6. In general, a higher degree of delignification occurs with increased application of oxidant in the alkaline extraction stage. The CED viscosity data, which is an indirect measure of cellulose degradation, are also given in Table 6. The viscosity data reveals that only minor carbohydrate damage occurs during the bleaching stages. In the alkaline extraction stage, hydrogen peroxide was more selective towards lignin removal than oxygen on the basis of Δkappa per Δviscosity (using brownstock for the initial values).
Table 6. Pulp characterization data.

<table>
<thead>
<tr>
<th>Pulp Description</th>
<th>Kappa Number</th>
<th>Klason Lignin</th>
<th>CED viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstock</td>
<td>30.4</td>
<td>1.895</td>
<td>30.27</td>
</tr>
<tr>
<td>D</td>
<td>14.6</td>
<td>1.583</td>
<td>26.40</td>
</tr>
<tr>
<td>D(E+Ar)</td>
<td>7.10</td>
<td>0.768</td>
<td>25.72</td>
</tr>
<tr>
<td>DE</td>
<td>6.37</td>
<td>0.709</td>
<td>22.57</td>
</tr>
<tr>
<td>D(E+O)</td>
<td>4.17</td>
<td>0.661</td>
<td>20.10</td>
</tr>
<tr>
<td>D(E+P)</td>
<td>4.80</td>
<td>0.671</td>
<td>22.64</td>
</tr>
<tr>
<td>D(E+O+P)</td>
<td>3.33</td>
<td>0.589</td>
<td>20.38</td>
</tr>
</tbody>
</table>

Brightness Ceiling. A brightness ceiling is the maximum brightness that can be achieved in a given bleaching stage after which further application of bleaching agent does not lead to an increase in brightness. The alkaline extracted pulps were further bleached with a D₁ED₂ sequence to generate a D₂ brightness ceiling (Figure 29).

![Figure 29. D₂ Stage Brightness Ceiling Data.](image-url)
The D₂ brightness ceiling data reveals that the use of hydrogen peroxide in the alkaline extraction stage, D(E+P) and D(E+O+P), results in the highest achievable brightness ceilings. When excluding all oxygen with argon, D(E+Ar), or incorporating air, D(E), or reinforcing with pressurized oxygen, D(E+O), in the alkaline extraction stage gives similar D₃ brightness ceiling values. Figure 29 demonstrates that pulp properties altered in the first alkaline extraction stage directly impact the bleachability of the pulp. Specifically, hydrogen peroxide decreases the content of structures which have a detrimental influence on the final brightness ceiling value.

Previous chemical pulp bleaching studies have investigated parameters influencing brightness ceiling values. For example, McDonough found that brightness ceiling development during D₂ stage bleaching (of a D₃(E+O)D₄ED₅ sequence) is dependent upon D₁ stage brightness [72]. In further studies of the D₃(E+O)D₄ED₅ bleaching sequence, McDonough et al. found that at a constant kappa factor the D₂ brightness ceiling is affected by the unbleached kappa number and the effective alkali charge during pulping [152]. These results suggest that lignin structural features may influence final brightness ceiling values.

Senior et al. showed that the brightness ceiling of a DEDP sequence is greater than that of a DEPD sequence [7, 74]. Senior et al. hypothesized that the higher brightness ceiling of the DEDP sequence is due to the presence of quinone or conjugated-carbonyl chromophores which survive the DED sequence only to be removed when hydrogen peroxide stage is subsequently applied [7, 74]. Similarly, the results of this investigation suggest that hydrogen peroxide, applied in the alkaline extraction stage, removes quinone (or conjugated carbonyl) structures that would otherwise cause a lower D₃ brightness ceiling value.

Visible Spectrum. The visible absorbance difference spectra for the series of residual lignins isolated from chlorine dioxide delignified brownstock and oxidative alkaline extracted pulps were acquired (Figure 30). Difference spectra were calculated by subtracting the brownstock residual lignin absorption spectrum from the absorption spectra of the isolated lignins. Analysis of difference spectra allows for the identification of chromo-
phore changes occurring in the alkaline extraction stage relative to the unbleached brownstock.

Clearly, the absorbance difference spectra are observed to cluster into groups based upon the oxidant applied to the alkaline extraction stage. Residual lignins arising from peroxide-treated pulps displayed considerably less visible absorbance than the initial unbleached brownstock residual lignin. Note that with the exception of hydrogen peroxide bleaching, D(E+P) and D(E+O+P), all residual lignins are darker than the initial brownstock residual lignin (Figure 30).

![Figure 30. Visible Absorption Difference Spectra for a Series of Residual Lignins.](image)

Quinone structures are potential chromophoric contributors to the brightness ceiling phenomenon. The \( n-\pi^* \) transition for quinones occurs in the visible region and may contribute to the colored nature of pulps. In general, the \( n-\pi^* \) transition for para-quinones occurs in the 420–460 nm region and 500–580 nm for ortho-quinones [40]. According to Furman and Lonsky, the absorption maximum for kraft lignin quinone structures occurs at \( \sim 430 \) nm [37]. If the residual lignins are ordered in terms of absorbance at 430 nm the following series is derived: \( D(E+Ar) > D = D(E) > D(E+O) >> D(E+P) > \)
D(E+O+P). It can be noted that this order corresponds to the brightness ceiling results shown in Figure 29. The correlation between brightness ceiling values and absorption spectra at the alkaline extraction stage indicates that lignin structural features, such as quinones, may be carried through from a previous bleaching stage and directly impact the final brightness value.

Trimethylphosphite Chemistry

**Ortho—Quinone Derivatization.** Both ortho- and para-quinones are known to form adducts with trimethylphosphite [127, 153-155]. The reaction of trimethylphosphite with the ortho-quinone 3,5-di-tert-butyl-1,2-benzoquinone (I) is shown in Figure 31. Attack of the trimethylphosphite phosphorus at the carbonyl is thought to initially give a zwitterionic structure (II). Cyclization of II then leads to a benzodioxaphospholene structure (III) [127, 153, 155]. The phosphorus chemical shift value, determined in this study (δ -45.3 ppm, DMSO-d₆ solvent), for the benzodioxaphospholene is similar to previously reported values: δ -46.5 ppm (CD₂Cl₂ solvent) [127] and δ -46.9 ppm (CDCl₃ solvent) [155].

![Reaction schematic](image)

**Figure 31.** Reaction of trimethylphosphite with 3,5-di-tert-butyl-1,2-benzoquinone (³¹P-NMR chemical shifts were determined in this study).

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The benzodioxaphospholene adduct can be hydrolyzed to give a cyclic phosphate ester (IV, Figure 31) [153, 156]. The phosphorus chemical shift value determined for cyclic phosphate ester was found to be $\delta 13.6$ ppm (DMSO-$d_6$ solvent) and this value is similar to that reported by Medvecz ($\delta 13.4$ ppm, CD$_2$Cl$_2$ solvent) [127]. During the present investigation it was found that the cyclic phosphate ester (IV) is unstable and further hydrolysis leads to a structure with a chemical shift similar to the open-chain phosphate ester. The expected structure of the cyclic phosphate ester hydrolysis product is V (R=H) [157].

An open-chain phosphate ester adduct (V, Figure 31) can also result from the direct action of water on the benzodioxaphospholene adduct [127]. Two possible isomeric open-chain phosphate esters products (V, $R = \text{CH}_3$) may be formed. The phosphorus chemical shift values ($\delta -2.2$ and $-2.4$ ppm, DMSO-$d_6$ solvent) for the open-chain phosphate esters were found to be similar to a reported value of $\delta -4.0$ ppm (CD$_2$Cl$_2$ solvent) [155]. Medvecz reported a similar phosphorus chemical shift for the open-chain phosphate ester adduct of 3-methoxy-1,2-benzoquinone ($\delta -2.3$ ppm, CD$_2$Cl$_2$ solvent) [127].

Para-Quinone Derivatization. Ramirez et al. demonstrated that trimethylphosphite can form an adduct with para-quinones [153, 154]. Figure 32 illustrates the reaction of trimethylphosphite with the para-quinone 2,6-dimethoxy-1,4-benzoquinone (VI). The mechanism is thought to proceed by attack of trimethylphosphite on the carbonyl oxygen leading initially to a phosphonium-phenoxide zwitterion (VII). Rapid methyl group translocation gives the open-chain phosphate ester in high yield (VIII) [153, 154]. Two isomeric adducts may be formed depending upon which quinone carbonyl group is initially attacked. The phosphorus chemical shift value for VIII was found to be $\delta 1.4$ ppm (DMSO-$d_6$ solvent). In a related study, Medvecz reported the chemical shift values for the trimethylphosphite/2-methoxy-1,4-benzoquinone isomeric adducts as $\delta 2.6$ and $3.15$ ppm (CD$_2$Cl$_2$ solvent) [127].
**Lignin Derivatization.** Using trimethylphosphate derivatization, Lebo and others have developed a solid-state \(^{31}\text{P}\)-NMR spectroscopic method for the detection of ortho-quinones [47-51]. Lebo *et al.* [47-51] and Argyropoulos *et al.* [50, 51] both used the cyclic phosphate ester adduct (III, Figure 31) as diagnostic for the presence of ortho-quinones in trimethylphosphate derivatized mechanical pulp. For this study, the literature procedure [47-51] was modified and applied to the determination of quinone structures in isolated lignins. The modification consisted of hydrolyzing the cyclic phosphate ester, ortho-quinone adduct (III), to the open-chain phosphate ester adduct (V). Therefore, after the addition of water, the combined lignin ortho- and para-quinone content can be determined by monitoring the open-chain phosphate ester structures with phosphorus chemical shifts in the \(\delta -2.5\) ppm region.

A solution \(^{31}\text{P}\)-NMR spectrum of trimethylphosphate derivatized D_{E+Ar} residual lignin is shown in Figure 33. The internal standard, tri-meta-tolylphosphate is observed as a sharp resonance with a chemical shift of \(\delta -16.3\) ppm. The broad Gaussian resonance corresponding to open-chain phosphate esters, arising from derivatized quinone structures, is observed with a peak centered at \(\delta -2.5\) ppm. Resonances downfield from the open-chain phosphate ester correspond to trimethylphosphate (\(\delta 3.5\) ppm, verified with pure material) and an expected series of phosphate esters arising from trimethylphosphate hydrolysis [158, 159].

**Lignin Quinone Content.** The combined ortho- and para-quinone content data (after subtraction of the softwood brownstock residual lignin quinone content) for the D_{E} and
alkaline extraction stage residual lignins is given in Figure 34. The brownstock residual lignin quinone content value, 1.6 quinones per 100 C₆, determined in this study was similar to literature values for softwood kraft lignin: 3 quinones per 100 C₆ (via reductive acetylation) [37] and 3 – 4 quinones per 100 C₆ (via visible absorbance) [52]. The ³¹P–NMR derived quinone content data (Figure 34) was found to cluster into groups in a manner similar to the visible difference absorbance data (Figure 30). The lowest quinone contents were observed when the alkaline extraction stage was reinforced with hydrogen peroxide, D(E+P) and D(E+O+P) (Figure 34), and this corresponds to the highest achievable brightness ceilings (Figure 29).

**Figure 33.** Phosphorus–NMR spectrum of D(E+Ar) residual lignin treated by trimethylphosphite.

**Chlorine Dioxide Stage.** The application of chlorine dioxide (D₃) was found to cause a dramatic increase in the quinone content relative to the brownstock residual lignin value (Figure 34). The D₃ residual lignin contained 0.135 mmol/g lignin (2.5 quinones per 100 C₆) more quinone structures than the brownstock residual lignin. These results are consistent with literature accounts which indicate that both phenolic and non-phenolic
lignin structures can react with chlorine dioxide to give ortho- and para-quinones [56, 58, 78, 79, 149-151]. The $^{31}$P-NMR derived quinone content data is also consistent with the visible absorption difference spectra which demonstrates that D$_b$ residual lignin is darker than brownstock residual lignin. Chlorine dioxide is an effective delignification agent (Table 6), but the residual lignin is darker than the unbleached brownstock residual lignin.

**Alkali Effect in the Alkaline Extraction Stage.** The influence of alkali on quinone chromophores was studied by performing the alkaline extraction under an argon atmosphere, D(E+Ar). Application of alkali resulted in the destruction of 55% of the quinone content introduced at the D$_b$ stage (Figure 34). Clearly, the influence of alkali is not merely lignin solubilization, but also involves the destruction of quinone chromophores.

![Figure 34. Residual lignin-quinone content data after subtraction of brownstock residual lignin-quinone content value.](image)

The visible absorbance difference spectra (Figure 30) reveal that the D(E+Ar) residual lignin is the darkest ($\lambda = 430$ nm) of all the studied lignins. According to the $^{31}$P-
NMR analysis (Figure 34), the D₆ stage residual lignin contains the highest quinone content and would be expected to have the greatest visible region absorbance (λ = 430 nm). One possible explanation for the apparent discrepancy between the ²³P-NMR and visible absorbance data may be that a portion of the quinone structures in the D(E+Ar) residual lignin are hydroxy substituted. Mechanical pulp [46] and model compound [64] studies have both suggested that hydroxy-quinone structures may contribute to the "alkali-darkening" phenomena. The action of alkali on quinone precursors may give rise to polyphenolic structures, which may be subsequently oxidized to hydroxy-quinones. Clearly, this and other alkali-based reactions that may generate chromophoric structures need to be investigated.

Table 7 gives spectral data, acquired in this study, for a number para-quinone models with various degrees of hydroxylation. The hydroxyl auxochrome causes a bathochromic shift and intensifies the π→π* transition in the quinone chromophore [40]. Furthermore, visible absorbance spectra were acquired in aqueous dioxane solution and ionization effects also intensify the molar absorptivity of hydroxy-substituted quinones [40, 64]. Table 7 shows that increased hydroxyl substitution results in greater visible region (λ = 430 nm) molar absorptivity. In particular, the spectrum of tetrahydroxy-1,4-benzoquinone was found to be characterized by a broad intense absorption throughout much of the visible region. Therefore, the data in Table 7 combined with both visible absorbance difference spectra (Figure 30) and ²³P-NMR analysis (Figure 34) suggests that although alkali is effective at removing lignin-quinone structures, a portion of the remaining quinones may be hydroxy-substituted and display enhanced chromophoric properties.

<table>
<thead>
<tr>
<th>Quinone</th>
<th>log ε₅₀₀ nm</th>
<th>log ε₄₃₀ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-benzoquinone</td>
<td>0.56</td>
<td>1.35</td>
</tr>
<tr>
<td>2,5-dihydroxy-1,4-benzoquinone</td>
<td>1.35</td>
<td>2.33</td>
</tr>
<tr>
<td>tetrahydroxy-1,4-benzoquinone</td>
<td>2.14</td>
<td>2.04</td>
</tr>
</tbody>
</table>

*90% 1,4-dioxane/10% water (v/v) solvent

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Oxygen Effect in the Alkaline Extraction Stage. Interestingly, incorporating air in the alkaline extraction stage, D(E), results in a greater quinone content than if only alkali is applied, D(E+Ar) (Figure 34). The higher quinone content of D(E) relative to D(E+Ar) can tentatively be assigned to the contribution of quinone formation during alkaline oxygen bleaching [93]. Table 6 reveals that a major benefit of incorporating air in the alkaline extraction stage is greater delignification relative to the effect of alkali alone.

When alkaline extraction is reinforced with pressurized oxygen, D(E+O), 81% of the quinone content introduced at the D₉ stage is removed (Figure 34). The D(E+O) residual lignin contains 0.026 mmol/g lignin (0.48 quinones per 100 C₆) more quinone structures than the brownstock residual lignin. The application of pressurized oxygen, D(E+O), versus air, D(E), suggests that the mechanism of quinone removal by oxygen is dependant on the oxygen concentration (pressure). The general mechanism of oxygen bleaching is known to be influenced by the concentration of oxygen [93, 160].

Peroxide Effect in the Alkaline Extraction Stage. The dramatic influence of hydrogen peroxide on quinone destruction is observed in Figure 34. Application of hydrogen peroxide in the alkaline extraction stage, D(E+P), results in the removal of more quinone structures than were introduced at the D₉ stage. The result in Figure 34 is consistent with the known reactivity of hydroperoxide anion towards conjugated carbonyl structures [62, 98, 99]. Although application of both hydrogen peroxide and pressurized oxygen in the alkaline extraction stage, D(E+O+P), gives a higher quinone content than hydrogen peroxide alone, D(E+P), greater delignification is a benefit of the concurrent application of both hydrogen peroxide and pressurized oxygen (Table 6).

Conclusions
The presence of chromophores such as ortho- and para-quinones may be important contributors to brightness ceiling development during chemical pulp bleaching. This investigation further suggests that brightness ceiling values may be dependent upon the chromophore content established in earlier bleaching stages. Although quinones are only one of a number of potential chromophoric structures in kraft lignin, analyzing residual lignin qui-
none contents may be useful for understanding the origin of bleachability differences between chemical pulps.

The utility of trimethylphosphite derivatization for investigating quinone chromophores in isolated kraft lignins was demonstrated for the first time. The results of this investigation are consistent with many of the suspected reactions of quinone structures in lignin. For example, the ability of chlorine dioxide to introduce lignin quinone structures and hydrogen peroxide to remove these was clearly observed. Further work is in progress applying $^{31}$P-NMR spectroscopy towards understanding the introduction and removal of quinone chromophores in multistage bleaching sequences.

Acknowledgments

The authors wish to thank Drs. McDonough, Dimmel, and Lucia for guidance. Financial support from the Institute of Paper Science and Technology (IPST) and its member companies is gracefully acknowledged. Portions of this work were used by M. Z. and T. R. as partial fulfillment of the requirements for the Ph.D. degree at IPST.

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Quinone contents of DE* effluent lignins were measured by the $^{31}$P-NMR and trimethylphosphophosphate method (Figure 35). The effluent lignins correspond to the alkaline extraction stage pulps as studied in publication number one (see also [131]). Analogous to the trend of quinone contents in DE* residual lignins (Figure 34), effluent lignin–quinone contents (Figure 35) were found to decrease with greater amount of oxidant applied in the alkaline extraction stage. Surprisingly, effluent lignin–quinone contents were very similar in value to those measured for the analogous residual lignins (Figure 35 and Appendix 4).

**Figure 35.** Quinone contents of DE* effluent lignins.

In the alkaline extraction stage, effluent lignin is present in homogeneous solution and should be more efficiently degraded than residual (pulp-bound) lignin. The similarity in effluent and residual lignin quinone content values may suggest that quinone structures present in residual and effluent lignins are somewhat resistant to chemical degradation. Certainly, small monomeric quinones are known to be very unstable in alkaline solution.
and undergo Diels–Alder dimerization, semiquinone formation/radical coupling, and hydroxylation reactions [91, 161, 162]. Possibly, the stability of both effluent and residual lignin–quinones may be explained by their existence in a hydroxy–substituted form. Hydroxy–substituted quinones are suspected to be formed during "alkali–darkening" reactions [62, 64, 163] and are thought to be resistant toward peroxide bleaching [46, 64]. Alternatively, the effluent lignins were reported to display relatively high molecular weights (average MWw ~ 6500 [131, 164]), and lignin–quinones may gain protection from dimerization and chemical attack due their low concentration in the low mobility lignin macromolecule.

6.2.2. Kinetics of Lignin Trimethylphosphite Derivatization

During this investigation, the kinetics of lignin–quinone trimethylphosphite adduct formation was studied on a D3 stage residual lignin (KF = 0.2, publication one). In a series of experiments, dimethylsulfoxide was used as the lignin solvent and derivatization was performed in homogeneous solution using excess trimethylphosphite. Figure 36 displays the measured dimethylphosphate (lignin–quinone) adduct content versus treatment time. Clearly, the measured quinone–adduct content reached a plateau near 7 days (168 hours) of treatment. After 24 and 54 hours of treatment the measured quinone contents were 81.5% and 87.5%, respectively, of the value achievable after 337 hours treatment. Therefore, nearly quantitative derivatization can be achieved after a 2–day trimethylphosphite treatment. Although a 2–day trimethylphosphite treatment should yield acceptable results, isolated lignins studied for publications 1–3 were treated for 7 days.

Ogata and Yamashita measured the kinetics of the reaction between benzil (an α–diketone) and trimethylphosphite in a variety of polar and non–polar solvents. Trimethylphosphite reacts with α–diketone structures to give products and intermediates analogous to the reaction with ortho–benzoquinones. Ogata and Yamashita found that the derivatization rate increased with solvent dielectric constant. Polar solvents, such as acetonitrile and methanol, gave the greatest reaction rates [165]. Interestingly, the
Figure 36. Quinone–trimethylphosphite formation versus treatment time for chlorine dioxide residual lignin using methanol and dimethylsulfoxide solvent systems.

reaction rate in methanol solvent was very large, 23.1 times the rate in benzene [165]. They postulated that this large increase in reaction rate was due to the acidic properties of the alcohol (pKₐ = 16.7). In support of this hypothesis, they showed that the reaction rate of trimethylphosphite with benzil in benzene solution was approximately doubled when acetic acid was added (54 mM) [165].

Figure 36 illustrates the results of a preliminary study into the use of methanol to accelerate the trimethylphosphite derivatization of a D₅₀ residual lignin. Two complications were found to seriously limit the use of the methanol. First, a qualitative study of the reaction of methanol/trimethylphosphite with 3,5-di-tert-butyl-1,2-benzoquinone revealed a very low conversion to the desired dimethylphosphate adduct. Interestingly, the low derivatization yield occurred despite an observed rapid and complete decolorization of the ortho-benzoquinone solution. Second, trimethylphosphite was found to be slowly degraded by methanol into dimethylphosphite (Figure 37, cf. [166]).

Figure 37. Methanalysis of trimethylphosphite.
The poor derivatization performance of methanol/trimethylphosphite can be interpreted in light of known trialklyphosphite chemistry. An intermediate in the reaction of trimethylphosphite with quinone structures is a tetraalkoxyphosphonium zwitterion (Figure 31 and Figure 32). Closely related tetraalkoxyphosphonium salts are among the most powerful alkylating agents known [167] and can undergo exchange reactions with alcohols [168]. Alcoholsysis of a tetraalkoxyphosphonium salt can lead to either a new substituted phosphonium salt or nucleophilic cleavage leading to a phosphate triester [168].

Figure 38 illustrates a possible reaction scheme for the alcoholysis of a benzoquinone-derived tetraalkoxyphosphonium structure (I). The most favored pathway of alcoholysis (cf. [169]) leads to trialkylphosphate and phenolic structures (II and III, Figure 38). The path to III involves alcohol exchange [168, 170-172]. Due to unproductive side-reactions, degradation of trimethylphosphite, and poor lignin-solvating ability, methanol was abandoned as a solvent for lignin trimethylphosphite derivatization.

Figure 38. The reaction of trimethylphosphite/methanol with tetraalkoxyphosphonium structures.

The apparent low quinone derivatization yield observed when using a methanol-based solvent system strongly suggested that the presence of hydroxyl containing compounds should be minimized during derivatization. Therefore, anhydrous solvents were
used during all subsequent treatments because of the likely similarity between hydrolysis with alcoholysis (Figure 38), and the reported ability of water/trimethylphosphate to act as a quinone reducing agent [173, 174]. Also, oxygen was excluded from the reaction mixture, with an argon atmosphere, because of published reports that oxygen may degrade dioxaphospholene structures (analogous to III, Figure 31) [175, 176].

6.2.3. Spin–Lattice Relaxation Time

In NMR spectroscopy the process of the excited magnetization state returning to thermal equilibrium is known as relaxation. Nuclear magnetic relaxation is critically important because small energy differences characterize NMR transitions and they are easy to saturate. The T1 parameter or spin–lattice relaxation time is the time constant necessary for establishing thermal equilibrium in longitudinal (z-) magnetization after a radio-frequency pulse. Quantitative NMR spectroscopy relies upon ensuring that the sample is fully relaxed before additional signal acquisitions.

The T1 relaxation rate is dependent upon a number of factors including: sample concentration, molecular size, presence of paramagnetic relaxation agents (such as Cr(acac)3), solvent, and field strength of the instrument (hence the Larmor precessional frequency ω0) [177-180]. T1 relaxation is related to the tumbling time of the molecule in solution (τc). When ω0τc = 1, the nuclear magnetic dipole–dipole relaxation mechanism is most efficient and T1 is at a minimum value [178]; for many small molecules ω0τc ~ 1. Conversely, when the solution is viscous or the target molecule is large ω0τc > 1 and T1 is larger.

T1 Relaxation can be measured by the inversion-recovery pulse sequence. The inversion-recovery pulse sequence has the following form: π-T1-π/2-acquire [177, 178]. The π (180°) pulse is used to invert magnetization from z in the longitudinal plane to -z. The magnetization will decay back to equilibrium at a rate 1/T1 (= R1). The second pulse is the read pulse (the last pulse in a sequence) which orients the magnetization in the transverse plane (xy) so it may be observed as a signal. The amplitude of the observed
signal is dependent upon the \( T_1 \) value of the spin system and the delay (\( T_d \)) between pulses (Equation 8) [177], where \( A_{\text{max}} \) is the maximum value of the signal amplitude as \( T_d \) is incremented. The results of the inversion–recovery experiment performed on a trimethylphosphite derivatized \( D_9 \) residual lignin sample are illustrated in Figure 39 and Figure 40.

\[
A = A_{\text{max}} (1 - 2\exp(-R_1 T_d))
\]  
(Equation 8)

Figure 39. Peak area measurements derived from the inversion–recovery experiment. A) tri-meta-tolylphosphate and B) lignin–quinone dimethylphosphate adduct.

Figure 40. Plot of individual spectra acquired during an inversion–recovery experiment on trimethylphosphite treated \( D_9 \) residual lignin.

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During this investigation, the spin–lattice relaxation times for trimethylphosphite derivatized lignin and tri-meta-tolylphosphate were determined by the inversion recovery pulse sequence to be 0.87 and 0.65 seconds respectively. Typical $T_1$ relaxation times for phosphorus nuclei in liquids are 0.01–10 seconds [179, 181, 182]. Consistent with the results of this study, Rossler and Eiermann previously reported the $T_1$ relaxation time for tri-meta-tolylphosphate to be 1.0 second (near, $\omega_0 = 121.49$ MHz, 300 K) [179]. Note that $T_1$ relaxation times were determined on an actual derivatized lignin sample.


Abstract

Ortho- and para-quinone structures were detected in isolated residual lignins by using trimethylphosphite derivatization and 31P-NMR spectroscopy. The methodology was validated with quinone model compounds and chemically modified kraft residual lignins. Under the conditions employed, model compound studies indicated that both ortho- and para-quinones yield stable phosphate adducts with 31P-NMR chemical shifts at approximately δ -2 ppm. A softwood kraft brownstock residual lignin was found to contain 0.088 mmol quinones/g lignin. Oxidation of the brownstock residual lignin with Fremy's reagent enriched the quinone content to 0.350 mmol quinones/g lignin. Residual lignin extracted from chlorine dioxide bleached pulp (D0) was also found to be enriched in quinone structures (0.244 ± 0.009 mmol quinones/g lignin) relative to the brownstock residual lignin. As expected, dithionite reduction of the D0 residual lignin substantially lowered the quinone content (0.050 mmol quinones/g lignin).

Introduction

Quinone structures are considered to be important chromophores in both mechanical and kraft pulps [29, 33, 44, 52, 141, 147]. During kraft pulp bleaching, chlorine dioxide and hydrogen peroxide have been shown to directly affect the quinone content in the pulp. Chlorine dioxide has been shown by several investigators [56, 58, 78, 79, 149-151] to react with phenolic lignin structures, giving ortho- and para-quinone structures among its
products. Conversely, hydroperoxide anion, generated during hydrogen peroxide bleaching, specifically removes conjugated carbonyl structures such as quinones [18, 62, 99]. These known bleaching reactions, combined with strong chromophoric properties, dictate that quinones are an important lignin functional group to monitor during bleaching studies.

Trimethylphosphite has been known, for over thirty years, to react specifically with ortho- and para-quinones [127, 153]. Lebo and others used trimethylphosphite derivatization and solid-state $^{31}\text{P}$-NMR for the detection ortho-quinone chromophores in mechanical pulp [47-51]. Similarly, Konya and Scaiano used a trialkylphosphite-based derivatization procedure to detect ortho-quinones in mechanical pulp by fluorescence spectroscopy [129]. In addition to trimethylphosphite, a number of other reagents have shown promise for quinone derivatization including: trifluoromethylphenylhydroxazine [145] and ortho-phenylenediamine [120]. Clearly, the importance of quinone structures in kraft and mechanical pulps has initiated substantial interest into developing analytical techniques to specifically measure their presence.

Recently, trimethylphosphite has been proposed as a specific reagent for the measurement of the combined ortho- and para-quinone contents of isolated lignins [183-185]. Medvecz [127], Zhang and Geléristedt [185], and Zawadzki et al. [184] have noted that trimethylphosphite derivatization of ortho-quinones, followed by controlled hydrolysis, yields stable dimethylphosphate adducts. The quinone adduct can readily be detected by $^{31}\text{P}$-NMR [127, 183, 184]. Similarly, para-quinone structures react with trimethylphosphite to give stable dimethylphosphate ester adducts [127, 153, 183, 184].

Zawadzki et al. have demonstrated that quinone structures in residual lignin, isolated from chlorine dioxide bleached pulp, can readily be detected by trimethylphosphite derivatization and $^{31}\text{P}$-NMR spectroscopy [183, 184]. The residual lignin–quinone contents were found to correlate with pulp brightness values, suggesting that these structures may be important to brightness development [183]. This paper describes our ongoing investigations into developing a specific method to measure the quinone content in isolated lignin by trimethylphosphite derivatization and $^{31}\text{P}$-NMR spectroscopy.
Experimental

Materials and Pulps. All chemicals were obtained commercially and used as received. Reverse osmosis water was used in all instances where water was required. An industrial softwood kraft pulp (kappa number 30.5 and viscosity 30.3 cP) was employed for all studies described in this report. Prior to using this pulp it was washed with distilled water until the effluents were pH neutral and colorless.

Bleached Pulp. Brownstock pulp was bleached in a D₂ stage under the following conditions: 2.3% charge of chlorine dioxide, 10% consistency, 45-minute reaction, 45°C, and final pH = 2.0. The bleached pulp was then washed with water and air-dried for testing. The pulp viscosity was found to be 26.4 cP and the pulp kappa number was found to be 14.6.

A portion of the D₂ pulp was further reacted in an alkaline extraction stage under the following conditions: 2.0% charge NaOH, 10% solids, 75-minute reaction, 70°C, and final pH = 11. The pulp was washed thoroughly with water (100 mL/g pulp), air dried and analyzed for lignin content and pulp viscosity. The pulp viscosity was found to be 22.6 cP and the pulp kappa number was found to be 6.4.

Residual Lignin. Residual lignins from the kraft brownstock, D and D(E) bleached pulps were isolated using a mild acidic dioxane hydrolysis method previously described in the literature [8, 26, 142, 143]. Yield of residual lignin, relative to the theoretical lignin amount calculated by kappa, is summarized as follows: BS = 51.8 %, D = 74.6 %, and DE = 40.8 %.

Reduced Residual Lignin. A 100 mg sample of D₂ residual lignin was dissolved in 50 mL of 0.1 N NaOH containing 100 mg sodium dithionite. The solution was stirred for 12 hours in the dark at room temperature. The reduced lignin was recovered by: acid precipitation at pH = 2.0, sample freezing, thawing, and then centrifugation. The recovered lignin was washed twice with water (pH = 2.0), freeze-dried and used for analysis.
Oxidized Residual Lignin. A portion of the brownstock residual lignin was oxidized by Frey's reagent using a procedure modified from the literature [113]. Residual lignin (100 mg) was dissolved in 15 mL of 50 % (v/v) 1,4-dioxane and 50 % water adjusted to pH = 8.0 with 0.1 N sodium hydroxide. To the solution was added 450 mg of potassium nitrosodisulfonate (Frey's reagent). The resulting mixture was stirred vigorously under an argon atmosphere for 1.5 hours. Excess Frey's reagent in the reaction mixture was decomposed by adding 5 mL of 1.0 N HCl. The 1,4-dioxane solvent was removed from the reaction mixture by vacuum evaporation at a temperature of 45°C. The oxidized lignin was recovered by: sample freezing, thawing, and then centrifugation. The recovered lignin was washed once with water (pH = 2.0), freeze-dried and used for analysis.

Phosphorylation and NMR Analysis. Dry residual lignin (30 mg) or model compounds (0.07 mmol) were reacted with 250 μL trimethylphosphite under an argon atmosphere at room temperature for seven days. (Note: Preliminary studies indicated that the measured quinone content reached a maximum after 7 days treatment.) The residual lignin samples were dried under vacuum at 40°C for 24 hours. Model compounds were dried under vacuum at room temperature over phosphorous pentoxide for three days before use. Treated lignin samples were prepared for 31P–NMR analysis by removing excess trimethylphosphite by application of vacuum at 40°C and reducing the material to near-dryness after each addition of the following solvents: three portions of 500 μL CH₂Cl₂ and then 500 μL DMSO. The treated lignins were dissolved in 250 μL of solvent consisting of DMSO–d₆, tri-methylphosphite (2.5 mg/mL), and chromium–acetyladonate (1.0 mg/mL). The resulting solution was analyzed with a Bruker 400 MHz NMR spectrometer. Using a standard inversion–recovery experiment [144], the T₁, (spin–lattice relaxation) value for the quinone adduct (-2 ppm) in trimethylphosphite derivatized lignin was found to be 0.7 seconds. The T₁ relaxation value for the internal standard, tri-methylphosphite, was found to be 0.9 seconds. Phosphorus–NMR spectra were recorded under quantitative conditions at 305°C. A 90° pulse was utilized with a 5-second pulse delay along with inverse–gated broadband proton decoupling. Generally, 1000–5000 scans were collected for each spectrum.
All phosphorus chemical shifts are reported relative to tri-meta-tolylphosphine, which was found to give a sharp resonance at 8 -16.3 ppm. Measurement of lignin-quinone content was achieved by use of the internal standard. The spectra were deconvoluted into a series of Lorentzian and Guassian curves (NUTS 95, Aeon NMR Software) and the areas of the fitted components were calculated.

Results and Discussion

Carbonyl groups in ortho- and para-quinones are known to undergo facile reaction with trimethylphosphite [153, 154]. Figure 41 illustrates the reactions of the model ortho-quinone, 3,5-di-tert-buty1-1,2-benzoquinone (I), with trimethylphosphite. Attack of the trimethylphosphite phosphorus at the carbonyl can lead to a cyclic benzodioxaphospholenone (II, Figure 41) [127, 153]. The formation of a benzodioxaphospholenone adduct is a specific product that can be expected to arise from the action of trimethylphosphite on an α-diketone, such as an ortho-quinone. Unfortunately, the benzodioxaphospholenone is hydrolytically labile [153, 156] and cannot reproducibly be formed in either pulp or residual lignin systems.

The action of water can lead to degradation of the benzodioxaphospholenone adduct giving a cyclic phosphite ester (III, Figure 41) [153, 156]. Lebo et al. [47-49] and Argyropoulos et al. [50, 51] both used the cyclic phosphite ester (III) as diagnostic for the presence of ortho-quinone structures in trimethylphosphite treated mechanical pulp. The cyclic phosphite ester is known to be unstable and in the presence of water farther degrades to give an open-chain phosphate ester (IV, Figure 41) [127, 184, 185].

Figure 42 illustrates the reaction of trimethylphosphite with the para-quinone model, 2,6-dimethoxy-1,4-benzoquinone (V). Again, trimethylphosphite may attack at the carbonyl group, but it is not possible to form the cyclic benzodioxaphospholenone. Instead the reaction is known to proceed in high yield to the open-chain phosphate ester (VI) [154, 184].
Prior to an investigation of quinone structures in isolated lignins, the trimethylphosphite derivatization reaction conditions were verified on ortho- and para-quinone compounds. Under the conditions employed in this investigation, the ortho-quinone model, 3,5-di-tert-butyl-1,2-benzoquinone, gave mainly the open-chain phosphate adduct upon reaction with trimethylphosphite (62%, Table 8). After addition of
water (100 \( \mu \)L) to the reaction mixture, all residual traces of the cyclic phosphate ester (III, Figure 41) were eliminated. The water-treated material was analyzed 48 hours after the water addition and the conversion of ortho–quinone into open–chain phosphate ester was found to be 92%. 

Table 8. Adducts formed during the reaction of quinone compounds with trimethylphosphite.

<table>
<thead>
<tr>
<th>Quinone</th>
<th>Before water addition</th>
<th>After water addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>II (^\circ)</td>
<td>III</td>
</tr>
<tr>
<td>3,5-di-tert-butyl-1,2-benzoquinone</td>
<td>0 %</td>
<td>36 %</td>
</tr>
<tr>
<td>2,6-dimethoxy-1,4-benzoquinone</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^\circ\)Roman numerals refer to adducts in Figure 41 and Figure 42

Adduct not detected

Treatment of the para–quinone model, 2,6-dimethoxy-1,4-benzoquinone, with trimethylphosphite gave only one major derivatization product. The dimethylphosphite ester (VI, Figure 42) was detected in high yield (92%, Table 1). The derivatized para–quinone was allowed to react with added water for 48 hours and the \(^{31}\text{P}-\text{NMR} \) spectrum was acquired again. Essentially no loss of derivatized product was observed after the water treatment. Interestingly, both ortho– and para–quinone model compounds were found to give phosphate ester products (IV, Figure 41 and VI, Figure 42) at approximately the same \(^{31}\text{P}-\text{NMR} \) chemical shift.

Shown in Figure 43 are \(^{31}\text{P}-\text{NMR} \) spectra of trimethylphosphite derivatized \( D_6 \) stage residual lignin. Spectra correspond to derivatization with 100% trimethylphosphite, as documented in this report, and derivatization with 50% trimethylphosphite/DMSO, as previously reported [183, 184]. In both spectra, the phosphate (quinone) adduct and internal standard are observed. Resonances downfield from the quinone adduct (δ -2 ppm) correspond to trimethylphosphate (δ 3.5 ppm, verified with pure material) and likely phosphate esters arising from trimethylphosphate hydrolysis. Further work is in progress to understand the full scope of trimethylphosphite reactions with other lignin functional
Figure 43. Phosphorus–NMR spectrum of trimethylphosphite treated D₈ stage residual lignin A) lignin treated with 100% trimethylphosphite and B) lignin treated with 50% trimethylphosphite/DMSO.

groups. Both spectra demonstrate the utility of vacuum removal of trimethylphosphite and its degradation products. Also, the use of 50% trimethylphosphite derivatization is of benefit to increase spectral resolution (Figure 43).

Under the derivatization and analysis conditions employed in this study, the benzodioxaphospholene adduct could not be detected in treated lignin. Possibly, traces of water introduced while preparing the sample for NMR analysis caused the labile structure to be degraded. In contrast to the previous mechanical pulp work of Lebo et al. [47-49] and Argyropoulos et al. [50, 51] the partially hydrolyzed cyclic phosphate ester also could not be reliably formed. Consequently, the open-chain phosphate adduct was selected as an indicator of the presence of lignin-quinone structures. The model compound studies indicate that both ortho– and para–quinone structures give open-chain phosphate adducts, consistent with previous reports [50, 127, 184]. Therefore, the developed method measures the combined ortho– and para–quinone content of isolated lignins.

Figure 44 displays measured quinone content data for a number of trimethylphosphite treated residual lignins. As expected, the combined ortho– and para–
quinone content of the brownstock lignin was found to be low (0.088 mmole quinones/g lignin). Freny’s reagent is known to specifically enrich the ortho-quinone content of lignin. When the brownstock residual lignin was oxidized with Freny’s reagent, the quinone content increased dramatically (0.350 mmole quinones/g lignin).

![Figure 44: Measured quinone contents for trimethylphosphite treated lignins (BS = brownstock, BS Freny = brownstock treated with Freny’s reagent, D = chlorine dioxide bleached, DE = chlorine dioxide bleached then alkaline extracted, and D reduced = dithionite reduced D lignin, TMP = trimethylphosphite).](image)

Chlorine dioxide bleaching leads to the formation of both ortho- and para-quinone structures in lignin [56, 58, 78, 79, 149-151]. Clearly, the introduction of quinone structures as a result of bleaching can be observed by comparing the treated D₀ stage residual lignin (0.244 mmole quinones/g lignin) with the brownstock residual lignin (Figure 44). Dithionite is expected to reduce ortho- and para-quinone lignin structures to the catechol and hydroquinone forms, respectively. Figure 44 reveals that dithionite reduction drastically lowered the quinone content of the D₀ stage residual lignin (0.050 mmole quinones/g lignin).

After trimethylphosphite treatment, lignin samples were amended with 100 μL water and analyzed after 24 hours. Generally a slight increase in the total quinone content was observed after addition of water, possibly indicating that a trace of the ortho-quinone

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cyclic adduct (III, Figure 41) was decomposed by hydrolysis. Therefore, the total combined ortho- and para-quinone content of residual lignins can be measured after adding water to trimethylphosphite treated material. For D₆ residual lignin, the accuracy of a triplicate quinone determination was shown to be ± 4% after water treatment. Currently, we are studying lignin derivatization in homogeneous solution (50% trimethylphosphite/DMSO [183, 184]) and Figure 44 reveals that this modification affords similar results to heterogeneous derivatization (100% trimethylphosphite) as documented in this report.

Conclusions

The combined ortho- and para-quinone content in isolated lignins can be reproducibly measured using trimethylphosphite derivatization and ³¹P-NMR spectroscopy. After addition of water to the treated lignin, a stable phosphate ester adduct may be used for determination of the quinone content. The derivatization conditions developed in this study were validated with ortho- and para-quinone model compounds and a brownstock residual lignin enriched in quinone content by Fremy's reagent. The technique demonstrated that Fremy's oxidation and chlorine dioxide bleaching both enrich the lignin-quinone content relative to the brownstock lignin. Furthermore, quinone structures in the D₆ stage residual lignin can be reduced, as expected, by the application of dithionite.

Acknowledgements

The authors wish to thank Drs. McDonough, Dimmel, and Lucia for guidance and the Institute of Paper Science and Technology (IPST) and its member companies for financial support. Valuable discussions of NMR spectroscopy with Dr. Patricia Stone Wilkinson, Senior Applications Scientist at Bruker Instruments, are gratefully acknowledged. Portions of this work were used by M. Z. and T. R. as partial fulfillment of the requirements for the Ph.D. degree at IPST.
Note Added During Review

Four months after our manuscript was submitted to JPPS, and while it was still under review, Argyropoulos and Zhang (loc. cit. below) reported that the trimethylphosphite derivatization yield of simple quinone compounds is ~70% when the reaction is performed in DMF containing both 0.5% water and lignin. As a result of this experiment, they concluded that the measured quinone content of trimethylphosphite derivatized lignin should be multiplied by 1.43 (i.e. 100/70) to give the actual content. Note, a correction factor (i.e. 1.43) would alter the quinone content values of the various lignin samples, but it would not impact their relative ranking. The application of trimethylphosphite derivatization for the routine determination of lignin-quinone contents will require additional study. Nonetheless, our results and previous reports suggest that trimethylphosphite derivatization is a promising strategy that may provide insight into the chemistry of an important chromophore in mechanical and chemical pulps.

6.4. Publication Three: Chromophore Properties of High Brightness Pulps


Abstract

The production of high brightness pulps remains one of the principal requirements for many high-value paper products. The need to accomplish this task under the recently proposed cluster rules makes this an especially challenging problem for softwood kraft pulps. Recently, our research group has begun to examine the chemical constituents of kraft pulps that may contribute to a brightness ceiling. As a preliminary study in this field we have examined the potential contribution of ortho- and para-quinone structures to brightness development during multistage bleaching. Employing literature methods, we have found a relationship between the quinone content after the first alkaline extraction stage and the final brightness values of a kraft pulp. The fate of quinones was explored using a D(E*)DED (E* = E, EAR, EO, EP, and EOP) bleaching sequence with a softwood kraft pulp.

Introduction

Chemical pulp bleaching involves both brightening and delignification reactions. Delignification can be conveniently studied by the well established measures of kappa number or Klason lignin content. Kappa number is a measure of the ease of oxidation of a pulp and has been correlated with Klason lignin content of chemical pulps [186]. Recent lignin and carbohydrate model compound studies by Li and Gellerstedt have begun to reveal the chemical significance of the kappa number test [187].

McDonough studied the fundamental parameters influencing brightness development during $D_E(E+O)D_E$ bleaching of softwood kraft pulps [72]. Significantly, the
kappa number of unbleached pulp was found to influence brightness response in the D₁ stage. Also, brightness ceilings were higher for modified versus conventional pulps and for pulps with lower unbleached kappa number. Clearly, chemical structures, as quantified by the kappa test, can have an influence that carries throughout the multistage bleaching process.

Pulp brightness is defined as the diffuse reflectance of visible blue light (central wavelength 457 nm) from an "infinitely" thick sheet of paper [68]. The brightening process is very important during chemical pulp bleaching and occurs concurrently with delignification. Brightening and delignification reactions both reduce the quantity of chromophoric (colored) structures in the pulp so the resulting paper reflects more light.

The brightening process is difficult to study because of the scarcity of specific methods to probe the nature and quantity of lignin chromophores. Ultraviolet and visible spectroscopy have been used to study chromophore removal during bleaching but precise structural information is difficult to derive from this technique. Also, studies of the brightening process are further complicated by the fact that the exact chemical nature of colored structures in pulp is not known with certainty. Hence, there is a need to understand the fundamental chemistry of brightening.

**Quinone Chromophores.** The color of chemical and mechanical pulps may arise from structures such as: catechol–metal complexes [30, 33, 147], quinone methides [147], stilbenes [147, 188], ortho– and para–quinones (Figure 45) [33, 38, 141, 147, 148]. In particular, quinones have been widely acknowledged to be important chromophores in ligno-cellulosic materials; they may have a major impact on the brightness of chemical pulps [29, 141].

In previous studies, we presented trimethylphosphite derivatization as a useful technique for both detection and quantification of the ortho– and para–quinone structures in kraft residual lignin [184, 189]. Trimethylphosphite derivatization was originally developed to study ortho–quinone structures in mechanical pulps [47-49, 51, 128]. Our research group has modified the literature procedure such that the combined ortho– and para–quinone content in isolated lignin samples can be quantified. The technique relies
on the ability of trimethylphosphite to form adducts specifically with ortho- and para-quinone structures. The "tagged" quinone structures are then quantified with $^{31}$P–NMR spectroscopy.

![Diagram of ortho- and para-quinones](image)

**Figure 45.** General structure of ortho- and para-quinones.

Lignin quinone structures are important because they are strongly colored. Also, commercially important bleaching agents are known to have reaction pathways involving both formation and destruction of quinone structures. Figure 46 illustrates the formation of a para-quinone lignin structure. During alkaline oxygen bleaching, para-quinone lignin structures may be formed via a Dakin reaction involving side-chain elimination at the C$_1$ position (Figure 46) [190]. Ortho- and para-quinone structures may also be formed during chlorine dioxide bleaching from phenolic and non-phenolic lignin structures [56, 58, 78, 79, 151]. The ability of chlorine dioxide to form lignin quinone structures has recently been studied by our research group [184, 189]. Furthermore, the brightening ability of hydrogen peroxide may be partially explained by the specific destruction of conjugated carbonyl structures, such as quinones, by the hydroperoxide anion [62, 98, 99].

One goal of comparing bleaching response with lignin structural changes is to suggest a more efficient use of bleaching chemicals. Potentially, multistage bleaching processes can be better controlled by understanding the chemical modifications that occur as lignin is removed and the pulp is brightened. Specifically, this study attempts to contribute to bleaching process improvement by understanding the impact quinone chromophores have on brightness development during chemical pulp bleaching.
Figure 46. Alkaline oxygen reactions of lignin leading to the formation of quinone chromophores.

Experimental

**Chemicals.** All chemicals were commercially purchased and used as received except for 1,4-dioxane, which was purified by distillation over sodium borohydride.

**Furnish.** All pulps were prepared from a single Loblolly pine (*Pinus taeda*) tree grown in Southeastern USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 and 8 mm. The chips were cooked under conventional kraft conditions to give a brownstock of kappa number 30.5.

**Chlorine Dioxide Bleaching.** D₀ stage pulp was prepared from brownstock under the following conditions: 2.3% ClO₂ charge, 10% consistency, 45°C, final pH = 2.0, and 45-minute reaction. The D₀ pulp was then washed with water; the viscosity was found to be 26.4 cP and the kappa number was 14.6. A portion of the D₀ pulp was alkaline extracted in a series of experiments and further bleached by application of a DED sequence. Bleached pulp was washed and characterized by kappa number (TAPPI 236 om–85), and Klassen lignin content (TAPPI 222 om–88).
Alkaline Extraction. A series of alkaline extracted pulps was prepared from the chlorine dioxide (D_{3}) delignified pulp. In a peg mixer, the following basic alkaline extraction stage conditions were used: 10% consistency, 70°C, final pH > 10.5, and 75-minute reaction. Specific details of the alkaline extraction stage conditions are given in Table 9.

### Table 9. Oxidative alkaline extraction stage conditions.

<table>
<thead>
<tr>
<th>Stage</th>
<th>NaOH Charge</th>
<th>Oxidative Reinforcement</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>2.0%</td>
<td>Ambient atmospheric pressure Air</td>
</tr>
<tr>
<td>EO</td>
<td>2.5%</td>
<td>Oxygen applied at 0.41 MPa (60 psig), decreased by 83 kPa (12 psig) per 5 minutes</td>
</tr>
<tr>
<td>EP</td>
<td>2.5%</td>
<td>0.5% Hydrogen peroxide</td>
</tr>
<tr>
<td>EOP</td>
<td>2.5%</td>
<td>0.5% Hydrogen peroxide; Oxygen applied at 0.41 MPa (60 psig) then decreased by 83 kPa (12 psig) per 5 minutes</td>
</tr>
<tr>
<td>EAr</td>
<td>2.0%</td>
<td>Air purged; argon applied at 69 kPa (10 psig)</td>
</tr>
</tbody>
</table>

D_{3} and D_{4} Bleaching. The alkaline extracted pulps were further bleached with a D_{3}ED_{2} sequence. The following D_{4} conditions were used: 0.75% ClO_{2} charge, 10% consistency, 70°C, and 3-hour reaction. Second alkaline extraction stage conditions were as follows: 1.0% NaOH charge, 10% consistency, 70°C, and 60-minute reaction. Washed E_{2} stage pulps were bleached in a D_{3} stage and the brightness ceiling was determined (at a maximum of 0.8% ClO_{2} charge).

Residual Lignin Isolation. Residual lignin was isolated from the pulps by a mild acidic 1,4-dioxane hydrolysis procedure modified from the literature [8, 26, 142, 143]. In brief, lignin was extracted from the pulp with 90% 1,4-dioxane/0.1 N HCl (v/v) solution (8% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. Purified lignin was freeze-dried and analyzed by 'H- and ^{31}P-NMR spectroscopy.

Lignin Quinone Quantification. The combined ortho- and para-quinone contents of isolated lignins were determined by ^{31}P-NMR spectroscopy after trimethylphosphate
derivatization [184, 189]. Dry residual lignin (30 mg) was treated with 500 μL, 50% trimethylphosphite/DMSO (v/v) under argon at room temperature. After seven days, excess trimethylphosphite was removed by vacuum at 40°C for 3 hours. Treated lignins were dissolved in 400 μL DMSO-d₆, containing tri-meta-tolylphosphate (2.5 mg/mL) and chromium-acetylacetonate (1.0 mg/mL). Then 5 μL water (0.3 mmol per 30 mg lignin) was added to the sample and after 12 hours, the 31P-NMR spectrum was acquired with a Bruker 400 MHz NMR spectrometer.

Quantitative 31P-NMR spectra were acquired at 305°K using a 90° pulse, a 5-second pulse delay, and inverse-gated broad-band proton decoupling. For each spectrum 1000–3000 scans were collected. The internal standard, tri-meta-tolylphosphate (δ-16.3 ppm vs. 85% H₃PO₄), was used both for quantification and as a shift reference. Quantification of lignin quinone content was achieved by integrating the areas of the internal standard and the quinone adduct resonance at δ-2.5 ppm [184, 189].

Functional Group Quantification. Lignin functional groups were determined by 1H-NMR spectroscopy using the method of Li and Lundquist [191]. Lignin samples (20 mg) were dissolved in anhydrous DMSO-d₆ containing sodium 3-trimethylsilyl-propionate-2,2,3,3-d₄ as an internal standard. Quantitative 1H-NMR spectra were acquired with a Bruker 400 MHz NMR spectrometer using a 90° pulse and a 15-second pulse delay. For each spectrum 200 scans were collected.

Results and Discussion

Residual Lignin Quinone Contents. From initial 31P-NMR studies, the combined ortho- and para-quinone content of brownstock residual lignin was found to be 0.088 mmol quinone/g lignin (≈ 1.6 quinones per 100 C9 units); this value compared favorably with literature values for softwood kraft lignins: Furman and Lonisky found 3 quinones per 100 C9 units using reductive acetylation [37] and Iiyama and Nakano found 3–4 quinones per 100 C9 units by using visible absorbance [52].

Quinone contents for a series of alkaline extraction treatments and D₅ stage residual lignins are given in Figure 47. Generally, the increased application of oxidative
reinforcement during alkaline extraction results in a lower quinone content. For example, the quinone content of alkaline extraction stage residual lignin with air excluded, D(EAR), is 190% more than when both hydrogen peroxide and pressurized oxygen, D(EOP), are applied. As shown in Figure 47, the order of increasing quinone content is as follows: D(EP) < D(EOP) < D(EO) < D(EAR) < DE. Hydrogen peroxide in the alkaline extraction stage, D(EP) or D(EOP), results in a dramatic decrease in quinone content [184] because of the specific reaction of hydroperoxide anion with quinone structures [62, 98, 99].

Figure 47. Quinone contents of E stage and D₁ stage residual lignins.

The quinone content, on a mmol/g lignin basis, is generally lower at the D₁ stage than at the alkaline extraction stage. Two notable exceptions are alkaline extraction with air excluded, D(EAR), and with applied pressurized oxygen, D(EO). Both D(EAR)D and D(EO)D residual lignins displayed a greater quinone content at the D₁ stage than at the previous alkaline extraction stage.

During this study it was noted that E₁ stage Klassen lignin content for D(EO) residual lignin was 4.4 g/kg pulp OD and similar in value to that for the D(EP) residual lignin (4.5 g/kg pulp OD). In contrast the E₁ quinone contents for the same residual lignins were vastly different, with 0.114 mmol quinone/g lignin for D(EO) residual lignin versus
0.076 mmol quinone/g lignin for D(EP) residual lignin (Figure 47). The E₁ quinone content values are consistent with the higher D₁ and D₂ brightness achievable for the D(EP)DED over the D(EO)DED sequence.

The direct precursors for quinone structures can be envisioned to be phenolic, aromatic, and/or methoxyl groups. Shown in Figure 48 are the unsubstituted phenolic, C₅–substituted phenolic, aromatic, and methoxyl proton contents for the series of alkaline extraction stage residual lignins. A correlation between precursor lignin functional groups and quinone contents was not readily apparent (Figure 47 with Figure 48). The difficulty encountered may suggest that a specific subset of these functional groups – such as catechols – is more amiable for conversion to quinones. Alternatively, conversion may be dependent on the oxidant applied, application conditions, and/or presence of other lignin functional groups not studied.

![Figure 48. Functional group content of E₁ stage residual lignins.](image)

In Figure 49 the quinone content data is plotted as “apparent” quinone concentration, that is, a measure of the concentration of the quinone chromophores in the pulp system. Klasson lignin content was used as an estimate of the quantity of lignin in the pulp. If residual lignin quinone content (mmol/g lignin) is multiplied by the pulp Klasson lignin
content (g/kg pulp OD), an estimation of quinone chromophore content in the pulp is derived (mmol/kg pulp OD).

**Figure 49.** The "apparent" quinone concentration in bleached kraft pulps (E<sub>I</sub> quinone content multiplied by the E<sub>I</sub> KIason lignin content).

**Quinone Content Brightness Correlation.** As we have presented above, a measure of the "apparent" concentration of quinone chromophores in the bleached pulps can be estimated by multiplying the residual lignin quinone content by the pulp KIason lignin content. If the "apparent" quinone chromophore concentration influences pulp brightness, then this chromophore concentration should obey the Kubelka–Munk relationship. The Kubelka–Munk equation (Equation 9) describes brightness (reflectance) of a sheet as a function of light absorbance and scattering:

\[
\frac{B}{100} = 1 + \frac{k}{s} - \left(\frac{k}{s}\right)^2
\]

(Equation 9)

where,

- \(B\) = brightness (%)
- \(k\) = absorption coefficient
- \(s\) = scattering coefficient

\(\text{note: } B_{100\%}/100 = R_{\infty} = \text{reflectivity of an "infinite" layer of sheets}\)
Generally, modern commercial bleaching has little influence upon the scattering coefficient (s) which is a function of the fiber dimensions and interfiber bonding [68, 69]. For this study, we assumed that altering oxidative reinforcement in the \( E_1 \) stage would have little influence on \( D_1 \) and \( D_2 \) scattering coefficients. We also assumed that the absorption coefficient (k) would be proportional to the chromophore content (Equation 10, Equation 11, and Equation 12) and that chromophores are evenly distributed throughout the pulp.

\[
\frac{k}{s} = \left( \frac{\phi}{s} \right) \times \frac{C}{s} \tag{Equation 10}
\]

where,
\( \phi \) = proportionality constant
\( C \) = chromophore concentration.

If \( s \) is assumed to be constant then,
\[
\frac{k}{s} = \phi_1 \times C \quad \text{or} \quad \frac{k}{s} \propto C \tag{Equation 11}
\]

where,
\( \phi_1 \) = proportionality constant.

If Equation 11 is substituted in Equation 9 then,
\[
B \propto 1 + C - \sqrt{2(C^2 + C)} \tag{Equation 12}
\]

Lignin is generally assumed to be the major component responsible for light absorption for wood, chemical and mechanical pulps [69, 192-196], although other studies have suggested that the carbohydrate component may also contribute [197, 198]. Given all of the above assumptions, the expected correlation between lignin chromophore content and pulp brightness is described in Equation 12. From Equation 12 it follows that, if a given lignin chromophore/structure has a significant impact on pulp brightness, a plot of \( 1+C-(2C+C^2)^{1/2} \) versus brightness should yield a linear line.

Table 10 illustrates data derived from plotting various functional group contents and "apparent" contents in pulp against \( D_1 \) and \( D_2 \) stage brightness values. The \( R^2 \) values were calculated for a linear line drawn through the data. Both \( E_1 \) stage kappa number and
Table 10. R^2 values for a linear line fit through brightness versus \(1+C-(2C+C^2)\) for DE*DED pulps.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Data Used for C^*</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D1 Brightness</td>
<td>D2 Brightness</td>
</tr>
<tr>
<td>Klason and Kappa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>E, Klason Content</td>
<td>0.81</td>
</tr>
<tr>
<td>2</td>
<td>D, Klason Content</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>E, Kappa Number</td>
<td>0.71</td>
</tr>
<tr>
<td>Quinone Contents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>E, Quinone Content</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>D, Quinone Content</td>
<td>0.81</td>
</tr>
<tr>
<td>&quot;Apparent&quot; Quinone Contents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(E, Quinone Content) x (E, Klason Content)</td>
<td>0.80</td>
</tr>
<tr>
<td>7</td>
<td>(D, Quinone Content) x (E, Klason Content)</td>
<td>0.95</td>
</tr>
<tr>
<td>8</td>
<td>(D, Quinone Content) x (D, Klason Content)</td>
<td>0.90</td>
</tr>
<tr>
<td>9</td>
<td>(D, Quinone Content) x (E, Kappa Number)</td>
<td>0.96</td>
</tr>
<tr>
<td>10</td>
<td>(E, Quinone Content) x (E, Kappa Number)</td>
<td>0.78</td>
</tr>
<tr>
<td>Proton Functional Group Contents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>E, Aromatic–H Content</td>
<td>0.30</td>
</tr>
<tr>
<td>12</td>
<td>E, Methoxy–H Content</td>
<td>0.05</td>
</tr>
<tr>
<td>13</td>
<td>E, Unsubstituted Phenolic–H Content</td>
<td>0.60</td>
</tr>
<tr>
<td>14</td>
<td>E, C–Substituted Phenolic–H Content</td>
<td>0.67</td>
</tr>
<tr>
<td>&quot;Apparent&quot; Proton Functional Group Contents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>(E, Aromatic–H Content) x (E, Klason Content)</td>
<td>0.72</td>
</tr>
<tr>
<td>16</td>
<td>(E, Methoxy–H Content) x (E, Klason Content)</td>
<td>0.74</td>
</tr>
<tr>
<td>17</td>
<td>(E, Unsubstituted Phenolic–H Content) x (E, Klason Content)</td>
<td>0.65</td>
</tr>
<tr>
<td>18</td>
<td>(E, C–Substituted Phenolic–H Content) x (E, Klason Content)</td>
<td>0.72</td>
</tr>
</tbody>
</table>

E* = E, EA, EO, EP, and EO*P
* Klason lignin content (g/kg pulp OD); quinone and proton functional group contents (mmol/g lignin); "apparent" quinone and proton functional group contents (mmol/kg pulp OD)
Klason lignin content are correlated with $D_1$ brightness and the $D_2$ stage brightness ceiling (Table 10 and Figure 51). These finding are consistent with results presented by McDonough who found $D_1$ and $D_2$ brightness values are dependent upon unbleached kappa numbers [72]. This study suggests that $E_1$ stage kappa number, and $E_1$ and $D_1$ Klason lignin contents are all expected to be good predictors of $D_1$ and $D_2$ stage brightness values for DE*DED pulps ($E^* = E$, EAr, EO, EP, and EOP).

It is apparent from examination of the data in Table 10 that certain lignin functional groups are not well correlated with $D_1$ and $D_2$ brightness values; these groups are unsubstituted phenolic, $C_1$-substituted phenolic, aromatic, and methoxy proton contents (weight-lignin basis, mmol/g lignin). Particularly, it can be noted that the methoxy proton absolute content displays a very poor correlation with the $D_1$ or $D_2$ stage brightness.

First alkaline extraction stage “apparent” phenolic proton content is better correlated with $D_1$ stage brightness values (Table 10 and Figure 50).

Table 10 reveals that both $E_1$ and $D_2$ stage lignin quinone contents are correlated with $D_1$ and $D_2$ brightness values. “Apparent” $D_1$ and $E_1$ quinone contents are also correlated with $D_1$ and $D_2$ brightness values (Table 10 and Figure 51). The correlation suggests that quinone structures may be important chromophores that impact on the brightness values for DE*DED pulps.

**Conclusions**

Trimethylphosphate derivatization combined with $^{31}P$-NMR spectroscopy is a useful technique for observing changes in the quinone chromophore contents of residual lignins. Further work is in progress exploring the fundamental nature of the technique and applying it to multistage bleaching sequences.

For DE*DED ($E^* = E$, EAr, EO, EP, and EOP) softwood kraft pulps, the “apparent” content (mmol/kg pulp OD) of quinone chromophores was found to be correlated with both $D_1$ and $D_2$ brightness values.
A) “Apparent” $E_i$ unsubstituted phenolic-H concentration correlated with $D_i$ and $D_2$ brightness.

B) “Apparent” $D_i$ quinone concentration correlated with $D_i$ and $D_2$ brightness.

(note: $1+C-(2C+C^2)$ is the right-hand side of the proportionality derived from the Kubelka–Munk equation (Equation 9, Equation 12))
Figure 51.

A) D₁ Klasson lignin content correlated with D₁ and D₂ stage brightness.
B) D₂ quinone content correlated with D₁ and D₂ brightness.

{note: $1+C(2C+C^2)^2$ is the right-hand side of the proportionality derived from the Kubelka-Munk equation (Equation 9, Equation 12)}
Acknowledgments

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6.5. Publication Four: Quantitative Determination of Quinone Chromophores in Isolated Lignins.


Abstract
Quinone substructures in lignin are important chromophores which are thought to negatively impact brightness development during industrial pulp bleaching. In this paper, a trimethylphosphite derivatization procedure is presented for the quantitative determination of lignin–quinone contents. Lignins investigated were isolated from chlorine dioxide, oxygen, alkaline extraction, and peracetic acid bleached pulps. Chlorine dioxide dramatically increased lignin–quinone content whereas subsequent alkaline extraction reduced the content. Oxygen delignification also resulted in quinone introduction, but to a lesser extent than with chlorine dioxide. Peracetic acid displayed a beneficial effect by eliminating quinone structures. Trimethylphosphite derivatization chemistry was investigated with small molecule benzoquinones and oxidized poly(4-vinylphenol). Generally small molecule benzoquinones were derivatized in good yield, except 3-methoxy-1,2-benzoquinone gave less than complete derivatization due to competing self-dimerization. Conditions necessary for optimum derivatization yield of isolated lignins, removal of trimethylphosphite degradation products, and quantitative NMR analysis are also discussed.

Introduction
The goals of kraft pulp bleaching are twofold: delignification, or removal of bulk residual lignin, and brightening. Generally, the lignin component may cause as much as 90% of the visible region light absorption coefficient of unbleached kraft pulps [199]. The pro-
duction of high value paper products relies upon bleaching pulps to high brightness. Therefore, knowledge of the fundamental chemistry of both brightening and delignification stages are crucial. Pulp delignification chemistry has been extensively studied [1, 16, 21, 62]. Unfortunately, fundamental knowledge of lignin and chromophore transformations during brightness development are much less developed.

Surprisingly, the structures responsible for color in mechanical and chemical pulps are only qualitatively known. Various studies have suggested that colored substructures present in the lignin macromolecule may include: quinone–methides [200], stable radicals [147], stilbenes [147, 148], conjugated carboxyls, and/or benzoquinones [29, 32, 52, 200].

Benzoquinones occur as either ortho (1,2-) or para (1,4-) forms, and are highly colored, $\lambda_{max}$ 420–580 nm [40]. It has often been suggested that quinones are involved in the yellowing of mechanical pulp [33, 44, 147]. Also, the color of kraft [32] and soda lignin [201, 202] has been attributed to the presence of benzoquinone structures. Lignin–quinones may arise during the alkaline pulp cooking process from methyl–aryl ether cleavage after subsequent air oxidation of phenolic units [21, 201, 202].

Benzoquinone structures play an important role in both chlorine dioxide and hydrogen peroxide bleaching processes. Chlorine dioxide has been demonstrated to react with phenolic lignin model compounds to give ortho- and para-benzoquinone products [56, 78, 79]. Hydrogen peroxide, conversely, acts as a powerful brightening agent by eliminating conjugated carbonyl structures, including quinones [62, 99]. Recently, Zawadzki et al. quantified the quinone contents of residual lignins isolated from chlorine dioxide bleached pulps (DE*DED) [183, 184]. Lignin–quinone levels were found to correlate with pulp brightness and brightness ceiling values, suggesting that quinones negatively impact brightness development [183].

Although lignin–quinones are widely acknowledged to be important chromophores, until recently few reliable methodologies were available for the quantitative analysis of these structures in lignocellulosic materials [118]. Visible absorption spectroscopy is not directly effective for lignin–quinone quantification because of the broad featureless nature of lignin absorption spectra [119]. Classical colorimetry–based [118]
and hydrazine oxidation [118] methods of quinone measurement are difficult to apply. Ortho–phenylenediamine derivatization and fluorescence spectroscopy has been used for the determination of ortho–benzquinone structures in mechanical pulps [120, 121]. Unfortunately, the technique is not applicable for the analysis of important para–benzquinone structures.

Recently, $^{31}$P–NMR–based spectroscopic techniques have been developed for the analysis of quinone structures in isolated lignins. 4–trifluoromethylphenyldrazine derivatization/$^{31}$P–NMR was applied for quinone analysis on a range of isolated lignins [122, 123]. Alternatively, derivatization by Ruppert's reagent has been suggested for lignin–carbonyl analysis [124], but model compound studies have revealed overlap between para–quinone and aldehyde derivatives [125].

A number of reports have described trimethylphosphite (TMP) derivatization of mechanical pulps. TMP has been reported to specifically form adducts with ortho–quinone structures [47, 49, 50, 129, 130]. Lebo et al. were first in applying TMP derivatization and phosphorus microanalysis for ortho–quinone quantification during mechanical pulp photoyellowing [47, 49]. Similarly, Konya and Scatano employed a trialkylphosphite–based derivatization procedure to detect ortho–quinones by fluorescence spectroscopy [129]. Argyropoulos et al. used solid–state $^{31}$P–NMR and TMP derivatization to qualitatively monitor ortho–quinone levels in a range of mechanical pulps [50]. Argyropoulos et al. also reported that carboxylic acid groups, but not carboxylic acid salts, interfere with solid–state $^{31}$P–NMR analysis of quinones [130].

Recent investigations of TMP derivatization has revealed that both ortho– and para–benzquinone structures in lignins can be quantified simultaneously. The fundamental chemistry of the method has been verified by model compound studies [184, 185, 189, 203]. The combined ortho– and para–quinone contents of isolated lignins can readily be detected by TMP derivatization and $^{31}$P–NMR spectroscopy [123, 183, 184, 189]. Similarly, Argyropoulos and Zhang have shown the application of TMP derivatization on a variety of isolated lignin samples [203]. Recently, Zhang and Gellerstedt applied the methodology towards the analysis of milled–wood lignin samples [204].
This paper describes ongoing research utilizing TMP derivatization and $^{31}$P-NMR spectroscopy as a tool for quantitative analysis of quinone structures in isolated lignins. The purpose of this study was to optimize quinone derivatization conditions and understand the TMP derivatization and degradation chemistries. Then, the developed procedure was applied for the analysis of residual lignins isolated from chlorine dioxide, oxygen, alkaline extraction and peracetic acid bleached pulps.

**Experimental Section**

All chemicals were purchased commercially and used without further purification, unless otherwise noted. 4-methyl-1,2-benzoquinone, 4-tert-butyl-1,2-benzoquinone, 3-methoxy-1,2-benzoquinone, and 2-tert-butyl-1,4-benzo-quinone were prepared by silver oxide oxidation of the analogous catechols and hydroquinone using the method of Cason [132]. Poly(4-vinylphenol) (PVP, MW ~ 22,000), enriched in quinone content, was prepared by Fremy's reagent oxidation according to a procedure modified from the literature [113]. Structures of quinone model compounds are illustrated in Figure 52.

![Figure 52. Structures of model compounds studied.](image)

Chlorine dioxide (D) and alkaline extracted (E) pulps were bleached as previously described [134]. Both conventional (kappa = 28) and EMCC™ (kappa = 29) laboratory
softwood kraft pulps were used. Chlorine dioxide bleaching was performed in a Quantum Technologies mixer at 45°C, 10% consistency, using a kappa factor of 0.2 and a 30-minute reaction [134]. The alkaline extraction stage was performed in a peg mixer at 70°C, 10% consistency, using ~1.2% NaOH charge and a 60-minute reaction.

Oxygen delignified and peracetic acid treated pulps were prepared as previously described [135]. A laboratory softwood polysulfide/anthraquinone (PS/AQ) kraft pulp (kappa = 45.4) was used [135]. Oxygen delignification was accomplished in a peg mixer at 110°C, with ~1.1% NaOH charge, using 70 psig oxygen pressure and a 60-minute reaction [135]. Equilibrium peracetic acid treatment was performed at 80°C using a 6% charge and 60-minute reaction.

Lignins were isolated from bleached pulps by an acidic 1,4-dioxane isolation procedure previously reported [134, 143]. Lignin was extracted from the pulp with 90% 1,4-dioxane/0.1 N HCl (v/v) solution (10% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. Isolated lignin yield was approximately 30–46% relative to pulp kappa number [134, 135]. Purified lignin was freeze-dried and used for further analysis.

Dry model compounds (0.2 mmol) and lignin (30 mg) were derivatized with 250 μL TMP and 250 μL anhydrous solvent under an argon atmosphere at room temperature for two days. TMP was previously purified by distillation from sodium metal. The following derivatization solvents were studied: dimethylformamide (DMF), DMF containing 2% water, and dimethylsulfoxide (DMSO). Derivatized samples were prepared for analysis by removing excess TMP under vacuum at 40°C. Then, 250 μL DMSO was added and the sample was placed under vacuum at 50°C until nearly dry.

Derivatized model compounds were dissolved in 450 μL of DMSO-δ6 containing 19.3 mg/mL tri-meta-tolylphosphate (TTP) and 6.0 mg/mL chromium-acetylacetonate (Cr(acac)3). Treated lignins were dissolved in 450 μL of DMSO-δ6 containing TTP (0.84 mg/mL) and Cr(acac)3 (1.0 mg/mL). Derivatized samples were hydrolyzed by the addition of water (10 μL for model compounds and 5 μL for lignin).

Phosphorus-NMR spectra were acquired with a Bruker 400 MHz NMR spectrometer using the following quantitative conditions: 90° pulse, 5-second pulse delay,
inverse–gated broadband proton decoupling, 64K time domain, and one degree of zero filling. For treated model compounds 100–400 scans/spectrum were collected. For treated lignin 2000 scans/spectrum were collected. The internal standard, TTP, gave a sharp resonance at δ -16.3 ppm (vs. 85% H$_3$PO$_4$) and was used for quantitative analysis and as a shift reference. To ensure quantitative spectral acquisition, the pulse delay exceeded five times the longest measured spin–lattice relaxation time.

Results and Discussion

**Derivatization Chemistry.** Trivalent phosphorous compounds, particularly trialkylphosphites, are well known to react specifically with ortho– and para–quinones. The chemistry of TMP reactivity with quinone structures has been extensively studied by Ramirez and others [153, 155, 175, 205].

In recent years, interest in detecting quinones in lignocellulosic materials has led to a reexamination of TMP/quinone derivatization chemistry. Shown in Figure 53 is the reaction of the ortho–quinone model compound 3–methoxy–1,2–benzoquinone (I) with TMP. The initial stages of TMP/quinone derivatization are obscure, but electron spin resonance spectroscopy has revealed that the reaction may proceed by a radical mechanism [206].

![Figure 53. Reaction of TMP with 3-methoxy-1,2-benzoquinone.](image)
Regardless of the initial mechanism of phosphorus attack, cyclization occurs and a benzodioxophospholene structure (Ia, Figure 53) is formed [153]. The benzo-dioxophospholene adduct can readily be detected by $^{31}$P-NMR spectroscopy at approximately $\delta$ -45 ppm. Many reports have extensively documented this facile reaction on a variety of ortho-quinone compounds [127, 155, 175, 184, 185, 189, 203].

Dioxophospholene structures are known to be unstable towards both water and oxygen [175, 207]. We envisioned that practical TMP derivatization of lignin would likely involve unavoidable exposure to water. Therefore, understanding the hydrolysis chemistry of benzodioxophospholenes is critical for the development of a robust quinone analysis method.

The literature contains a number of reports regarding the hydrolysis of dioxaphospholene structures with water. Early reports by Ramirez [153, 156, 208] indicated that the addition of water to aliphatic-diketone derived dioxaphospholenes resulted in nearly quantitative conversion to the cyclic phosphate ester (analogous to Ib, Figure 53, $\delta$ -12 ppm, cf. [209]). Later, studies of the hydrolysis reaction on related substrates found complete hydrolysis to the open-chain phosphate ester form (analogous to Ic) [169, 175, 210].

Until recently, few hydrolysis studies on (orth-quinone-derived) benzodioxaphospholene structures have been reported. Kirillova and Kukhtin found that the hydrolysis of dioxaphospholenes derived from TMP/1,2-naphthoquinones gave predominantly the dimethyl-phosphate ester with little cyclic phosphate adduct [211]. A number of workers, including this group [184, 189], have recently confirmed that TMP derivatization of ortho-quinones, followed by hydrolysis, yields stable dimethylphosphate ester products and negligible cyclic phosphate ester content [127, 155, 185, 203, 211].

For 3-methoxy-1,2-benzoquinone, the stable products of hydrolysis are two dimethylphosphate esters (Ic, Figure 53) with resonances at $\delta$ -2.0 and $\delta$ -2.7 ppm (Table 11). Note, ring opening of the benzodioxaphospholene structure leads to either C1 or C2 substituted isomers (Ic, Figure 53). The chemical shifts of adduct(s) Ic compare favorably with $\delta$ -2.3 ppm reported in related studies (CDCl$_3$ solvent) [127, 203]. 4-tert-
Butyl- and 4-methyl-1,2-benzoquinone were derivatized by TMP and also displayed adducts in the δ -2.5 ppm region (Table 11).

**Table 11. Chemical shifts for TMP-quinone adducts.**

<table>
<thead>
<tr>
<th>Benzoquinone</th>
<th>δ^{31}P (ppm) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methoxy-1,2-benzoquinone (I)</td>
<td>-2.0, -2.7</td>
</tr>
<tr>
<td>4-tert-butyl-1,2-benzoquinone (II)</td>
<td>-2.3, -2.6</td>
</tr>
<tr>
<td>4-methyl-1,2-benzoquinone (III)</td>
<td>-2.4, -2.6</td>
</tr>
<tr>
<td>2,6-dimethoxy-1,4-benzoquinone (IV)</td>
<td>-1.6, -1.7</td>
</tr>
<tr>
<td>2-tert-butyl-1,4-benzoquinone (V)</td>
<td>-2.6, -2.7</td>
</tr>
</tbody>
</table>

*chemical shift of dimethylphosphate ester products.

We further explored characterization of adduct 1c (Figure 53) by ^{31}P-^1H heterocorrelation spectroscopy using the COLOC pulse sequence [212]. Selecting a phosphorus-proton spin coupling constant of 11.0 Hz, indicative of a POCH$_3$ moiety, we found the expected correlation between the phosphorus signal at δ -2.0 and -2.7 ppm with methoxyl proton, δ 3.8 ppm, thereby further supporting assignment of the adducts as dimethylphosphate esters (Figure 54).

![Figure 54. ^{31}P-^1H heterocorrelation spectrum (COLOC) of TMP treated 3-methoxy-1,2-benzoquinone.](image)

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The reaction of TMP with \textit{para}–benzoquinone structures has been well documented [127, 153, 154, 174, 175, 184, 189, 203, 205, 213]. In Figure 55 the reaction of TMP with 2–\textit{tert}–butyl–1,4–benzoquinone (V) is shown. Initial attack of the phosphorus is reported to give a tetraalkoxyphosphonium intermediate. The intermediate (Va, Figure 55) is a very reactive alkylating agent (cf. [167]) and is readily degraded by water to the analogous hydroquinone (Vb, Figure 55) [154, 173, 214].

\begin{center}
\includegraphics[width=0.8\textwidth]{figure55.png}
\end{center}

Figure 55. Reaction of TMP with 4–\textit{tert}–butyl–1,4–benzoquinone.

If water is excluded from the reaction mixture, methyl group translocation to another molecule Va (Figure 55) gives the dimethylphosphate ester (Vc) in high yield [184, 189, 203, 213]. Note, although the reaction intermediate (Va, Figure 55) is hydrolytically unstable, the dimethylphosphate ester product(s) are stable to the presence of water [173]. As with the \textit{ortho}–benzoquinone substrates, TMP derivatized \textit{para}–benzoquinones may give two isomeric dimethylphosphate ester products. From Table 11, chemical shift data for the 2–\textit{tert}–butyl– and 2,6–dimethoxy–1,4–benzoquinone derived phosphate esters were found at δ -1.6 to -2.7 ppm — in the same region as derivatized \textit{ortho}–benzoquinones.

\textbf{Yield Data.} Table 12 lists dimethylphosphate ester yield data for TMP derivatized of \textit{ortho}– and \textit{para}–benzoquinone model compounds. The initial derivatization conditions in-

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volved 50% TMP/DMF treatment for two days. The most sterically hindered benzoqui-
nones, II and IV (Table 12), were found to give high yield (>83.7%) of the desired di-
methylephosphate adduct. Generally, the dimethylephosphate yield appeared to correlate
with benzoquinone structure.

Table 12. Reaction yields of quinone compounds derivatized with TMP.

<table>
<thead>
<tr>
<th>Benzoquinone</th>
<th>Yield * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methoxy-1,2-benzoquinone (I)</td>
<td>53.5 (80.8k, 22.2 *)</td>
</tr>
<tr>
<td>4-tert-butyl-1,2-benzoquinone (II)</td>
<td>83.7 (84.1 b)</td>
</tr>
<tr>
<td>4-methyl-1,2-benzoquinone (III)</td>
<td>69.9 (71.7 b)</td>
</tr>
<tr>
<td>2,6-dimethoxy-1,4-benzoquinone (IV)</td>
<td>95.7</td>
</tr>
<tr>
<td>2-tert-butyl-1,4-benzoquinone (V)</td>
<td>70.1</td>
</tr>
<tr>
<td>oxidized PVP (VI)</td>
<td>0.116 mmol/g</td>
</tr>
<tr>
<td>PVP</td>
<td>0.006 mmol/g</td>
</tr>
</tbody>
</table>

*yield determined by 31P-NMR spectroscopy.

k cooled to -52°C then treated with 100% TMP for 16 hr.

b dissolved in DMF then after 24 hr treated with TMP for 2 days.

We suspected that lower derivatization yields observed for some benzoquinone
compounds (Table 12) were related to instability of the model. Quinones are well known
to be unstable to the presence of light [215] and can also undergo self dimerization via the
Diels–Alder reaction (4π + 2π cycloaddition) [116]. Note, when quinone I was merely
dissolved in DMF solvent (light excluded) for 24 hours before TMP derivatization, the
yield was drastically lowered (22.2%, Table 12).

A series of ortho–benzoquinone compounds were studied using 100% TMP deri-
vatization and, in all cases, the yield increased, especially so for 3-methoxy-1,2–
benzoquinone (I, Table 12). For small ortho–benzoquinone compounds, derivatization
yield may be dependent on the relative rates of self-dimerization and TMP derivatization.
Although, small molecule quinones have been used to represent lignin–quinone structures
[185, 189, 203], in some cases their ephemeral stability in solution may preclude
extrapolation of the yield results to lignin–quinones. Nevertheless, sterically hindered

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benzoquinones, as described in this report (Table 12) and others [185, 189, 203], have given very high dimethylphosphate yields.

During the course of this investigation, PVP enriched with ortho-benzoquinone structures (VI, Figure 52) was prepared and derivatized by TMP (Table 12). An increase in quinone content, relative to unoxidized PVP, was noted. The estimated ortho-benzoquinone enrichment was ~5% of the monomer units. Polymeric quinones such as oxidized PVP should serve as realistic models for lignin–quinones. Like lignin, quinone substructures in oxidized PVP are present at low level in a low mobility matrix. Dimerization reactions should be much less likely to occur than with small molecule quinones. Further work is in progress to verify the quinone content data determined for the oxidized PVP by an alternative method.

**TMP Degradation Products.** Trialkyl- and triaryl-phosphites are well known to degrade to hydrogen–phosphate, (RO)₃P(=O)H, structures by the action of water or acids [158, 166, 172]. Potentially during TMP (VI, Figure 56) treatment of lignin, dimethylphosphate (CH₃O)₂P(=O)H may form because of the presence of traces of water in the reaction mixture and/or lignin–acid or hydroxyl functional groups (VI→VII, Figure 56). Methyl-dimethylphosphonate (IX, Figure 56) is a degradation product that can arise by a facile Arbuzov rearrangement of TMP [216, 217]. TMP oxidation by α, particularly in the presence of quinones [176], can give trimethylphosphate (VIII, Figure 56) [184, 185, 189, 203]. Ideally, degradation products from TMP should either be noninterfering or removed prior to quinone analysis.

![Figure 56. TMP degradation scheme.](image-url)
Although the concentration of degradation products in the TMP reagent is low, their presence can make quinone analysis particularly challenging. An understanding of the potential interference of TMP degradation products is especially important in connection with lignin-quinone analysis in which the quinone content is very low.

Figure 57 illustrates a $^{31}$P–NMR spectrum of TMP and its degradation products (DMSO–d$_6$ solvent). Chemical shifts and $^{31}$P–$^1$H coupling constants for TMP-derived structures are given in Table 13. Clearly, all degradation products, as illustrated in Figure 56, are observed in the spectrum (Figure 57). The component with a chemical shift at δ 12.6 ppm gives a doublet of two septets ($J_{p,CH_3} = 12.1$ Hz) when observed with protons coupled (Figure 57A). The septet indicates the presence of two –OCH$_3$ groups directly bonded to phosphorus [218]. The large dispersion between the two septets is due to a 699.4 Hz coupling constant ($J_{pm}$), which is a unique signature for hydrogen–phosphites [146], arising from dimethylphosphite (Figure 57). The noted presence of dimethylphosphite is consistent with TMP hydrolysis.

![Figure 57. Proton decoupled $^{31}$P-NMR spectrum of TMP and degradation products. Inset: A) Proton coupled, and B) Waltz–16 proton decoupled.](image-url)
<table>
<thead>
<tr>
<th>δ $^{31}$P (ppm)$^a$</th>
<th>Lit. δ $^{31}$P (ppm)$^a$</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>140.9 (10.7°)</td>
<td>140.9 (10.5–10.7°)</td>
<td>trimethylphosphate (VI)</td>
</tr>
<tr>
<td>33.8 (17.5°, 11.0°)</td>
<td>29.1–32.3 (17.3°, 10.9°)</td>
<td>dimethylethylphosphonate (IX)</td>
</tr>
<tr>
<td>12.6 (699.4°, 12.1°)</td>
<td>9.3–14.3 (710°, 12°)</td>
<td>dimethylphosphate (VII)</td>
</tr>
<tr>
<td>3.5 (11.1°)</td>
<td>-2.4–2.4 (10.2–11.4°)</td>
<td>trimethylphosphate (VIII)</td>
</tr>
</tbody>
</table>

$^a$ DMSO–d$_6$ solvent, ~10% v/v, H$_2$PO$_4$ external standard

coupling constants: $J_{PH}$ (Hz)$^b$, $J_{PC}$ (Hz)$^c$, $J_{PC}$ (Hz)$^d$

$^b$ literature: [146, 181, 218-221]

Our experience has indicated that the presence of dimethylphosphate causes difficulty with trace quinone quantification. Proton decoupling is often used in $^{31}$P–NMR spectroscopy because an increase in peak sharpness and sensitivity can be gained. Standard 1D $^{31}$P (and $^{13}$C) pulse sequences on modern NMR spectrometers typically use the Waltz–16 (1H) decoupling scheme. Unfortunately, Waltz–16 1H decoupling of dimethylphosphate was found to introduce cycling sideband interference [222] into the spectrum (Figure 57 B). The decoupling artifacts can clearly be seen in Figure 57 B as spurious spikes symmetrical about the central resonance. The spurious resonances were observed to occur well within the δ-2 ppm region used to monitor benzoquinone derivatives.

Preliminary $^{31}$P–NMR studies of TMP–derivatized lignin (containing dimethylphosphate) were found to suffer from severe cycling sideband interference when Waltz–16 1H decoupling was used. Two strategies were selected to give a robust method for trace quinone analysis. First, the negative influence of dimethyl-phosphite was substantially reduced by removing the volatile compound using vacuum and heat [183, 184, 189]. Second, residual dimethylphosphate was found to be effectively 1H decoupled by using classical high-power broadband decoupling (Figure 57) instead of the Waltz–16 sequence. To further mitigate TMP degradation, quantitative derivatization was conducted under an argon atmosphere, in the dark, and using anhydrous solvents.
Quinone Contents of Isolated Lignins. We applied TMP derivatization/\(^31^P\)-NMR analysis to a series of lignins isolated from bleached and unbleached kraft pulps. An important NMR parameter that must be evaluated prior to quantitative NMR acquisition is the spin–lattice (\(T_1\)) relaxation parameter. Typically five times the \(T_1\) parameter is selected as the shortest pulse delay that may be used during quantitative NMR acquisition [178].

The applicable \(T_1\) parameters were determined in this study on actual derivatized lignin samples and oxidized PVP (Table 14). Additionally, the \(T_1\) parameter for the internal standard was determined at a concentration typical of routine analysis (Table 14). It should be noted that the \(T_1\) parameter is a dynamic parameter that is influenced by a number of factors including: concentration of Cr(acac)\(_3\), sample concentration, solvent, and others [178, 182]. Quantitative NMR acquisition can be assured for any of the samples listed in Table 14 when a 5-second (90°) pulse delay is used.

Table 14. Chemical shifts and spin–lattice relaxation times for TMP–quinone adducts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta \ ^{31}P) (ppm)</th>
<th>(T_1) (sec)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxidized PVP</td>
<td>-2.7 (^b)</td>
<td>0.70</td>
</tr>
<tr>
<td>TMP treated D(_b) (KF = 0.2, SW brownstock kappa = 29)</td>
<td>-2.5 (^b)</td>
<td>0.70</td>
</tr>
<tr>
<td>TTP (0.84 mg/mL, 1.0 mg/mL Cr(acac)(_3))</td>
<td>-16.3</td>
<td>0.77 (0.75 (^c))</td>
</tr>
</tbody>
</table>

\(^a\)\(T_1\) of dimethylphosphate adduct (\(<-2\) ppm) or TTP.
\(^b\)determined by line shape analysis (NUTS, Acorn NMR).
\(^c\)in the presence of derivatized D\(_b\) lignin (KF = 0.2, SW brownstock kappa = 29).

Table 15 gives quinone content data for a series of residual lignins isolated from bleached pulps. Referring to item X (Table 15), the lignin–quinone content was measured after 2 and 7 days of TMP treatment. The content measured after 2 days was 98% of the 7-day result, indicating that a 2-day reaction is sufficient for quantitative derivatization. Similarly, the quinone contents for various other isolated lignins also had second day values close to the 7 day result (\(>93\%), XI, XIII, and XIV, Table 15). In a few cases, deriva-
tization was studied using DMSO as a solvent instead of DMF (XII and XV–XVIII, Table 15) (cf. [123, 183, 184, 189]). The quinone content values were close in value when either solvent was used (XII, Table 15).

Table 15. Quinone contents of TMP derivatized lignins.

<table>
<thead>
<tr>
<th>Residual Lignin</th>
<th>Quinone concentration (mmol/g lignin)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF (2-day)*</td>
</tr>
<tr>
<td>SW kraft pulps 5</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Dₜ (KF = 0.2, EMCC™ BS kappa = 29)</td>
</tr>
<tr>
<td>XI</td>
<td>BS (kappa = 28)</td>
</tr>
<tr>
<td>XII</td>
<td>Dₜ (KF = 0.2, BS kappa = 28)</td>
</tr>
<tr>
<td>XIII</td>
<td>DE (KF = 0.05)</td>
</tr>
<tr>
<td>XIV</td>
<td>DB (KF = 0.2)</td>
</tr>
<tr>
<td></td>
<td>PS/AO kraft pulps 5</td>
</tr>
<tr>
<td>XV</td>
<td>BS (kappa = 45)</td>
</tr>
<tr>
<td>XVI</td>
<td>O</td>
</tr>
<tr>
<td>XVII</td>
<td>OO</td>
</tr>
<tr>
<td>XVIII</td>
<td>OPa</td>
</tr>
</tbody>
</table>

5 = not determined, * treatment time, 7 see Frouss et al. [25], 8 7 days 50% TMP/DMSO, 9 2 days 50% TMP/DMF (2% water), * see Moe et al. [135].

In a recent effort, Argyropoulos and Zhang found that the TMP derivatization yield of simple quinone compounds is ~70% when the reaction is performed in DMF containing both 0.5% water and lignin [203]. As a result of this experiment, they concluded that the measured quinone content of TMP derivatized lignin must be multiplied by 1.43 (i.e. 100/70) to give the actual content. From a review of the literature, the lower derivatization yield, observed by Argyropoulos and Zhang [203], is consistent with reports indicating that TMP, in the presence of water, acts as a quinone reducing agent [154, 173, 214].

To verify the hypothesis that water reduces derivatization yield, we derivatized a chlorine dioxide residual lignin using DMF solvent containing 2% water. The measured
quinone content was found to be 53% of the value when anhydrous DMF solvent was used (X, Table 15). Therefore, the use of both dry samples and reagents during TMP treatment are likely essential for quantitative derivatization.

Chlorine dioxide has been reported in several studies [56, 58, 78, 79, 149-151] to oxidize phenolic lignin model compounds to ortho- and para-benzoquinone structures. Table 15 documents the dramatic introduction of colored lignin-quinone structures as a result of chlorine dioxide bleaching. Comparing residual lignins isolated from unbleached (XI, Table 15) and chlorine dioxide bleached (XII) pulps [25], a ~3-fold increase in the quinone is measured.

Increased lignin-quinone content after chlorine dioxide bleaching may be counterintuitive because it strongly suggests the bleaching stage darkens the lignin remaining in the pulp. In fact, by visible spectroscopy, we have demonstrated that chlorine dioxide darkens lignin [184]. These results suggest that chlorine dioxide bleaching involves both productive lignin removal and counterproductive lignin darkening reactions.

Industrially, after chlorine dioxide bleaching, pulps are processed with an alkaline extraction stage. Residual lignins isolated from pulps at this stage showed a dramatically reduced quinone content (XIII and XIV, Table 15). The lower quinone content is consistent with reports indicating alkali degrades quinones to α-hydroxy-carboxylic acid structures via a benzylic acid-type rearrangement [62]. Alternatively, alkali can transform quinones into more highly colored hydroxy-quinone structures [62, 163] that may be resistant to subsequent bleaching operations.

Residual lignins, isolated from oxygen delignified and peracetic acid pulps [135], were also investigated. The quinone contents of residual lignin from the unbleached pulp (XV, Table 15) was found to be low. Oxygen (XVI) and double-stage oxygen (XVII) caused an increase in the measured quinone content, although not as dramatic as observed with chlorine dioxide. Peracetic acid was applied after oxygen delignification gave a beneficial reduction of the quinone content. This result is consistent with higher brightness, as previously reported [135] and its known chemistry [104].

Figure 58 illustrates 31P-NMR spectra of TMP-derivatized chlorine dioxide residual lignin, oxidized PVP, and PVP. The broad Gaussian resonances (Figure 58), centered
at δ -2.5 ppm (Table 14), are attributed to dimethylphosphate TMP/quinone adducts. Note, the resonances from derivatized quinone structures are well separated from downfield signals due to trimethylphosphate (VIII, Table 13) and other aliphatic phosphate esters. The reproducibility of quinone measurement was found to be ±3.5% using an alkaline extraction stage residual lignin (XIV, 2-day treatment, Table 15) derivatized in triplicate.

![Diagram of quinone adducts and internal standard with peaks labeled A, B, and C, and ppm scale from 0 to -20.](image)

**Figure 58.** $^3$P–NMR spectra of compounds treated with 50% TMP/DMF for 2 days: A) D$_5$ residual lignin, B) oxidized PVP, and C) PVP.

**Quinone Content of Oxidized PVP.** Factor and Donahue used TMP derivatization/$^3$P–NMR to quantitatively determine ortho–quinone structures in γ-irradiated bisphenol–A polycarbonate [223]. They monitored derivatized ortho–quinones as the unstable benzo-dioxaphospholene derivative (analogous to Ia, Figure 53). Their work confirmed the presence of quinones as potential colored bodies in these polymers. Similarly, this present study demonstrated the ability to quantify quinone structures in polymeric oxidized PVP (Table 12 and Figure 58). Potentially, TMP derivatization may have broad applicability for the quantitative study of quinone contents in a variety of aromatic–based polymeric materials.

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Secondary Lignin/TMP Reactions. Lignin is rich in a variety of hydroxyl functional groups, and our studies have indicated that a portion of these structures may form TMP-derived products. Identification of these "secondary" reaction products was critical because they may have been falsely attributed to quinone-TMP adducts.

Figure 59 reveals $^{31}$P-NMR spectra of TMP-treated 3,4-dimethoxybenzyl alcohol (A and B) and 3,4-dimethoxybenzoic acid (C). The benzoic acid did not form any apparent adducts with TMP ($\delta$ 140 to -50 ppm monitored) and is shown as a blank spectrum. Clearly, in the blank spectrum (Figure 59C) TMP degradation products are observed, including: dimethylphosphite (VII, Figure 56) and methylphosphate esters ($\delta$ 3.5 (VIII), 1.8, and 0.8 ppm).

**Figure 59.** $^{31}$P-NMR spectra of TMP treated compounds: 3,4-dimethoxybenzyl alcohol A) $^1$H coupled, B) $^1$H decoupled and C) 3,4-dimethoxybenzoic acid $^1$H decoupled.

Hoffmann [170] and others [168, 217, 224] have noted that trialklyphosphites can undergo transesterification with alcohols. Figure 60 illustrates a pathway of TMP benzyl alcohol exchange with subsequent hydrolysis of the mixed trialklyphosphite. Note, the $^1$H decoupled spectrum of 3,4-dimethoxybenzyl alcohol shows the appearance of two new resonances after TMP treatment and hydrolysis ($\delta$ 11.6 and 10.2 ppm, Figure 59B). These signals were tentatively assigned to hydrogen-phosphites formed from single
(XIX, Figure 60) and multiple exchange reactions. The assignment of this structure type is strongly supported by $^{31}$P–$^1$H coupling constant data (~700 Hz, Figure 59A).

$$\text{CH}_3\text{OH} \xrightarrow{\text{P(OCH}_3\text{)}} \text{P(OCH}_3\text{)$_3$OCH}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HP(OCH}_3\text{)$_3$OCH}_2\text{H} \xrightarrow{\text{CH}_3\text{OH}} \text{XIX}$$

**Figure 60.** Alcohol exchange reaction between TMP and benzyl alcohol.

Figure 61 reveals the presence of hydrogen–phosphate structures in TMP–derivatized chlorine dioxide residual lignin. Adducts can be identified in the $^1$H coupled spectra (Figure 61A) as hydrogen–phosphites ($J_{PH} = 716$ Hz), possibly derived from lignin hydroxyl groups such as benzyl alcohol. The lignin polymer is much less mobile than the small molecule benzyl alcohol, hence, only a single alcohol exchange reaction is most likely to occur. Interestingly, the chemical shift of the hydrogen–phosphate product is coincident with cyclic phosphate adducts expected from TMP derivatized ortho-quinones (δ ~ 12 ppm, see Figure 53). But, $^{31}$P–$^1$H spin coupling data excludes the possibility that the δ ~ 12 ppm signal can be assigned to an ortho-quinone derived cyclic phosphate ester.

Figure 61. $^{31}$P–NMR spectra of TMP treated D$_6$ residual lignin: A) $^1$H coupled and B) $^1$H decoupled.

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Conclusions

Trimethylphosphite derivatization and $^{31}$P-NMR spectroscopy has proved useful for a study of the introduction and removal of colored benzoquinone structures during kraft pulp bleaching. Chlorine dioxide bleaching dramatically increased lignin-quinone content whereas subsequent alkaline extraction reduced the content. Oxygen delignification also resulted in quinone formation, but to a lesser extent than with chlorine dioxide. Peracetic acid displayed a beneficial effect by eliminating quinone structures. Consistent with known chemistry, trimethylphosphite in the presence of water gave drastically lower derivatization yield for an isolated chlorine dioxide residual lignin. The optimum derivatization treatment time for isolated lignin in anhydrous DMF solution was found to be approximately two days.

The fundamental chemistry of TMP derivatization of lignin was explored using quinone model compounds, 3,4-dimethoxybenzyl alcohol, and 3,4-dimethoxybenzoic acid. Both ortho- and para-benzoquinone model compounds were found to give dimethylphosphosphate ester products consistent with our previous studies and literature reports. 3,4-Dimethoxybenzoic acid was found to be unreactive with trimethylphosphite. Conversely, 3,4-dimethoxybenzyl alcohol gave dialkylhydrogen phosphate adducts after transesterification with trimethylphosphite and subsequent hydrolysis.

Derivatization yields for quinone model compounds were generally high; cases of incomplete derivatization may be explained by competing self-dimerization and degradation reactions. Hence, some monomeric thermally unstable quinone model compounds are not effective models for benzoquinone structures in isolated lignins. A model polymeric ortho-quinone was prepared by the oxidation of poly(4-vinylphenol) and characterized by trimethylphosphite/$^{31}$P-NMR spectroscopy. Therefore, the developed method may have broader applicability for the study of quinone structures in other aromatic and phenolic polymers.

Major degradation products of the derivatization reagent, TMP, were identified by $^{31}$P-NMR chemical shifts and $^{31}$P-$^1$H coupling constants. Dimethylphosphite was found to cause difficulty with trace lignin-quinone analysis. The negative influence of di-
methylphosphite was substantially reduced by removing the volatile compound using vacuum and heat and using classical high-power broadband decoupling $^1$H decoupled during NMR acquisition.

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6.6. Addendum For Publication Four

6.6.1. Trimethylphosphite Derivatization of Non–Benzoquinone Compounds

To properly establish the utility of the benzoquinone determination by trimethylphosphite derivatization, it was essential to uncover any possible side-reactions that may occur during the derivatization of lignin. Previously, Argyropoulos et al. [51, 130] reported trimethylphosphite forms adducts with a variety of non–benzoquinone compounds particularly carboxylic acid and cinnamaldehyde structures. Conversely, publication four of this study presented evidence that 3,4-dimethoxybenzoic acid does not form a detectable product with trimethylphosphite. Also, 3,4-dimethoxybenzyl alcohol was found to form trimethylphosphite adducts. In a comprehensive treatise on lignin, Sarkanen and Ludwig briefly mentioned trimethylphosphite treatment and reported the product of the reaction as lignin–phosphite (transesterification) derivatives [108]. The $^3$P-NMR spectra of trimethylphosphite treated aldehyde and carboxylic acid model compounds are shown in Figure 62. Note, the carboxylic acid compound was found unreactive with trimethylphosphite (Figure 62, see also Figure 59). Similarly, a recent patent exploited the low reactivity of trimethylphosphite with carboxylic acids for the removal of trace levels of $para$–benzoquinone stabilizer from bulk monomeric acrylic acid solution [225].

A number of workers [166, 172] have indicated that acids cause the degradation of trimethylphosphite to dimethylphosphite ($\delta$ 12.6 ppm, publication four, Figure 56). Alternatively, Batyeva et al. reported that trialkylphosphites can form an adduct with carboxylic acids if the coproduct alcohol is removed (by distillation) from the reaction mixture (Figure 63). The derivatization product is a phosphite–carboxylic acid ester with an expected $^3$P chemical shift in the $\delta \sim 130$ ppm region (cf. [146]). Note, if a phosphite–carboxylic acid adduct was formed during lignin derivatization, then the resulting $^3$P–NMR signal would be well removed from those of trimethylphosphite–cinnone adducts.

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Figure 62. $^{31}$P-NMR spectra of non-benzoquinone model compounds treated with trimethylphosphite A) 4-hydroxy–3–methoxycinnamic acid and B) 4–hydroxy–3–methoxy–cinnamaldehyde.

$$(\text{RO})_3\text{P} + \text{RCOOH} \rightleftharpoons (\text{RO})_2\text{POC}=\text{O}+\text{ROH}$$

Figure 63. Arbuzov product of the reaction of trimethylphosphite with carboxylic acids.

Trialkylyphosphate chemistry is complex; potential reactions of trimethylphosphate with non–benzoquinone carbonyl structures can occur [153, 224, 226, 227]. Figure 62 indicates that 4–hydroxy–3–methoxycinnamaldehyde (I, Figure 64) can react with trimethylphosphite to give a phosphonate product(s) in the δ 30 ppm region (cf. [146]). One possible reaction scheme [153] of I leading to a phosphonate product (II), is shown in Figure 64.

Figure 64. Reaction scheme of 4–hydroxy–3–methoxycinnamaldehyde with trimethylphosphite.
During this study, trans-chalcone (III, Figure 66) was found to react with trimethylphosphite initially giving a oxyphosphorane product [227] at δ -26.51 ppm (Figure 65A, IV Figure 66). The oxyphosphorane was hydrolytically unstable [153] and gave a phosphonate structure at δ 31.50 ppm (Figure 65B, V Figure 66) after water treatment. An expanded spectrum trimethylphosphite derivatized D₆ residual lignin is shown in Figure 67. Possible phosphonate structures (δ 30 ppm region, Figure 67) are observed in the spectrum suggesting that non−benzoquinone lignin structures have been derivatized by trimethylphosphite. Further work would be necessary to catalog all the potential reaction of lignin functional groups but model compound work suggests that the δ -2 ppm region of derivatized lignin (Figure 67) can reasonably be assigned to benzoquinone adducts.

![Diagram of chemical structures](image)

**Figure 65.** ¹³P−NMR spectra of trans−chalcone with derivatized by A) trimethylphosphite B) followed by hydrolysis.

![Diagram of reaction scheme](image)

**Figure 66.** Reaction scheme of trans−chalcone with trimethylphosphite.

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6.6.2. Visible Absorbance Study of Benzoquinone Model Compound Derivatization

Trimethylphosphite derivatization of 4-tert-butyl-1,2-benzoquinone was studied by visible absorption spectrometry. Qualitatively, derivatization of all studied ortho-benzoquinone compounds was found to proceed with decolorization of the reaction mixture. Figure 68 shows that, during trimethylphosphite derivatization, reduction of visible absorbance of 4-tert-butyl-1,2-benzoquinone was essentially complete within 2 days. This derivatization study supports the results previously given for the derivatization of lignin in DMSO (Figure 36) and DMF (Table 15).

When trimethylphosphite derivatization of 2-methoxy-1,4-benzoquinone was studied by visible absorbance spectrometry, the absorbance was found to increase with time (Figure 69). The visible absorbance spectrum, after a 2-day trimethylphosphite treatment (Figure 69, #4), is very similar to the spectrum published by Forsskahl et al. for 2-methoxy-1,4-benzoquinone after exposure to light [215]. Forsskahl interpreted the
dark color of the solution as resulting from dimeric products arising from radical coupling of quinones. The visible absorbance study provides further evidence that dimerization of small monomeric quinones can occur before complete trimethylphosphite derivatization. Clearly, trimethylphosphite derivatization studies on quinone model compounds should be carefully interpreted in light of the known reactivity of some quinone compounds.

Figure 68. Reaction of 4-tert-butyl-1,2-benzoquinone with trimethylphosphite monitored by visible spectroscopy.

Figure 69. Reaction of 2-methoxy-1,4-benzoquinone with trimethylphosphite monitored by visible spectroscopy.
6.7. Quinone Contents of Isolated Lignins

6.7.1. Chlorine Dioxide Bleached Lignin

The formation of lignin-quinone chromophores during chlorine dioxide bleaching was explored by treating an isolated kappa 28 brownstock residual lignin (Appendix 3) in homogeneous solution with various charges of chlorine dioxide. Figure 70 and Figure 71 give lignin-quinone contents versus the applied chlorine dioxide kappa factor (KF, Equation 6) and actual consumed KF, respectively. For a hypothetical kappa 30 pulp the KF data can be expressed as an equivalent % ClO₂ (wt/wt) as in Equation 13. For example, 0.2 KF would be equivalent to 2.3 % chlorine dioxide (wt/wt) applied on the hypothetical kappa 30 pulp.

\[ \text{KF (11.39) = % ClO}_2 (\text{wt/wt}) \]  
(Equation 13)

![Figure 70. Quinone contents versus chlorine dioxide KF applied.](image)

The data in Figure 70 show that the application of chlorine dioxide to the isolated lignin results in the introduction of quinone structures. An increase in quinone content is measured with increasing application of chlorine dioxide. Interestingly, a plateau is reached at approximately 0.30 mmol quinone/g lignin using 0.2 KF applied chlorine dioxide charge. A very high chlorine dioxide dosage of 1.92 KF failed to increase the
Quinone content further. A series of spectra demonstrating the enrichment of lignin–quinone structures as a result of applied chlorine dioxide are shown Figure 72. The concentration of lignin–quinone structures observed during solution bleaching is similar to those determined in a separate pulp bleaching study (publication one, 2.3% D = 0.2 KF), [Q] = 0.223 mmol/g lignin).

Figure 72. $^{31}$P–NMR spectra of trimethylphosphite treated residual lignins bleached in homogeneous solution with chlorine dioxide (KF chlorine dioxide applied).
At the end of the solution bleaching experiment, residual chlorine dioxide was measured. Figure 71 shows the quinone content data expressed on an actual KF chlorine dioxide consumed basis. The chlorine dioxide residual was found to increase dramatically after the application of more than 0.2 KF. Possibly, application of greater than 0.2 KF chlorine dioxide results in little further lignin oxidation and certainly no greater introduction of quinone structures (Figure 71).

The data in Figure 71 suggest possible pathways of chlorine dioxide bleaching. Firstly, lignin–quinone structures may be rapidly formed until phenolic and non-phenolic lignin precursors are exhausted. Indeed, in a separate study, Froese found a leveling off of total consumed phenolic structures at 0.1–0.2 KF (applied chlorine dioxide) [25]. If this pathway is predominant, then further application of chlorine dioxide appears not to degrade the already formed lignin–quinone structures. Alternatively, a balance may be reached between lignin–quinone formation and destruction.

Interestingly, the introduction of lignin–quinone structures follows the general form of brightness ceiling development as documented by McDonough [72, 73, 76]. Possibly, brightness ceiling development may be partly accounted for by the accumulation of lignin–chromophores. Alternatively, lignin–quinone introduction may be a surrogate for gross lignin oxidation that occurs during chlorine dioxide bleaching.

6.7.2. Residual Lignins From Peracetic Acid and Oxygen Delignified Pulps

The trimethylphosphite derivatization technique was further applied to a series of residual lignins isolated from oxygen delignified pulps. A more detailed analysis of pulp properties and residual lignin functional group contents is given in Appendix 10 (publication six). During this study, an alternate method of quinone analysis was used to verify the results determined by ^19F–NMR spectroscopy. The alternate method relied on 4–trifluoromethylphenylhydrazine derivatization and analysis by ^19F–NMR spectroscopy.
Both kappa 24 and 47 brownstock pulps were oxygen delignified under various conditions. Oxygen delignification was targeted at two levels ~42% or "standard" delignification (O) and an "aggressive" degree of delignification (~68%, O*) employing additional alkali and higher temperature. Selected experiments used peracetic acid pretreatment before oxygen delignification. Peracetic acid treatment was performed at pH ~ 8 and pulps were not washed before subsequent oxygen delignification. The peracetic acid pretreatment method was selected so that it could easily be implemented at the mill level. Potentially, brownstock may be treated with peracetic acid in the brownstock storage chest without pH adjustment. After 1 hour residence time, and moderate treatment temperature (70°C), the pulp may only need to be dewatered before an oxygen delignification stage. Selected properties for the Pa/O series of pulps are given in Figure 73 and Figure 74.

![Figure 73. Brightness versus kappa number for PaO pulps.](image)

Note in Figure 73 that, in comparison, the kappa 47 brownstock pulps gave higher brightness values than the kappa 24 pulps. Although a limited and low brightness range was studied, we can see from Figure 73 that the high and low kappa pulps follow parallel curves with the kappa 47 brownstock pulps brighter at any given kappa number. A similar effect was noted by Gajdos [228] and Steffes et al. [229] who found that high kappa pulps gave higher brightness values after oxygen delignification.
The data in Figure 73 indicate that peracetic acid pretreatment between two oxygen stages results in greater kappa reduction relative to the OO sequence. Other researchers have noted the activating influence of peracetic acid applied between two oxygen stages [230]. Peracetic acid pretreatment followed by (single-stage) oxygen delignification gave a greater kappa number drop than oxygen delignification alone. For the kappa 47 pulp, peracetic acid pretreatment followed by aggressive oxygen delignification (BS(47)PaO*), gave higher pulp viscosity, similar kappa number, and slightly lower brightness than interstage pretreatment (BS(47)OPaO).

The high kappa pulp showed higher viscosity at any given brightness value (Figure 74). Apparently the high intrinsic viscosity of the kappa 47 brownsstock is preserved during oxygen delignification. Steffes et al. noted that viscosity selectivity (Δ viscosity per Δ kappa) is relatively constant for oxygen delignification over the pulp kappa number 18.9–57.1 [229]. Generally, 50% delignification is taken as a rule of thumb for the maximum delignification that can be achieved without unacceptable loss of viscosity. Clearly, for this study, the kappa 47 pulp can adequately withstand >50% oxygen delignification, possibly because of its high intrinsic viscosity.

Due to the range of brightness values exhibited for the PaO pulps, quinone analysis was explored as a probe of chromophore changes during oxygen delignification. Figure 75 and Figure 76 display the quinone contents, measured by $^{31}$P-NMR.
spectroscopy, for a series of residual lignins isolated from the Pa/O pulps. In contrast to previous reports on chlorine dioxide bleaching (publication one through four), the quinone contents were found to be uniformly low regardless of the exact oxygen delignification or peracetic acid pretreatment conditions used.

**Figure 75.** Quinone contents of BS(47) Pa/O residual lignins determined by trimethylphosphite derivatization and $^{31}$P-NMR spectroscopy.

**Figure 76.** Quinone contents of BS(24) Pa/O residual lignins determined by trimethylphosphite derivatization and $^{31}$P-NMR spectroscopy.

Oxygen/alkali can potentially cause the formation of quinone products from phenolic-lignin precursors by Dakin or Dakin–like reactions [190]. The low quinone content results observed during this investigation supports model compound studies [59, 190, 131]
231] that indicate quinone intermediates are unstable and further oxidized to muconic acid and other structures. From a UV/visible spectroscopy-based investigation, Pasco and Suckling speculated that simple quinone structures may not be the sole cause of visible-region absorbance in oxygen/alkali treated kraft lignins [232]. Therefore, the low quinone content measured in the Pa/O residual lignins, appears to indicate that these structures may not be the major chromophores present in oxygen delignified pulps.

The quinone content values determined by trimethylphosphite\(^{31}\)P-NMR were verified by using the \(^{19}\)F-NMR spectroscopic technique proposed by Scvillano et al. [122, 145]. For example, the quinone content for periodate and chlorine dioxide (KF = 0.2) residual lignins were found be 0.503 and 0.322 mmol/g lignin respectively by \(^{19}\)F-NMR (Figure 77 and Figure 78), and 0.431 and 0.302 ± 0.004 (LSD = 0.02) mmol/g lignin by \(^{31}\)P-NMR (Figure 79). Similarly, the quinone contents for kappa 47 Pa/O residual lignins determined by both \(^{19}\)F- and \(^{31}\)P-NMR were also close in value (Figure 75 and Figure 77). Notable exceptions were the values determined for BS(47) and BS(47)O lignin samples; \(^{19}\)F-NMR values are 3.3 and 1.7 times higher, respectively, than the \(^{31}\)P-NMR values (Figure 75 and Figure 76). The \(^{19}\)F-NMR-derived results for BS(47) and BS(47)O residual lignins were replicated.

![Graph showing quinone and carbonyl contents of BS(47) Pa/O residual lignins as determined by \(^{19}\)F-NMR spectroscopy.]

Figure 77. Carbonyl and quinone contents of BS(47) Pa/O residual lignins as determined by \(^{19}\)F-NMR spectroscopy.
For accurate results, the $^{19}$F–NMR method relies on the formation of the azo(-phenol) derivative ($\delta \approx -61.2$ ppm) for quinones and the hydrazone derivative ($\delta \approx -60.5$ ppm) for other carbonyl structures (Figure 78, cf. [233, 234] re. azo-phenol/hydrazone tautomerism). Note, the $^{19}$F–NMR method [122, 145] has been verified on only a small number of model compounds. The $^{19}$F–NMR methodology should be applied to non-benzoquinone carbonyl structures to confirm that only derivatized
quinone structures can exist in the azo tautomer. Additionally, the influence of sample preparation conditions on the potential oxidation of lignin-hydrazone to the azo form is not yet known. Otherwise, the close correspondence of $^1$H- and $^3$P-NMR values for most of the examined pulps serves to verify both methods for the determination of quinones in lignins.

The $^1$H-NMR method was useful for the determination of lignin-carbonyl functional groups. For kappa 47 Pa/O residual lignins, application of oxygen caused an increase in carbonyl content above the brownstock value but very little difference in carbonyl content was observed between the individual Pa/O lignins (Figure 77). The result for the BS(47)O residual lignin is similar to carbonyl content data determined by Lachenal et al. for an oxygen-stage residual lignin (BS kappa 30, 53% d(w/g), C=O content of 0.16/200g lignin = 0.9 mmol/g lignin) [5].
7. Conclusions

This study was focused on the development of a quantitative analytical methodology for the determination of benzoquinone structures in isolated lignins. Previously, Lebo et al. [47, 49] and others [130] developed and used trimethylphosphite derivatization, phosphorus microanalysis, and qualitative solid-state $^{31}$P-NMR spectroscopy for the determination of ortho–benzoquinone structures in mechanical pulps. This study extended the original method and yielded a procedure for the simultaneous determination of both ortho– and para–quinone structures in isolated lignins.

The developed methodology was applied toward the analysis of lignin–quinone introduction and removal during chlorine dioxide bleaching of kraft pulp. Chlorine dioxide bleaching was found to dramatically increase the quinone content of residual lignin. Lignin–quinone contents, of DE*DED pulps, correlated well with pulp brightness and brightness ceiling values indicating that these structures may negatively impact upon pulp brightness.

This investigation further suggested that brightness ceiling values may be dependent upon the chromophore content established in earlier bleaching stages. The results of this investigation are consistent with many of the suspected reactions of quinone structures in lignin. For example, the ability of chlorine dioxide to introduce lignin quinone structures and hydrogen peroxide to remove them was clearly observed.

An isolated lignin, treated in homogeneous solution with chlorine dioxide, revealed increased lignin–quinone formation with greater application of chlorine dioxide. The lignin–quinone content reached a maximum value of 0.30 mmol/g lignin and further chlorine dioxide application did not alter the amount. The results are consistent with previous studies which indicated that quinone compounds are relatively stable toward further oxidation by chlorine dioxide.

Interestingly, the introduction of lignin–quinone structures follows the general form of brightness ceiling development as documented by McDonough [72, 73, 76]. Possibly, brightness ceiling development may be partly accounted for by the accumulation of
lignin—chromophores. Alternatively, lignin—quinone introduction may be a surrogate for
gross lignin oxidation that occurs during chlorine dioxide bleaching.

Benzoquinone contents of a series of lignins isolated at the oxidative alkaline ex-
traction stage reveal that alkali alone causes a significant reduction of lignin—quinone
content. Hydrogen peroxide and oxygen reinforcement of the alkaline extraction stage
resulted in enhanced degradation of lignin—quinone structures.

The fundamental chemistry of trimethylphosphite derivatization was explored on
a series of ortho— and para—benzoquinone model compounds. Both ortho— and para—
benzoquinones were found to give dimethylphosphate ester isomers of the analogous
catechol or hydroquinone structures. Assignment of the products was accomplished by
one— and two—dimensional 31P—NMR spectroscopy. The phosphorus chemical shifts of
the trimethylphosphite adducts of both ortho— and para—benzoquinones were found to
occur in the δ—2 ppm region. Derivatization yields for quinone model compounds were
generally high, and cases of less than complete derivatization may possibly be explain by
competing self—dimerization and degradation reactions. Hence, some monomeric ther-
mally unstable quinone model compounds are not effective models for quinone structures
in isolated lignins.

Non—benzoquinone model compounds representing additional lignin functional
groups were also studied. Notably, 3,4—dimethoxybenzyl alcohol was found to undergo
trianetization with trimethylphosphite giving, after hydrolysis, hydrogen—phosphite
adducts with phosphorus NMR signals in the δ—12 ppm region. Analysis of a
trimethylphosphite—derivatized chlorine dioxide lignin revealed the presence of these hy-
drogen—phosphite products.

The hydrogen—phosphite product (δ—12 ppm) was found to be more abundant
than quinone—derived resonances (δ—2 ppm). Interestingly, the chemical shift of the
hydrogen—phosphite product was coincident with the chemical shift expected for the cy-
clic phosphate of derivatized ortho—benzoquinone (δ—12 ppm). But, 31P—1H spin cou-
pling data excluded the possibility that the large signal observed at δ—12 ppm could be
assigned to an ortho—benzoquinone derived cyclic phosphate ester.
Benzoic acid and cinnamic acid model compounds were found to be inert under the derivatization conditions studied, in contrast to previous literature reports. Trans-chalcone gave a oxophosphorane adduct at δ -26.51 ppm, the adduct was unstable to the presence of water and yielded products including a phosphonate at δ 31.50 ppm.

Major degradation products of the derivatization reagent, trimethylphosphite, were identified by \(^{31}\)P-NMR chemical shifts and \(^{31}\)P-\(^{1}\)H coupling constants. Hydrolysis of trimethylphosphite gave dimethylphosphate as a product. Dimethylphosphite was found to severely impact upon \(^{31}\)P-NMR quantification of lignin–quinone adducts. The influence of this trimethylphosphite degradation compound was substantially reduced by its elimination with vacuum and heat.

A series of peracetic acid pretreated and oxygen delignified pulps (PaO) were prepared using both aggressive and standard oxygen delignification conditions. Regardless of the delignification conditions, the quinone contents of these pulps were uniformly low. These results suggest that lignin–quinone structures may not be a major chromophore influencing brightness development of PaO pulps.
8. **Recommendations for Further Research**

The trimethylphosphite derivatization methodology, as developed during this thesis work has shown great promise to study one important class of lignin chromophore — benzoquinones. The analysis of benzoquinone chromophores in isolated lignins is virtually an unexplored area of study because previously no reliable and quantitative methods were available [118].

The trimethylphosphite$^{31}$P-NMR methodology opens up many new avenues for research. In particular, this work has revealed that chlorine dioxide causes a dramatic enrichment of quinone structures in treated lignin samples. The method could be useful for the analysis of chlorine dioxide bleaching parameters influencing lignin–quinone introduction, for example: pH, temperature, and reaction time. Potentially the chlorine dioxide bleaching stage may be optimized to minimize lignin-quinone formation.

Lignin-quinone structures initially formed in the chlorine dioxide are likely altered in a subsequent alkaline extraction stage. The method should be used to further explore the alkali-darkening reaction. Furthermore, the exact contribution of lignin–quinone structures to visible region absorption coefficient should be determined using this quantitative technique.

Finally, this work has explored aggressive (~68% delignification) oxygen delignification of a high kappa pulp. Aggressive oxygen delignification using a high kappa pulp is a promising approach which should be explored further. Pulp properties should be determined after bleaching to market brightness. Quinone analysis of the oxygen delignified pulps suggest that lignin–quinone structures are not an important chromophore for these pulps. Further lignin structural studies should be undertaken to determine the exact nature of the chromophoric structures in these pulps.
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10. Appendix 1. $^1$H-, $^{13}$C-, and $^{31}$P-NMR Spectroscopy for Lignin Analysis.

The analytical techniques of $^1$H-NMR, $^{13}$C-NMR, and $^{31}$P-NMR are essential tools for the determination of residual lignin structural features impacting upon delignification and brightening reactions. Below is a brief review of the application of NMR spectroscopy for lignin analysis.

Proton–NMR is able to quantify a number of important residual lignin structural features [25, 191, 235] including: carboxylic acid ($\delta$ 12.6–13.5 ppm), aldehyde ($\delta$ 9.4–10.0 ppm) [191, 256], phenolic hydroxyl ($\delta$ 8.0–9.4 ppm), $\beta$–5 phenolic hydroxyl ($\delta$ 8.99 ppm), syringyl C5 phenolic hydroxyl ($\delta$ 8.0–8.5 ppm), aromatic protons ($\delta$ 6.3–7.7 ppm), and aliphatic protons [237, 238]. Proton-NMR has also been used for the quantification of structures in lignin related humic acid and fulvic acid samples [239].

The major advantages of $^1$H-NMR are no modification of the residual lignin is required and the high intrinsic sensitivity allows for the use of a small sample size and a short acquisition time. Figure 80 illustrates a typical $^1$H-NMR spectrum of a nonacetylated kraft softwood residual lignin.

Acetylation of lignins may cause unwanted chemical modification of the lignin sample. Because of the danger of lignin structure modification the use of underivatized samples is preferable. Unfortunately, lignin has an abundance of hydroxyl functional groups and the chemical shift of hydroxyl groups in proton NMR spectroscopy is strongly dependent upon experimental conditions [235, 240]. Also, exchange of acidic protons with traces of water limits quantitative analysis. Fortunately, DMSO–$d_6$ is an excellent lignin solvent and the chemical shift of hydroxyl protons in this solvent is characteristic and proton exchange is slow [240]. Li and Lundquist have stated that $^1$H–NMR spectroscopic analysis of lignin–phenolic groups in DMSO–$d_6$ solvent is possible if the following conditions are maintained: the amount of water present is minimized, no acid is present except for the small number of lignin–carboxylic acid groups, and no base is present [191]. The $T_1$ relaxation parameter for lignin in DMSO–$d_6$ solution has been found to be $< 1$ second and a pulse delay of 7 seconds has been used [191]. In support of the $T_1$ data
for lignin, the $T_1$ relaxation parameter for fulvic acid in D$_2$O solution is reported to be $\sim$1.2 seconds [239].

![Figure 89. Quantitative $^1$H–NMR spectrum of a residual isolated from an oxygen delignified softwood kraft pulp (brownstock, kappa = 47, prepared in this study).](image)

Carbon($^{13}$C)–NMR is a powerful technique capable of revealing a large amount of lignin structural information including the presence of aryl ether, condensed and uncondensed aromatic and aliphatic carbons [4, 241-247]. Table 16 lists an extensive compilation of structural assignments that have been derived from model compound studies [247]. The major disadvantage of $^{13}$C–NMR spectroscopy is the inherent low sensitivity which requires that a large sample size and a long acquisition time be used. Nonacetylated lignin samples are dissolved in either DMSO–d$_6$ or acetone–d$_6$/D$_2$O (9:1 v/v) at a concentration of 400–600 mg lignin / 1.8 mL solvent [244]. Functional group chemical shift differences between the two solvent systems are generally less than 1 ppm [243].

Quantitative $^{13}$C–NMR analysis requires a number of conditions to be fulfilled [244]. First, the lignin sample must be free of contaminants such as carbohydrates or extractives. Also, the lignin/solvent solution must be made as concentrated as possible to maximize signal-to-noise and minimize baseline and phasag distortions. Generally, $^{13}$C–NMR spectra of concentrated lignin/DMSO–d$_6$ are acquired at 50°C in order to reduce
viscosity. A 11-second pulse delay has been used [4, 244] which is five times the longest lignin-carbon T1 relaxation time [248]. Finally, the inverse—gated decoupling sequence is used which involves turning off the proton decoupler during the recovery between pulses so that the NOE effect is avoided.

Figure 81. Quantitative 13C-NMR spectrum of softwood residual lignin (brownstock, kappa = 47, prepared in this study).

Phosphorous–NMR has been exploited to determine hydroxyl functional groups in various substrates [249] including coal [250, 251], and isolated lignin [8, 25, 128, 134, 252-254]. Trivalent and pentavalent phosphorous reagent have been used [249]. The largest diastereomeric shift differences [249] and substituent influences [255] are observed with trivalent phosphorous reagents.

Hydroxyl functional groups in isolated lignins have been identified by a 31P–NMR technique that involves derivatization with the phosphorylating agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) [8, 25, 128, 134, 252-254]. The reaction of TMDP with hydroxyl functional groups is illustrated in Figure 82. TMDP reacts with hydroxyl functional groups to give phosphate products which are resolvable by 31P–NMR into separate regions arising from aliphatic hydroxyl, phenolic, and carboxylic acids groups. Figure 83 illustrates typical spectra of a TMDP treated softwood residual lignin.

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<table>
<thead>
<tr>
<th>δ 13C-NMR (ppm)</th>
<th>Structure *</th>
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<tr>
<td>193.4</td>
<td>C=O in (\phi)-CH=CH-CHO, C=O in (\phi)-C(=O)CH(-O (\phi)-C-)</td>
</tr>
<tr>
<td>191.6</td>
<td>C=O in (\phi)-CHO</td>
</tr>
<tr>
<td>169.4</td>
<td>Ester C=O in R-C(=O)OCH₃</td>
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<tr>
<td>166.2</td>
<td>C=O in (\phi)-COOH, Ester C=O in (\phi)-C(=O)OR</td>
</tr>
<tr>
<td>156.4</td>
<td>C-4 in H-units</td>
</tr>
<tr>
<td>152.9</td>
<td>C-3/C-3' in etherified 5-5 units, C-(\alpha) in (\phi)-CH=CH-CHO units</td>
</tr>
<tr>
<td>152.1</td>
<td>C-3/C-5 in etherified S units and B ring of 4-O-5 units</td>
</tr>
<tr>
<td>151.3</td>
<td>C-4 in etherified G units with (\alpha)-C=O</td>
</tr>
<tr>
<td>149.4</td>
<td>C-3 in etherified G units</td>
</tr>
<tr>
<td>149.1</td>
<td>C-3 in etherified G type (\beta)-O-4 units</td>
</tr>
<tr>
<td>146.8</td>
<td>C-4 in etherified G units</td>
</tr>
<tr>
<td>146.6</td>
<td>C-3 in non-etherified G units ((\beta)-O-4 type)</td>
</tr>
<tr>
<td>145.8</td>
<td>C-4 in non-etherified G units</td>
</tr>
<tr>
<td>145.0</td>
<td>C-4/C-4' of etherified 5-5 units</td>
</tr>
<tr>
<td>143.3</td>
<td>C-4 in ring B of (\beta)-5 units, C-4/C-4' of non-etherified 5-5 units</td>
</tr>
<tr>
<td>134.6</td>
<td>C-1 in etherified G units</td>
</tr>
<tr>
<td>132.4</td>
<td>C-5/C-5' in etherified 5-5 units</td>
</tr>
<tr>
<td>131.1</td>
<td>C-1 in non-etherified 5-5 units</td>
</tr>
<tr>
<td>129.3</td>
<td>C-(\beta) in (\phi)-CH=CH-CHO</td>
</tr>
<tr>
<td>128.0</td>
<td>C-(\alpha) and C-(\beta) in (\phi)-CH=CH-CH₂OH</td>
</tr>
<tr>
<td>125.9</td>
<td>C-5/C-5' in non-etherified 5-5 units</td>
</tr>
<tr>
<td>122.6</td>
<td>C-1 and C-6 in (\phi)-C(=O)C=C units</td>
</tr>
<tr>
<td>119.9</td>
<td>C-6 in G units</td>
</tr>
<tr>
<td>118.4</td>
<td>C-6 in G units</td>
</tr>
<tr>
<td>115.1</td>
<td>C-5 in G units</td>
</tr>
<tr>
<td>114.7</td>
<td>C-5 in G units</td>
</tr>
<tr>
<td>111.1</td>
<td>C-2 in G units</td>
</tr>
<tr>
<td>110.4</td>
<td>C-2 in G units</td>
</tr>
<tr>
<td>86.6</td>
<td>C-(\alpha) in G type (\beta)-5 units</td>
</tr>
<tr>
<td>84.6</td>
<td>C-(\beta) in G type (\beta)-O-4 units (threo)</td>
</tr>
<tr>
<td>83.8</td>
<td>C-(\beta) in G type (\beta)-O-4 units (erythro)</td>
</tr>
<tr>
<td>71.8</td>
<td>C-(\alpha) in G type (\beta)-O-4 units (erythro)</td>
</tr>
<tr>
<td>71.2</td>
<td>C-(\alpha) in G type (\beta)-O-4 units (threo), C-(\gamma) in G type (\beta)-(\beta)</td>
</tr>
<tr>
<td>63.2</td>
<td>C-(\gamma) in G type (\beta)-O-4 units with (\alpha)-C=O</td>
</tr>
<tr>
<td>62.8</td>
<td>C-(\gamma) in G type (\beta)-5, (\beta)-1 units</td>
</tr>
<tr>
<td>60.2</td>
<td>C-(\gamma) in G type (\beta)-O-4 units</td>
</tr>
<tr>
<td>55.6</td>
<td>C in (\phi)-OCH₃</td>
</tr>
<tr>
<td>53.9</td>
<td>C-(\beta) in (\beta)-(\beta) units</td>
</tr>
<tr>
<td>53.4</td>
<td>C-(\beta) in (\beta)-5 units</td>
</tr>
</tbody>
</table>

* data from [247], G = guaiacyl, S = syringyl, see Figure 2 for substructures.
sample. Table 17 gives a comprehensive compilation of integration region that have been used for the TMPD/31P–NMR analysis of softwood isolated lignins.

Figure 82. Derivatization of phenolic structures with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP).

The major advantages of the TMPD/31P–NMR is that the technique is well developed and a database of model compound spectral information is available [256]. An additional derivatizing agent, 2-chloro-1,3,2-dioxaphospholane, has been reported to allow for the discrimination between primary and secondary hydroxyl groups and also to differentiate between erythro- and threo- conformations [128]. Quantitative information gained from the technique has been verified against other techniques (benzyl acetate/GC, 1H–NMR, 13C–NMR and 31P–NMR) during a recent international round robin lignin study [252, 257].

Figure 83. Quantitative 31P–NMR spectrum of softwood residual lignin (brownstock, kappa = 47, prepared in this study, derivatized with TMDP).
<table>
<thead>
<tr>
<th>Structure</th>
<th>δ 31P-NMR</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Aliphatic OH</td>
<td>145.1 – 148.1, 145.4 – 150.0, 145.5 – 149.5</td>
<td>[256], [258] *, [259]</td>
</tr>
<tr>
<td>(2) Phenols</td>
<td>137.6 – 144.0, 137.3 – 144.4, 136.6 – 145.5</td>
<td>[256], [258], [259]</td>
</tr>
<tr>
<td>Para-HO-phenyl and catechol</td>
<td>137.5 – 138.2, 137.3 – 138.2</td>
<td>[260], [258]</td>
</tr>
<tr>
<td>Para-hydroxyphenyl</td>
<td>~137.8, 137.4 – 138.2, 136.6 – 138.2</td>
<td>[261], [258] *, [259]</td>
</tr>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>139.0, 138.8</td>
<td>[256]</td>
</tr>
<tr>
<td>3,4-dihydroxyphenylethanol</td>
<td>139.0 – 140.0</td>
<td>[260]</td>
</tr>
<tr>
<td>Guaiacyl</td>
<td>137.5 – 140.0</td>
<td>[260]</td>
</tr>
<tr>
<td>(2a) Combined p-OH-Φ and guaiacyl</td>
<td>137.5 – 140.0</td>
<td>[260]</td>
</tr>
<tr>
<td>(2b) C₅ substituted &quot;condensed&quot;</td>
<td>140.0 – 144.5, 140.3 – 144.4, 140.2 – 144.5</td>
<td>[260], [258], [262]</td>
</tr>
<tr>
<td>β-5</td>
<td>~143.5, 143.0 – 144.3, 144.3 – 142.8</td>
<td>[261], [260] *, [263]</td>
</tr>
<tr>
<td>4-O-5</td>
<td>141.7 – 142.8</td>
<td>[263], [260] *, [263]</td>
</tr>
<tr>
<td>5-5</td>
<td>~141.9, 140.2 – 141.5, 140.2 – 141.7</td>
<td>[261], [260] *, [263]</td>
</tr>
<tr>
<td>(3) Carboxylic acid OH</td>
<td>134.6 – 135.2, 133.6 – 136.0</td>
<td>[256], [258] *, [256]</td>
</tr>
<tr>
<td>Cyclohexanol (Internal standard)</td>
<td>145.1 (T₁ &lt; 4.6 sec)</td>
<td>[256]</td>
</tr>
<tr>
<td>(30° pulse 5T₁ delay &lt; 20 sec)</td>
<td>[262]</td>
<td></td>
</tr>
<tr>
<td>Cholesterol (Internal standard)</td>
<td>144.9 (T₁ &lt; 20 sec)</td>
<td>[260]</td>
</tr>
<tr>
<td>(30° pulse 5T₁ delay &lt; 7 sec)</td>
<td>[262]</td>
<td></td>
</tr>
<tr>
<td>TMDP</td>
<td>176.0</td>
<td>[256], [261]</td>
</tr>
<tr>
<td>TMDP hydrolysis product</td>
<td>132.2</td>
<td>[256]</td>
</tr>
</tbody>
</table>

* regions estimated by examination of figures in the citation.
*b after thioacidolysis, expected 0.2–0.5 ppm upfield shift relative to untreated lignin.

11.1. Proton–NMR

Proton–NMR spectra of isolated lignins were acquired using the method of Li and Lundquist [191]. Approximately 25 mg of dried isolated lignin was dissolved in 450 µL DMSO–d_6 containing 0.70 mg/mL sodium 3-(trimethylsilyl)propionate–2,2,3,3–d_4 (TSP, Isotech, δ 0.00 ppm [264]) as an internal standard. Before analysis, the lignin/DMSO–d_6/TSP solution was dried, for one hour, over two active 3Å molecular sieves. Proton–NMR spectra were acquired under quantitative conditions: 90° pulse, 16 ppm sweep width, time domain size of 32K, one degree of zero filling, 1.0 Hz line broadening, 15–second pulse delay, and 200 acquisition transients. Integration regions, consistent with the literature [235, 236, 238, 239], are given in Table 18 were used for quantitative analysis.

Table 18. Integration regions for ¹H–NMR analysis of isolated lignins.

<table>
<thead>
<tr>
<th>Structure</th>
<th>δ ¹H–NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid</td>
<td>14.0 – 11.0</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>11.0 – 9.4</td>
</tr>
<tr>
<td>Unsubstituted phenolic</td>
<td>9.4 – 8.5</td>
</tr>
<tr>
<td>Substituted phenolic</td>
<td>8.5 – 7.9</td>
</tr>
<tr>
<td>Aromatic and vinyllic</td>
<td>7.9 – 6.3</td>
</tr>
<tr>
<td>Aliphatic (H₆ and H₅)</td>
<td>6.3 – 4.0</td>
</tr>
<tr>
<td>Methoxy and H₆</td>
<td>4.0 – 3.5</td>
</tr>
<tr>
<td>H₅ in β–1</td>
<td>2.9 – 2.8</td>
</tr>
<tr>
<td>Internal standard, TSP</td>
<td>0.08 – (-0.08)</td>
</tr>
</tbody>
</table>

11.2. Carbon(13)–NMR

Generally, 80–220 mg of dried lignin was weighed into a 2 ml vial. To the vial was added 450 µL DMSO–d_6. The lignin sample was solubilized by using a microstir bar and slight
heating (-50°C). The solvent, DMSO-$_d_6$, was used as both NMR solvent and internal shift reference. Quantitative NMR parameters used were: 90° pulse with inverse-gated decoupling (Waltz-16), 11-second pulse delay, and approximately 4,000-11,000 acquisition transients (# of scans ~ -50(mg lignin) + 15000). Spectra were acquired at 50°C and acquisition time was 13 to 36 hours. Integration regions, consistent with the literature [25, 244, 245, 247, 265], were used (Table 19).

An oxygen delignification stage residual lignin was further analyzed by $^{13}$C-NMR using the DEPT-135 (Distortionless Enhancement by Polarization Transfer) spectral editing sequence in a manner similar to Gellersdorff and Robert [242]. The DEPT spectrum was run with a chosen coupling constant of 145 Hz ($J_{CA}$) and under qualitative conditions with a pulse delay of 2.2 seconds ($T_2$). The number of transients acquired was 12000. The DEPT-135 spectral editing sequence displays CH and CH$_2$ carbons as positive signals and CH$_3$ carbons are displayed as negative signals.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\delta^{13}$C-NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconjugated --CO$_2$H</td>
<td>178.0 – 167.5</td>
</tr>
<tr>
<td>Conjugated --CO$_2$H</td>
<td>167.5 – 162.5</td>
</tr>
<tr>
<td>C3, C4 Aromatic ether or hydroxyl</td>
<td>154.0 – 140.0</td>
</tr>
<tr>
<td>C1, Aromatic C–C bond</td>
<td>140.0 – 127.0</td>
</tr>
<tr>
<td>C5, Aromatic C–C bond</td>
<td>127.0 – 123.0</td>
</tr>
<tr>
<td>C6, Aromatic C–H bond</td>
<td>123.0 – 117.0</td>
</tr>
<tr>
<td>C5, Aromatic C–H bond</td>
<td>117.0 – 114.0</td>
</tr>
<tr>
<td>C2, Aromatic C–H bond</td>
<td>114.0 – 106.0</td>
</tr>
<tr>
<td>Aliphatic C–O bond, Cβ in β–O–4, Cα in β–5 and β–β</td>
<td>90.0 – 78.0</td>
</tr>
<tr>
<td>Aliphatic C–O bond, Cα in β–O–4</td>
<td>79.0 – 67.0</td>
</tr>
<tr>
<td>Aliphatic COR</td>
<td>65.0 – 61.5</td>
</tr>
<tr>
<td>Aliphatic C–O Cγ in β–O–4</td>
<td>61.5 – 57.5</td>
</tr>
<tr>
<td>Methoxyl OCH$_3$</td>
<td>57.5 – 54.0</td>
</tr>
<tr>
<td>Cβ in β–β and Cβ in β–5</td>
<td>54.0 – 52.0</td>
</tr>
<tr>
<td>OCH$_3$ in NAME structure</td>
<td>52.0 – 49.0</td>
</tr>
<tr>
<td>CH$_3$ in diarylmethane</td>
<td>29.9 – 27.5</td>
</tr>
</tbody>
</table>

Table 19. Integration regions used for $^{13}$C-NMR analysis of softwood residual lignins.
11.3. Phosphorus(31)–NMR

11.3.1. Hydroxyl Content

Hydroxyl functional groups in isolated lignins were quantified by $^{31}$P–NMR spectroscopy using a slight modification of the procedure developed by Argyropoulos and others. Approximately 35 mg of dried isolated lignin was weighed into a 2 mL vial. To the vial was added 280 μL pyridine containing chromium–acetiaacetionate (2 mg/mL) and cyclohexanol (2 mg/mL). After the lignin was completely solubilized by the pyridine solvent 175 μL CDCl₃ was added with stirring. Fifteen minutes before NMR analysis, 75 μL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, Aldrich Chemical Company) was added to the lignin solution with vigorous stirring. Phosphorous–NMR analysis indicated that excess derivatization reagent was present in the solution (δ 176.0 ppm).

Integration regions previously discussed in the review section of Appendix 1 were used and a summary is given in Table 20 and shown in Figure 84. Integration regions were supported by additional model compounds derivatized with TMDP (see Appendix 3). Note, in Figure 84 that the internal standard (δ 145.1 ppm) is not baseline resolved. For all analyses involving TMDP/$^{31}$P–NMR the calculated integration areas were compared to the area of the internal standard after baseline correction in the immediate vicinity of the peak.

Quantitative NMR analysis was acquired under the following conditions: 25-second pulse delay, inverse–gated decoupling (Waltz–16), 30° pulse angle, a time domain of 32K with one degree of zero filling, 200 acquisition transients, and 4.0 Hz line broadening.
Table 20. Integration regions used for $^{31}$P–NMR analysis of TMDP treated SW lignin.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\delta$ $^{31}$P–NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Aliphatic OH</td>
<td>150.0 – 145.5</td>
</tr>
<tr>
<td>1S) Cyclohexanol (Internal standard)</td>
<td>144.7 – 145.5</td>
</tr>
<tr>
<td>2) Phenols</td>
<td>136.6 – 144.7</td>
</tr>
<tr>
<td>2a) Combined para–OH–φ and guaiacyl</td>
<td>137.3 – 140.0</td>
</tr>
<tr>
<td>2b) C₅ substituted &quot;condensed&quot;</td>
<td>140.0 – 144.7</td>
</tr>
<tr>
<td>2b1) β–5</td>
<td>142.8 – 144.7</td>
</tr>
<tr>
<td>2b2) 4–O–5</td>
<td>141.7 – 142.8</td>
</tr>
<tr>
<td>2b3) 5–5</td>
<td>140.2 – 141.7</td>
</tr>
<tr>
<td>2c) Guaiacyl</td>
<td>139.0 – 140.0</td>
</tr>
<tr>
<td>2d) Catechol</td>
<td>138.2 – 139.0</td>
</tr>
<tr>
<td>2e) Para–hydroxy–phenyl</td>
<td>137.3 – 138.2</td>
</tr>
<tr>
<td>3) Carboxylic acid OH</td>
<td>133.6 – 136.6</td>
</tr>
</tbody>
</table>

TMDP                                | 176.0                  |
TMDP hydrolysis product             | 132.2                  |

Figure 84. Phosphorous–NMR spectrum, with integration regions, of a softwood kraft effluent lignin treated with TMDP.

Kraft Cook Conditions.

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA, % on wood</td>
<td>21.00</td>
<td>21.80</td>
<td>19.00</td>
</tr>
<tr>
<td>Sulfidity, % AA basis</td>
<td>28.90</td>
<td>29.70</td>
<td>28.90</td>
</tr>
<tr>
<td>Liquor to wood ratio</td>
<td>4.5</td>
<td>6.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Max temperature</td>
<td>174</td>
<td>160</td>
<td>168</td>
</tr>
<tr>
<td>Time to max temperature</td>
<td>60</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>Time at max temperature</td>
<td>97</td>
<td>224</td>
<td>85</td>
</tr>
<tr>
<td>Total cook (min)</td>
<td>157</td>
<td>314</td>
<td>145</td>
</tr>
<tr>
<td>H factor</td>
<td>2209</td>
<td>1550</td>
<td>1200</td>
</tr>
<tr>
<td>Residual EA, g/L</td>
<td>12.52</td>
<td>15.11</td>
<td>11.68</td>
</tr>
<tr>
<td>Residual EA, % on wood</td>
<td>5.63</td>
<td>9.07</td>
<td>5.26</td>
</tr>
<tr>
<td>Blow pH</td>
<td>13.26</td>
<td>13.17</td>
<td>13.18</td>
</tr>
<tr>
<td>Screened yield, % on wood</td>
<td>44.09</td>
<td>46.30</td>
<td>48.06</td>
</tr>
<tr>
<td>Rejects, % on wood</td>
<td>1.59</td>
<td>0.37</td>
<td>3.91</td>
</tr>
<tr>
<td>Total yield, % on wood</td>
<td>45.68</td>
<td>46.6%</td>
<td>51.97</td>
</tr>
<tr>
<td>Kappa number</td>
<td>24.0</td>
<td>28.3</td>
<td>47.1</td>
</tr>
</tbody>
</table>

Chip Size Classification Data.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Specific Gravity</th>
<th>Overlength &gt;45 mm</th>
<th>Overthick &gt;8 mm</th>
<th>Accepts &gt;7 mm</th>
<th>Pins &gt;3 mm</th>
<th>Fines &lt;3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.396</td>
<td>0.0%</td>
<td>12.6%</td>
<td>82.5%</td>
<td>4.8%</td>
<td>0.1%</td>
</tr>
<tr>
<td>2</td>
<td>0.390</td>
<td>0.0%</td>
<td>14.9%</td>
<td>79.0%</td>
<td>6.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>3</td>
<td>0.394</td>
<td>0.0%</td>
<td>8.4%</td>
<td>86.4%</td>
<td>5.1%</td>
<td>0.1%</td>
</tr>
<tr>
<td>4</td>
<td>0.396</td>
<td>0.0%</td>
<td>9.7%</td>
<td>80.7%</td>
<td>5.2%</td>
<td>0.1%</td>
</tr>
<tr>
<td>5</td>
<td>0.402</td>
<td>0.0%</td>
<td>9.8%</td>
<td>81.6%</td>
<td>8.4%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Average</td>
<td>0.395</td>
<td>0.0%</td>
<td>11.9%</td>
<td>82.0%</td>
<td>5.9%</td>
<td>0.1%</td>
</tr>
<tr>
<td>SD</td>
<td>0.004</td>
<td>0.0%</td>
<td>2.7%</td>
<td>2.8%</td>
<td>1.5%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

SD = standard deviation
Summary of Physical Properties For Peracetic Acid Pretreated and Oxygen Delignified Pulps.

<table>
<thead>
<tr>
<th>Bleaching * Sequence</th>
<th>O Stage End pH</th>
<th>Kappa Final</th>
<th>% Delig.</th>
<th>Yield, wt %</th>
<th>Brightness</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS(24)</td>
<td>na</td>
<td>24.00</td>
<td>na</td>
<td>45.68</td>
<td>nd</td>
<td>20.66</td>
</tr>
<tr>
<td>BS(24)O</td>
<td>10.54</td>
<td>13.74</td>
<td>42.75</td>
<td>44.10</td>
<td>33.89</td>
<td>17.47</td>
</tr>
<tr>
<td>BS(24)O*</td>
<td>10.32</td>
<td>7.76</td>
<td>67.67</td>
<td>44.36</td>
<td>42.39</td>
<td>13.66</td>
</tr>
<tr>
<td>BS(24)PaO</td>
<td>10.53</td>
<td>6.79</td>
<td>71.71</td>
<td>44.11</td>
<td>50.31</td>
<td>15.87</td>
</tr>
<tr>
<td>BS(24)PaO*</td>
<td>10.53</td>
<td>4.50</td>
<td>81.24</td>
<td>43.48</td>
<td>57.22</td>
<td>14.65</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bleaching * Sequence</th>
<th>O Stage End pH</th>
<th>Kappa Final</th>
<th>% Delig.</th>
<th>Yield, wt %</th>
<th>Brightness</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS(47)</td>
<td>na</td>
<td>47.10</td>
<td>na</td>
<td>51.97</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>BS(47)O</td>
<td>10.51</td>
<td>27.30</td>
<td>42.04</td>
<td>49.17</td>
<td>27.80</td>
<td>31.41</td>
</tr>
<tr>
<td>BS(47)O*</td>
<td>10.11</td>
<td>14.34</td>
<td>69.55</td>
<td>48.15</td>
<td>35.91</td>
<td>22.41</td>
</tr>
<tr>
<td>BS(47)OPaO</td>
<td>11.28</td>
<td>19.10</td>
<td>59.45</td>
<td>49.49</td>
<td>31.91</td>
<td>25.01</td>
</tr>
<tr>
<td>BS(47)OO</td>
<td>11.06</td>
<td>9.60</td>
<td>79.62</td>
<td>47.63</td>
<td>50.84</td>
<td>19.53</td>
</tr>
<tr>
<td>BS(47)PaO</td>
<td>10.55</td>
<td>18.89</td>
<td>59.88</td>
<td>48.77</td>
<td>37.67</td>
<td>26.66</td>
</tr>
<tr>
<td>BS(47)PaO*</td>
<td>10.36</td>
<td>9.99</td>
<td>78.78</td>
<td>47.33</td>
<td>46.83</td>
<td>22.22</td>
</tr>
</tbody>
</table>

* see Table 3 for an explanation of bleaching sequence abbreviations.

Preparation of Peracetic Acid

Glassware that was used for peracetic acid preparation was cleaned by the following procedure:
- wash with alkaline detergent
- rinse with deionized water
- rinse with 10% sodium hydroxide solution
- rinse well with water
- soak overnight in a 50% (v/v) aqueous nitric acid solution
- rinse with water

Distilled peracetic acid was prepared by simple distillation of equilibrium peracetic acid. The vacuum source used for the distillation was a water-aspirator. Using
the water-aspirator vacuum, peracetic acid could be distilled using a water bath temperature of approximately 60°C.

Equilibrium peracetic acid was either prepared during this study or purchased commercially (Aldrich Chemical Company). Distillation gave a maximum concentration of peracetic acid in the distillate of ~36%. Typical composition of the distillate was: 29% peracetic acid, 0.9% hydrogen peroxide, and ~23% acetic acid. According to the literature, peracetic acid concentrations greater than 50% are potentially detonable at room temperature [266]. Therefore, by using a relatively inefficient distillation apparatus safe operation was ensured.

A drawback to the use of the inefficient distillation apparatus was that a significant quantity of acetic acid codistilled with the peracetic acid. The final concentration of acetic acid in the distilled mixture was ~23%. This high level of acetic acid demanded that alkali be added during bleaching for pH adjustment.

Equilibrium peracetic acid can be prepared by a number of routes. The most widely used synthetic route is the oxidation of acetic acid by hydrogen peroxide in the presence of an acid catalyst [267]. Approximately 200 mL of 50% hydrogen peroxide and 200 mL of glacial acetic acid were mixed in a large beaker immersed in an ice bath. Concentrated sulfuric acid catalyst (25 mL) was then cautiously added to the mixture. The acid was added at a rate to keep the mixture temperature between 10 and 15°C. After addition of the acid, the reaction mixture was stirred for three hours and allowed to warm to room temperature.

Peracetic Acid Analysis

Peracetic acid samples were analyzed according to the procedure developed by Greenspan and Mackellar [268]. A sample of peracetic acid (0.15–1.00 g) was accurately weighed into an 500 mL Erlenmeyer flask. To the flask was added ice chips, 25 mL 10% sulfuric acid, 50 mL deionized water, and three drops of ferroin indicator. The mixture was rapidly titrated with 0.1 N cerium (IV) sulfate to the first appearance of the colorless.
endpoint. The cerium (IV) sulfate titration is used to determine the hydrogen peroxide content of the sample.

Immediately after determining the hydrogen peroxide content, 10 mL of 10% potassium iodide solution was added to the sample. The resulting solution was then titrated with 0.1 N sodium thiosulfate solution to a starch endpoint. The sodium thiosulfate titration was used to determine the peracetic acid content of the sample.

$$\text{Hydrogen peroxide (wt %) =}$$


$$\text{Peracetic acid (wt %) =}$$


The combined acetic and peracetic acid contents of the sample were determined by titration with 0.1N sodium hydroxide to a phenolphthalein endpoint. A sample of peracetic acid (~1.00 g) was accurately weighed into an Erlenmeyer flask. To the flask is added ice chips and 50 mL deionized water and three drops of phenolphthalein indicator. The mixture was rapidly titrated to the first faint appearance of the slight pink endpoint. The sample was rapidly analyzed using ice-cold conditions to prevent degradation of peracetic acid to acetic acid.

$$\text{Acetic acid + peracetic acid (wt%)} =$$

$$\frac{\text{(volume of 0.1N NaOH used)(6.005)(wt of Pa sample)}}{\text{(volume of 0.1N NaOH used)(6.005)(wt of Pa sample)}}$$
Carbon(13)–NMR Spectral Data for Quinone Model Compounds

All spectra were acquired using: ZGIG30 = 30° carbon pulse with inverse-gated 1H decoupling (Waltz–16)
where: D1 = pulse delay (seconds), NS = number of scans

3-methoxy-1,2-benzoquinone
(CDCl₃ solvent, D1 = 5, NS = 565)

4-methyl-1,2-benzoquinone
(DMSO-d₆ solvent, D1 = 1, NS = 26)

4-tert-butyli-1,2-benzoquinone
(DMSO-d₆ solvent, D1 = 5, NS = 400)

2-methoxy-1,4-benzoquinone
(DMSO-d₆ solvent, D1 = 15, NS = 635)

2-tert-butyl-1,4-benzoquinone
(DMSO-d₆ solvent, D1 = 15, NS = 229)

Oxidized Poly(4-vinyl-phenol)
(DMSO-d₆ solvent, D1 = 11, NS = 10282)

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2,6-dimethoxy-1,4-benzoquinone
(25% CDCl₃, 75% CD₃CN solvent, D₁ = 7, NS = 5000)

Note, for the above spectra the solvent was used as a chemical shift reference:
CDCl₃ = δ 77.23 ppm (triplet) and DMSO-d₆ = δ 39.51 ppm (septet).

Simulated Carbon(13)-NMR Spectra of Quinone Compounds. Simulation by ACD/CNMR Spectrum Generator Version 3.50

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>CH₃</th>
<th>Chem. Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃</td>
<td>1.96</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>9.8</td>
</tr>
<tr>
<td>3</td>
<td>CH₃</td>
<td>99.4</td>
</tr>
<tr>
<td>4</td>
<td>CH₃</td>
<td>102.43</td>
</tr>
<tr>
<td>5</td>
<td>CH₃</td>
<td>107.23</td>
</tr>
<tr>
<td>6</td>
<td>CH₃</td>
<td>119.88</td>
</tr>
<tr>
<td>7</td>
<td>CH₃</td>
<td>119.88</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>122.96</td>
</tr>
<tr>
<td>9</td>
<td>CH₃</td>
<td>133.96</td>
</tr>
<tr>
<td>10</td>
<td>CH₃</td>
<td>135.54</td>
</tr>
<tr>
<td>11</td>
<td>CH₃</td>
<td>143.4</td>
</tr>
<tr>
<td>12</td>
<td>CH₃</td>
<td>156.18</td>
</tr>
<tr>
<td>13</td>
<td>CH₃</td>
<td>160.1</td>
</tr>
<tr>
<td>14</td>
<td>CH₃</td>
<td>163.17</td>
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<tr>
<td>15</td>
<td>CH₃</td>
<td>166.72</td>
</tr>
<tr>
<td>16</td>
<td>CH₃</td>
<td>168.65</td>
</tr>
<tr>
<td>17</td>
<td>CH₃</td>
<td>198.88</td>
</tr>
<tr>
<td>18</td>
<td>CH₃</td>
<td>199.88</td>
</tr>
<tr>
<td>19</td>
<td>CH₃</td>
<td>207.51</td>
</tr>
</tbody>
</table>

3-methoxy-1,2-benzoquinone

4-methyl-1,2-benzoquinone
Simulated Carbon(13)-NMR Spectra of Quinone Compounds. Simulation by ACD/CNMR Spectrum Generator Version 3.50

4-tert-buty-1,2-benzoquinone

2-methoxy-1,4-benzoquinone

2-tert-buty-1,4-benzoquinone

Oxidized Poly(4-vinyl-phenol)

3,5-di-tert-buty-1,2-benzoquinone

2,6-dimethoxy-1,4-benzoquinone

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Phosphorous(31)–NMR Spectral Data for Compounds Derivatized with TMDP.

A) trans,trans–muconic acid (135.0 ppm) and cyclohexanol
B) 4–methyl–catechol (139.2 ppm, 138.9 ppm, $J_{POCCP} = 10$ Hz) and cyclohexanol.

4–hydroxy–3–methoxycinnamaldehyde (147.2, 139.6, 139.3 ppm) and cyclohexanol.

The above spectrum reveals that the aldehyde functional group (CHO) is reactive with TMDP and give two phosphite products (147.2 and 139.6 ppm).
3,5-di-tert-butyl-catechol (137.9 ppm, 144.0 ppm, $J_{PCOCOC} = 9$ Hz)
A) TMDP/catechol spirophosphorane adduct (proton coupled, $J_{PP} = 852$ Hz)
A) TMDP/catechol spirophosphorane adduct (proton decoupled, -30.1 ppm)

The above spectrum demonstrates that a catechol compound can give two widely separated phenolic-phosphite signals (δ 137.9 and 144.0 ppm). Also, the catechol is derivatized in less than quantitative yield. A side-product of the reaction was found to be a spirophosphorane (δ -30.1 ppm).

Lignin–Quinone Content Data for DE* Residual Lignins.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Region (ppm)</th>
<th>BS</th>
<th>D</th>
<th>D(E+Ar)</th>
<th>DE</th>
<th>D(E+O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L Phosphate</td>
<td>12.5 - 8.8</td>
<td>0.574</td>
<td>0.466</td>
<td>0.539</td>
<td>0.482</td>
<td>0.619</td>
</tr>
<tr>
<td>TMPO</td>
<td>4.2 - 2.8</td>
<td>0.191</td>
<td>0.333</td>
<td>0.317</td>
<td>0.409</td>
<td>0.394</td>
</tr>
<tr>
<td>L Quinone</td>
<td>(-0.3) - (-7.0)</td>
<td>0.088</td>
<td>0.223</td>
<td>0.149</td>
<td>0.167</td>
<td>0.114</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Region (ppm)</th>
<th>D(E+P)</th>
<th>D(E+O+P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L Phosphate</td>
<td>12.5 - 8.8</td>
<td>0.260</td>
<td>0.609</td>
</tr>
<tr>
<td>TMPO</td>
<td>4.2 - 2.8</td>
<td>0.233</td>
<td>0.446</td>
</tr>
<tr>
<td>L Quinone</td>
<td>(-0.3) - (-7.0)</td>
<td>0.076</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Lignin–quinone content data for DE* effluent lignins.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Region (ppm)</th>
<th>D(E+Ar)</th>
<th>DE</th>
<th>D(E+O)</th>
<th>D(E+P)</th>
<th>D(E+O+P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L Phosphate</td>
<td>12.5 - 8.8</td>
<td>0.683</td>
<td>0.569</td>
<td>0.731</td>
<td>0.675</td>
<td>0.607</td>
</tr>
<tr>
<td>TMPO</td>
<td>4.2 - 2.8</td>
<td>0.359</td>
<td>0.463</td>
<td>0.316</td>
<td>0.328</td>
<td>0.411</td>
</tr>
<tr>
<td>L Quinone</td>
<td>(-0.3) - (-7.0)</td>
<td>0.160</td>
<td>0.151</td>
<td>0.122</td>
<td>0.063</td>
<td>0.088</td>
</tr>
</tbody>
</table>

All quantities are mmol/g lignin.
L Phosphate = lignin hydrogen–phosphite product
TMPO = trimethylphosphate
L Quinone = lignin–quinone adduct

Spectral Parameters for Para–Benzoquinone Model Compounds.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>abs</th>
<th>ε (abs L/mol cm)</th>
<th>log ε</th>
<th>Quinone</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>0.975</td>
<td>262.285</td>
<td>2.42</td>
<td>2,6-di-MeO–PQ</td>
</tr>
<tr>
<td>500</td>
<td>0.023</td>
<td>6.258</td>
<td>0.80</td>
<td>2,6-di-MeO–PQ</td>
</tr>
<tr>
<td>430</td>
<td>1.045</td>
<td>22.383</td>
<td>1.35</td>
<td>PQ</td>
</tr>
<tr>
<td>500</td>
<td>0.171</td>
<td>3.663</td>
<td>0.56</td>
<td>PQ</td>
</tr>
<tr>
<td>430</td>
<td>0.365</td>
<td>24.236</td>
<td>1.38</td>
<td>PQ</td>
</tr>
<tr>
<td>500</td>
<td>0.383</td>
<td>108.769</td>
<td>2.04</td>
<td>tetrahydroxy–PQ</td>
</tr>
<tr>
<td>430</td>
<td>0.482</td>
<td>136.885</td>
<td>2.14</td>
<td>tetrahydroxy–PQ</td>
</tr>
<tr>
<td>430</td>
<td>0.905</td>
<td>212.024</td>
<td>2.33</td>
<td>2,5-di–OH–PQ</td>
</tr>
<tr>
<td>500</td>
<td>0.095</td>
<td>22.257</td>
<td>1.35</td>
<td>2,5-di–OH–PQ</td>
</tr>
</tbody>
</table>

PO = 1,4-benzoquinone

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$^{31}$P-NMR Spectra of DE* residual lignins treated with 50% trimethylphosphite/DMSO.

$^{31}$P-NMR Spectra of DE* effluent lignins treated with 50% trimethylphosphite/DMSO.
$^{31}$P-NMR Spectra of a D$_6$ residual lignin treated with 250 μL DMSO/250 μL trimethylphosphite for various time periods.

$^{31}$P-NMR Spectra of a D$_6$ residual lignin treated with 200 μL DMSO/150 μL methanol/20 μL trimethylphosphite for various time periods.
Quinone Content Data for a D<sub>6</sub> Residual Lignin Treated with Excess Trimethylphosphite and Either Methanol/DMSO or DMSO Solvent Systems.

<table>
<thead>
<tr>
<th>Treatment (hr)</th>
<th>TMP/Methanol&lt;sup&gt;a&lt;/sup&gt; [Q] mmol/g lignin</th>
<th>Treatment (hr)</th>
<th>TMP/DMSO&lt;sup&gt;b&lt;/sup&gt; [Q] (mmol/g lignin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>0.0556</td>
<td>0.42</td>
<td>0.0997</td>
</tr>
<tr>
<td>1.75</td>
<td>0.0657</td>
<td>24.00</td>
<td>0.2158</td>
</tr>
<tr>
<td>4.75</td>
<td>0.0794</td>
<td>54.00</td>
<td>0.2318</td>
</tr>
<tr>
<td>24.00</td>
<td>0.0971</td>
<td>168.00</td>
<td>0.2498</td>
</tr>
<tr>
<td>54.00</td>
<td>0.1023</td>
<td>168.00</td>
<td>0.2559</td>
</tr>
<tr>
<td></td>
<td></td>
<td>222.00</td>
<td>0.2659</td>
</tr>
<tr>
<td></td>
<td></td>
<td>337.00</td>
<td>0.2648</td>
</tr>
</tbody>
</table>

<sup>a</sup> 200 µL DMSO/150 µL methanol/20 µL trimethylphosphite.

<sup>b</sup> 250 µL DMSO/250 µL trimethylphosphite.
**14. Appendix 5. Supporting Data for Publication Two.**

Quinone Content Data for Residual Lignins Treated with 100% Trimethylphosphite.

**[Q] (mmol/g Lignin) before addition of water.**

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>Structure</th>
<th>BS</th>
<th>BS Fremy</th>
<th>D (ave)</th>
<th>DE</th>
<th>D reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.2</td>
<td>quinone adduct</td>
<td>0.075</td>
<td>0.314</td>
<td>0.236</td>
<td>0.154</td>
<td>0.050</td>
</tr>
<tr>
<td>11.8</td>
<td>L phosphite</td>
<td>0.164</td>
<td>0.320</td>
<td>0.505</td>
<td>0.527</td>
<td>0.228</td>
</tr>
</tbody>
</table>

**[Q] (mmol/g Lignin): after addition of water.**

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>Structure</th>
<th>BS</th>
<th>BS Fremy</th>
<th>D (ave)</th>
<th>DE</th>
<th>D reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.2</td>
<td>quinone adduct</td>
<td>0.088</td>
<td>0.350</td>
<td>0.244</td>
<td>0.161</td>
<td>0.050</td>
</tr>
<tr>
<td>11.8</td>
<td>L phosphite</td>
<td>0.853</td>
<td>0.286</td>
<td>0.352</td>
<td>0.390</td>
<td>0.205</td>
</tr>
</tbody>
</table>

Average [Q] of Dₙ residual lignin treated in triplicate without water addition.

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>Structure</th>
<th>D #1</th>
<th>D #2</th>
<th>D #3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.2</td>
<td>quinone adduct</td>
<td>0.231</td>
<td>0.256</td>
<td>0.222</td>
<td>0.236</td>
</tr>
<tr>
<td>11.8</td>
<td>L phosphite</td>
<td>0.388</td>
<td>0.554</td>
<td>0.574</td>
<td>0.505</td>
</tr>
</tbody>
</table>

Average [Q] of Dₙ residual lignin treated in triplicate after water addition.

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>Structure</th>
<th>D #1</th>
<th>D #2</th>
<th>D #3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.2</td>
<td>quinone adduct</td>
<td>0.245</td>
<td>0.252</td>
<td>0.234</td>
<td>0.244</td>
</tr>
<tr>
<td>11.8</td>
<td>L phosphite</td>
<td>0.359</td>
<td>0.405</td>
<td>0.292</td>
<td>0.352</td>
</tr>
</tbody>
</table>

Difference: quinone content after water addition - [Q] without water addition.

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
<th>Structure</th>
<th>BS</th>
<th>BS Fremy</th>
<th>D (ave)</th>
<th>DE</th>
<th>D reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.2</td>
<td>quinone adduct</td>
<td>0.012</td>
<td>0.036</td>
<td>0.007</td>
<td>0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>11.8</td>
<td>L phosphite</td>
<td>0.689</td>
<td>-0.034</td>
<td>-0.153</td>
<td>-0.137</td>
<td>-0.024</td>
</tr>
</tbody>
</table>

L Phosphate = region encompassing cyclic phosphate and PH derivatized lignin structures
Quinone adduct = derivatized lignin-quinone structures
BS = brownstock residual lignin
BS Fremy = brownstock residual lignin oxidized with Fremy's reagent
D(ave) = average quinone content of Dₙ residual lignin treated in triplicate
D #1, D #2, and D #3 = replicates of quinone content measurements on a Dₙ residual lignin extracted from a single pulp
D reduced = Dₙ residual lignin reduced with dithionite

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Example of lineshape analysis applied to a $^{31}$P-NMR spectrum:

A) D$_6$ residual lignin after 100% trimethylphosphite treatment and addition of water.
B) lines fitted to the quinone adduct and internal standard components.
C) simulated spectrum.

$^{31}$P–NMR Spectra of DE* and DE* D Residual Lignins Treated with 50% Trimethylphosphite/DMSO.

Lignin–Quinone Content and "Apparent" Pulp Quinone Content Data for DE* and DE* D Residual Lignins.

<table>
<thead>
<tr>
<th>Item</th>
<th>$D(EAr)$</th>
<th>$D(EAr)D$</th>
<th>$DE$</th>
<th>$DED$</th>
<th>$D(EO)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Quinone (mmol/g lignin)</td>
<td>0.149</td>
<td>0.164</td>
<td>0.167</td>
<td>0.138</td>
<td>0.114</td>
</tr>
<tr>
<td>Klasson lignin (g/kg pulp OD)</td>
<td>0.590</td>
<td>0.193</td>
<td>0.503</td>
<td>0.133</td>
<td>0.437</td>
</tr>
<tr>
<td>Quinone content * Klasson (mmol/kg pulp OD)</td>
<td>0.877</td>
<td>0.317</td>
<td>0.843</td>
<td>0.184</td>
<td>0.496</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Quinone (mmol/g lignin)</td>
<td>0.151</td>
<td>0.076</td>
<td>0.066</td>
<td>0.098</td>
<td>0.080</td>
</tr>
<tr>
<td>Klasson lignin (g/kg pulp OD)</td>
<td>0.117</td>
<td>0.450</td>
<td>0.117</td>
<td>0.347</td>
<td>0.097</td>
</tr>
<tr>
<td>Quinone content * Klasson (mmol/kg pulp OD)</td>
<td>0.176</td>
<td>0.341</td>
<td>0.078</td>
<td>0.339</td>
<td>0.077</td>
</tr>
</tbody>
</table>

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Phosphorus–NMR Spectrum Illustrating Decoupler Artifacts Introduced During Proton Decoupling of Dimethylphosphite with the Waltz–16 Decoupling Sequence.

Proton Coupled $^{31}$P–NMR Spectra of Trimethylphosphite Degradation Compounds.
Phosphorous(31)-NMR Spectra of Quinone Model Compounds Treated with 50% DMF/Trimethylphosphite for 2 Days.

4-methyl-1,2-benzoquinone

4-tert-buty1-1,2-benzoquinone

4-tert-buty1-1,2-benzoquinone (before hydrolysis)

3-methoxy-1,2-benzoquinone

2,6-dimethoxy-1,4-benzoquinone

3-methoxy-1,2-benzoquinone (24 hr DMF then 2 days TMP)
Chemical Shifts and Spin–Lattice Relaxation Times for TMP–Quinone Adducts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{31}P$ (ppm)</th>
<th>$T_1$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methoxy–1,2–benzoquinone</td>
<td>-2.0, -2.7</td>
<td>0.28</td>
</tr>
<tr>
<td>4-tert–butyl–1,2–benzoquinone</td>
<td>-2.3, -2.6</td>
<td>0.35</td>
</tr>
<tr>
<td>4-methyl–1,2–benzoquinone</td>
<td>-2.4, -2.6</td>
<td>0.34</td>
</tr>
<tr>
<td>2,6-dimethoxy–1,4–benzoquinone</td>
<td>-1.6, -1.7</td>
<td>0.36</td>
</tr>
<tr>
<td>2-tert–butyl–1,4–benzoquinone</td>
<td>-2.6, -2.7</td>
<td>0.32</td>
</tr>
<tr>
<td>TTP (19.3 mg/mL, 6.0 mg/mL Cr(acac)$_3$)</td>
<td>-16.3</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Phosphorous(31)-NMR Spectra of Residual Lignins Treated with Trimethylphosphite.

$D_6$ (KF = 0.2, EM(CCMW, BS kappa = 29) 50% DMF/TMP)

BS (SW, kappa = 28) 7d 50% TMP/DMF

$D_6$ (SW, KF = 0.2) 50% DMSO/TMP

DE (SW, KF = 0.05) 50% DMF/TMP

DE (SW, KF = 0.2) 2d 50% DMF/TMP

treated in triplicate

DE (SW, KF = 0.2) 7d 50% DMF/TMP

treated in triplicate
PS/AQ res. lignins 7d 50% TMP/DMSO

D₄ (KF = 0.2, EMCC™, BS kappa = 29)
2d 50% TMP/DMF (2% water)

PS/AQ OPa, 2d DMF

PS/AQ OPa, 7d DMF
Quinone Contents of a Kappa 28 Brownstock Residual Lignin Bleached in Homogeneous Solution with Various Charges of Chlorine Dioxide.

<table>
<thead>
<tr>
<th>[Q]</th>
<th>calc. KF</th>
<th>calc. KF left</th>
<th>KF used</th>
<th>% D used</th>
<th>end pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.067</td>
<td>0.000</td>
<td>na</td>
<td>0.000</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>0.084</td>
<td>0.004</td>
<td>0.000*</td>
<td>0.004</td>
<td>100.00</td>
<td>3.16</td>
</tr>
<tr>
<td>0.156</td>
<td>0.06</td>
<td>0.000*</td>
<td>0.057</td>
<td>100.00</td>
<td>2.35</td>
</tr>
<tr>
<td>0.219</td>
<td>0.10</td>
<td>0.022</td>
<td>0.080</td>
<td>78.24</td>
<td>2.02</td>
</tr>
<tr>
<td>0.299</td>
<td>0.20</td>
<td>0.021</td>
<td>0.18</td>
<td>89.52</td>
<td>2.03</td>
</tr>
<tr>
<td>0.300</td>
<td>0.77</td>
<td>0.53</td>
<td>0.23</td>
<td>30.39</td>
<td>nd</td>
</tr>
<tr>
<td>0.297</td>
<td>1.92</td>
<td>1.57</td>
<td>0.35</td>
<td>78.35</td>
<td>nd</td>
</tr>
<tr>
<td>0.288</td>
<td>0.20</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>0.287</td>
<td>0.20</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

[Q] = lignin-quinone (mmol/g lignin) content determined by trimethylphosphite derivatization and 31P-NMR spectroscopy.
calc. KF = KF chlorine dioxide applied calculated on the basis of the amount of lignin and chlorine dioxide solution used (see Equation 6).
calc. KF left = chlorine dioxide remaining after the reaction; calculated by thiosulfate titration; expressed on a KF basis.
KF used = actual chlorine dioxide consumed expressed on a KF basis.
% D = percentage of the applied chlorine dioxide charge consumed.
end pH = pH of the bleaching solution measured at the end of the reaction.
nd = not determined.
na = not applicable; corresponds to brownstock lignin not bleached with chlorine dioxide.
* no detected chlorine dioxide residual.

Submitted for publication in Holzforschung.
N-HYDROXY COMPOUNDS AS NEW INTERNAL STANDARDS FOR THE $^{31}P$-NMR DETERMINATION OF LIGNIN HYDROXYL FUNCTIONAL GROUPS.

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500 10th St., N.W., Atlanta, GA 30318.

Keywords: $^{31}P$-NMR, residual lignin, hydroxyl and phenolic group determination, N-hydroxy compounds.

Introduction

TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) is a very powerful reagent for tagging hydroxyl groups as the $^{31}P$-NMR active phosphate derivative (Figure 1). TMDP derivatization $^{31}P$-NMR spectroscopy has been effectively applied to analyze lignin structural changes during Kraft pulping [263, 269] and various bleaching operations [8, 270].

Figure 1. Phosphorylation of a hydroxy group by TMDP.

Usually, cyclohexanol is selected as an internal standard for the TMDP/$^{31}P$-NMR method [261]. In our experience, we have found that occasionally the cyclohexanol-phosphate product overlaps with derivatized aliphatic and phenolic lignin structures (Figure 2, also see [123]). Cholesterol has also been used as an internal standard [260], but unfortunately, the chemical shift for the phosphate product is very similar to that of cyclohexanol (Table 1).

Clearly, an internal standard that is baseline resolved would be useful when investigating lignin samples displaying disperse aliphatic- and phenolic-phosphate regions. TMDP is known to react with a variety of heteroatom functional groups containing labile hydrogen; for example, OH, CO$_2$H, NH, and SH [251]. Because of the range of TMDP reactivity, we have investigated the phosphate reaction products arising from a variety of substrates. In this paper, we propose that N-hydroxy compounds may be useful new internal standards for TMDP/$^{31}P$-NMR analysis of isolated lignins.

Method

TMDP derivatization and phosphorus-NMR analysis was performed according to the literature [256, 261] using ~30 mg lignin or ~30 μmol model compounds. Spin-lattice (T$_1$) relaxation parameters were determined by the standard inversion recovery experiment [144]. All chemicals were purchased commercially and used without further purification.

Results and Discussion

Experiments were focused on the development of a new internal standard that was baseline resolved from lignin-derived adducts. Chemical shift and spin-lattice relaxation (T$_1$) values for the studied compounds are given in Table 1. The structures of the compounds studied are illustrated in Figures 3–5.

Piperidine (VIII, Figure 5) was studied, and rejected, as a potential internal standard because the chemical shift of its TMDP product (δ 13.8 ppm) overlaps with lignin phenolic adducts. Potentially stable triarylphosphites may be used as internal standards. One triarylphosphite studied was hindered tri(2,4-dioctyloxyphenyl)phosphite (VII, Figure 5).

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The $^{31}$P-NMR chemical shift (δ 130.7 ppm) was found to occur in a region where occasionally TMDP derivatization products are observed (δ ~130 ppm, Figure 2).

Figure 3. Commonly used internal standards for $^{31}$P-NMR/TMDP analysis.

Table 1. Phosphorus-NMR parameters for TMCP treated compounds.

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>$\delta$ $^{31}$P (ppm)</th>
<th>T$_{1}$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>cyclohexanol</td>
<td>145.1$^*$</td>
<td>4.6$^+$</td>
</tr>
<tr>
<td>II</td>
<td>cholesterol</td>
<td>144.9$^+$</td>
<td>&lt;5$^+$</td>
</tr>
<tr>
<td>III</td>
<td>N-hydroxy- phthalimide</td>
<td>150.7</td>
<td>nd</td>
</tr>
<tr>
<td>IV</td>
<td>1-hydroxy-7-azabenzo triazole</td>
<td>150.6</td>
<td>1.9</td>
</tr>
<tr>
<td>V</td>
<td>N-hydroxy-5-norborne-2,3-dicarboxamide</td>
<td>151.9</td>
<td>1.3</td>
</tr>
<tr>
<td>VI</td>
<td>N-hydroxy-1,8-napthalimide</td>
<td>153.6</td>
<td>1.5</td>
</tr>
<tr>
<td>VII</td>
<td>tris(2,4-di-tert-butylphenyl) phosphite</td>
<td>130.7</td>
<td>0.5</td>
</tr>
<tr>
<td>VIII</td>
<td>Piperidine</td>
<td>138.7</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd = not determined
$^*$ref. [261]
$^+$ref. [260], not stated explicitly.

The most promising candidates for new internal standards are the N-hydroxy compounds (III–VI, Table 1). After TMCP derivatization, these compounds were found to give phosphite products with $^{31}$P-NMR chemical shifts in the δ 150.7–153.6 ppm region.

For a preliminary investigation, N-hydroxy-5-norborne-2,3-dicarboximide (V, Table 1, Figure 4) was selected as a potential new internal standard. After TMCP derivatization, the N-hydroxy internal standard was found to be nearly baseline resolved from the lignin-derived resonances (Figure 1).

Figure 4. N-hydroxy compounds.

Figure 5. Additional compounds.

A reproducibility study was performed on a softwood kraft (brownstock, kappa = 47) residual lignin isolated by acidolysis [143]. Integration regions used were consistent with the literature [256, 258-261]. Integration measurement results for residual lignin samples treated in triplicate are given in Table 2 and 3. Both cyclohexanol and N-hydroxy-5-norborne-2,3-dicarboximide were used as internal standards.

Referring to Figure 1, the reader will notice that cyclohexanol is not baseline resolved from lignin-derived resonances. Therefore, for the residual lignin samples studied, when using cyclohexanol as an internal standard, the baseline was 'locally' corrected about the
cyclohexanol peak inorder to establish the proper integration areas. Nevertheless, the OH functional group reproducibility of measured lignin functional groups was very good when either cyclohexanol or N-hydroxy-5-norbornene-2,3-dicarboximide was used as the internal standard.

Table 2. Functional group values for a softwood kraft (kappa = 47) residual lignin treated in triplicate using cyclohexanol as an internal standard.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Average</th>
<th>Std. Dev.</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic OH</td>
<td>2.81</td>
<td>0.052</td>
<td>0.30</td>
</tr>
<tr>
<td>Phenolic</td>
<td>3.55</td>
<td>0.044</td>
<td>0.25</td>
</tr>
<tr>
<td>Acid</td>
<td>0.49</td>
<td>0.010</td>
<td>0.06</td>
</tr>
</tbody>
</table>

all values in mmol/g lignin
LSD = least significant digit

Table 3. Functional group values for a softwood kraft (kappa = 47) residual lignin treated in triplicate using N-hydroxy-5-norbornene-2,3-dicarboximide as an internal standard.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Average</th>
<th>Std. Dev.</th>
<th>LSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic OH</td>
<td>2.55</td>
<td>0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>Phenolic</td>
<td>3.20</td>
<td>0.010</td>
<td>0.26</td>
</tr>
<tr>
<td>Acid</td>
<td>0.44</td>
<td>0.0002</td>
<td>0.01</td>
</tr>
</tbody>
</table>

all values in mmol/g lignin
LSD = least significant digit

Previous reports have defined the T1 relaxation time range of TMDP phosphitylated lignin as 0.5–2.0 seconds [261]. Phosphites derived from TMDP/N-hydroxy compounds were found to display shorter T1 relaxation times relative to TMDP/cyclohexanol-phosphite (Table 1). Therefore, a shorter pulse delay may potentially be selected if an N-hydroxy internal standard is used instead of cyclohexanol. A shorter pulse delay will allow for the more rapid analysis of TMDP phosphitylated lignin. Further work is in progress determining the generality of N-hydroxy internal standards for routine lignin analysis.

Summary
A series of commercially available N-hydroxy compounds were studied by 31P-NMR spectroscopy after TMDP derivatization. The 31P-NMR chemical shifts of phosphitylated N-hydroxy compounds (δ 150.7–153.6 ppm) were found to be well separated from lignin derived components. These compounds show promise as new internal standards for the 31P-NMR analysis of lignin hydroxyl groups.

Acknowledgements
The authors wish to thank Drs. McDonough, Dimmel, and Lucia for guidance. Financial support from the Institute of Paper Science and Technology (IFST) and its member companies is gratefully acknowledged. Portions of this work were used by M. Z. as partial fulfillment of the requirements for the Ph.D. degree at IFST.

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PULP PROPERTIES INFLUENCING OXYGEN DELIGNIFICATION BLEACHABILITY

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ABSTRACT

The influence of peracetic acid pretreatment and interstage treatment on subsequent oxygen delignification was evaluated for both kappa 24 and 47 softwood kraft pulps. Both pulps were oxygen delignified under standard (~42% delig.) and aggressive (~68% delig.) conditions. Selected pulps were also pretreated with distilled peracetic acid under slightly alkaline conditions (pH = 8). Peracetic acid pretreatment was found to increase the efficiency of the oxygen delignification stage with no loss of pulp viscosity. A kappa of pulp could be oxygen delignified under aggressive conditions to give a pulp of comparable viscosity and brightness as standard oxygen delignified kappa 24 pulp. The fundamental chemistry of the process was studied by TSC-, T2-, and 2H-NMR spectroscopy. Residual lignin quinone contents were quantified by trimethylphosphine/31P-NMR and 1H-NMR spectroscopy. Oxygen delignification conditions were found to have little influence on the introduction of colored quinone and carbonyl structures. Condensed dihydroxymethylene and carboxylic acid lignin structures were enriched and/or formed, particularly under aggressive oxygen conditions.

INTRODUCTION

Kraft pulping, oxygen delignification, and subsequent bleaching processes all interact and should be considered on a "system approach" basis to meet environmental and cost constraints. The trend in recent years toward low kappa pulping has resulted in lower bleaching costs due to decreased brownstock kappa number entering the bleach plant. Alternatively, a higher proportion of delignification can be shifted to the (multiple-stage) oxygen delignification stage by cooking the pulp to a higher kappa number. Oxygen delignification is more selective than the kraft cook process and potentially an increased final product yield can be realized [229, 271-273]. The higher pulp yield can translate into a lower organic load to the recovery boiler, and for recovery-limited mills an increase in capacity can be achieved. A strong environmental incentive to use oxygen delignification is that it is chlorine-free and effluents are compatible with mill closure.

Peracetic acid is a TCF bleaching agent with excellent brightening properties [103]. The electrophilic bleaching agent is highly selective for delignification. Peracetic acid is being used at the mill level for TCF bleaching in Scandinavia [100, 101]. In Scandinavia, the bleaching agent is transported chilled in diluted form [100, 102]. Generally, DOT shipping regulations limit large-scale shipping of peracetic acid in the United States and the material has to be prepared on-site.

Peracetic acid can be used in either equilibrium or distilled form. The equilibrium form contains appreciable residual hydrogen peroxide. Unless metals are sequestered, the residual peroxide can damage pulp viscosity. Distilled peracetic acid contains low residual peroxide content and pulp damage is much less likely. Peracetic acid [135, 274] and other peracids [275] can "activate" or increase the efficiency of a subsequent oxygen stage, although the fundamental reasons for this effect are not yet clear.

The broad goal of this study was to consider oxygen delignification and a low capital implementation of peracetic acid activation to improve oxygen delignification. Pulp parameters were studied after various PaO delignification conditions for both low and high kappa pulps. A specific focus was to use a range of novel and standard NMR methods to structurally analyze residual lignins and understand the fundamental chemistry of oxygen delignification/peracetic acid activation.
EXPERIMENTAL

Chemicals
All chemicals were commercially purchased and used as received except for 1,4-dioxane, which was purified by distillation over sodium borohydride.

Furnish
Pulps were prepared from a single softwood wood source which was chipped and screened with accepts between 3 and 8 mm. The chips were cooked under conventional kraft conditions in the laboratory to give two brownstock pulps of kappa number 24.0 (L/W = 4.5, E/AS = 21, S/AS = 28.9, H = 2209) and 47.1 (L/W = 4.5, E/AS = 19, S/AS = 28.9, H = 1209).

Percarboxylic Acid Treatment
Distilled percarboxylic acid (Pa) was prepared by simple vacuum distillation of equilibrium percarboxylic acid. The distilled percarboxylic acid was analyzed according to Greenan and MacKellar [268] and found to have the following typical composition: Pa 29%, hydrogen peroxide 0.9%, and acetic acid 52%. Pulps were treated at a 4% charge of percarboxylic acid at 6% consistency in sealed polyethylene bags. The pH of the medium was adjusted to −8 with alkali. The pulp was treated at 70°C for one hour. After treatment, pulps were thickened by dewatering using a Böhringer funnel and were not washed before oxygen delignification.

Oxygen Delignification
A series of oxygen delignified (O) pulps were prepared from brownstock and percarboxylic acid pretreated pulps. In a modified digester, the following basic oxygen delignification conditions were used: 5.5% consistency, final pH >10.5, 75 psi oxygen, and 60-minute reaction. Specific details of the percarboxylic acid-oxygen delignification experiments and bleaching sequence abbreviations are given in Table 1. Bleached pulps were washed and characterized by kappa number (TAPPI 254 om-85), CED viscosity (TAPPI 230 om-94), and brightness (TAPPI 205 sp-95).

Table 1. Oxygen delignification conditions and bleaching sequence abbreviations.

<table>
<thead>
<tr>
<th>Bleach sequence</th>
<th>Bleaching conditions</th>
<th>abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS(47)</td>
<td>brownstock, kappa = 47</td>
<td></td>
</tr>
<tr>
<td>BS(47)O</td>
<td>oxygen delig.: 2.3% alkali charge, 90°C</td>
<td></td>
</tr>
<tr>
<td>BS(47)PhO</td>
<td>percarboxylic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C</td>
<td></td>
</tr>
<tr>
<td>BS(47)PhO*</td>
<td>percarboxylic acid: 4% charge, oxygen delig.: 4.2% alkali charge, 105°C</td>
<td></td>
</tr>
<tr>
<td>BS(47)POO</td>
<td>double oxygen delig.: 2.3% alkali charge, 90°C each stage</td>
<td></td>
</tr>
<tr>
<td>BS(47)OPaO</td>
<td>oxygen delig.: 2.3% alkali charge, 90°C, percarboxylic acid: 4% charge, oxygen delig.: 2.3% alkali charge, 90°C</td>
<td></td>
</tr>
<tr>
<td>BS(24)</td>
<td>brownstock, kappa = 24</td>
<td></td>
</tr>
<tr>
<td>BS(24)O</td>
<td>oxygen delig.: 1.3% alkali charge, 90°C</td>
<td></td>
</tr>
<tr>
<td>BS(24)O*</td>
<td>oxygen delig.: 2.2% alkali charge, 105°C</td>
<td></td>
</tr>
<tr>
<td>BS(24)POO</td>
<td>percarboxylic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 90°C</td>
<td></td>
</tr>
<tr>
<td>BS(24)POaO*</td>
<td>percarboxylic acid: 4% charge, oxygen delig.: 1.3% alkali charge, 105°C</td>
<td></td>
</tr>
</tbody>
</table>

* for additional conditions see experimental text.

Residual Lignin Isolation
Residual lignin was extracted from the pulp samples by an acidic 1,4-dioxane isolation procedure previously reported [134, 143]. Prior to lignin isolation, pulps were Soxhlet extracted for 24 hours with acetone, washed with water and air-dried. Lignin was extracted from the pulp with a 90% 1,4-dioxane/0.1 N HCl (v/v) solution (10% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture
Functional Group Quantification

Lignin functional groups were determined by 1H-, 13C-, 31P-, and 3P-NMR using a Bruker 400 MHz NMR spectrometer. Proton- and 13C-NMR spectroscopy was performed according to Li and Landquist [191] using anhydrous DMSO-<sup>d6</sup> as the solvent and 3-(trimethylsilyl)propionate-2,2,3,3-d<sub>4</sub> as the internal standard. Carbon-13 NMR spectroscopy was employed according to the procedure of Robert [244] using integration regions consistent with the literature [244, 245, 247].

Lignins hydroxyl groups were measured by using a modification of the phosphorus-NMR-based procedure previously reported [251, 256, 258-261]. Lignin, 55 mg, was completely dissolved in 280 mL pyridine containing chromium-acetylacetonate (2 mg/mL) and cyclohexanol (2 mg/mL), then 175 mL CDCl<sub>3</sub> was added. Fifteen minutes before NMR analysis, 75 mL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was added to the lignin solution with stirring. Phosphorus-NMR analysis indicated that excess derivatization reagent was present in the solution (δ 176.0 ppm). NMR analysis was performed using the following conditions: 30° pulse angle, 25-second pulse delay, inverse-gated decoupling, and 200 scans per spectrum. Integration regions consistent with published data and model compound studies were used [256, 258-261], and the baseline was locally corrected about the internal standard (cyclohexanol).

The ortho- and para-quinone contents of isolated lignins were quantified by 31P-NMR spectroscopy after trimethylphosphite derivatization [183, 184, 189, 276]. Lignin, 55 mg, was treated with 500 mL 50% trimethylphosphite/DMF (v/v) under argon. After two days, excess trimethylphosphite was removed by adding 250 mL DMSO and applying vacuum at 45°C until the sample was nearly dry. Treated lignins were dissolved in 400 mL 60% DMSO-<sup>d6</sup>/pyridine (v/v) containing tri-meta-tolylyphosphate (0.7 mg/mL, δ -16.3 ppm vs. 85% H<sub>3</sub>PO<sub>4</sub>, T<sub>1</sub> = 0.8 sec.) and chromium-acetylacetonate (0.9 mg/mL). Then, 5 mL water was added to the sample and after 12 hours, the 31P-NMR spectrum was acquired. Quantitative 31P-NMR spectra were acquired using: 90° pulse, 5-second pulse delay, inverse-gated broadband proton decoupling, and 1500 scans per spectrum. Lignin-quinone quantification was achieved using the following integration areas: tri-meta-tolylyphosphate (internal standard) δ -14.9 to -17.4 ppm, and the quinone adduct δ -0.3 to -7.0 ppm.

Lignin-carbonyl groups were determined by using a modification of the 13C-NMR procedure developed by Sevillano et al. [122, 145]. Lignin, 60 mg, was dissolved in 500 mL DMF, then 1 mL 50% DMF/water (v/v) containing 110 mg 4-trifluoromethylphenylhydrazine was added. After 12 hours, the derivatized lignin was precipitated by the addition of ~20 mL of water (pH = 2.0). The aqueous layer was discarded and the lignin was freeze-dried. The resulting lignin was Soxhlet extracted with CH<sub>2</sub>Cl<sub>2</sub>. A total of three hours were required for complete extraction. Approximately 25 mg of derivatized lignin was dissolved in 450 mL DMSO-d<sub>6</sub> containing 3-trifluoromethoxybenzoic acid (0.5 mg/mL, δ -57.2 ppm vs. CO,F, T<sub>1</sub> = 1.6 sec) as an internal standard. NMR analysis was performed under the following conditions: 90° pulse angle, 10-second pulse delay, and 400 scans per spectrum. Lignin-carbonyl quantification was achieved by lineshape analysis using NUTS NMR Transform Utility Software (Acorn-NMR).

RESULTS AND DISCUSSION

Pulp Properties

Both kappa 24 and 47 brownstock pulps were oxygen delignified under various conditions. Oxygen delignification was targeted at two levels ~42% or "standard" delignification (O) and an "aggressive" degree of delignification (~68%, O*) employing additional alkali and higher temperature. Selected experiments used peracetic acid pretreatment before oxygen delignification. Peracetic acid treatment was performed at pH ~8 and pulps were not washed before subsequent oxygen delignification. The peracetic acid pretreatment method was selected so that it could easily be implemented at the mill level. Potentially, brownstock may be Pa treated without pH adjustment, using 1 hour treatment time, moderate temperature (70°C), and only dewatering (without washing) before the oxygen delignification stage. Figures 1-4 give pulp property data for the series of Pa/O pulps.
Note in Figure 1 that in comparison, the kappa 47 brownstock pulps gave higher brightness values than the kappa 24 pulps. Although a limited and low brightness range was studied, from Figure 1 we can see that the high and low kappa pulps follow parallel curves with the kappa 47 brownstock pulps brighter at any given kappa number. A similar effect was noted by Czajkos [228] and Steffen et al. [229] who also found that high kappa pulps gave greater brightness values after oxygen delignification.

Referring to Figure 1, peracetic acid pretreatment between two oxygen stages results in greater kappa reduction relative to the OO sequence. Other researchers have noted the activating influence of peracetic acid applied between two oxygen stages [230]. Peracetic acid pretreatment also allows for the decreased kappa number after subsequent oxygen delignification. For the kappa 47 pulp, peracetic acid pretreatment followed by aggressive oxygen delignification (BS/47/O^+O^-) gave higher pulp viscosity, similar kappa number, and slightly lower brightness than intermediate pretreatment (BS/47/O^-O^-).

On the basis of viscosity versus brightness (Figure 2), the high kappa pulp showed higher viscosity at any given brightness value. Apparently the high intrinsic viscosity of the kappa 47 pulp is preserved during oxygen delignification. Steffen et al. noted that viscosity selectivity (Δviscosity/kappa) is relatively constant for oxygen delignification over the pulp kappa number 18.9-57.1 [229]. Generally, 50% delignification is taken to be a rule of thumb as the maximum delignification that can be achieved without unacceptable loss of viscosity. For this study, the kappa 47 pulp can adequately withstand >50% oxygen delignification because of its higher intrinsic viscosity.

![Figure 1](image1.png)  
**Figure 1.** PaO pulp brightness/kappa properties.

![Figure 2](image2.png)  
**Figure 2.** PaO pulp brightness/viscosity properties.

![Figure 3](image3.png)  
**Figure 3.** Pulp properties relative to the BS(24)O standard pulp.

![Figure 4](image4.png)  
**Figure 4.** Bleachability of PaO pulps.

### Residual Lignin Functional Group Contents
Quinone group contents. Oxo-, and para-quinone lignin structures are potentially important groups to consider during bleaching because they are highly colored. Quinone structures are widely thought to be the major colored bodies present in a wide range of pulps and lignins [32, 34, 37, 51, 147, 183, 188, 252]. Recently our group demonstrated that chlorine dioxide dramatically increases the lignin-quinone content relative to the brownstock value [185, 184, 189]. DE-DED residual lignin quinone contents were found to
correlated with pulp brightness and brightness ceiling values suggesting these structures may blander brightness development [183]. Quinone structures have also been implicated in the alkali darkening reaction of mechanical [277] and chemical pulps [184].

Lebo et al. [47, 49] and Argyropoulos et al. [130] developed an used trimethylphosphine derivatization for the study of ortho-quinone structures in mechanical pulps. Both phosphorus microanalysis and qualitative solid-state 31P-NMR spectroscopy were used to investigate derivatized mechanical pulps. Recently, trimethylphosphine derivatization/31P-NMR was extended for the simultaneous determination of both ortho- and para-quinone structures in isolated lignins [183-185, 189, 203, 204]. The method is currently in the process of development, but experimental evidence indicates quantitative results can be acquired, provided sample derivatization takes place under dry conditions [173, 174, 189, 203].

Figure 4 displays the quinone contents, measured by 31P-NMR spectroscopy, for a series of residual lignins isolated from Pa/O pulps. In contrast to previous reports on chlorite dioxide bleaching [183, 184, 189], the quinone contents were found to be uniformly low regardless of the exact oxygen delignification of peracetic acid pretreatment conditions used.

Oxygen/alkali can potentially cause the formation of quinone products from phenolic-lignin precursors by Dikin or Dakin-like reactions [190]. The result of this investigation supports model compound studies [59, 190, 231], which indicate that quinone intermediates are unstable and further oxidized to muconic acid and other structures. From a UV/Visible spectroscopy-based investigation, Pasco and Suckling speculated that simple quinone structures may not be the sole cause of visible-region absorbance in oxygen/alkali treated Kraft lignins [232]. Therefore, the low quinone content measured in the Pa/O residual lignins appears to indicate that these structures may not be the major chromophores present in oxygen-delinified pulps.

![Figure 4. Ortho- and para-quinone contents of residual lignins from kraft 24 and 47 Pa/O pulps.](image)

In a preliminary study, the quinone content values determined by trimethylphosphine/31P-NMR were verified by applying the 31P-NMR method developed by Sevillano et al. [122, 145]. For example, the quinone content for periodate and chlorine dioxide (KF = 0.2) residual lignins were found to be 0.50 and 0.322 mmol/g lignin respectively by 31P-NMR (Figure 5), and 0.431 and 0.302 ± 0.004 (LSD = 0.02) mmol/g lignin by 31P-NMR. Similarly, the quinone contents for kraft 47 Pa/O residual lignins determined by both 31P- and 31P-NMR are also close in value (Figures 4 and 5). Notable exceptions are the values determined for BS47 and BS47O lignin samples, 31P-NMR values are 3.3 and 1.7 times higher, respectively, than the 31P-NMR values (Figures 4 and 5). The 31P-NMR-derived results for BS47O and BS47O residual lignins were replicated.

For accurate results, the 31P-NMR method relies on the formation of the azo-phenol) derivative (λ ~ 612 ppm) for quinones and the hydrzone derivate (λ ~ 403 ppm) for other carbonyl structures (Figure 6, of [233, 234] re-azo-phenol/hydrzone tautomerism). Note, the 31P-NMR method [122, 145] has been verified on a small number of model compounds. The 31P-NMR methodology should be applied to additional non-quinone carbonyl compounds to confirm that only derivatized quinone structures can exist in the tautomer. Additionally, the influence of sample preparation conditions on the potential
oxidation of lignin-hydroxyl to the azo form is not yet known. Otherwise, the close correspondence of $^{13}$F- and $^{31}$P-NMR values serves to verify both methods for the determination of quinones in lignins.

**Carbonyl group contents.** The $^{13}$F-NMR method was useful for the determination of lignin-carbonyl functional groups. For kappa 47 Pa/O residual lignins, application of oxygen caused an increase in carbonyl content above the brownstock value but very little difference in carbonyl content was observed between the individual Pa/O lignins (Figure 5). The result for the BS/47O residual lignin is similar to carbonyl content data determined by Lachnial et al. for an oxygen-stage residual lignin (BS kappa 30, 53% delign., CrO$_3$ content of 0.16/00g lignin = 0.0 mmol/g lignin [5].

**H1- and P31-NMR derived data.** Figures 7 and 8 show a comparison of $^1$H-NMR and $^{31}$P-NMR/TMDP derived residual lignin functional group data. Generally, the correlation between $^1$H- and $^{31}$P-NMR derived data was very good. A surprising result of this study is that the total phenolic content of the Pa/O residual lignins does not dramatically decrease with the application of aggressive oxygen, double-oxygen, or intermediate peracetic acid conditions. From model compound studies, a dramatic decrease in total phenolic content would be expected because of the known reactivity of oxygen with phenolic structures [93], although these results are consistent with other residual lignin studies [4].

McDonough and Rapson [104] reported that peracetic acid under alkaline conditions degrades phenolic structures to a plethora of acid products. The reaction proceeds by electrophilic attack of peracetic acid on the phenolate, demethylated, and finally nucelophilic attack of peracetic on the ortho-benzoquinone intermediate. Additionally, alkaline peracetic acid may cause lignin side-chain oxidation, Beyer-Villiger rearrangement to an aromatic ester, hydrolysis, and degradation to acid products [105]. During this study, the ability of peracetic acid to cause phenolic structures degradation was not readily apparent in the $^1$H- and $^{31}$P-NMR data (Figures 7 and 8). Only a marginal decrease in phenolic content as a result of peracetic acid pretreatment was observed (for example, BS/25O$_2$ versus BS/24PaO$_2$, Figure 8).

Overall, oxygen delignification, especially using aggressive conditions (O$_2$, PaO$_2$) or intermediate peracetic acid treatment (OPMO), results in a dramatic increase in the lignin carboxylic acid content as measured by $^1$H- and $^{31}$P-NMR techniques (Figures 7 and 8). The increase in carboxylic acid content is consistent with model compound investigations, which have shown ring-opening and side-chain elimination reactions resulting in carboxylic acid formation [93]. Similarly, Gellendest et al. [4] and Argyropoulos et al. [9] and others have noted that oxygen delignification introduces carboxylic acid structures into lignin.

Refer to Figures 7 and 8 the residual lignin carboxylic acid contents determined by $^1$H-NMR were consistently higher than those determined by $^{31}$P-NMR. The deviation is particularly large for the BS/47O/PAO residual lignin (Figure 7). From preliminary model compound studies we found that the $^{31}$P-NMR method may underestimate the presence of some hydroxyl functional groups, such as α-hydroxy acid structures. Related side reactions have been reported by Argyropoulos et al. [278] and others [279]. Potentially, the $^{31}$P-NMR carboxyl content value for the BS/47O/PAO residual lignin is lower than the $^1$H-
NMR value because of the presence of structures such as α-hydroxy acids that are not quantitatively derivatized. Further work needs to be done to determine the fundamental reason for the deviation of \(^{1}H\) and \(^{31}P\)-NMR determined carboxylic acid content values for the BS(47)O/P/O residual lignin.

Figure 7. Comparison of \(^{1}H\) and \(^{31}P\)-NMR determined OH functional group contents: BS(47) Pa/O residual lignin.

Figure 8. Comparison of \(^{1}H\) and \(^{31}P\)-NMR determined OH functional group contents: BS(24) Pa/O residual lignin.

C(13)-NMR derived data. Carbon(13)-NMR data is considered to be semiquantitative, because functional group data is expressed on a carbons per aromatic ring basis. Figure 9 and Table 2 give \(^{13}C\)-NMR determined functional group data for both kappa 24 and 47 Pa/O residual lignins.

Diaryl methane–lignin structures can easily be detected by \(^{13}C\)-NMR spectroscopy. The signal due to this ‘condensed’ lignin substructure can be observed as a sharp signal at δ = 29 ppm [4]. Diaryl methane structures are known to be formed by the phenol–formaldehyde reaction [280]. Formation of diaryl methane structures have been reported from the alkali treatment of guaiacylglycerol–δ-aryl ether model compounds [281]. Also, vanillyl alcohol has been reported to undergo condensation via a quinomethide intermediate to give diaryl methane structures [282, 283]. Interestingly, diaryl methane structures have been shown to undergo air oxidation to give chromophoric extended quinonemethide structures stable to borohydride reduction [281-283]. Lai has indicated that diaryl methane structures are resistant to oxygen/alkali degradation relative to uncondensed structures [96].

Figure 9. \(^{13}C\)-NMR functional group data for residual lignins from PaO pulps.

Figure 9 shows the distribution of diaryl methane structures in the PaO residual lignins. From Figure 9 we can see that the content of diaryl methane structures is apparently greater in BS(24) pulps. Interestingly, the application of oxygen (BS(24)O), and particularly under aggressive conditions, (BS(24)O*) causes a dramatic increase and/or enrichment of these condensed structures. In the case of the BS(24) pulps, peracetic acid pretreatment appears to prevent the accumulation of the condensed
diaryl methane structures. The influence of peracetic acid pretreatment is less clear on BS(47) pulps, although the diaryl methane content is greater in the BS(47)OO versus BS(47)OpaO residual lignin.

The data in Figure 9 also demonstrate the introduction of conjugated and unconjugated carboxylic acid structures into the residual lignin as a result of oxygen and peracetic acid treatment. The trend of the data is consistent with the results gained by 1H- and 31P-NMR spectroscopy (Figures 7 and 8). Again, aggressive oxygen conditions are more effective for lignin carboxylic acid group formation. Peracetic acid pretreatment appears to have a beneficial effect on the introduction of carboxylic acid groups, consistent with its reported chemistry [104, 105].

Additional lignin functional group data are assembled in Table 12. Differences in the C=O (CH2OH) carbon content were observed. A decrease in this functional group could potentially indicate the elimination of formaldehyde during oxygen delignification. Subsequently, the formaldehyde can participate in the formation of diarylmethylene structures. Interestingly, the C=O content appears to increase with oxygen delignification and particularly when the pulps are pretreated with peracetic acid. Generally, there was a noted increase in all aliphatic carbon functional groups as a result of oxygen delignification/peracetic acid treatment.

| Table 2. 13C-NMR data for Pa/O residual lignins (values expressed as carbons/aromatic ring). |
|-----------------|------|-----|-----|-----|-----|-----|
| **Structure**   | BS(47) | O   | *O* | PaO | PaO* | O/O |
| Aliphatic C-O: C=O in β-O-4; C=O in β-5 and β-β | 0.32  | 0.35 | 0.34 | 0.44 | 0.50 | 0.40 | 0.47 |
| Aliphatic C-O: C=O in β-O-4 | 0.33  | 0.35 | 0.46 | 0.46 | 0.52 | 0.40 | 0.49 |
| Aliphatic COR | 0.07  | 0.07 | 0.08 | 0.09 | 0.10 | 0.07 | 0.08 |
| Aliphatic C-O: C=O in β-O-4 | 0.17  | 0.16 | 0.18 | 0.21 | 0.20 | 0.18 | 0.20 |
| Methoxy OCH3 | 0.77  | 0.76 | 0.72 | 0.78 | 0.76 | 0.75 | 0.76 |
| C=O in β-β and C=O in β-5 | 0.06  | 0.06 | 0.06 | 0.06 | 0.06 | 0.05 | 0.06 |

| **Structure**   | BS(24) | O   | *O* | PaO | PaO* | O/O |
| Aliphatic C-O: C=O in β-O-4; C=O in β-5 and β-β | 0.22  | 0.24 | 0.30 | 0.36 | 0.38 |
| Aliphatic C-O: C=O in β-O-4 | 0.24  | 0.30 | 0.36 | 0.41 | 0.45 |
| Aliphatic COR | 0.04  | 0.04 | 0.04 | 0.04 | 0.05 |
| Aliphatic C-O: C=O in β-O-4 | 0.10  | 0.10 | 0.10 | 0.13 | 0.12 |
| Methoxy OCH3 | 0.70  | 0.67 | 0.64 | 0.67 | 0.68 |
| C=O in β-β and C=O in β-5 | 0.04  | 0.04 | 0.02 | 0.40 | 0.02 |

**CONCLUSIONS**

Lignin functional group data revealed little quinone and carbonyl content differences between the various Pa/O residual lignins. The contents of these potentially chromophoric structures do not appear to be extensively altered by the oxygen delignification conditions. The data suggest that quinone and carbonyl lignin structures may not be major chromophoric structures and therefore may not have an impact on pulp brightness. The detected quinone contents were very low for all residual lignins studied. Carbonyl group contents did not vary appreciably for the kappa 47 Pa/O residual lignins. Further work remains to be done so understand the fundamental nature of brightness differences between the kappa 24 and 47 Pa/O pulps.

Standard 1H-, 13C-, and 31P-NMR analyses of the residual lignins revealed that diarylmethane and carboxylic acid structures are enriched and/or formed as a result of Pa/O treatment. Surprisingly, the total phenolic contents of the residual lignins were lowered, but not dramatically by Pa/O treatment. Possibly, lignin phenolic structures are more resistant toward oxygen delignification and peracetic acid than has been suggested by previous model compound studies.

Potentially, oxygen delignification can be interpreted as a wholesale removal of lignin fragments with little apparent evidence of the delignification mechanism residing in structural features of the (residual) lignin left in the pulp. Similarly, Gillenstedt et al. interpreted the unexpectedly low level of observed lignin structural changes after oxygen delignification in the following manner: "...bleaching
seems to follow a pattern which resembles the peeling of an onion layer by layer and, once a layer has been chemically modified and removed, the lignin is again reactive and available for new chemical attack. [4]

Both low (24) and high (47) kappa softwood kraft pulps were oxygen delignified under standard (~42% delig.) and aggressive (~68% delig.) conditions. A series of pulps were treated with distilled peracetic acid (pH = 8). Peracetic acid applied before and between oxygen delignification stages was beneficial and allowed for a greater kappa number reduction.

Apparently, under the conditions of application in this study, peracetic acid caused no loss of pulp viscosity. Generally, 50% delignification is taken to be a rule of thumb as the maximum delignification that can be achieved without unacceptable loss of viscosity (pulp strength). Clearly, for this study the kappas 47 pulp could adequately withstand > 50% oxygen delignification and still give a pulp with properties similar to the standard case (BS3423).

ACKNOWLEDGMENTS

The authors wish to thank Drs. McDonough, Dimmel, and Lucia for guidance. We would also like to thank the Institute of Paper Science and Technology (IPST) and its member companies for their financial support. Portions of this work were used by M. Z. as partial fulfillment of the requirements for the Ph.D. degree at IPST.

Phosphorous(31)-NMR Spectra of Residual Lignins Treated with Trimethylphosphite.

D (KF = 0.2) replicate #1

D (KF = 0.2) replicate #2

D (KF = 0.2) replicate #3
(Ave. = 0.302, SD = 0.004, LSD = 0.02)

Periodate treated kappa = 28 brownstock

186
Phosphorus(31)-NMR Spectra of Trimethylphosphite Treated Residual Lignins isolated From Oxygen and Peracetic Acid Bleached Kappa 47 Brownstock Softwood Kraft Pulp.
Phosphorus(31)-NMR Spectra of Trimethylphosphite Treated Residual Lignins Isolated From Oxygen and Peracetic Acid Bleached Kappa 47 and 24 Brownstock Softwood Kraft Pulp.
Phosphorus(31)-NMR Spectra of Residual Lignins Isolated From Oxygen and Peracetic Acid Bleached Kappa 47 Softwood Kraft Pulp.
Summary of Hydroxyl Functional Group Data for Oxygen and Peracetic Acid Bleached, Kappa 47 Softwood Kraft Pulps (Determined by $^{31}$P–NMR and TMDP Derivatization).

<table>
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<th>PaO</th>
<th>PaO*</th>
<th>OO</th>
<th>OPaO</th>
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<td>2.62</td>
<td>2.47</td>
<td>2.86</td>
<td>2.03</td>
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<td>$p$-OH–$\phi$ &amp; G</td>
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<td>1.52</td>
<td>1.48</td>
<td>1.70</td>
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<td>0.31</td>
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<td>1.08</td>
<td>1.61</td>
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* see Table 3 for an explanation of bleaching sequence abbreviations.
Phosphorus(31)-NMR Spectra of Residual Lignins Isolated From Oxygen and Peracetic Acid Bleached Kappa 24 Softwood Kraft Pulp.

BS(24)

BS(24)O

BS(24)O*

BS(24)PaO*
Summary of Hydroxyl Functional Group Data for Oxygen and Peracetic Acid Bleached, Kappa 24 Softwood Kraft Pulps (Determined by $^{31}$P-NMR and TMDP Derivatization).

<table>
<thead>
<tr>
<th>Structure</th>
<th>ES</th>
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<th>O*</th>
<th>PaO*</th>
</tr>
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<tbody>
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</tr>
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<td>0.63</td>
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<td>1.11</td>
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<td>2.05</td>
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* See Table 3 for an explanation of bleaching sequence abbreviations.

Phosphorous($^{31}$)-NMR Spectral Data for α-Hydroxy-Acids Derivatized with TMDP.

- A) TMDC/citric acid spirophosphorane adduct (proton decoupled, $\delta$ -37.8 ppm)
- B) TMDC/citric acid spirophosphorane adduct (proton coupled, $J_{HH} = 891$ Hz)

Citic acid ($\delta$ 134.9, 134.7 ppm) and cyclohexanol
Mandelic acid (δ 146.7, 134.6 ppm) and cyclohexanol
A) TMDP/mandelic acid spirophosphorane adduct (proton decoupled, δ -36.7, -37.1 ppm)
B) TMDP/mandelic acid spirophosphorane adduct (proton coupled, $J_{RR} = 866$ Hz)

Argyropoulos et al. [256, 261] previously reported carboxylic acid–phosphate (δ ~ 135 ppm) ester products from the reaction of carboxylic acids and TMDP. During this study, α-hydroxy–carboxylic acids (citric acid and mandelic acid, see above) were found to be converted to the carboxylic acid–phosphate esters in less than quantitative yield. An unexpected side–product of the derivatization reaction was a spirophosphorane product (δ ~ -37 ppm, $J_{RR} = 700$ Hz). Spirophosphorane structures exist in equilibrium with the open chain form and react further with the derivatizing agent (see scheme below) [279].
Proton-NMR Spectra of Residual Lignins Isolated From Oxygen and Peracetic Acid Bleached Kappa 24 and 47 Softwood Kraft Pulps.
Summary of $^1$H-NMR Determined Functional Group Data (mmol/g Lignin) for Oxygen and Peroxidic Acid Bleached Kappa 47 Softwood Kraft Pulps

<table>
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<tr>
<th>Structure</th>
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<th>PaO</th>
<th>PaO*</th>
<th>OO</th>
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<td>15.16</td>
<td>13.66</td>
<td>11.93</td>
<td>14.62</td>
</tr>
<tr>
<td>Aliphatic (H$b$ &amp; H$a$)</td>
<td>10.74</td>
<td>15.83</td>
<td>15.25</td>
<td>15.00</td>
<td>15.22</td>
<td>11.80</td>
<td>16.11</td>
</tr>
<tr>
<td>Methoxy (Hy &amp; OH)</td>
<td>16.68</td>
<td>20.00</td>
<td>21.31</td>
<td>21.29</td>
<td>18.93</td>
<td>15.61</td>
<td>20.03</td>
</tr>
<tr>
<td>H$b$ in b–1</td>
<td>7.38</td>
<td>7.86</td>
<td>11.08</td>
<td>8.56</td>
<td>7.78</td>
<td>6.81</td>
<td>8.38</td>
</tr>
</tbody>
</table>

* see Table 3 for an explanation of bleaching sequence abbreviations.
Summary of $^1$H-NMR Determined Functional Group Data (nmol/g Lignin) for Oxygen and Peracetic Acid Bleached Kappa 24 Softwood Kraft Pulps.

<table>
<thead>
<tr>
<th>Structure</th>
<th>BS</th>
<th>O</th>
<th>O*</th>
<th>PaO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid</td>
<td>0.85</td>
<td>1.33</td>
<td>2.31</td>
<td>2.57</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>1.05</td>
<td>1.22</td>
<td>1.06</td>
<td>0.90</td>
</tr>
<tr>
<td>Unsub phenolic</td>
<td>2.68</td>
<td>1.65</td>
<td>1.34</td>
<td>1.28</td>
</tr>
<tr>
<td>Substituted phenolic</td>
<td>1.39</td>
<td>1.24</td>
<td>1.14</td>
<td>1.08</td>
</tr>
<tr>
<td>Total Phenolic</td>
<td>4.06</td>
<td>2.89</td>
<td>2.48</td>
<td>2.36</td>
</tr>
<tr>
<td>Aromatic and vinylic</td>
<td>15.91</td>
<td>13.79</td>
<td>12.86</td>
<td>15.40</td>
</tr>
<tr>
<td>Aliphatic (Hβ &amp; Ho)</td>
<td>10.99</td>
<td>14.24</td>
<td>13.44</td>
<td>16.16</td>
</tr>
<tr>
<td>Methoxy (Hy &amp; OH)</td>
<td>20.04</td>
<td>17.79</td>
<td>15.95</td>
<td>20.12</td>
</tr>
<tr>
<td>Hβ in β-1</td>
<td>8.57</td>
<td>7.27</td>
<td>7.81</td>
<td>13.21</td>
</tr>
</tbody>
</table>

* see Table 3 for an explanation of bleaching sequence abbreviations.

13C NMR Residual 360 ppm:450 psi DMF-d6

13C NMR Residual 360 ppm:450 psi DMF-d6

13C NMR Residual 360 ppm:450 psi DMF-d6

201
## Summary of $^{13}$C-NMR Data (data expressed on carbon's/aromatic ring basis).

<table>
<thead>
<tr>
<th>BS(47)</th>
<th>O</th>
<th>O*</th>
<th>PzO</th>
<th>PzO*</th>
<th>GO</th>
<th>OPaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconjugated COOH</td>
<td>0.153</td>
<td>0.253</td>
<td>0.362</td>
<td>0.313</td>
<td>0.411</td>
<td>0.288</td>
</tr>
<tr>
<td>Conjugated COOH</td>
<td>0.043</td>
<td>0.087</td>
<td>0.133</td>
<td>0.098</td>
<td>0.135</td>
<td>0.104</td>
</tr>
<tr>
<td>C₅, C₆ Arom ether or -OH</td>
<td>1.994</td>
<td>2.028</td>
<td>1.970</td>
<td>1.958</td>
<td>1.953</td>
<td>1.984</td>
</tr>
<tr>
<td>C₁, Aromatic C-C bond</td>
<td>1.381</td>
<td>1.394</td>
<td>1.411</td>
<td>1.392</td>
<td>1.407</td>
<td>1.408</td>
</tr>
<tr>
<td>C₅, Aromatic C-C bond</td>
<td>0.520</td>
<td>0.532</td>
<td>0.522</td>
<td>0.477</td>
<td>0.488</td>
<td>0.531</td>
</tr>
<tr>
<td>C₆, Aromatic C-H bond</td>
<td>0.799</td>
<td>0.795</td>
<td>0.816</td>
<td>0.839</td>
<td>0.855</td>
<td>0.809</td>
</tr>
<tr>
<td>C₅, Aromatic C-H bond</td>
<td>0.482</td>
<td>0.454</td>
<td>0.452</td>
<td>0.493</td>
<td>0.466</td>
<td>0.442</td>
</tr>
<tr>
<td>C₂, Aromatic C-H bond</td>
<td>0.824</td>
<td>0.796</td>
<td>0.828</td>
<td>0.840</td>
<td>0.851</td>
<td>0.826</td>
</tr>
<tr>
<td>Aliphatic C-O bond, C₅ in β-O-4; C₆ in β-5 and β-</td>
<td>0.323</td>
<td>0.345</td>
<td>0.425</td>
<td>0.438</td>
<td>0.501</td>
<td>0.402</td>
</tr>
<tr>
<td>Aliphatic C-O bond, C₆ in β-O-4</td>
<td>0.326</td>
<td>0.349</td>
<td>0.460</td>
<td>0.460</td>
<td>0.519</td>
<td>0.395</td>
</tr>
<tr>
<td>Aliphatic COR</td>
<td>0.071</td>
<td>0.072</td>
<td>0.084</td>
<td>0.087</td>
<td>0.096</td>
<td>0.066</td>
</tr>
<tr>
<td>Aliphatic C-O-CY in b-O-4</td>
<td>0.172</td>
<td>0.155</td>
<td>0.180</td>
<td>0.205</td>
<td>0.203</td>
<td>0.182</td>
</tr>
<tr>
<td>Methoxy OCH₃</td>
<td>0.773</td>
<td>0.757</td>
<td>0.747</td>
<td>0.778</td>
<td>0.758</td>
<td>0.747</td>
</tr>
<tr>
<td>C₅ in β-5 and C₅ in β-5</td>
<td>0.059</td>
<td>0.057</td>
<td>0.055</td>
<td>0.057</td>
<td>0.055</td>
<td>0.050</td>
</tr>
<tr>
<td>OCH₃ in MAME structure</td>
<td>0.118</td>
<td>0.090</td>
<td>0.115</td>
<td>0.115</td>
<td>0.115</td>
<td>0.113</td>
</tr>
<tr>
<td>CH₃ in diarylmethane</td>
<td>0.028</td>
<td>0.034</td>
<td>0.120</td>
<td>0.088</td>
<td>0.135</td>
<td>0.111</td>
</tr>
</tbody>
</table>

## BS(24) O  O*  PzO  PzO* GO  OPaO

<table>
<thead>
<tr>
<th>BS(24)</th>
<th>O</th>
<th>O*</th>
<th>PzO</th>
<th>PzO*</th>
<th>GO</th>
<th>OPaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconjugated COOH</td>
<td>0.170</td>
<td>0.298</td>
<td>0.406</td>
<td>0.420</td>
<td>0.489</td>
<td></td>
</tr>
<tr>
<td>Conjugated COOH</td>
<td>0.024</td>
<td>0.102</td>
<td>0.151</td>
<td>0.150</td>
<td>0.148</td>
<td></td>
</tr>
<tr>
<td>C₅, C₆ Arom ether or -OH</td>
<td>1.815</td>
<td>1.962</td>
<td>1.926</td>
<td>1.955</td>
<td>1.930</td>
<td></td>
</tr>
<tr>
<td>C₁, Aromatic C-C bond</td>
<td>1.395</td>
<td>1.449</td>
<td>1.466</td>
<td>1.445</td>
<td>1.472</td>
<td></td>
</tr>
<tr>
<td>C₅, Aromatic C-C bond</td>
<td>0.576</td>
<td>0.593</td>
<td>0.586</td>
<td>0.516</td>
<td>0.529</td>
<td></td>
</tr>
<tr>
<td>C₆, Aromatic C-H bond</td>
<td>0.822</td>
<td>0.785</td>
<td>0.795</td>
<td>0.821</td>
<td>0.830</td>
<td></td>
</tr>
<tr>
<td>C₅, Aromatic C-H bond</td>
<td>0.476</td>
<td>0.425</td>
<td>0.405</td>
<td>0.454</td>
<td>0.449</td>
<td></td>
</tr>
<tr>
<td>C₂, Aromatic C-H bond</td>
<td>0.915</td>
<td>0.786</td>
<td>0.821</td>
<td>0.809</td>
<td>0.790</td>
<td></td>
</tr>
<tr>
<td>Aliphatic C-O bond, C₅ in β-O-4; C₆ in β-5 and β-</td>
<td>0.221</td>
<td>0.240</td>
<td>0.303</td>
<td>0.357</td>
<td>0.383</td>
<td></td>
</tr>
<tr>
<td>Aliphatic C-O bond, C₆ in β-O-4</td>
<td>0.237</td>
<td>0.301</td>
<td>0.363</td>
<td>0.406</td>
<td>0.453</td>
<td></td>
</tr>
<tr>
<td>Aliphatic COR</td>
<td>0.036</td>
<td>0.043</td>
<td>0.038</td>
<td>0.043</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Aliphatic C-O-CY in b-O-4</td>
<td>0.100</td>
<td>0.104</td>
<td>0.104</td>
<td>0.127</td>
<td>0.120</td>
<td></td>
</tr>
<tr>
<td>Methoxy OCH₃</td>
<td>0.703</td>
<td>0.671</td>
<td>0.643</td>
<td>0.668</td>
<td>0.680</td>
<td></td>
</tr>
<tr>
<td>C₅ in β-5 and C₅ in β-5</td>
<td>0.039</td>
<td>0.035</td>
<td>0.023</td>
<td>0.395</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>OCH₃ in MAME structure</td>
<td>0.001</td>
<td>0.013</td>
<td>0.003</td>
<td>0.012</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>CH₃ in diarylmethane</td>
<td>0.052</td>
<td>0.180</td>
<td>0.321</td>
<td>0.052</td>
<td>0.153</td>
<td></td>
</tr>
</tbody>
</table>
Fluorine(19)-NMR Spectra of Residual Lignins Treated with 4-Trifluoromethylphenyl-Hydrazine.

BS(47) #1

BS(47)PaO*

BS(47)O*

Chlorine dioxide (KF =0.2) residual lignin

Periodate oxidized softwood, kappa = 28, brownstock

BS(47)OO
Fluorine(19)-NMR Original and Simulated Spectrum Of 4-Trifluoromethylphenyl-Hydrazine Treated BS(47) Residual Lignin Showing Contaminants Derived From The Reagent.

The upper spectrum is a simulated spectrum produced by lineshape analysis. Individual fitted components are shown under the original spectrum (lower trace). The sharp resonances at δ -59.2, -60.2, and -61.3 ppm are contaminants arising from the reagent. The derivatized lignin was washed two times with diethyl ether but, this procedure did not remove all of the residual reagent and contaminants. Soxhlet extraction of the treated lignin with dichloromethane (see Experimental section) was found to substantially reduce the level of contamination.
Fluorine(19)-NMR Spectra of Model Compounds in DMSO-<i>d</i><sub>6</sub> Solvent.

4-<i>CF<sub>3</sub></i>-4-hydrazine (-59.0 ppm),
3-<i>CF<sub>3</sub></i>O-benzoic acid (-57.2 ppm)

4-<i>CF<sub>3</sub></i>-benzamide (-61.5 ppm)

4-fluorobenzoic acid (-106.9 ppm)

trans-4-<i>CF<sub>3</sub></i>-cinnamic acid (-60.3 ppm)

CCL<sub>3</sub>F (Freon, neat) reference standard
(0.000 ppm)
Residual Lignin Quinone and Carbonyl Contents (mmol/g Lignin) Determined by $^{19}$F-NMR spectroscopy.

<table>
<thead>
<tr>
<th>Structure</th>
<th>BS (#1)</th>
<th>O (#1)</th>
<th>O*</th>
<th>PaO*</th>
<th>OO</th>
<th>OPaO</th>
<th>Per.*</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>0.810</td>
<td>1.101</td>
<td>1.145</td>
<td>1.207</td>
<td>1.215</td>
<td>1.179</td>
<td>1.367</td>
<td>1.643</td>
</tr>
<tr>
<td>Quinone</td>
<td>0.159</td>
<td>0.097</td>
<td>0.074</td>
<td>0.069</td>
<td>0.079</td>
<td>0.087</td>
<td>0.503</td>
<td>0.322</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>BS (#2)</th>
<th>O (#2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>0.860</td>
<td>1.193</td>
</tr>
<tr>
<td>Quinone</td>
<td>0.163</td>
<td>0.096</td>
</tr>
</tbody>
</table>

* see Table 3 for an explanation of bleaching sequence abbreviations.
* residual lignins treated in homogeneous solution: periodate (per.) and chlorine dioxide (D, KF = 0.2), see Experimental section for details.

Fluorine(19) Spin–Lattice ($T_1$) Relaxation Parameters Determined by the Inversion–Recovery Pulse Sequence for 4-Trifluoromethylphenylhydrazine Treated BS(47)O* Residual Lignin.

$T_1$ values:
- Internal standard = 1.6 sec
- Carbonyl = 1.1 sec
- Quinone = 1.2 sec

Delay list:
0.01, 0.1, 0.25, 0.5, 1, 3, 5, 10, 20 sec.

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Appendix 11. Additional Publications.
ECF BLEACHABILITY OF SOFTWOOD AND HARDWOOD KRAFT PULPS MADE WITH ALTERED LIQUOR CONCENTRATION PROFILES


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ABSTRACT

This paper reports the results of a systematic study of the ECF bleachability of softwood and hardwood pulps prepared in a laboratory digester equipped with instrumentation that allows monitoring and controlling the concentrations of individual liquor components during the kraft cook. Conventional kraft control cooks were compared with cooks in which the concentrations of disolved lignin and other dissolved organic solids were limited to very low levels and the alkali concentration profile was flat in comparison to a normal batch cook alkali profile. Bleachability was characterized in terms of the specific requirement for oxidant in the delignifying stages and the total chloride dioxide requirement for the whole sequence as a function of final brightness, for various charge levels in the third and fifth stages of the DEQOJED sequence. The bleachability was characterized in terms of the parameters of a mathematical model, which allowed determination of each pulp’s minimum ClO2 requirement for a specified target brightness. Bleachability was correlated with fundamental pulp characteristics, including hexenuronic acid content, and the contents in the residual lignin of condensed structures, free phenolic hydroxyl groups, methoxyl groups, and carboxyl groups.

It was concluded that, compared to conventional control pulps, pulps produced under conditions of low and relatively constant alkali concentration and low dissolved organic solids concentration, here denoted low-solids pulp, have higher unleached brightness and better bleachability. The bleachability improvement is manifested as a reduction in ClO2 requirement in the last three stages of the bleach sequence; the efficiency of lignin removal in the first two stages is unaffected. The bleachability differences are very large in the case of oak pulps and smaller for southern pine pulps. The results may be interpreted in terms of reduced propensity of the low solids pulps to form quinonoid chromophores during bleaching. Thus, the low solids pulps have residual lignin that contains fewer free phenolic hydroxyl groups to serve as quinone precursor. In hardwood (oak) low solids pulps, the shortage of quinone precursors is even greater because these pulps have higher hexenuronic acid contents and, therefore, lower lignin contents at the same kappa number.

INTRODUCTION

Modifications of the kraft pulping process for improved selectivity and/or extended delignification are perceived, primarily as a result of the growing need to limit bleaching chemical requirements and bleaching byproduct generation rates. All of these modifications involve changing the time courses (“profiles”) of the concentrations of one or more pulping liquor components, usually hydroxide ion, sulfide sulfur, or dissolved organic material. In addition to improving selectivity, such profile changes may affect bleachability. Although there have been studies of the bleachabilities of pulps from particular modified pulping processes, literature contains little information on effects of establishing well-defined profiles of individual liquor component concentrations during the kraft cook. Such information is needed to allow pulping liquor concentration profiles to be optimized for even greater reductions in bleaching chemical requirements. Consequently, we have conducted laboratory pulping experiments in which the alkali and lignin concentration profiles were altered in controlled ways, and have systematically studied the bleaching response of the resulting pulps. We have also isolated residual lignins from some of the pulps and have analyzed them by nuclear magnetic resonance to correlate lignin structural features with pulping conditions and bleaching response.

EXPERIMENTAL

Pulping

All pulping was carried out at Auburn University in an M/K Systems 6-liter laboratory digester, modified to accommodate ultraviolet and conductivity sensors, and equipped for continuously injecting and/or removing liquor during the cook. All cooks were done according to the same temperature schedule, which incorporated a 40-minute rise from ambient temperature to a maximum cooking temperature of 170°C.

Both softwood (SW) and hardwood (HW) chips were pulped, the species being southern pine and oak, respectively. In the case of SW, duplicate cooks of each of three different types were performed. In all three types, the effective alkali (EA) charge was 20% (dry wood basis), the sulfidity was 30%. One type, a
softwood control (SW-C) was done in the conventional batch mode, all of the pulping chemicals being charged at the beginning of the cook, with no addition or removal of liquor during the cook. In a second type, black liquor was charged at the beginning of the cook, together with the pulping chemicals. This type was denoted SW-BL. The third type is referred to as "prefilled" or "low solids" cook, denoted SW-LS. SW-LS cooks were started by charging all of the sulfite required to give a sulfidity of 30% based on the total alkali, together with a fraction of the alkali corresponding to the desired total alkali charge level. Both the EA and dissolved lignin (DL) concentration profiles were controlled. When the EA concentration had fallen to a predetermined value, alkali addition was begun to maintain that value. The rate of addition was controlled by continuous, on-line measurement of EA concentration. Alkali addition was continued until the DL-concentration had risen to the value at which it was to be controlled. At this point a black liquor bleed stream was initiated to control the DL concentration, while at the same time alkali was continuously fed to maintain the EA level and liquor-to-wood ratio constant. Duplicate softwood cooks of each type were done to reach a kappa number target of 25-30. During the constant alkali concentration period, the EA concentration was maintained at 14 g/L. Final lignin concentrations were 14-22 g/L in the SW-LS cooks, 51-52 g/L in the SW-C cooks and 55-57 g/L in the SW+BL cooks.

In the case of HW, duplicate cooks of each of the HW+BL type and a single cook of the HW-LS type were performed. In both types, the EA charge was 22% (o.d. wood basis), and the sulfidity was 30%. The final kappa number was 15-16. During the constant alkali concentration period, the EA concentration was maintained at 14-16 g/L. The final lignin concentration was 10 g/L in the HW-LS cook and 47-49 g/L in the HW+BL cooks.

All pulps were prepared at Auburn University, washed and shipped to the Institute of Paper Science and Technology, where they were screened, further characterized, and bleached.

Bleaching:
All bleaching employed the D₂(EO₈)(EP₄)₂ sequence, each stage, except the D₁ and (EO₈)₂ stages, being conducted at 10% consistency in sealed polyester bags. The first stage was carried out at kappa factor 0.20 for 30 min at 45°C in a Quantum mixer. The (EO₈) stage was done at 70°C and 10% consistency in a horizontal shaft mixer rotating at 200 rpm, and lasted for 60 minutes. The oxygen pressure, initially at 60 psig, was decreased by 12 psig every five minutes during the first 30 minutes, and the alkali charge was either 1.6% (HW pulps) or 2.4% (SW pulps), giving an oxir pH of 11 or higher. The D₁ and D₂ stages were conducted for 180 minutes at 70°C, and the D₃ stage was at 70°C for 60 minutes, with a NaOH charge of 6.4%.

After the (EO₈) stage, each pulp was divided into three equal portions, which were then bleached in the D₁ stage, usually with 0.2, 0.6, and 1.8% CI₉. Each of the resulting D₂ pulps was further subdivided for bleaching with 0.1, 0.3, and 0.9% CI₉ in the D₃ stage.

Residual Lignin Isolation and NMR Analysis
Residual lignin was isolated from the pulps by employing a mild, acidic 1,4-dioxane hydrolysing procedure. In brief, lignin was extracted from the pulp (50 g oven-dry weight) with 90% 1,4-dioxane/0.1 N HCl (v/v) solution (4% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by acid precipitation (pH = 2.5). Purified lignin was freeze-dried, extracted with pentane and analyzed by ¹³C- and ²⁹P-NMR spectroscopy.

All NMR data were acquired with a Bruker DMX 400 MHz spectrometer. Lignin hydroxyl functional groups were quantitatively determined according to the standard literature method by ²⁹P-NMR spectroscopy. Approximately 25 mg dry lignin was dissolved in 1.61 ml (v/v) pyridine/chloroform-d containing cyclo-hexanol (6.0 mmol) and chromium acetylacetonate (0.6 mg) and then derivatized with 75 μl 2-chloro-4,4,4,5,5-pentamethyl-1,3,2-dioxaphospholane. Carbon- ¹³ NMR spectra were acquired under quantitative conditions, and using integration regions compiled by Roettig. Ag D₃ pulps were again isolated. Lignin was dissolved in 500 μl DMSO-d₆ and ¹³C-NMR spectra were acquired at 50°C, using a 90° pulse, inverse-gated decoupling, a 11-second pulse delay, and 16,000 scans.

Pulp Testing
Kappa number and ISO brightness were determined according to TAPPI Test Methods.
Hexenuronic acids were determined in unbeached pulp by the method of Vuurmond et al. Briefly, 50 g o.d. pulp was refluxed with 150 ml of 10 mM sodium formate solution at 100°C. 3.0% consistency for 5.0 hours. The pH of the reaction was 3.5. After the treatment the hydrolysate was analyzed by ultraviolet spectroscopy for the reaction product, 2-hydroxy acetic acid. The absorbance at 245 nm corresponds to the hexenuronic acid level.

RESULTS AND DISCUSSION
Unbleached Pulps
Table 1 shows the results obtained when the unbeached pulps were characterized. The LS pulps
had slightly higher brightness in the SW case and significantly higher brightness in the HW case.

D_2E(O) Bleaching
Table 2 compares the D_2E(O) response of pulps from low solids and conventional Kraft cooks. Liquor concentration profiling had no effect on delignification efficiency, as measured by Kappa number decrease per unit of active chlorine consumed. Similarly, there was no effect on the brightness gain in the (EI) stage for the softwood pulps. There was, however, a significant benefial effect of profiling on the brightness gain of the hardwood pulps.

D_2E(O)D_1 Bleaching
The pulps of Tables 2 and 3 were further bleached in a D_1 stage by applying three different levels of CIOT, usually 0.2, 0.6, and 1.5% (c.p.d. pulp basis). The end pH was close to 4.0.

Table 1. Properties of unbleached pulps.

<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>RaRicate</th>
<th>Kappa</th>
<th>Number</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>1</td>
<td>26.6</td>
<td>24.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.4</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>SW + BL</td>
<td>1</td>
<td>25.1</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>29.0</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>SW - LS</td>
<td>1</td>
<td>27.3</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30.6</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>HW + BL</td>
<td>1</td>
<td>15.5</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15.5</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>HW - LS</td>
<td>1</td>
<td>15.0</td>
<td>27.5</td>
<td></td>
</tr>
</tbody>
</table>

SW = softwood; HW = hardwood; "+ BL" denotes addition of black liquor prior to cook; "- LS" denotes low solids profiling.

Table 2. D_2E(O) bleaching of conventional and low solids cooks.

<table>
<thead>
<tr>
<th>Unbleached Pulp</th>
<th>D_2E(O) Stage</th>
<th>D_2E(O) Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>25.6</td>
<td>20.4</td>
</tr>
<tr>
<td>SW + BL</td>
<td>26.4</td>
<td>26.4</td>
</tr>
<tr>
<td>SW - LS</td>
<td>29.0</td>
<td>26.1</td>
</tr>
<tr>
<td>HW + BL</td>
<td>15.5</td>
<td>23.4</td>
</tr>
<tr>
<td>HW - LS</td>
<td>15.5</td>
<td>23.2</td>
</tr>
</tbody>
</table>

D_2E(O) D_1 stage bleaching of conventional and low solids cooks.

<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>Kappa</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>25.6</td>
<td>20.4</td>
</tr>
<tr>
<td>SW + BL</td>
<td>26.4</td>
<td>26.4</td>
</tr>
<tr>
<td>SW - LS</td>
<td>29.0</td>
<td>26.1</td>
</tr>
<tr>
<td>HW + BL</td>
<td>15.5</td>
<td>23.4</td>
</tr>
<tr>
<td>HW - LS</td>
<td>15.5</td>
<td>23.2</td>
</tr>
</tbody>
</table>

The data presented in Table 3 shows that the response of the low solids pulps to D_1 stage bleaching is superior to that of the controls. In the case of the softwood pulps, the difference took the form of a one-point increase in the brightness ceiling. There was no effect of addition of black liquor at the start of the cook. In the case of the hardwood pulps, there was a very large increase in brightness ceiling : 5.5 units, and the response factor of the low solids pulps was significantly better than that of the control.

\[ y = b_0 + b_1 \left(1 - \exp(-b_2 x)\right) \]
Each of the 9 pulp streams represented by the entries in 
Table 4 and 5 were alkali extracted and further 
bleached in a D1 stage, by applying three different 
levels of CI\textsubscript{2}: 0.1, 0.5, and 0.9% (d.b. pulp basis). In 
each case, nonlinear regression analysis of the 
resulting brightness response curve was used to 
determine the parameters in Equation 1. The values of 
these parameters were dependent on the brightness of 
the pulp before the D2 stage.

The response factor, \( b_2 \), for the D2 stage is plotted in 
Fig. 1 as a function of the brightness after the D1 stage. 
It is apparent that the value of \( b_2 \) varies nonlinearly as 
the D1 brightness is increase from 65 to 90, and may 
pass through a minimum within this range. It can also 
be seen that, at given D1 stage brightness, the pulps do 
not differ significantly with respect to \( b_2 \) value in the 
D2 stage. This is not true for the other important D2 
stage parameter, the maximum achievable brightness 
value, \( b_h \).

For hardwood pulps, the maximum achievable 
brightness gain of the low solids pulp exceeded that 
of the control pulp by a greater margin, as shown in Fig. 
4. The practical significance of the parameter variations 
shows in Figs. 1-4 is that bleaching chemical costs are 
strongly impacted by the pulping liquor concentration 
profile differences investigated. The model-based 
approach we have used in characterizing the bleaching 
response allows the effect of bleaching costs to be 
precisely determined. This is done by using the model 
to find, for each pulp, the smallest possible total CI\textsubscript{2} 
application for a given final brightness. The parameters in 
the D2 stage model are expressed in terms of the D1 stage brightness using the regression 
relationships shown in Figs. 1, 2, and 4. Then for any 
given CI\textsubscript{2} charge in D1, the brightness after the D2 
stage is calculated from the D1 stage model equation. 
The D2 stage model parameters are then calculated 
from this brightness and, finally, the D2 stage 
brightness is calculated from the D2 stage model. The 
resulting values are then searched to minimize the sum 
of the CI\textsubscript{2}charges in D1 and D2 for any given 
bleached pulp target brightness. Figures 5 and 6 Show 
the results of these calculations.

For softwood pulps, the brightness ceiling of the low solids pulp is lower than that of the control pulp by a statistically 
significant margin. The difference, though small, 
Corresponds to a significant difference in 
brightness ceiling, as shown in Fig. 3.

It is apparent from Figure 5 that, for the softwood 
pulps, the amount of CI\textsubscript{2} required to reach a given 
target brightness is appreciably lower for the low 
solids pulp than for the controls. This is especially true 
at high brightness levels, where the differences can be 
as high as 20-30%. It is also apparent that the low 
solids pulp can be bleached to higher brightnesses 
than the control pulps. These differences are the 
combined result of the low solids pulp having higher 
ubleached brightness, together with a correspondingly 
higher D1 stage brightness ceiling, and better brightness gains in the D2 stage.
Corelation of Bleachability with Chemical Differences

Differences in residual lignin structural features between low solids and control pulps were small or nonexistent, with the exception of uncondensed phenolic group content, which was lower in the low solids pulps than in the corresponding controls. For softwoods the guaiacol group content of the lignin, in \( \text{mmol/g} \), was 0.88 ± 0.05 for low solids pulp and 1.06 \( \pm 0.03 \) for the controls. For hardwood, the corresponding content of uncondensed guaiacol and syringol groups was 1.36 ± 0.08 for low solids pulp and 1.56 ± 0.05 for the controls. The absence of major structural differences in the lignins is consistent with the observation of no difference in ease of lignin removal in the early part of the bleach sequence. Bleachability in the latter part of the sequence may be controlled by unbleached residual lignin structural features that are not easily detected by the standard \( ^{13} \text{C} \) and \( ^{31} \text{P} \)-NMR methods. Generally, we observed a negative correlation between bleachability and isolated lignin free phenolic group contents. This correlation may reflect the role of phenolics as quinine precursors. Recent work suggests that lignin-quinone chromophores are produced in high concentration in the first chlorine dioxide stage and brightness values in later stages are negatively impacted by their presence. The literature also suggests that these structures may be stable to chlorine dioxide and modified in alkali to structures of low bleachability. Although difficult to detect, lignin structural features altered by modified pulping may have an important influence on brightness development.

In the case of the hardwood pulps there was one other significant chemical difference between the low solids and control pulps. The hexaacetone acid contents of the two hardwood control pulps, measured as 2-furoic acid in the pulp hydrolysates, were 10.0 and 10.9 \( \text{mmol/g} \), while the corresponding figures for duplicate low-solids cooks were 28.3 and 29.7. This indicates that the lignin content of the low solids pulps was lower, even though the kappa numbers were the same. This is consistent with the explanation offered above, since the lower lignin content represents a lower concentration of precursor for quinoid chromophores.

CONCLUSIONS

Compared to conventional control pulps, pulps produced under conditions of low and relatively constant alkali concentration and low dissolved organic solids concentration, here denoted low-solids pulps, have higher unbleached brightness and better bleachability. The bleachability improvement is manifested as a reduction in \( \text{ClO}_{2} \) requirement in the last three stages of the bleach sequence; the efficiency of lignin removal in the first two stages is unaffected.
The bleachability differences are very large in the case of oak pulps and smaller for southern pine pulps. The results may be interpreted in terms of reduced propensity of the low solids pulps to form quinonoid chromophores during bleaching. Thus, the low solids pulps have residual lignin that contains fewer free phenolic hydroxyl groups to serve as quinone precursors. In hardwood (oak) low solids pulps, the shortage of quinone precursors is even greater because these pulps have higher hexenuronic acid contents and, therefore, lower lignin contents at the same kappa number.

LITERATURE CITED


HIGH-YIELD PULPING AND BLEACHING STRATEGY FOR ASPEN KRAFT PULPS

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ABSTRACT

A study was conducted on aspen chips that would identify conditions of pulping, oxygen delignification and bleaching which were optimal for the overall production of aspen kraft pulp. Screened yields were determined for kraft pulps produced with a range of kappa numbers from 12 to 32. At a constant kappa of 16, the kraft screened yield was 57.1%. When this pulp was oxygen delignified to 8 kapps, a yield loss of 2.6% resulted. Kraft pulps cooked to 31.7 and 24.0 kappa, followed by oxygen delignification to 16 kapps also had 1.0 and 1.7% yield loss, respectively, relative to kraft pulp of 16 kapps. Use of anatroposine (AO) improved yield by 0.7%. Combined application of AO and oxygen also gave positive yields. Thus, the use of AO appears to have protected the pulp from yield loss during oxygen treatment. Kraft AO pulps were more easily bleached than kraft pulps and had higher heteroaromatic acid and syringyl lignin contents at constant kappa. The most easily bleached pulps were oxygen delignified and had the lowest levels of heteroaromatic acids. The highest brightness pulp was kraft O2 produced from highest kappa brownstock and had the lowest heteroaromatic acid content prior to oxygen delignification. Xylanase pretreatment raised the brightness of all pulps by up to 1-2% ISO. The use of AO and oxygen pretreated production of kraft pulps with increased yields over kraft and kraft O2. Since these pulps were made from high initial brownstock kappa, the potential to increase production also exists. These high yield pulps were also readily bleached when used in conjunction with oxygen delignification and enzymes. Structural analysis of isolated lignins provided a partial explanation of the bleachability of the pulps.

INTRODUCTION

The Pulp and Paper Industry has seen an increasing trend in the production of low kappa pulps through the early to mid 1990's. This trend has largely been driven by an attempt to reduce or eliminate chlorine chemicals. In the latter case, TCF bleaching sequences require the lowest possible kappa number of the pulp prior to the bleach plant if high brightness are to be achieved (1). A major concern with the production of low kappa pulps for TCF and ECF bleaching is an associated yield loss. Loss in yield creates obvious economic consequence for a mill (2,3) and is of particular concern to fibre-short mills in Northern United States and Western Canada. Oxygen delignification of kraft pulps is the most widespread method of producing low kappa pulps. In the case of hardwood pulps, oxygen-stage yields and fully-bleached yields can fall uncontrollably, if delignification during cooking or oxygen treatment is too extensive (4,5). The major reason for bleaching low kappa pulps is the reduction in chlorine chemical requirement and an associated reduction in formation of chlorinated organic compounds in effluents (6). In many instances however, mills cannot take advantage of extended delignification due to limitations in recovery furnace capacity. Similarly, with the constraints of fibre costs and availability, an economic balance has to be reached between yield loss from extended delignification and savings from reductions in bleaching chemicals. A mill may reduce chemical costs and cut chlorinated compound release but the cost in terms of yield loss can be too high. Earlier work on oxygen delignification of hardwoods has shown that it is possible to increase pulp yields and still take advantage of the potential cuts to bleach plant chemicals. Janssen and Fossom (4) recognized that, although oxygen-stage yields fall sharply beyond a certain delignification level, the treatment of high kappa pulps with oxygen can lead to increased yields. Similarly, Lindblad and Lindstrom identified that there is an optimal balance between cooking, oxygen delignification, and bleaching (5). From an environmental perspective, latest developments in ECF bleaching and effluent treatments have shown that it is possible to continue to take advantage of the potential for high brightness development with chlorine-containing chemicals and still significantly reduce the environmental impact of the effluents from mills (7). Even more impressive is the fact that new technologies being developed allow recycle of effluents from ECF
bleaching (8). Thus, a process that permits the high brightness benefits of ECF bleaching along with the reduction in chemical usage and an increase in pulp yield would be desirable. Ironically, pulps prepared by TCF methods (extended delignification with oxygen followed by non-chlorine bleaching) have been shown in some cases to produce effluents of greater toxicity than by ECF bleaching (9).

It has been shown that it is possible to increase pulp yield by selective application of oxygen on higher yield pulps, rather than accepting a loss in yield with overcooking. In 1953, it was demonstrated that this strategy can permit extended delignification while still increasing yield and reducing boiler loading (10). Recently, Partanen et al. discussed how high kappa pulpizing with oxygen delignification and digester additives plus the use of ECF bleaching will improve yields of softwoods and allow mills to achieve Cluster pulp requirements (11).

An opportunity exists to improve pulp yields by optimization of cooking and oxygen delignification. At the same time, a bleaching strategy could be identified that would minimize the cost of bleaching and still produce highest brightness pulps. The overall effect would be the production of high brightness pulp with higher yield and reduced bleaching costs and environmental impact. The result would be a combined strategy of cooking, oxygen delignification and bleaching that has the highest economic return for overall bleached pulp production.

**EXPERIMENTAL**

**Furnish.**

Aspen chips were obtained from a Northern mill in the United States. Chips were air dried and screened to remove overstock fractions. The 2-4, 4-6, and 6-8 mm fractions made up 31%, 59%, and 10%, respectively, of the accept. Moisture content of air-dried chips was determined using a Sirhartin MASO moisture analyzer at 105°C.

**Pulping.**

The accept chips were re-combined in the correct proportion and were cooked in a laboratory-scale digester (200 g chips or basis oven dried). Synthetic white liquor was prepared using sodium sulfite and a 10% solution of sodium hydroxide. Sulphidity was 32%, liquor/wood ratio was 3.4 L/kg and % Inactive Alkali (EA) and B-Factor were as specified in Tables 1 and 2. IMPART™ Plus Antrona Plus Dispersion was applied to cooks as specified in the table. At the end of each cooking cycle, the pulp was disintegrated with a Cowlin blade mixer for five minutes in the presence of a defoamer (Advantage 95, supplied by Hercules Canada Inc.). Disintegrated pulp was washed and dewatered in a Bock Centrifuge. Kappa sheets were prepared and analyzed according to TAPPI Method T236 cm-85. Pulp yields were determined from the total mass of wet pulp recovered and consistency. Pulps that were subsequently bleached were screened with a Valley Flat screener (0.36 mm) at least 1.25% consistency. Pulps that were oxygen delignified were not screened prior to oxygen treatment.

**Oxygen Delignification.**

Oxygen delignification was carried out in 200 g, o.d. batches with the use of a Quantum Mixer at 10% consistency, 60 p.s.i.g. of oxygen pressure (0.4 MPa) and 0.25% MgSO4 for 60 minutes with temperature variation from 75-90°C and % NaOH from 0.5-2.75. The reactor was preheated prior to each run, purged of air and instrumentally mixed at 400 rpm for a total of 60 minutes. Upon completion of each oxygen run, the pulp was collected and thickened to approximately 25% consistency by pressing. The pulp was then filtered and washed with 8 L of deionized water and thickened. Pulps were screened as above and screened yields were determined based on total mass recovered and consistency. Kappa number determinations were as described above and brightnesses were measured according to CUPA STD E.1 using standard 4 g sheets and a Zeiss Elabor brightness meter.

**Bleaching.**

**Enzyme Stage.** Ecopulp®-TX-200 was applied at a dose of 3 lb/g pulp at pH 7 and a temperature of 70°C for a retention of 60 minutes. Pulps were mixed using a Hobart mixer and immediately transferred into polyethylene bags and placed into a water bath. Control pulps were prepared in an identical manner but with water replacing the enzyme.

**Bleaching Stages.** Enzyme-bleached and control pulps were bleached using a DED sequence with the following conditions:

**D1 Stage:** Each pulp was divided into three 30 g, o.d. portions and chlorine dioxide was applied at kappa factors of 0.14, 0.18 and 0.20, respectively in sealed Mason jars. Intensified time, 30 minutes, consistency,
5.5%; temperature, 50°C. Sulphuric acid was added as required to maintain an exit pH of about 2.5.

Extraction Stage (E): A charge of 1.6% sodium hydroxide was applied to pulp at 10% consistency for 60 minutes at 70°C in polyethylene bags.

Dl Stage: 1.0% chlorine dioxide was applied at 70°C, 6% consistency for 240 minutes. Exit pH was maintained at pH 4 by addition of 0.35% NaOH based on dry pulp.

Blanched Yield Determination: These were conducted on selected control and enzyme-treated brownstocks as specified in Table 4. Pulps were treated under conditions that were predetermined (as above) to provide 89% ISO brightness. Pulps moved from stage to stage without removal of any pulp for testing until the end of the bleaching. Yields were determined from the change in mass from start to completion of bleaching.

Structural Analyses of Pulps

Residual Lignin Isolation Procedure

Residual lignin were isolated by mild acid hydrolysis as described by Gellcrsdf (17) with the following slight modifications. The pulps were acetone extracted and air dried then washed with distilled water and air dried. Residual lignin extraction was achieved by refluxing for 2 h at 4% consistency with 9:1 dioxane to water acidified to 0.1N with HCL. The solution was filtered and the filtrate was passed through celite. The solution was then neutralized (pH 7) and concentrated. After all the dioxane was removed, the solution was precipitated by acidifying to pH 2.5. The residual lignins were centrifuged, washed with distilled water three times and then freeze-dried. The average yield was 40% (based on kappa numbers).

Hexenuronic Acid Determination.

Pulp samples were washed until the filtrate pH was neutral and colourless. Pulp samples were then diluted to 3% consistency and, using a formic acid-sodium formate solution, buffered to pH 3.0, similar to the procedure described by Vouraen et al. (16). After refluxing for 6 hours, the pulp samples were washed, air dried and analyzed for kappa number. The drop in kappa number is attributed to the removal of hexenuronic acids.

3P-NMR Analysis of Residual Lignin

Residual lignin characterization was performed by 3P-NMR analysis described by Argyropoulos (19-20). 2-Chloro-4,5,5-trimethyl-1,3,2-diazaphospholene was used as the phosphitylation reagent in this quantitative analysis. Two stock solutions were prepared. The first was a solution of pyridine and deuterated chloroform in p.d, 1 (v/v) ratio, which was used as the solvent for the residual lignins. The second solution was chromium (III) acetylacetonate in cyclohexane (5.0 mg/mL). This was used as the relaxation reagent and the cyclohexane was used as the internal standard. The 3P-NMR samples were prepared by adding 400 μL of the solvent solution and 150 μL of the relaxation reagent solution to 25 mg of residual lignin. This solution was stirred while 45 μL of phosphitylation reagent was added and was allowed to sit for two minutes before being transferred into an NMR tube and tested. NMR analysis was performed on a Bruker 400 DMX with a 25 second delay and 200 scans. All chemical shifts are quoted relative to the signal from the reaction product of water with the phosphitylation reagent which gives a sharp signal at 132.2 ppm.

RESULTS AND DISCUSSION

1. Pulping and Oxygen De lignification

A series of hardwood (aspen) pulps were produced by conventional kraft cooking over a kappa number range of 12 to 32 and yields were measured (Table 1). For some of these pulps, oxygen de lignification was carried out (Table 2) and screened yields were also determined (Figure 1). Modification of the kappa number was done in most cases by adjusting H-Factor. A second series of pulps was prepared using arbraglucose in the pulping liquor. Rejets for pulps are expressed as the difference between screened and unscreened yields and are shown in Figure 2.

Samples of brownstock pulps were analyzed for content of hexenuronic acid and lignin was isolated from selected pulps and analyzed for lignin functional groups including: carboxylic acids; syringyl; guaiacyl and demethylated phenolics; 5-substituted phenolics; aliphatic hydroxyl groups; and condensed lignins. An attempt was made to correlate bleeding responses to differences in lignin structure.

The Effect of AQ on Yield at Constant Kappa

Conventional cook # 6 had a total yield of 57.1% at 15.5 kappa and reflected the high yields obtained with aspen pulps (12). The mean total yield from the AQ cooks 2.7 and 14 was 57.8% at a mean kappa of 15.4, showing the yield improvement derived from AQ. The same yield improvement was observed after screening (compare screened yields of cooks 6 and 7). Table 3

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summarized differences in yields at 16 kappa while the differences in screened yields are shown graphically over the range of kappa numbers in Figure 1. The yield gain with AQ pulping was about 0.7% at 16 kappa.

Hexenuronic acids were measured for kraft and Kraft-AQ pulps and are expressed as the percentage of the kappa number, which they constitute (Figure 3). The hexenuronic acid content of kraft and Kraft-AQ pulps rises faster than the decrease in kappa alone can account for, indicating that these groups are being generated as the kappa drops. Kraft-AQ pulps had a slightly higher content of hexenuronic acids which is likely due to the higher retention of hemicelluloses during cooking with anthraquinone.

The Effect of Oxygen on Yield at Constant Kappa
Surprisingly, the kraft-oxygen pulps from aspen had lower screened yields than comparable kraft pulps. For example, in Table 3, kraft O2 pulps after oxygen delignification to 16 kappa, had screened yields of about 56% compared to 57.1% yield for a conventional kraft cook in 15.5 kappa. I.e., at a constant kappa number of 16, the oxygen delignified pulp had 1.0-1.3% lower screened yield than the kraft cook. Figure 3 tells the story; oxygen delignification of kraft aspen pulp provides no better yield-kappa performance than conventional cooking, instead. yields were worse with oxygen. However, as pulp kappa numbers drop below 15, yields from conventional kraft pulps drop sharply whereas the oxygen delignified pulp yield declines gradually.

Markham (13), Parsead (10), Guillaumech (14), Pursharathra (11), McCulloh (15), Young et al. (16) and others have all indicated that oxygen delignification of softwoods is more selective than kraft cooking. Consequently, high kappa pulping followed by oxygen delignification is being proposed as a route to more efficient wood use. In contrast, this work indicates that, for aspen pulps, high kappa pulping followed by oxygen delignification does not offer the possibility of yield increases.

The Effect of AQ and Oxygen on Yield at Constant Kappa
When AQ and oxygen were used together, the yield results at constant kappa were the same as for Kraft-AQ cooking (compare AQ/oxygen bleached pulps with AQ pulps in Table 3). In other words, AQ appeared to counteract the adverse effect of oxygen delignification. This does not, however, provide any additional yield incentive for using oxygen as an AQ pulp.

Kraft O2 and Kraft AQ/O2 pulps had lower hexenuronic acid levels than the non-oxygen delignified cases (Figure 3). These pulps were prepared from brownstock pulps of higher initial kappa number and lower initial hexenuronic acid contents. Hexenuronic acids are considered unreactive in oxygen delignification (21). The data for oxygen pulps in Figure 3 can be explained by assuming that hexenuronic acids are neither created nor destroyed in high kappa pulps by oxygen delignification.

2. Bleaching
All of the pulps were bleached using a DDD sequence, with and without a pretreatment with electrolyte (urea), so that a comparison of the relative bleachabilities could be made. The results are shown in Figures 4 and 5. Following the bleaching studies, conditions were identified that permitted bleaching to 88% ISO brightness. Selected pulps were then rebleached using these conditions and pulp yields were determined.

Lignin functional group analyses were determined by 39 NMR. Carbonyllic acids, guaiaeryl and demethylated phenolic, 5-substituted phenolics and aliphatic hydroxyl contents were measured for the conventional kraft series (Kappa range 51.7 to 12.3) and the Kraft AQ series (Kappa range 24.0 to 15.7) as shown in Table 5, respectively. For these pulps, carbonylic acids, guaiacyl and demethylated phenolic and 5-substituted phenolics contents increased per gram of extracted lignin, as kappa number decreased.

Effect of Oxygen
The oxygen delignified aspen pulps were more easily bleached than kraft pulps; as expected, the chlorine dioxide consumption was decreased, but also the brightness ceiling was higher for the oxygen pulps by 1-2% ISO (compare Figures 4a and 5a). Kappa 16 oxygen bleached pulp made from 32 kappa brownstock reached a high brightness ceiling; higher than that was achieved when starting with 24 kappa brownstock. The high per-O2 kappa pulp also had the lowest hexenuronic acid content prior to bleaching. A comparison of phenolic lignin content of kraft pulp (Kappa 15.5) in Table 5 with kraft O2 pulp of kappa 15.8 revealed a higher concentration of phenolic groups, particularly syringyl lignin, per gram of isolated lignin in the kraft pulp. It is known that, under the practical conditions of bleaching, chlorine dioxide reacts mainly with phenolic lignin (22). Thus, since the kraft lignin had a higher concentration of phenolic lignin per gram of isolated lignin, it could be expected that the kraft pulp would be more easily bleached, but this was not the case. Since the kraft O2 pulp was more easily bleached than its Kraft analogue at 16 kappa, suggests the improvement in
The bleaching of oxygen pulps may be related to the lower level of hexuronic acid. The most easily bleached oxygen pulps also had the lowest hexuronic acid content.

Effect of AQ

The effect of AQ was different for oxygen and non-oxygen pulps. For pulps bleached without oxygen, the AQ pulps were most easily bleached (Figure 4a). The Kraft AQ pulps had a consistently higher content of hexuronic acids compared to Kraft pulps of similar kappa (Figure 3). A comparison of Kraft and Kraft AQ pulps at either kappa 15.5 or kappa 24 reveals similar levels of guaiacyl and demethylsulfonyl protons; however, the AQ pulp had a higher level of syringyl and coniferyl lignin (Table 5) which are expected to be more reactive to chlorine dioxide.

For the ODED sequence, the oxygen pulp made without AQ seemed to bleach slightly easier. Only one Kraft AQ/O2 pulp was examined for hexuronic acid content and was comparable to two Kraft O2 pulps of similar post-O2 kappa. The Kraft AQ/O2 pulp had a starting brownstock kappa of 24.0 and bleached similarly to the Kraft O2 pulp of brownstock kappa 24.4 (Figure 5a). These pulps also had similar hexuronic acid contents. However, as with the above findings, the Kraft AQ/O2 pulp did not bleach as easily as the Kraft O2 pulp of higher kappa number (35.7) and also had a higher hexuronic acid content.

Effect of Xylanase

Prior bleaching with xylanase enzymes improved the bleachability of all pulps by up to 2% ISO brightness units (Figure 4b, Kraft pulps and Figures 5b, oxygen-treated pulps). The brightness celling of the oxygen-treated pulps was raised with enzymes from 89% to 90% ISO and the Kraft pulps were increased in brightness from 86% to 88% ISO. The use of enzymes on Kraft-AQ pulp resulted in brightness ceilings comparable to those of Kraft-O2 of similar brownstock kappa number.

At constant post oxygen kappa number, highest brightness was reached for pulps of highest pre-oxygen kappa number.

Bleached and Overall Yields

Following the bleaching evaluation, conditions were identified that permit bleaching of each pulp to 88% ISO brightness. Selected pulps of kappa number 16 were bleached using these conditions, with and without enzyme additions, and bleached yields were measured (see Table 4). The bleached yield of the 16 kappa pulps was approximately 97%, regardless of whether AQ or oxygen were used, or not. The use of xylanase enzyme produced extra shrinkage for the Kraft control and Kraft oxygen pulps; xylanase did not change the shrinkage on the Kraft AQ and Kraft O2 pulp at 8 kappa. That a difference in bleached yields was observed for enzymes on oxygen pulps prepared using different methods, suggests enzyme effect is complete and potential yield loss or gain should be examined for each specific pulp.

The lowest overall pulp yields were produced when using oxygen delignification (Table 6). Conversely, highest yields were obtained when anthraquinone was added to the cook and also when anthraquinone was used along with oxygen delignification. AQ appeared to counteract the negative effect of oxygen on yield.

CONCLUSIONS:

1. Aspen chips cooked using conventional Kraft methods to 16 kappa number resulted in a screened yield of 37.1% and is consistent with previous literature (32,33). Pulps of the same final kappa number produced using AQ were obtained with 0.7% higher yield.

2. Pulps of 16 kappa number prepared from high kappa cooks (24 or 32 kappa number) followed by oxygen delignification to 16 kappa number were obtained with an average screened yield of 55.9%. This is a 1.2% yield loss in comparison to the conventional Kraft cook to 1.9% loss compared to the Kraft-AQ cook.

3. Kraft AQ pulps had higher contents of hexuronic acids than Kraft pulps at all comparable kappa numbers. This is likely due to the increased retention of hemicelluloses associated with AQ use.

4. Pulps cooked with anthraquinone to kappa numbers of 20 or 24, followed by oxygen delignification to 16 were obtained in similar yield as Kraft-AQ pulp, also at 16 kappa number. The use of AQ appears to have protected the pulp from yield loss during the oxygen treatment.

5. Pulps cooked by conventional Kraft means to 16 kappa number followed by oxygen delignification to 7.9 was obtained with a yield of 54-4% which is 2.6% lower than yield of pulp prepared to 16 kappa by conventional Kraft methods.
6. Pulps prepared using oxygen delignification or enzyme pretreatment achieved higher brightnesses. The benefit of either technology was nearly comparable. When enzymatic was applied on oxygen delignified pulps, further increases in brightness were obtained. The highest brightness (89.8% ISO) was obtained using enzymes and oxygen.

7. Pulp cooked to 15.5 kappa number followed by oxygen delignification to 7.0 was bleached to 88% ISO brightness with 1.4% total applied chlorine dioxide. Kraft-O2 pulp of 16 kappa number was bleached to 80% ISO using 1.8% chlorine dioxide or 1.35% chlorine dioxide with enzymes.

8. Kraft AQ pulps were more easily bleached than kraft pulps at similar kappa numbers. The kraft AQ pulps also had higher hexenuronic acid contents and slightly higher xylan oligosaccharide levels.

9. Kraft O2 pulps were the most easily bleached and had the lowest levels of hexenuronic acids.

10. Pulps of 16 kappa number were more easily bleached when prepared by cooking to high kappa number and applying greater delignification with oxygen than by cooking extensively and applying less oxygen delignification. The highest brightness pulp produced was made using oxygen delignification on the highest kappa brownstock pulp, this pulp had the lowest hexenuronic acid content prior to bleaching of all the Kraft O2 pulps.

11. Enzyme pretreatment raised the brightness of all of the pulps. The highest brightnesses obtained were on the two pulps cooked to highest kappa number (31.7 and 33.7 - AQ) followed by oxygen delignification to 16.2 and 30.2, respectively.

Overall yields were determined for various pulps produced with and without AQ and oxygen delignification. Relative bleachabilities of these pulps were also determined. For more efficient production at a mill, this work provides data to help select the optimum combination of pulping and bleaching methods.

REFERENCES


15. Caslden, J., keynote Speaker of the International Recoveries Conference Toronto (Badaliment), (April 1997).


### Table 1

Pulping Results for Kraft and Kraft-AQ Aspen Furnish

<table>
<thead>
<tr>
<th>Cook #</th>
<th>% A.Q</th>
<th>% EA</th>
<th>H-Factor</th>
<th>Kappa #</th>
<th>% Yield</th>
<th>% Screened Yield</th>
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### Table 2

Oxygen Delignification Results from Aspen Furnish

<table>
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<th>Cook #</th>
<th>% A.Q</th>
<th>H-Factor</th>
<th>% Yield</th>
<th>Kappa #</th>
<th>% Screened Yield</th>
<th>% NaOH</th>
<th>Temp, °C</th>
<th>Kappa #</th>
<th>% Yield</th>
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### Table 3
**Brownstock Screened Pulp Yields at Constant Kappa**

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<tr>
<th>Pulp</th>
<th>%AQ</th>
<th>Brownstock Kappa #</th>
<th>O₂-Stage Kappa #</th>
<th>Screened Yield</th>
<th>% Yield</th>
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<td>Kraft</td>
<td>0</td>
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<td>Kraft O₂</td>
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<td>24</td>
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<td>56.1</td>
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<td>Kraft O₄</td>
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<td>Kraft AQ*</td>
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<td>Kraft AQ/₀₂</td>
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<td>Kraft AQ/₀₃</td>
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* Average of cooks 2, 7 & 14

### Table 4
**Bleaching Yields**

<table>
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<th>Pulp</th>
<th>Brownstock Kappa Number</th>
<th>O₂-Stage Kappa Number</th>
<th>Yield (%)</th>
<th>Brightness (% ISO)</th>
<th>Yield (%)</th>
<th>Weightness (% ISO)</th>
<th>% Yield</th>
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<td>Kraft</td>
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<tr>
<td>Kraft O₄</td>
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- Bold indicates statistically significant results.
## Table 5

Functional Group Content of Lignin Extracted from Brownstock Pulps (Concentrations expressed as mmol functional group per gram lignin)

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Brownstock Kappa</th>
<th>Carbonylic Acid</th>
<th>Carboxylic Benzenesulfonated Phenolics</th>
<th>S-Substituted Phenolics</th>
<th>Aliphatic Hydroxyl</th>
<th>Syringyl Phenolics</th>
<th>Coniferyl Phenolics</th>
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## Table 6

Overall Yields of Pulps after Pulping and Bleaching

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<tr>
<th>Cook</th>
<th>Brownstock Kappa #</th>
<th>O2-Stage Kappa #</th>
<th>Pulping Yield (%)</th>
<th>Bleaching Yield (+ enzymes) (%)</th>
<th>Bleaching Yield (- enzymes) (%)</th>
<th>Net Yield (no enzyme) (%)</th>
<th>Net Yield with enzyme (%)</th>
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Figure 1: Effects of Pulping Variables on Sulfate Pulp Yields. In the case of pulps prepared using oxygen delignification, the original bleached stock kappa numbers from which the pulps were prepared are indicated on the figure.

Figure 2: - Hemicellulose Acid Contents of Kraft and Kraft-AQ Pulps.

Figure 3: - AEPs Produced from Kraft and Kraft-AQ Pulps.

Figure 4: Brightness Results for Conventional Kraft Control Pulps (4a) and Xylanase-Treated Pulps (4b). Final brightnesses are shown for pulps bleached using a DED sequence. Kappa numbers of the pulps that were bleached are indicated.

Figure 5: Brightness Results for Oxygen Delignified Control Pulps (5a) and Xylanase-Treated Pulps (5b). Final brightnesses are shown for pulps bleached using a DED sequence. Kappa numbers of the pulps that were bleached are indicated and kappa numbers of brownstock pulp, prior to oxygen treatments, are shown in parentheses.

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CHLORINE DIOXIDE BLEACHABILITY OF PINE KRAFT PULPS MADE WITH
CONTROLLED LIQUOR CONCENTRATION PROFILES

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ABSTRACT
In an effort to assign a cause for the superior bleachability of pulps made by modified pulping
processes, we have conducted systematic bleaching studies of southern pine pulps prepared with two
types of controlled liquor concentration profiles. In one type, the alkali concentration, after an initial decrease, was
maintained at a constant value. In the second type, the same kind of alkali profile was augmented by
continuous liquor replacement to limit the concentration of dissolved lignin and other reaction
products. Neither type of profiling had any effect on the bleachability of the resulting pulps in the D(E)O35D,E)D,
bleaching sequence. Structural analyses of residual lignins showed that alkali profi led cooks gave residual
lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as
lower contents of aliphatic hydroxyl groups. These differences may contribute to the lability of the pulps
from the profi led cooks to exhibit better whiteness than those from conventional cooks.

INTRODUCTION
The chlorine dioxide bleachability of softwood pulps
made by modifi ed continuous kraft pulping processes
is known to be superior to that of conventional kraft pulps
having the same kappa number (1,2). Since, in modifi ed
kraft cooking, the time profiles of the concentrations of
al l pulp lignin components are different from the
corresponding profi les in conventional cooks, it is not
yet possible to associate the improved bleachability with
particular lignin component concentrations.
Consequently, we have conducted laboratory pulping
experiments in which the alkali and lignin concentration
prof i les were altered in controlled ways, and have
systematically studied the bleaching response of the
resulting pulps. We have also isolated residual lignins
from some of the pulps and have analyzed them by
nuclear magnetic resonance to correlate lignin structural
features with pulping conditions and bleaching response.

EXPERIMENTAL
Pulp
All pulping was carried out at Auburn University in an
MK Systems 6-line laboratory digester, modifi ed to
accommodate ultraviolet and conductivity sensors, and
equipped for continuously injecting and/or removing
liquor during the cook. All cooks were done according to
the same temperature schedule, which included a 40-minute
rise from ambient temperature to a maximum
cooking temperature of 170°C.

Two types of profi led cooks were conducted. Both were
started by charging all of the sulfide required to give a
sulfide of 30% based on the total alkali added in cooks of
"Type I," together with a fraction of the alkali corresponding
to the desired total alkali charge level. In "Type I" cooks, the alkali concentration was allowed to
fall from its initial value to some predetermined level, at
which point alkali was added at a rate equal to the rate at
which it was consumed, to maintain a constant
concentration. The rate of addition was controlled by
continuous, on-line measurement of EA concentration.
Duplicate cooks of this type were done to reach a kappa
number target of 17 at each of two total eff ective alkali
(EEA) charge levels, 24% and 28% (as NaO0, based on
o.d. wood). Although these charge levels are somewhat
higher than those found industrially, they corresponded to
alkali concentrations typically found in commercial
digesters because of the somewhat higher than normal
lignin-to-wood ratio (5.5) used in our experiments. This
was necessary because at any given time, a significant
fraction of the pulp liquor was in the external
circulation loop used for indirect heating and cooling of
liquor component concentrations. During the constant
alkali concentration period, the EA concentration was
maintained at 14 g/L in the 24% EEA cooks and 18 g/L in
the 28% EEA cooks. Figure 1 shows the EA and
dissolved lignin (DL) profiles in a typical cook of this
type.

In the second type of profi led cook, both the EA and DL
concentration prof i les were controlled. When the EA
concentration had fallen to the desired value, alkali
addition was begun to maintain that value, and was
continued until the DL concentration had risen to the
value at which it was to be controlled. At this point a
black liquor bleed stream was initiated to control the DL
dissolution of a single line of the same alkali was
continuous lysis was initiated to maintain the EA level constant.
Figure 2 shows the EA and dissolved lignin (DL)
profiles in a typical cook of this type.

All pulps were prepared at Auburn University, washed
and shipped to the Institute of Paper Science and
Technology, where they were screened, further
caracterized and bleached.
Residual Lignin Isolation and NMR Analysis

The isolation of lignin from the Kraft pulp was accomplished employing standard literature methods (15). In brief, air-dried pulp (50 g oven-dry weight) was added to an aqueous 0.1 M HCl (90 ml 1 N HCl), 100 ml dioxane (300 ml freshly distilled solvent), and this mixture was then refluxed for 2 hr, under a argon atmosphere. The mixture was then filtered and, the filtrate was filtered through celite. The solution was neutralized with sodium bicarbonate and concentrated under reduced pressure. After the filtrate was vacuum distilled to less than 10% of the original volume, water was added (3 x 200 ml) and the mixture was reconcentrated under reduced pressure. The aqueous solution was then acidified to pH 2.5 with an aqueous (N HCl) solution. The resulting precipitate was collected, washed several times with distilled water, and freeze-dried.

NMR data were acquired with a DMX 400 MHz Bruker spectrometer. Quantitative $^1$H-NMR experiments were performed following standard literature methods (4).

Pulp Testing

Kappa number, viscosity and ISO brightnesses were determined according to TAPPI Test Methods.

RESULTS AND DISCUSSION

Unbleached Pulps

Table 1 shows the results obtained when the unbleached pulps were characterized. Alkali profiling resulted in significant viscosity improvements, and solids profiling gave a slight increase in brightness. Decreasing the unbleached kappa number significantly increased brightness.

Dy(O)/Bleaching

Table 2 compares the dyed (DyO) response of pulps from alkali profiled and conventional-kraft cooks at the two different CA concentrations levels. It is apparent that, with the possible exception of a slight improvement in deinking efficiency, profiling had little effect on either the kappa-number reduction or the brightness increase in the first two stages of the bleaching sequence.

Table 3 compares pulp from conventional and solids profiling (Type III cooks) with respect to their DyO bleaching results. Again, little difference was observed between the two types of cooks in this respect.

Dy/O/Dy, Bleaching

The pulps of Tables 2 and 3 were further bleached in a D$_2$ stage, by applying three different levels of CIEO: 0.8, 1.2 and 1.6% (odi pulp basis). The end pH was 4.0.

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with a standard deviation of 0.6, and the residual ClO₂ ranged from 0.0% up to 0.36%, with the exception of two bleaches (out of a total of 36) in which only a trace of residual was found.

Table 1. Properties of unbleached pulps.

<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>Rep. Kappa</th>
<th>Visc.</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C</td>
<td>1</td>
<td>16.3</td>
<td>16.9</td>
</tr>
<tr>
<td>2</td>
<td>16.2</td>
<td>16.7</td>
<td>32.1</td>
</tr>
<tr>
<td>24AP</td>
<td>1</td>
<td>17.3</td>
<td>22.9</td>
</tr>
<tr>
<td>2</td>
<td>17.0</td>
<td>23.9</td>
<td>28.6</td>
</tr>
<tr>
<td>28C</td>
<td>1</td>
<td>16.3</td>
<td>15.3</td>
</tr>
<tr>
<td>2</td>
<td>16.3</td>
<td>13.6</td>
<td>31.1</td>
</tr>
<tr>
<td>28AP</td>
<td>1</td>
<td>17.8</td>
<td>18.2</td>
</tr>
<tr>
<td>2</td>
<td>17.3</td>
<td>16.7</td>
<td>28.4</td>
</tr>
<tr>
<td>20C</td>
<td>1</td>
<td>31.9</td>
<td>32.5</td>
</tr>
<tr>
<td>2</td>
<td>31.2</td>
<td>31.1</td>
<td>25.1</td>
</tr>
<tr>
<td>20AP</td>
<td>1</td>
<td>34.1</td>
<td>39.5</td>
</tr>
<tr>
<td>2</td>
<td>32.8</td>
<td>40.2</td>
<td>25.2</td>
</tr>
<tr>
<td>20SP</td>
<td>1</td>
<td>33.6</td>
<td>46.0</td>
</tr>
<tr>
<td>2</td>
<td>30.5</td>
<td>35.5</td>
<td>27.5</td>
</tr>
</tbody>
</table>

*First two digits indicate EA chart; Letter codes as follows: C = conventional control; AP = alkali profiled; SP = solids (dissolved) (unlim) profiled.*

Table 2. D(EO) of bleaching of conventional and alkali profiled pulps.

<table>
<thead>
<tr>
<th>Unbleached Pulp</th>
<th>D(EO)</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA Type</td>
<td>Kappa</td>
<td>Brightness</td>
</tr>
<tr>
<td>24</td>
<td>C</td>
<td>16.3</td>
</tr>
<tr>
<td>24AP</td>
<td>17.3</td>
<td>29.2</td>
</tr>
<tr>
<td>25C</td>
<td>16.3</td>
<td>28.4</td>
</tr>
<tr>
<td>28AP</td>
<td>17.8</td>
<td>32.5</td>
</tr>
<tr>
<td>20C</td>
<td>17.3</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Table 3. D(EO) of bleaching of conventional and solids profiled cookys.

<table>
<thead>
<tr>
<th>Unbleached Pulp</th>
<th>D(EO)</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA Type</td>
<td>Kappa</td>
<td>Brightness</td>
</tr>
<tr>
<td>24</td>
<td>C</td>
<td>31.9</td>
</tr>
<tr>
<td>24AP</td>
<td>39.6</td>
<td>26.1</td>
</tr>
<tr>
<td>20SP</td>
<td>30.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>

For all pulps, plots of brightness vs. ClO₂ consumed assumed the same form and could be described by the equation (2):

\[ y = b_0 + b_1 \left( 1 - \exp(-b_2 x) \right) \]  

(Equation 1) in which \( y \) is the brightness after the stage and \( x \) is the amount of ClO₂ consumed, as % of o.d. pulp. The equation describes a brightness that rises to the amount of ClO₂ consumed is increased, rapidly at first and at an increasingly slower rate as the brightness asymptotically approaches an upper limit, or “brightness ceiling.”

Fitting this equation to data obtained by bleaching a particular pulp sample provides values of the three parameters, \( b_0, b_1, b_2 \), which collectively describe the brightness of the sample. Thus, \( b_0 \) represents the brightness when no ClO₂ has been consumed, or the brightness of the pulp before bleaching; \( b_2 \) represents the maximum possible brightness gain; and \( b_1 \) indicates how rapidly the brightness ceiling is approached as the amount of ClO₂ consumed is increased, and may therefore be referred to as the response factor.

Differentiation of the equation shows that the slope at \( x = 0 \) is \( b_2 \), from which it is apparent that \( b_2 \) is the slope normalized by the maximum possible gain. For given values of \( b_0 \) and \( b_1 \), pulps having higher values of \( b_2 \) require less ClO₂ to reach any given brightness.

Table 4 gives the experimentally determined values of these parameters for D₁ stage bleaching of conventional and alkali profiled pulps at two different alkali levels.

Table 5. D₁ stage bleaching parameters for pulps from conventional and alkali profiled cooks.

It may be concluded from these data there were no significant differences in either brightness ceiling or response factor in the D₁ stage attributable to alkali profiling.

The corresponding comparison of conventional and solids profiled (Type III) cooks is shown in Table 5. A slight increase in D₁ response factor, but no change in D₁ brightness ceiling, can be attributed to solids profiling.

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Table 5: D3 stage bleachability parameters for pulps from conventional and solids profiled cooks.

<table>
<thead>
<tr>
<th>Unbleached Pulp</th>
<th>D3 Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brightness Ceiling</td>
</tr>
<tr>
<td></td>
<td>Brown</td>
</tr>
<tr>
<td></td>
<td>Value</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 3: Final brightness ceiling for pulps from conventional (24C1 and 24C3) and Type 1 alkali profiled (24AP1 and 24AP2) cooks with 24% EA.

Figure 4: Final brightness ceiling for pulps from conventional (28C1 and 28C2) and Type 1 alkali profiled (28AP1 and 28AP2) cooks with 28% EA.

Residual Lignin Structure

Table 6 contains the results of analyses of residual lignins isolated from pulps prepared by conventional and profiled cooks with 24% EA. The data suggest that the alkali profiled cooks gave residual lignins having slightly lower contents of phenolic groups, both uncondensed and condensed, as well as lower contents of aliphatic hydroxyl groups. The lower difference is consistent with an earlier observation that phenolic content alone cannot be used to predict bleachability (5).

The lower content of aliphatic hydroxyl groups may suggest that elimination of side-chain carbons as formaldehyde occurred to a greater extent in the profiled cooks. This, in turn, suggests a greater degree of accompanying rooth hair formation, which might be
CONCLUSIONS

Controlling alkali profiles during Kraft cooking of southern pine under the conditions used in this study had no significant effect on the bleachability of the resulting pulps at an unbleached kappa number of 16-18. The conditions prevailing during the profiled coooks were as follows: 24-28% EA, 5.5:1 liquor-to-wood ratio, temperature maintained from ambient to a maximum temperature of 170 °C during the period from t=0 to t=40 min., 30% sulfidity, all sulfite added at beginning of cook, initial EA concentration 19% g/l, falling linearly to 14% g/l, from t=0 to t=30 min., then falling linearly to 15% g/l at t=60 min., at which point the cook was terminated. In the same coooks, the concentration of dissolved lignin increased from 0 at t=0 to 44 g/l at t=60 min.

A lower content of aliphatic hydroxyl groups in pulps from profiled coooks may suggest a greater degree of endothermic formation which, together with a lower phenolic content, may contribute to the failure of the pulps from profiled cooks to exhibit better bleachability than those from conventional cooks.

Controlling both alkali and dissolved solids profiles under the conditions used in this study had no significant effect on the bleachability of the resulting pulps at an unbleached kappa number of 55-74. The conditions prevailing during the profiled cooks were as follows: 20% EA, 5.5:1 liquor-to-wood ratio, temperature maintained from ambient to a maximum temperature of 170 °C from t=0 to t=40 min., 50% sulfidity, all sulfite added at beginning of cook, initial EA concentration 28 g/l, falling linearly to 14 g/l from t=0 to t=30 min., and maintained at 14 g/l from t=30 to t=155 min., at which point the cook was terminated. In the same cook, the concentration of dissolved lignin increased from 0 at the beginning of the cook to 25 g/l at t=60 min, after which it fell approximately linearly to 20 g/l at t=55 min.

The beneficial effect of modified cooking on bleachability must be attributed to effects not simulated in our profiling experiments to date.

ACKNOWLEDGMENTS

Financial assistance for this research by the United States Department of Energy, the Member Companies of the Aspenh University Pulp and Paper Industry Advisory Committee, and the Member Companies of the Institute of Paper Science and Technology is gratefully acknowledged. We thank Miss Michelle Alger for assistance with the bleaching experiments.

REFERENCES

Pilot Study of Impulse Drying Industrial Sludge

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Institute of Paper Science and Technology, 500 10th Street N.W., Atlanta, Georgia 30318

In impulse drying, a moving sheet of pressed sludge contacts a hot roll under pressure, thereby converting water to the sludge—roll interface to steam. The resulting pressure expresses a part of the water from the sludge in liquid form. Belt-pressed primary sludge from two paper mills was impulse-dried on a pilot scale. In one case, solids increased from 33 to 96%, in the other, an increase from 32 to 46% was realized. Roll sticking or blinding of the belt did not occur at roll temperatures exceeding 300 °C, whereas pressing at ambient temperature extruded the sludge into the belt to the point where the sludge could not be processed further. Energy costs are projected at about $60 KWh/ton of dry solids. The technology provides an inexpensive energy-efficient means of increasing drying solids.

Introduction

Impulse drying was initially developed for dewatering a wet web of paper (1, 2). A hot roll contacts the web, flashing the moisture at the roll—web interface to steam. The resulting pressure then forces out some of the water in the web in liquid form, thereby conserving the heat of evaporation. The application is quite complex for paper, since heat transfer to the web must be tightly controlled in order to prevent sheet delamination (3, 4). These difficulties are absent for sludge, where properties of the dewatered product are relatively unimportant. Laboratory-scale work has shown that impulse drying belt-pressed industrial, municipal, and a mixture of municipal and industrial sludges removes up to an additional 20 percentage points of water (5–7), most of it as liquid. Here, a hot plate briefly imparts a layer of sludge retting on a blower, and the weight gained by the blower is taken as an assessment of the water lost from the sludge in liquid form.

The laboratory measurements represent a batch process, and extension of the impulse concept to a continuous operation must address several additional uncertainties. For example, it is well known that there is a practical limit to the solids gain achievable by retting alone (8, 9). Also, belts or rolls are used to draw the sludge, frequently blinding under pressure (10). Potential sticking of the sludge to the hot surface is yet another issue. In this paper, we demonstrate a pilot application of impulse dewatering of a primary paper mill sludge, conveyed by a metal belt through a heated up.

Experimental Section

Primary sludge was obtained from two paper mills: Riverwood International's Macon, GA, mill, and the Hawkinsville, GA, facility of Hollingsworth and Vose (H&V). Riverwood makes coated board, and the sludge consisted of fiber and

<table>
<thead>
<tr>
<th>Sludge</th>
<th>Riverwood</th>
<th>H&amp;V</th>
<th>percentage solids</th>
<th>32 ± 2</th>
<th>33 ± 1</th>
<th>44.6 ± 0.6</th>
<th>4.2 ± 0.1</th>
<th>15.7 ± 0.2</th>
<th>2.69 ± 0.02</th>
</tr>
</thead>
</table>

**TABLE 1. Properties of the Sludges Used**

![FIGURE 1: Side view schematic diagram of the pilot-scale sludge impulse dewatering system.](image)

Inorganic filter press, etc. clay. H&V is a small specialty mill whose products include filter paper. Sludge was collected on intact sheets as it emerged from the belt press, placed on 1 × 4-foot melamine-coated boards, and wrapped in plastic to prevent moisture loss. The sheets were cut separately to prepare compaction, and were used within 48 h of collection. The properties of the sludges are provided in Table 1. The Riverwood sludge had a higher ash content than did the H&V material on account of its higher inorganic fiber content.

Pilot work was done on the custom-built unit illustrated in Figure 1. The heated upper roll measures 2 ft in diameter and 2 ft in width, and the roll consists of a circular drum (which is the roll surface) and 2 bush/shaft units. The upper roll shafts ride on oil-filled bearings that are fixed to the frame of the machine. The oil recirculates through the bearings back to a reservoir, where it is circulated through a heat exchanging water jacket. This system avoids high temperatures at the bearings due to heat conduction through the roll shaft. Power is generated from a 75 hp DC shunt wound electric motor, and is transferred to both rolls via a drivetrain, which transfers the torque to the rolls through a magnetic particle clutch for the lower roll, and a pneumatic clutch for the upper roll.

The upper roll is heated by a 100 kW induction heater located directly above the upper roll. The rectangular heater coils are coated with a high-temperature epoxy which prevents acting from the coils to the piece being heated. The coils curve to the shape of the roll and are positioned approximately 3/16 to 1/4 in. from the roll surface. The output of the control unit is regulated by a Barber–Colman temperature controller which has continued feedback from a single-point pyrometer focused on the substrate of the upper roll as it exits the heater unit. Although a 100 kW induction heater was used to heat the top roll, only 15% of its output was sufficient for maintaining steady temperatures of up to 300 °C. The surface temperature of the hot roll was measured using a AGEMA 900/WTWE Thermovision system, which combines a thermocouple/irradiated infrared scanner and a high-speed systems computer. The calibration function of the system compensator, which

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FIGURE 3. Schematic diagram of the Mits electrohydraulic press.

The test was originally designed to operate at speeds over 2400 (ft/min) for densification purposes. A 1000 psi gear reduction and adjustment of the variable speed motor allowed operation in the 5-25 rpm range. The individual rolls were driven from four face-centered crank systems for independent control. By design, variation in roll surface speed due to thermal expansion was compensated for by slipage in the upper roll clutch (located at 50 ft-min) as the nip was closed. Clutch slipage was detrimental for our application since it limited the maximum allowable nip pressures, and the clutch was removed. The upper roll was dished directly from the lower roll, which was linked to a hydraulic clutch. However, with these modifications, the Finesseur sludge could be processed at a peak pressure of 300 psi, beyond which the nip was insufficient to drive the web through the nip.

The peak nip pressure in the pin sludge dryer was determined by a Yokogawa 5501 pinch roll sensor. The load was provided on hydraulic cylinders connected to the bottom of the lower swing sets. The fabric usually used for paper applications was replaced by a belt supplied by Eilton (60 x 3/8 x 3/8, 500 psi air flow). The belt was 26 ft in length and had a width of 18 in. It was tensioned at 200 psi using a pinch roll to reduce nip pressure at the pinch on the other side of the tensioning roll. Sludge sheets were placed on a wooden platform at the height of the belt and were gradually pulled into the moving belt. The nip was closed just after the leading edge of the sheet entered the nip. An early concern was that the sheet would not have the strength to pass through the nip at high pressure, but would bunch up at the front end of the roll. This is not an issue with paper, since the nip area is a minimum of about 100 psi, but the belt has an optimum nip pressure of 150-200 psi. On the other hand, the sludge sheets were much thicker, and was cut at much lower nip pressure due to the absence of a web structure. However, the sheet was strong enough to cleanly pass through the nip under the conditions used.

Laboratory measurements were conducted on a Matts and Testing Systems electrohydraulic press. Illustrated in Figure 2, this device consists of a heated upper plate attached to the load cell of the press, a hydraulic supply system, a load cell, and a lower ground cold plate. With a maximum load capacity of 25,000 lb, a force response time of 0.15 s, and a 98-psi (1.4-mbar) test pressure, it is well suited for the present study. The contact pressure is maintained between 10 and 15 psi, while the pressure is adjusted to provide pressure profiles of a commercial sludge dryer. Transmec Corporation's \n
Dyke.png

Results and Discussion

From the pilot trial for the Finesseur sludge are illustrated in Figure 3. A control measurement was of room temperature (28°C) to isolate the effect of pressure and steam temperature on the process. However, the belt was folded slightly and severe sludge extrusion was observed, very difficult to clean. Hence, essentially no solid gain would be realized when the belt returned to contact fresh sludge. It is well known that pressure, alone, leads to minimal additional densification. For example, Figure 5 shows that no throughput pressure rises to suggest that the belt is independent of the pressure applied for compressible solids. The extrusion problem disappeared at 155°C, although now, a new amount of material to the dryer. Depressurizing the system at more than 20°C, where both cold glad and extrusion were consistent. Figure 2 shows that the sludge dryer's material temperature, increasing pressure and temperature. For the best case, an increase of 17°C to 14°C of water was extruded, giving a final solids of 58% at a peak pressure of about 143 psi (10 bar = 1.4 mbar). Higher pressures appear to lead to poorer results, probably because of sludge consolidation. In earlier laboratory work (5), we noted that the bulk of the water was retained as liquid, rather than as steam. This was qualitatively confirmed in the pilot study. A valve placed in the nip before the dryer mouth with the nip-cold plate interface. It was minimum compared to the liquid.
water lost at the lower roll. We estimate that evaporation accounted for less than 1% of the total water removed.

The same batch of H&V sludge used in the pilot study was processed in the laboratory electrohydrodynamic press, and the results are included in Figure 4. The pilot results are much better at both room temperature and at 100 °C and are more sensitive to pressure than are the laboratory data. The most likely reason is that the laboratory press can only de-water in a single stage, whereas in dewatering can occur in the nip of the pilot unit. Differences in water may be an additional factor.

At 100 °C, the pilot dryer processed about 80% of the sludge solids. Energy use was approximately 15 kW h, which translates to 80 kW h/dry ton. A similar value can also be estimated from theory. Heat is principally utilized to evaporate the small amount of water lost as steam. Other losses occur through heating the sludge and the expressed water, heat transferred to the belt, and radiative heat loss from the roll. The heat requirement was estimated for the following typical conditions: top roll, 200 °C; bottom roll, 50 °C; ingoing sludge, 50% solids; outgoing sludge, 42% solids; belt, air at 10 ft/min; sheet thickness, 0.5 in.; sludge density, 2.7 lbs/ft³; loss as steam, 3%; outgoing sludge temperature, 40 °C. Under these conditions, 1.46 lb of dry solids were processed, and 1.36 lb of water was removed.

The radiative heat lost from the hot roll is given by

\[ Q_{rad} = \epsilon \sigma T^4 - \epsilon \sigma T_{roll}^4 \]

where \( T \) is the roll temperature in °C, \( \epsilon \), the emissivity, equals 0.2, \( \sigma \), the Stefan-Boltzmann constant, equals 5.67 x 10⁻⁸ W/m²K⁴ and \( B \) is 3,339 m³. From which \( Q_{rad} = 1,192 \times 8 \times 10² \) J/lb. The heat required to warm the expressed water to 40 °C in 14 x 10² lb, and is 2 x 10² J/lb for heating the outgoing water and sludge. The heat lost through steam is 28 x 10² J/lb, based on the estimated 5% evaporation of water as steam. We assumed that the dry primary sludge is mainly comprised of wood fiber whose specific heat was taken to be that of paper, i.e., 1,345 J/g K⁻¹. Finally, the heat required to heat the stainless steel belt (100 kg/m) in 1 x 10³ lb, assuming a heat capacity of 460 J/kg K. The total heat requirement is, therefore, 0.5 x 10¹ J/lb or 78 KW-hr/ton. Despite the many assumptions, the correspondence between theory and experiment is acceptable, demonstrating that the energy costs, while significant, are minor compared to present and projected disposal costs.

The Riverwood sludge was more compressible than the H&V material, and the sludge would not traverse the nip at pressures exceeding 324 psi. The high compressibility of the Riverwood sludge resulted in a relatively larger nip width, which increased the dwell. The results illustrated in Figure 5 for a trial at 5 ft/min (3.8 dwell) show a gain of about 7 percentage points over ambient temperature pressing. However, the room temperature data is misleading, since the belt temperature was as high as 100 °C. The 7 percentage point gain achieved could not have been sustained. No other improvements were obtained at room temperature or temperature conditions. Importantly, the solid gain is consistent with the results with the dry electrohydrodynamic press on Riverwood sludge sampled earlier, where a 9 percentage point gain was realized at 50 psi of pressure, 700 °C temperature, and 0.1 psi dwell (5). Similar percentage points were obtained at 1200 psi in the laboratory study, an equivalent performance can be anticipated with a higher torque machine, particularly in view of our experience with the Hollingsworth and Vose sludge, where the pilot unit outperformed the laboratory.
press. The morphology of the Riverwood sludge before and after impulsive drying is illustrated in Figure 6. Internal voids in the cross-section of the belt-grooved sludge are removed after impulse drying (to 42% solids).

In summary, impulsive drying overcomes the traditional limitation of high-pressure dewatering, namely skin formation and sludge extrusion from the belt, and is able to appreciably increase sludge solids. Pressing at ambient temperature blunts the belt to a point where the sludge could not be dewatered, but this limitation was removed at higher temperatures. It is likely that deposition is prevented during the much higher pressures developed during the impulse process. This ability to use high pressures without plugging the belt is perhaps the most significant benefit of impulse drying. The energy costs for heating the roll are significant, but result in a commensurate amount of water removed. Since the protein solutes were superior to the laboratory-derived values, the performance realized with secondary sludge in earlier laboratory work (5) should be at least matched, if not exceeded, on a pilot scale. Commercialization of the technology is being collaboratively pursued with Ashland Chemical Corporation, Houston, TX, and a commercial unit will be available in mid-1998. The 10 lpm rate used for the pilot apparatus that is of a typical belt press, and methods of scaling pressures should be feasible. Also, since the impulse unit has a small footprint, installation cost should be relatively low.

Acknowledgments

This study was funded by the State of Georgia’s Traditional Industries Program for Poly and Paper. We are indebted to Dave Cristoff for making the pilot unit available and Chad Kerash, Paul Pfahler, and Tim Patterson for their active participation. We also thank Greg Hoiland and Heather Lemke of Riverwood Instrumental and Marshall Bums of Hollingsworth and vose for help in sludge collection, and Robert Sackellas of Georgia-Pacific for several discussions.

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Sludge Dewatering by Impulse Drying

Michael Zawadzki, Talat Mahmood, Sujit Banerjee,
Institute of Paper Science and Technology, 500 Tenth Street, NW, Atlanta, GA 30318.

Abstract

An innovative and energy efficient sludge dewatering technology has been developed. The technology, impulse drying, involves briefly contacting the sludge under pressure with a heated surface. A unique feature of impulse drying is that the majority of moisture removal occurs as liquid water.

A pilot and laboratory scale demonstration was performed on low ash primary papermill sludge. The pilot scale impulse dryer was able to increase the sludge solids level 23.2% points greater than belt pressing alone. The pilot scale equipment was not optimized and further gains are expected. Laboratory scale demonstrations suggest that impulse drying is effective on a wide variety of sludge types: primary (high and low ash), secondary, and mixed sludges.

Impulse drying efficiency depends upon the presence of sufficient moisture in the sludge. Preliminary results indicate that the process is effective for sludges with initial solids content in the range of 15% to 50%. Since, a sludge solids content of 30% is typical of the performance of an inexpensive belt press these experiments demonstrate the potential of retrofitting existing belt presses with an add-on impulse dryer. A high percentage of liquid water removal is achieved by the impulse drying process, which gives the technology an economic advantage relative to thermal drying. The liquid water removal has major cost reduction potential for either sludge burning or landfilling.
Introduction

Since the 1980s impulse drying has been under extensive development in the field of paper drying (Lavery 1988). Essentially, the impulse drying process involves pressing in a nip between heated and unheated rolls. Paper impulse drying involves pressing a moist paper sheet with a felt against a heated roll (200°C to 350°C). Nip dwell of less than one second are generally used. Impulse drying induces an intense dewatering process that gives a higher dryness level than (wet) pressing and it is more energy efficient than thermal drying. Unfortunately, for paper impulse drying the useful range of operating conditions is limited by sheet delamination and product quality concerns (Crouse, Woo, and Sprague 1989; Oloff 1992). Sludge dewatering is an ideal application for the impulse drying technology because sludge delamination is not a concern. This paper describes recent work being done at the Institute of Paper Science and Technology (IPST) on the application of impulse drying to the field of sludge dewatering.

The water removal mechanism of impulse drying is different from that involved in either thermal drying or pressing. A combination of related phenomena likely contributes to dewatering. Initially impulse drying involves a compression and heating period during which the unsaturated material is mechanically compressed. In wet pressing, the water removal is limited by the compressibility of the web. The higher temperatures used in impulse drying may increase material compressibility and allow more water to be pressed out. Also, at high temperature, the viscosity of water is reduced and therefore more easily pressed from the small pores of the sludge matrix. The intense heat transfer may result in the generation of a vapor zone near the heated surface. One of the unique mechanisms of impulse dewatering is thought to be the creation of a vapor phase within the sheet that displaces sheet moisture as liquid water (Lavery 1988).
Experimental

Belt pressed sludge was acquired from Hollingsworth and Vose's (H&V) Hawkesville, Georgia, papermill. The H&V sludge was determined to have an initial solids content of 33 ± 1% and an inorganic ash content of 4.2 ± 0.1% (ashing at 525°C). The sludge is broadly characterized as a primary sludge composed of fiber, filler, and inorganic components.

At the papermill, sludge was sampled as it emerged from the belt press. The sludge samples were taken as intact sheets and stored on melamine coated 1 foot by 4 foot boards. Immediately after sampling the sludge was sealed with PVC plastic to avoid moisture loss. The sludge samples were stored separately to avoid compression during transport and storage.

The pilot scale experiments were performed on the IPST pilot scale paper impulse dryer (Figure 1). The purpose of these experiments was to access scale up from the one-dimensional laboratory study to the two-dimensional pilot impulse dryer. The pilot equipment used an inductively heated top roll, grooved lower roll and a metal wire. The wire run was 26 feet and had a width of 18 inches. The stainless steel wire was supplied by National Filtration (510 cfm airflow, 70 gal/min water flow rate). Both upper and lower rolls were 24 inches in diameter with a 24 inch width. Peak nip pressure was verified using a TekScan 5501 pinch roll sensor. The pinch roll sensor was calibrated over a range of known pressures using the laboratory-scale electrohydraulic press. Static nip measurements were made on the pilot impulse dryer to provide a measure of peak pressure, nip width, and pressure uniformity.

Comparison experiments using the same batch of sludge were performed in the laboratory on an electrohydraulic Material and Testing Systems (MTS) press. The MTS press system used flat stainless steel platens. The MTS press system was configured to simulate
both the thermal and mechanical pressure profiles of the pilot scale equipment. A haversine pressure profile was used during the study.

Figure 1: Schematic of the sludge impulse dewatering pilot scale equipment.

Results and Discussion

H&V sludge was impulse dewatered in a laboratory study and results are presented in Figure 2. This figure reveals that increasing peak nip pressure and upper platen temperature both give greater dewatering. The lower line in Figure 2 represents dewatering at room temperature. For the laboratory case, room temperature pressing gives little additional dewatering of previously belt pressed sludge.

Impulse drying at 200°C (Figure 2, data not shown) gave 5.8% points greater final sludge solids than room temperature pressing (dwell = 1 sec, P = 700 psi). By use of mass balances the amount of liquid water removal from the sludge was calculated. For the 200°C case 82 ± 6 % of the moisture was removed as liquid water. This estimate of liquid
water removal is expected to underestimate the actual amount of liquid water removal because some liquid water is lost on the platen surfaces.

At 350°C, 6.7% points greater solids were achieved relative to room temperature pressing (dwell = 1 sec, P = 700 psi) and 57 ± 6 % of the moisture was removed as liquid water. The upper line in Figure 2 represents dewatering with a two second nip dwell. In this case the final sludge solids content achieved was 60% (P = 780 psi) with 45 ± 7 % liquid water removal.

![Figure 2: Impulse drying H&V primary sludge in a laboratory demonstration.](image)

The results of the pilot scale investigation are shown in Figure 3. The general trend of water removal is similar to that of the laboratory case. The nip dwell for the pilot scale data presented in Figure 3 was one second. For the pilot scale equipment a one second dwell corresponds to a linear wire speed of ten feet per minute.

At a peak nip pressure of 707 psi room temperature pressing was able to achieve a 44.3% final solids content. By increasing the upper roll temperature to 200°C a final solids
content of 51.7% can be achieved. The greatest percentage solids, 56.2%, are achieved by using a roll pressure of 820 psi. Clearly, the pilot study has demonstrated that the solids content of 33% belt pressed sludge can be increased 23.2% points by the impulse drying technology.

Figure 4 illustrates the influence of sludge initial solids on final solids after either pressing (25°C) or impulse drying (350°C). The results were acquired in a laboratory study with a nip pressure of 800 ± 200 psi and a nip dwell of one second. Data in the white region of the figure represents dewatering conditions under which final sludge solids is greater than the initial values. Pressing alone achieves little additional dewatering over the range of initial solids studied. Impulse drying was more effective than pressing alone. Impulse drying is effective over a wide range of initial solids contents with efficiency being lost only at high dryness levels. Liquid water removal for the impulse drying case was found to be approximately 80% (Figure 4).

![Figure 3: Impulse drying H&V primary sludge in a pilot scale demonstration.](image-url)
Impulse drying offers the advantage of increasing the solids content from previously belt pressed sludge. Both the laboratory and pilot studies display similar dewatering trends but, greater dewatering is observed in the pilot configuration. With increasing roll temperatures, similar increases in sludge solids were observed for both MTS and pilot studies. The laboratory study appears to simulate the results of the pilot study if the influence of pressing alone is considered.

From the pilot trial a further advantage of the impulse drying technique was noted. Attempting to dewater previously belt pressed sludge at temperatures below 150°C resulted in sticking of the sludge to the wire and blinding the wire. It was found that under impulse dewatering conditions (>200°C) sticking of the sludge to the roll or wire did not occur. It is hypothesized that steam generated by the impulse drying process prevents sludge from sticking to the wire. Similarly, sticking has been observed in the laboratory experiments. Therefore, there is likely a practical limit to the level of pressure alone that can be used to increase the sludge solids content. Impulse drying can be used to extend range of practical pressures and increase sludge solids.

From the laboratory impulse drying study (200°C, dwell = 1 sec), 82 ± 6 % of the sludge moisture was removed as liquid water. Increasing the roll temperature to 350°C resulted in liquid water removal of 57 ± 6%. Therefore, high liquid water removal is observed over a range of practical roll temperatures. The high liquid water removal suggests that the impulse drying process can have an economic advantage relative to sludge thermal drying. Impulse drying is energetically favorable because liquid water removal does not involve energy introduction to overcome the enthalpy of vaporization of water. The liquid water removal has major cost reduction potential for either sludge burning or landfilling.

Impulse drying efficiency depends upon the presence of sufficient moisture in the sludge. Preliminary results suggest that the process is effective for sludges with an initial solids content between 15% and 50% (Figure 4). A sludge solids content of 30% is typical of the performance of an inexpensive belt press. Hence, these experiments
demonstrate the potential of retrofitting existing belt presses with an add-on impulse dryer.

![Graph showing sludge initial solids contents versus final solids for impulse drying and wet pressing.](image)

**Figure 4**: Sludge initial solids contents versus final solids for impulse drying and wet pressing.

Experimental results suggest that the technology is useful for a wide range of sludge types: primary (high and low ash), secondary and mixed (Banerjee et al., 1997; Banerjee, Phelan and Foulkes, 1996). Impulse drying has been successfully applied to municipal waste activated sludge (City of Houston, TX). The belt pressed sludge was supplied at 16% solids and impulse drying (350°C, dwell = 0.7 sec) gave approximately 10% point increase in the solids content. Mixed primary papermill and secondary sludge (~50:50) benefited from impulse drying. A nip dwell of 0.5 seconds and a roll temperature of 200°C was able to give a 15% point increase in the solids level. Finally, high ash primary papermill sludge was investigated. Preliminary pilot and laboratory results reveal that the dewatering behavior is similar to H&V sludge and again the pilot scale configuration is more effective than the laboratory.
The process technology has recently been licensed to Ashbrook Corporation (Houston, TX). Ashbrook plans to manufacture impulse dryers as both retrofits for exiting belt presses and as new units. The commercial configuration of sludge impulse dryers is expected to be similar to the pilot configuration shown in Figure 1.

Acknowledgement

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References


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Front View of the Pilot Scale Impulse Dryer.

Side View of the Pilot Scale Impulse Dryer.

Sludge Storage Box.
21. References


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