THE GENERATION OF QUINONES FROM LIGNIN AND LIGNIN-RELATED COMPOUNDS

DIELS-ADLER REACTIONS OF LIGNIN-DERIVED QUINONES

LIGNIN-DERIVED QUINONES AS PULPING ADDITIVES

JOHN C. WOZNIAK, DONALD R. DIMMEL, AND EARL W. MALCOLM

FEBRUARY, 1990
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Portions of this work were used by JCW as partial fulfillment of the requirements for the Ph.D degree at the Institute of Paper Science and Technology. This manuscript has been submitted for consideration for publication in the Journal of Wood Chemistry and Technology.

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The following three papers discuss research generated in the course of John Wozniak's Ph.D. Thesis. These papers will be appearing in the Journal of Wood Chemistry and Technology, issue 4, 1989. The technical paper was slow in its release due to patent restrictions and due to the Institute's move.

The research is continuing (IPST project #3661) and is receiving financial support from the Department of Energy. The research team also involves personnel at the Solar Energy Research Institute in Golden, Colorado. The goal of the present research is to develop an economic pulping process based on the use of anthraquinone and analogs which are generated from lignin. Such a process may be quite selective and thus have a positive impact on mill productivity, energy requirements, bleaching requirements, and environmental concerns. Several of these effects are related to the possibility of eliminating sulfur species from the pulping process.
THE GENERATION OF QUINONES FROM LIGNIN AND LIGNIN-RELATED COMPOUNDS

John C. Wozniak, Donald R. Dimmel,* and Earl W. Malcolm
Institute of Paper Science and Technology
Atlanta, GA 30318

ABSTRACT

Lignin and lignin-related compounds were oxidized with potassium nitrosodisulfonate, hydrogen peroxide, and peracetic acid, with the aim of producing o- and p-benzoquinones. Depending on the substrate and oxidant, yields of p-benzoquinones from lignin model compounds were as high as 80-95%. The best yield of p-benzoquinones from lignin (16%) was with the use of potassium nitrosodisulfonate and an aspen hardwood lignin; corresponding yields obtained with hydrogen peroxide and peracetic acid were 0-2%. Electrochemical oxidation was examined briefly and found to be inferior to the chemical oxidants with regard to yields of benzoquinones from lignin models (max. 40%) and from lignin (1%). The nitrobenzene oxidation of several lignin samples revealed that the highest syringaldehyde and combined aldehyde yields (for subsequent oxidation to quinones) were obtained from an organosolv lignin obtained through the acid-catalyzed pulping of aspen with ethanol.

INTRODUCTION

Quinone pulping catalysts, such as anthraquinone (AQ), can be used to increase pulping selectivity, improve productivity, and save energy. However, the widespread use of AQ in pulping systems has been limited because of its relatively high cost to benefit ratio. One possible way to lower the cost of AQ is to prepare it from an inexpensive starting material, such as lignin. Lignin is

*Address inquiries to this author.
a major component of both wood and pulping liquors and contains oxygenated aromatic rings which have some similarity to AQ.

This paper describes our attempts to use various oxidative techniques to generate simple quinone structures from lignin, lignin fragments, and lignin model compounds. Modification of these lignin-derived quinones through Diels-Alder reactions with various dienes can enhance their ring structure by converting them into higher order quinones such as naphthoquinones and anthraquinones. Some of these enhanced quinones have characteristics needed to act as effective delignification catalysts.

Lignin and degraded lignin consists predominantly of phenolic and etherified phenolic units with one or two methoxyl groups adjacent to the phenolic hydroxyl group, and an alkyl side chain para to the phenolic hydroxyl group. As shown in Eq. 1, oxidation of the phenolic hydroxyl group and an adjacent methoxyl group converts a lignin unit to an \( \text{O-benzoquinone} \) (2 or 3). Oxidation of the phenolic hydroxyl group, together with oxidative degradation of the p-alkyl side chain, can convert a lignin unit into a \( \text{p-benzoquinone} \) (4 or 5).

A number of chemical oxidative techniques have been used to generate both \( \text{o-quinones} \) and \( \text{p-quinones} \) in lignin and lignin-related compounds. Potassium nitrosodisulfonate and sodium periodate are known to produce \( \text{o-quinones} \) from lignin model compounds of the substituted guaiacol type or to introduce \( \text{o-quinone} \) structures into various lignin preparations. Hydrogen peroxide and peracetic acid have been found to generate
p-quinones from lignin-related compounds. Several other chemical oxidants have also been used to produce either quinones or the related hydroquinones from various samples.13-15

Electrochemical oxidation has been applied to phenols, lignin model compounds, and lignin itself; often demethylation and quinone formation results.16-19 The enzymatic degradation of lignin and lignin-related compounds has also been investigated,20-22 and the production of p-benzoquinones from model compounds has been demonstrated.20,21

Our work described here focuses on the use of three chemical and various electrochemical oxidative techniques for the generation of specific benzoquinones. The use of these benzoquinones in catalyst production is described in the publications which follow.1,2

RESULTS AND DISCUSSION

The lignin-related compounds used in the experimental work are shown below. These compounds possess common structural characteristics of lignin or may be derived from lignin; both hardwood and softwood models are represented. In addition to the simple monomeric lignin-related compounds, several lignin preparations were also investigated. These include samples resulting from soda, kraft, and sulfite pulping as well as a lignin obtained through the acid-catalyzed pulping of aspen with ethanol (ethanol lignin) and a low molecular weight fraction of this lignin (LMW ethanol lignin).

Potassium Nitrosodisulfonate

Although the use of potassium nitrosodisulfonate (Fremy's salt) often results in the generation of o-quinones,7 recent work has shown that high yields of p-benzoquinones can be produced through the oxidation of p-hydroxybenzyl alcohols, p-hydroxybenzoic acids, and p-hydroxybenzaldehydes.23,24
The results obtained from Fremy's salt oxidation of selected lignin-related compounds are summarized in Table 1. In many cases several variations in the reaction conditions were attempted to try to improve the yield; the best results observed are presented. It should be pointed out that the yields reported were determined by a gas chromatography (GC) technique in which an internal standard was added after all reaction, extraction, and washing of the

**TABLE 1**

Fremy's salt oxidation of lignin-related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product(^a)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Guaiacyl Type:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Methylvanillyl Alcohol</td>
<td>MBQ</td>
<td>79</td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>Vanillin</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>Vanillic Acid</td>
<td>MBQ</td>
<td>77</td>
</tr>
<tr>
<td><strong>Syringyl Type:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Methylsyringyl Alcohol</td>
<td>DMBQ</td>
<td>79</td>
</tr>
<tr>
<td>Acetosyringone</td>
<td>DMBQ</td>
<td>3</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>DMBQ</td>
<td>65</td>
</tr>
<tr>
<td>Syringic Acid</td>
<td>DMBQ</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^a\)MBQ = Methoxy-p-benzoquinone (4); DMBQ = 2,6-Dimethoxy-p-benzoquinone(5).
extract had been done; consequently, the yields reported may be somewhat lower than the crude yields and in no case reflect isolated, purified product yields.

The importance of the α-hydroxyl group is clearly evident. High quinone yields were obtained from both the alcohols and the acids. Except for syringaldehyde, the yields from compounds containing α-carbonyl groups were, on the other hand, very low or nonexistent. Rapid conversion to an o-quinone would explain why the oxidation of vanillin does not lead to the desired product; o-quinones have been shown to be relatively unstable compounds. The additional methoxyl group present in syringaldehyde may inhibit reactions at C₅ and lessen the level of undesirable by-products.

The Fremy's salt oxidation of various isolated lignin samples is presented in Table 2. Numerous unsuccessful attempts were made to try to increase the yield of quinone from the ethanol lignin sample above the 4% initially obtained. Increasing temperature, reaction time, and amount of Fremy's salt used generally had detrimental effects on the yield.

**TABLE 2**

Fremy's salt oxidation of various lignin samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quinone Obtaineda</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood Ethanol</td>
<td>DMBQ</td>
<td>4</td>
</tr>
<tr>
<td>LMW Ethanol 1</td>
<td>DMBQ</td>
<td>11</td>
</tr>
<tr>
<td>LMW Ethanol 2</td>
<td>DMBQ</td>
<td>16</td>
</tr>
<tr>
<td>Softwood Soda</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>Hardwood Kraft</td>
<td>DMBQ</td>
<td>4</td>
</tr>
<tr>
<td>Softwood Kraft</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>Hardwood Sulfite</td>
<td>DMBQ</td>
<td>1</td>
</tr>
<tr>
<td>Softwood Sulfite</td>
<td>--</td>
<td>0</td>
</tr>
</tbody>
</table>

*aDMBQ = 2,6-Dimethoxy-p-benzoquinone (5).*

The oxidations of the low molecular weight (LMW) sample differed only in the product isolation method. Unlike the rest of the samples, the chloroform-extract of the reaction mixture from
the second reaction was not extensively washed and, consequently, more product was retained in the chloroform. The result serves to illustrate the earlier point made regarding compound yields and indicates that washing losses may be as high as 25%.

The ethanol, hardwood kraft and sulfite lignin samples appeared to be very reactive toward Fremy's salt, resulting in deep red solutions indicative of the presence of quinones. Unlike the reactions of ethanol and hardwood kraft lignin, the sulfite lignin reactions showed little tendency to produce compounds that could be readily extracted with chloroform. Possibly, Fremy's salt generates o-quinones from all of the lignins; these structures may remain attached to the lignin matrices and, therefore, are not observed as extracted reaction products.

As can be seen from Table 2, a p-benzoquinone was obtained only from the hardwood samples. This result parallels the finding in the model compound study that syringyl units have a greater tendency to generate p-benzoquinones than guaiacyl units. The soda lignin appeared to be the least reactive sample.

Hydrogen Peroxide

Several researchers have studied the effect of alkaline hydrogen peroxide on lignin and lignin model compounds. Reeves and Pearl\textsuperscript{10} found that softwood lignin model compounds containing α-carbonyl groups were reactive when a free hydroxyl group was present in the position \textit{para} to the side chain. Under these conditions the side chain was cleaved to yield methoxyhydroquinone.

In many studies of the hydrogen peroxide oxidation of lignin or lignin-related compounds, quinones or related hydroquinones are only reaction intermediates,\textsuperscript{8,9,26} which with subsequent oxidation leads to low molecular weight dicarboxylic acids. In general, syringyl model compounds have been found to react more readily with peroxide than guaiacyl models. With both models, unetherified phenolic rings seem to be necessary for reaction to occur.\textsuperscript{9}
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Time (min)</th>
<th>Products</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Methylvanillyl Alcohol</td>
<td>300</td>
<td>2-Methoxy-4-vinylphenol</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-Methylvanillyl Alcohol</td>
<td>93</td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>60</td>
<td>Methoxy-p-benzoquinone</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methoxyhydroquinone</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetovanillone</td>
<td>15</td>
</tr>
<tr>
<td>Vanillin</td>
<td>10</td>
<td>Methoxy-p-benzoquinone</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methoxyhydroquinone</td>
<td>95</td>
</tr>
<tr>
<td>Vanillic Acid</td>
<td>330</td>
<td>No Reaction</td>
<td></td>
</tr>
<tr>
<td>α-Methylsyringyl Alcohol</td>
<td>300</td>
<td>2,6-Dimethoxy-4-vinylphenol</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-Methylsyringyl Alcohol</td>
<td>59</td>
</tr>
<tr>
<td>Acetosyringone</td>
<td>120</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,6-Dimethoxyhydroquinone</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetosyringone</td>
<td>31</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>80</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,6-Dimethoxyhydroquinone</td>
<td>[72]</td>
</tr>
<tr>
<td>Syringic Acid</td>
<td>330</td>
<td>Unidentified Compound</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Syringic Acid</td>
<td>29</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields are based on a GC using 4-isopropyl phenol as an internal standard technique; because authentic samples were not always available, values in brackets are approximations based on a typical response factor of 0.4 for related compounds.

In contrast to Fremy's salt oxidation, hydrogen peroxide oxidation of lignin-related compounds gave poor results when the compounds contained α-hydroxyl groups (Table 3). In the attempted oxidation of the two alcohols, even after several hours, most of the starting compounds remained; only small amounts of dehydration products were obtained. Attempted reactions of the aromatic acids also went poorly or not at all.

On the other hand, high yields of quinone or hydroquinone were obtained from both the aldehydes and the ketones. Because hydroquinones may be easily oxidized to quinones, high yields of these compounds are also significant. Methoxyhydroquinone was
identified as the major product obtained from the oxidation of both acetovanillone and vanillin. A good yield of 2,6-dimethoxyhydroquinone was obtained from the oxidation of acetosyringone and syringaldehyde.

Hydrogen peroxide oxidations were also attempted on the hardwood ethanol, kraft, and sulfite lignins. Although each sample appeared to react to some extent with the hydrogen peroxide, GC analysis indicated no measurable amounts of either methoxy- or 2,6-dimethoxy-p-benzoquinone. It appears, that in the direct hydrogen peroxide oxidation of lignin, quinones are either produced in amounts which are too low for practical use or are degraded almost as quickly as they are produced.

The hydrogen peroxide oxidation of some lignin-derived compounds, however, is more promising. The yields of 2,6-dimethoxy-p-benzoquinone and 2,6-dimethoxyhydroquinone from syringaldehyde appear to be quite good. Using similar reaction conditions, a group of Japanese researchers have also obtained a good yield of 2,6-dimethoxy-p-benzoquinone from syringaldehyde.27

Peracetic Acid

Like hydrogen peroxide, peracetic acid can cause extensive oxidative degradation of lignin-related compounds and result in complex mixtures of aliphatic dibasic acids. In some cases, however, good yields of quinones or hydroquinones have been obtained from lignin-related compounds. Peracetic acid oxidations of guaiacyl lignin model compounds containing α-carbonyl groups proceed (via Baeyer-Villiger rearrangements) to form esters which upon hydrolysis produce methoxyhydroquinones. The hydroquinones may be further oxidized to quinones, or they may be degraded into smaller carboxylic acids. Compounds containing α-hydroxyl groups are first oxidized to the corresponding α-carbonyl compounds.

The results obtained from the peracetic acid oxidation of selected lignin-related compounds are presented in Table 4; again
the values presented indicate the current best, but not necessarily the optimum, results. Table 4 shows that peracetic acid may be used to obtain p-benzoquinones from compounds which contain either α-hydroxyl groups or α-carbonyl groups. Although little has been reported in the literature on the peracetic acid oxidation of syringyl type compounds, our results show that these compounds are more prone to yield quinone products than are their guaiacyl analogs.

The yields of the acetoxy and formoxy esters shown in Table 4 suggest that much higher quinone yields are possible from several

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Time (min)</th>
<th>Products</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Methylvanillyl Alcohol</td>
<td>20</td>
<td>Methoxy-p-benzoquinone</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Acetoxy-2-methoxyphenol</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unidentified Compounds</td>
<td>[14]</td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>95</td>
<td>Methoxy-p-benzoquinone</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methoxyhydroquinone</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Acetoxy-2-methoxyphenol</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetovanillone</td>
<td>4</td>
</tr>
<tr>
<td>Vanillin</td>
<td>25</td>
<td>Methoxy-p-benzoquinone</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methoxyhydroquinone</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Formoxy-2-methoxyphenol</td>
<td>[5]</td>
</tr>
<tr>
<td>Vanillic Acid</td>
<td>540</td>
<td>No Reaction</td>
<td></td>
</tr>
<tr>
<td>α-Methylsyringyl Alcohol</td>
<td>20</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>30</td>
</tr>
<tr>
<td>Acetosyringone</td>
<td>35</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Acetoxy-2,6-dimethoxyphenol</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unidentified Compounds</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetosyringone</td>
<td>5</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>25</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unidentified Compounds</td>
<td>[2]</td>
</tr>
<tr>
<td>Syringic Acid</td>
<td>360</td>
<td>2,6-Dimethoxy-p-benzoquinone</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unidentified Compounds</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Syringic Acid</td>
<td>16</td>
</tr>
</tbody>
</table>

aYields are based on a GC technique using 4-isopropylphenol as an internal standard; because authentic samples were not always available, values in brackets are approximations based on an estimated response factor of 0.5.
of the compounds. The generation of the ester compounds is in agreement with the mechanism of the Baeyer-Villiger reaction; the esters should be easily converted to the corresponding quinones by hydrolysis and mild oxidation. Thus, it is the combined quinone, hydroquinone, and ester yield that is of significance in the table.

The oxidation of each of the lignin samples was carried out using the same procedure that was used for the model compounds. The fact that quinones were obtained from the alcohols and acids, and in particular the 30% yield of 2,6-dimethoxy-\(p\)-benzoquinone from \(\alpha\)-methylsyringyl alcohol, indicates that peracetic acid should be capable of generating quinones directly from lignin. Table 5 shows that this is, in fact, the case; however, the yields are relatively low.

### Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quinone Obtained</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood Ethanol</td>
<td>DMBQ</td>
<td>1</td>
</tr>
<tr>
<td>LMW Ethanol</td>
<td>DMBQ</td>
<td>2</td>
</tr>
<tr>
<td>Hardwood Kraft</td>
<td>DMBQ</td>
<td>2</td>
</tr>
<tr>
<td>Hardwood Sulfite</td>
<td>DMBQ</td>
<td>trace</td>
</tr>
</tbody>
</table>

\(\text{aDMBQ} = 2,6\text{-Dimethoxy-}\(p\)\text{-benzoquinone (5).}\)

As with the other oxidative techniques used, peracetic acid oxidation is clearly more effective in generating quinones from simple lignin-related compounds than from lignin itself. Syringaldehyde stands out as a good compound for the generation of 2,6-dimethoxy-\(p\)-benzoquinone.

**Electrochemistry**

Electrochemical oxidation of lignin-related phenolic compounds to form quinones has been briefly studied by Steelink and Britton. They found that \(\alpha\)-methylsyringyl alcohol could be converted into 2,6-dimethoxy-\(p\)-benzoquinone in water/acetonitrile; in the absence of water, acetosyringone was produced.
We, too, have examined the anodic electrochemical oxidation of α-methylsyringyl alcohol, along with several other compounds. A summary of our best results, obtained after repeated attempts, is presented in Table 6. Many variables were examined, including changes in pH, temperature, solvent, and electrode materials. Reaction conditions that were found to give good results (high quinone yields) with the lignin models were then applied to the oxidation of lignin.

Reports on electrochemical oxidations indicate that quinones or quinone precursors (4-hydroxycyclohexa-2,5-dienones) generally are produced in acidic media using a lead dioxide anode. The majority of the reactions presented in Table 6, therefore, were carried out using these conditions.

A problem with acidic conditions, however, is that lignin is generally not soluble in acid. Various solvents were therefore examined with the hope to promote solubility. However, even with acetone, which gave the best quinone yield from α-methylsyringyl alcohol, the yields from lignin were poor (exp. 10 and 11).

The use of other oxidative techniques had shown that higher quinone yields may be obtained from lignin-derived compounds, such as vanillin and syringaldehyde, than from lignin itself. Some time was therefore spent in an investigation of the possible electrochemical conversion of lignin-derived compounds to quinones. This work mainly involved the use of syringic acid as the substrate. Syringic acid was selected for two reasons. First, it may be easily obtained from the oxidation of syringaldehyde which, in turn, may be obtained directly from lignin. Second, there is some precedence in the literature for the electrochemical decarboxylation of carboxylic acids to yield compounds which then might be further oxidized to quinones.

Greatest success in the generation of 2,6-dimethoxy-p-benzoquinone from syringic acid was obtained by setting the anode potential as high as the equipment would allow, using a cell potential of approx. 37 volts (Expt. 7). To maintain syringic
### TABLE 6

Electrochemical oxidation of lignin and lignin-related compounds

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Anode,(^a) Potential(^b)</th>
<th>Conditions(^c)</th>
<th>Quinone(^d)</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td><strong>Oxidations of α-Methylvanillyl Alcohol:</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Pb, 1.8V</td>
<td>CH(_3)CN/1.0M H(_2)SO(_4) (7/1), 3°C</td>
<td>MBQ</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Pb, 1.8V</td>
<td>p-Dioxane/0.67M H(_2)SO(_4) (7/3), 28°C</td>
<td>MBQ</td>
<td>7</td>
</tr>
<tr>
<td><strong>Oxidations of α-Methylsyringyl Alcohol:</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pb, 1.8V</td>
<td>CH(_3)CN/1.0M H(_2)SO(_4) (7/1), 3°C</td>
<td>DMBQ</td>
<td>21</td>
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<tr>
<td>4</td>
<td>Pb, 1.8V</td>
<td>p-Dioxane/0.67M H(_2)SO(_4) (7/3), 28°C</td>
<td>DMBQ</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Pb, 1.6V</td>
<td>DMSO/1.0M H(_2)SO(_4) (7/3), 35°C</td>
<td>DMBQ</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>Pb, 1.7V</td>
<td>Acetone/1.0M H(_2)SO(_4) (7/1), 28°C</td>
<td>DMBQ</td>
<td>39</td>
</tr>
<tr>
<td><strong>Oxidations of Syringic Acid:</strong></td>
<td></td>
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<tr>
<td>7</td>
<td>C, 1.5-2.3V</td>
<td>0.1N NaOH, 27°C</td>
<td>DMBQ</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>C, 2.0V</td>
<td>0.1N NaOH, pH 7, 25°C</td>
<td>DMBQ</td>
<td>5</td>
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<tr>
<td><strong>Oxidation of Syringaldehyde:</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C, 2.0V</td>
<td>0.1N NaOH, pH 7, 25°C</td>
<td>DMBQ</td>
<td>2</td>
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<td><strong>Oxidation of Ethanol Lignin:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Pb, 2.0V</td>
<td>Acetone/1.0M H(_2)SO(_4) (7/1), 28°C</td>
<td>DMBQ</td>
<td>trace</td>
</tr>
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<td><strong>Oxidation of LMW Ethanol Lignin:</strong></td>
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<tr>
<td>11</td>
<td>Pb, 2.0V</td>
<td>Acetone/1.0M H(_2)SO(_4) (7/1), 28°C</td>
<td>DMBQ</td>
<td>1</td>
</tr>
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</table>

\(^a\)Pb = Lead electrode (lead oxide under reaction conditions); C = Graphite electrode.  
\(^b\)Volts relative to a saturated calomel electrode.  
\(^c\)Substrate concentration was 0.05M for model compound oxidations; 10 mg/mL was used for lignin oxidations.  
\(^d\)MBQ = Methoxy-\(p\)-benzoquinone (4); DMBQ = 2,6-Dimethoxy-\(p\)-benzoquinone (5).
acid solubility, 1N NaOH was periodically added. An attempt to oxidize syringaldehyde, using similar reaction conditions (Expt. 9), resulted in a very slow reaction and only a 2% yield of 2,6-dimethoxy-p-benzoquinone.

Although the direct electrochemical oxidation of lignin gave some positive results, the yields were far below those obtained through direct chemical techniques. The results of the oxidation of syringic acid were also not encouraging. It appears that electrochemical oxidation might be a viable alternative to chemical oxidants, but considerable developmental work in the experimental conditions would be needed in order to get significantly better results.

Nitrobenzene Oxidation

The use of several of the oxidative techniques has shown that higher p-benzoquinone yields result from the oxidation of the simpler lignin-related compounds than from the oxidation of lignin itself. Syringaldehyde is a particularly attractive starting material for the production of 2,6-dimethoxy-p-benzoquinone.

The technology for the production of simple compounds such as vanillin and syringaldehyde from lignin is fairly well established.\textsuperscript{29,30} To gain a better understanding of which pulping processes might give rise to lignins that are most highly susceptible to conversion into these compounds, we conducted several nitrobenzene oxidations of pulping-based lignin samples (Table 7).

It is clear from the data given in the table that aldehyde yields increase with increasing reaction temperature and that the ethanol lignin sample gave the highest aldehyde yields. Lignin generated through acid-catalyzed ethanol pulping may therefore be very useful as a starting material for the generation of p-benzoquinones.
TABLE 7
Nitrobenzene oxidation of various lignin samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidations at 140°C:</th>
<th>Oxidations at 159°C:</th>
<th>Oxidations at 179°C:</th>
<th>Oxidation at 178°C:</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Vanillin Yield (%)</td>
<td>Syringaldehyde Yield (%)</td>
<td>Total Yield (%)</td>
<td>Vanillin Yield (%)</td>
</tr>
<tr>
<td>HW Ethanol</td>
<td>5.0</td>
<td>12.9</td>
<td>17.9</td>
<td>5.8</td>
</tr>
<tr>
<td>SW Soda</td>
<td>10.1</td>
<td>trace</td>
<td>10.1</td>
<td>12.9</td>
</tr>
<tr>
<td>HW Kraft</td>
<td>3.4</td>
<td>4.8</td>
<td>8.2</td>
<td>4.6</td>
</tr>
<tr>
<td>SW Kraft</td>
<td>7.9</td>
<td>0.4</td>
<td>8.3</td>
<td>9.9</td>
</tr>
<tr>
<td>HW Sulfite</td>
<td>5.1</td>
<td>8.9</td>
<td>14.0</td>
<td>5.6</td>
</tr>
<tr>
<td>SW Sulfite</td>
<td>12.1</td>
<td>trace</td>
<td>12.1</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.9</td>
<td></td>
<td></td>
<td>20.4</td>
</tr>
</tbody>
</table>

SUMMARY AND CONCLUSIONS

The purpose of this investigation was to determine which oxidative technique(s) might give rise to high p-benzoquinone yields from lignin and lignin-related compounds. It is clear that in all cases simple lignin-related compounds or compounds which may be derived from lignin, such as vanillin and syringaldehyde, are much more prone to yield these quinones than is lignin itself.

Fremy's salt is most useful on compounds which contain a benzyllic hydroxyl group. Hydrogen peroxide is more effective on compounds which contain an α-carbonyl group. Peracetic acid will
oxidize either type of compound, but the yields are generally lower. Electrochemical oxidation provides reasonable quinone yields from α-methylvanillyl alcohol and α-methylsyringyl alcohol. However, much more developmental work is needed to establish the best reaction conditions and most suitable substrates for producing quinones via any of the above techniques.

Syringyl compounds generally give higher quinone yields than guaiacyl compounds. This may be due to the greater stability of the dimethoxy-p-benzoquinone or to lower amounts of radical combination reactions associated with the presence of the additional methoxyl group. The lignin obtained through the acid-catalyzed ethanol pulping process appears to be a very reactive sample and more prone to quinone generation than the other lignins.

EXPERIMENTAL

Most of the lignin model compounds were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. Recrystallized samples of α-methylvanillyl and α-methylsyringyl alcohol were obtained by the procedure of Bailey and Dence and had melting points in agreement with literature values.

Softwood Soda Lignin. The lignin was isolated from the black liquor resulting from a soda cook of loblolly pine chips by acidification to a pH between 2 and 3 through the dropwise addition of 6M H₂SO₄. The precipitated lignin was centrifuged and repeatedly washed with distilled water until the pH of the supernatant was between 5 and 6. Carbohydrate removal was achieved by dissolving the lignin in 2-methoxyethanol followed by successive filtration through coarse and medium sintered-glass Buchner funnels. The solvent was then removed on a rotary evaporator at 40-45°C, and the resulting syrup was dried in a vacuum desiccator over P₂O₅. The dry lignin residue was removed from the flask with distilled water and freeze dried.
Hardwood Ethanol Lignin. An organosolv lignin was obtained by cooking 150.0 g of oven dry aspen chips in a mixture of 750 mL 95% ethanol and 750 mL 0.025M HCl at 156°C. After reaction, the contents of the reaction vessel was filtered and washed with 50% ethanol. The pulp was then defiberized in a Waring blender, filtered, and again washed with 50% ethanol. The lignin was isolated from the combined wash liquor by evaporating the liquor to approximately one-half volume, centrifuging, washing with water, and freeze drying. To retain the fine lignin particles, the lignin/water mixture was centrifuged after each wash, and the supernatant obtained after each centrifugation was filtered through a fine sintered-glass Buchner funnel. The lignin yield was 19.0 g (12.7%).

Low Molecular Weight Ethanol Lignin. After the isolation of the first lignin fraction, a low molecular weight fraction was isolated from the remaining solution. This was done by first reducing the solution, to approx. 250 mL under reduced pressure, generally keeping the temperature below 40°C. This concentrated solution was extracted with CHCl₃ (8 x 50 mL); the extract was washed with 50 mL of distilled water, dried over anhydrous Na₂SO₄, and then evaporated. The LMW sample was then dried over P₂O₅ in a vacuum desiccator to give 8.6 g (5.8%). No direct determination of molecular weight was made.

Other Lignin Samples. The origin of the other lignin samples used in the oxidation studies are presented in Table 8.

TABLE 8

Sources of lignin samples used in the oxidation studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood Kraft</td>
<td>Westvaco RLX 4713-3A, Charleston Research Center, North Charleston, SC</td>
</tr>
<tr>
<td>Softwood Kraft</td>
<td>Isolated in the thesis work of Furman³²</td>
</tr>
<tr>
<td>Hardwood Sulfite</td>
<td>Reed Lignin D-312-13, Rothschild, WI</td>
</tr>
<tr>
<td>Softwood Sulfite</td>
<td>Reed Lignin D-300-2</td>
</tr>
</tbody>
</table>
General Work-Up and Analytical Procedure. Gas chromatography was used to analyze the product mixtures obtained through the oxidative techniques described below. In general, the reaction mixture was acidified with dilute HCl or neutralized with saturated NaHCO₃ solution to attain a pH of approx. 3 and extracted with CHCl₃. The extract was dried over anhydrous Na₂SO₄ and analyzed on a Hewlett-Packard 5890A GC using a 530-μm 50% phenylmethyl silicone, fused silica, open tubular column. For quantitative work, a known amount of 4-isopropylphenol was added as an internal standard prior to analysis. For some analyses a Hewlett-Packard 5985B GC/MS system was used which employed a 6-ft, 1/4-in. glass column packed with 3% silicone OV-17 on 100/120 chromosorb W-HP.

Potassium Nitrosodisulfonate Oxidation. The material being investigated (1.00 mmol of model compound or 200 mg of lignin) was dissolved in 10 mL of ethylene glycol monomethyl ether. The reaction flask was then cooled to approx. 0°C in an ice bath. Under a stream of nitrogen, 3.0 mmol of potassium nitrosodisulfonate was added to 20.0 mL of a 0.2M KH₂PO₄/K₂HPO₄ buffer solution (pH 6.0) which had also been cooled in an ice bath. The Fremy's salt mixture was then added dropwise to the solution of the material to be oxidized with fairly vigorous stirring, again using a stream of nitrogen to blanket the reaction. The reaction mixture was then removed from the ice bath and allowed to come to room temperature. Total reaction time was generally 2 hr.

Hydrogen Peroxide Oxidation. Hydrogen peroxide stock solution was standardized through sodium thiosulfate titration of iodine liberated upon the addition of potassium iodide. The material to be oxidized (1.00 mmol of model compound or 200 mg of lignin) was added to 1.00 mL of 1.00N NaOH in an 8-ml vial equipped with a small stirring bar. Hydrogen peroxide (2.50 mL of 1.00M solution) was then added.

Peracetic Acid Oxidation. Peracetic acid is commercially available from FMC, Industrial Chemicals Division, Downers Grove, IL.
The percentage of hydrogen peroxide and peracetic acid in the stock solution was determined both before and after the series of peracetic acid oxidations was performed, using a slightly modified procedure of Greenspan and MacKellar. There was found to be no change in composition during the course of the experiments. The material to be oxidized (1.00 mmol of model compound or 200 mg of lignin) was added to 1.60 mL of glacial acetic acid in an 8-mL vial equipped with a small stirring bar. Peracetic acid stock solution (0.60 mL, found by the standardization procedure to be 36% peracetic acid and 6.7% $\text{H}_2\text{O}_2$) was then added.

Electrochemical Oxidations. The cell used for the electrochemical oxidations was a 100-mL Model C-600 membrane cell obtained from The Electrosynthesis Co., Inc., East Amherst, NY, with a Dupont Nafion #117 membrane. The cell was connected in series with an Electrosynthesis Model 415 potentiostatic controller, supplied by an Model 420X accessory power unit, and an Electrosynthesis Model 640 coulometer equipped with a Model 645 shunt. A digital voltmeter was used to obtain the cell voltage.

Working electrodes generally consisted of 1-in. square sheets of metal of the highest available purity (at least 99.997%) to which a copper connecting wire was attached by using an electrically conductive epoxy adhesive. The connecting wire was surrounded by a 1/4-in. glass tube which was attached to the metal sheet with a chemically resistant resin; this resin also covered any of the connecting wire and the silver epoxy bond which remained exposed. A graphite anode was constructed from a 1/4-in. graphite rod by covering the upper portion of the rod with Teflon tape so that only a 1-in. section remained exposed. Metal anodes were prepared prior to use by successive polishing with 1.0-, 0.3-, and 0.05-μm Buehler alumina micropolish as a water suspension. The counter electrode consisted of a platinum wire coil; the reference electrode was a Beckman 39417 calomel electrode with a ceramic frit.
After cell assembly, the solution in the anode compartment was purged with nitrogen, and the anode was pretreated at an appropriate potential (normally the voltage at which the electrolysis was carried out) for 10 min. Background polarization curves (current vs. potential) were obtained before and after the addition of the substrate and used to help determine the electrolysis potential. Substrate concentration was generally 0.05M. The electrolysis was monitored by periodically withdrawing and analyzing 2.00-mL samples.

Nitrobenzene Lignin Oxidations. The lignin sample (30.0 mg), 2.00 mL of 2.00M NaOH, and 0.12 mL of nitrobenzene were added to a 4.5-mL stainless steel pressure vessel. The vessel was sealed, preheated at 60°C for 30 min, and then heated at an elevated temperature for 2.5 hr. The contents of each bomb was transferred to a 60-mL separatory funnel; the bomb was rinsed twice with approx. 1.5 mL of 1M NaOH and once with approx. 1.5 mL of water. Excess nitrobenzene and its reduction products were removed by extraction with CHCl3 prior to acidification, extraction and analysis of the product mixture.

ACKNOWLEDGMENTS

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REFERENCES


DIELS-ALDER REACTIONS OF LIGNIN-DERIVED QUINONES

John C. Wozniak, Donald R. Dimmel,* and Earl W. Malcolm
Institute of Paper Science and Technology
Atlanta, GA 30318

ABSTRACT

The Diels-Alder reactions of methoxy-p-benzoquinone and 2,6-dimethoxy-p-benzoquinone, which may be obtained from lignin and lignin model compounds, and of o-quinones (4-methyl, 4-acetyl, and 4-(1-hydroxyethyl)-o-benzoquinone) were investigated using 2,3-dimethylbutadiene, isoprene and styrene as dienes. Dimethylbutadiene and isoprene were found to be effective reactants, resulting in the generation of several Diels-Alder addition products. Loss of the methoxyl group and the side chain were observed under certain conditions. Reactions of the p-benzoquinones went more smoothly than the reactions of the o-quinones, and product yields were generally higher. Higher yields of anthraquinone products were obtained from 2,6-dimethoxy-p-benzoquinone than from methoxy-p-benzoquinone.

INTRODUCTION

Quinones, and especially anthraquinone (AQ, 1), are well known for their ability to promote pulping at catalytic levels.1 While not as effective as AQ, naphthoquinone (2) and o-phenanthrenequinone (3) have some pulping catalytic activity. The lower ring members of this homologous series, namely p- and o-benzoquinone (4 and 5), do not promote pulping, presumably because of their low stability in pulping liquors.

*Address inquiries to this author.
We have found that \( \text{p-benzoquinone} \) compounds can be generated through oxidation of lignin and lignin-related compounds. We sought ways of building up the rings (homologizing) the simple methoxy substituted \( \text{p-benzoquinones} \) and \( \text{o-benzoquinones} \) to generate effective pulping catalysts from lignin. This paper addresses the homologization of benzoquinones related to lignin. A subsequent paper describes the catalytic activity of resulting products.

The Diels-Alder chemistry of some quinones is well known. As shown in Fig. 1, a homologous quinone synthesis, using the Diels-Alder reaction, involves three steps: the addition of a conjugated diene to a starting quinone, aromatization of the adduct, and oxidation of the resulting quinol to a quinone.

![Figure 1. Quinone synthesis using the Diels-Alder reaction.](image)

In order to achieve conversion of lignin-related benzoquinones to effective pulping catalysts (which normally have three
rings), we need to react both double bonds of the benzoquinones with dienes, even though one or more double bonds may be deactivated because of attached methoxyl groups. This paper describes the conditions needed to accomplish these homologizations. Yield optimization was not our main goal, but attempts to develop good yield procedures were addressed.

RESULTS AND DISCUSSION

Synthesis of Lignin Model Quinones

The basis for the selection of the benzoquinones studied (6-10) was related to our anticipated ability to generate these quinones from lignin or lignin-related compounds. Through oxidative cleavage of the lignin phenylpropane side chain, methoxy- and dimethoxy-p-benzoquinones (6 and 7) can be generated. However, the samples of 6 and 7 used in this study were synthesized from readily available commercial compounds.6,7

Oxidation of a phenolic hydroxyl group together with an adjacent methoxyl group in a lignin macromolecule would lead to generation of an o-benzoquinone. This quinone, of course, would remain attached in the lignin matrix via the propyl side chain. The three o-quinones selected for investigation have side chains which represent common features of the side chains actually found in lignin: an α-hydroxyl group, an α-carbonyl group, and a fully saturated carbon atom in the α-position.
It was found that 4-methyl-o-benzoquinone (8) could be obtained in low yield (14%) by the oxidation of 4-methylcatechol with silver (II) oxide; only small amounts of the compound could be isolated at one time. A second procedure involved the oxidation of 4-methylcatechol with o-chloranil. The yield from this reaction was much higher (64%), but the compound readily degraded after a few minutes under room conditions.

Because of their high reactivity, 4-acetyl- and 4-(1-hydroxyethyl)-o-benzoquinone (9 and 10) were not isolated but were generated, in the presence of a diene, through the sodium periodate oxidation of acetovanillone and o-methylvanillyl alcohol.

Because sodium periodate can also react with o-benzoquinones, the reactions were monitored by GC; ethylene glycol was added after an appropriate reaction time to consume any unreacted sodium periodate.

Diene selection was based on reactivity considerations, ease of product characterization, and possible industrial applications.

Reactions of Methoxy-o-Benzoquinone

Reaction of 6 with a 50% molar excess of 2,3-dimethyl-1,3-butadiene in methanol resulted in a 24% yield of 11 (Scheme 1).

Scheme 1
Enolization of 11 to a hydroquinone, 12, (79% yield) was achieved by treatment with acid.\textsuperscript{11} Hydroquinone 12 was oxidized to quinone 13 (37% yield) using ferric chloride in ethanol.\textsuperscript{11} The overall yield to quinone 13 was only 7%.

By performing the Diels-Alder reaction in acetic acid and directly oxidizing the product with chromic acid,\textsuperscript{12} we were able to by-pass several intermediates and obtain naphthoquinone 16 directly in 71% yield (Eq. 1). Unless noted otherwise, this single-pot procedure was employed in all subsequent reactions.

Attempts to obtain an anthraquinone structure by combining methoxy-p-benzoquinone with two units of diene were largely unsuccessful. When a 2.5 to 1 mole ratio of diene to dienophile was used and the reaction was run at a higher temperature, tetramethylanthraquinone (18) was observed, but only in trace amounts; the major product was still the naphthoquinone, 16.

When 6 and 14 were heated together in the absence of a solvent, only the enolized monoadduct, 12, was obtained (36% yield). This result is significant in that it indicates that following the addition of one unit of the diene, the adduct has a stronger tendency to enolize (11 to 12) than to add another diene unit. A one-step synthesis of an anthraquinone derivative starting with methoxy-p-benzoquinone, therefore, would appear to be difficult.

The above results also show the strong influence of the electron donating methoxyl group in the formation of the initial Diels-Alder adducts. Both steric and electronic factors may be
significant in causing reaction to occur much more readily at the unsubstituted double bond of the quinone.

Reaction of methoxy-\( p \)-benzoquinone with 1.5 equiv. of isoprene (15) gave 17a and 17b in 53% yield (Eq. 1). A complex product mixture (as indicated by gas chromatography) resulted when styrene was reacted with methoxy-\( p \)-benzoquinone in acetic acid. The reaction without a solvent gave a low (5%) yield of phenanthrenequinone 20 (Eq. 2).

Reactions of 2,6-Dimethoxy-\( p \)-benzoquinone (7)

Heating a 1.5 to 1.0 mixture of 2,3-dimethyl-1,3-butadiene and 7 in acetic acid, followed by oxidation with chromic acid, gave a product mixture which was approx. 90% naphthoquinone 16 and 10% tetramethylanthraquinone 18 (Eq. 1). When a 2.5 to 1 mole ratio of diene to dienophile was used, compounds related to 18 became the major products, but the yield was low.

Heating a mixture of 7 and 1.5 equiv. of isoprene at 114°C for 18 hr resulted in a 19% yield of the mixture of methyl-naphthoquinones 17a and 17b. A small percentage (approx. 6%) of dimethylanthraquinone (19a and 19b) was detected by GC/MS. When the mole ratio was increased to 2.5 to 1 and the reaction was run under more vigorous conditions (180°C, 24 hr), the precipitated product was entirely dimethylanthraquinone (25-30% yield).

These results indicate that the yields of the diadduct are greater from dimethoxy-\( p \)-benzoquinone than from methoxy-\( p \)-benzoquinone, although more vigorous reaction conditions are required. It is apparent that the methoxyl groups are liberated as methanol during the reaction; this gives rise to a quinone, rather than a
hydroquinone, intermediate and, therefore, favors further Diels-Alder reactions.

Only the starting material was recovered when 7 was heated with styrene even though the conditions were more vigorous than those employed for the corresponding reaction with 6. The additional methoxyl group is quite effective in blocking the addition of styrene to the compound.

Reactions of 4-Methyl-o-benzoquinone (8)

Because of the high reactivity of 8, the Diels-Alder reactions were performed on a freshly prepared, unpurified sample of the compound. Since the amount of 8 employed in the reactions was not determined, yields for the Diels-Alder reactions were based on the 4-methylcatechol used in its preparation.

Reaction of 8 with 2,3-dimethyl-1,3-butadiene was carried out at room temperature for 3 hr in chloroform using a diene to quinone mole ratio of at least 6 to 1 (based on the amount of 4-methylcatechol used).\textsuperscript{13} A 43\% yield of an o-naphthohydroquinone, 21, was obtained. Apparently the enolized form of the adduct is more stable than the quinone form, and the initially formed adduct is immediately converted to the hydroquinone form. Oxidation of 21 with o-chloranil in ether\textsuperscript{13} resulted in an 83\% yield of o-naphthoquinone 23 (Eq. 3).

\[
\begin{align*}
& \text{CH}_3 \quad \text{R}_1=\text{CH}_3 \quad 14, \text{R}_1=\text{CH}_3 \\
& 15, \text{R}_1=\text{H} \quad 21, \text{R}_1=\text{R}_2=\text{CH}_3 \\
& 22a, \text{R}_1=\text{H}, \text{R}_2=\text{CH}_3 \quad 22b, \text{R}_1=\text{CH}_3, \text{R}_2=\text{H} \quad 23, \text{R}_1=\text{R}_2=\text{CH}_3 \\
& 24a, \text{R}_1=\text{H}, \text{R}_2=\text{CH}_3 \quad 24b, \text{R}_1=\text{CH}_3, \text{R}_2=\text{H}
\end{align*}
\]

Reaction with isoprene was conducted in a similar manner but with a longer reaction time (17 hr). This resulted in a 32\% yield of a mixture of naphthohydroquinones, 22a and 22b. Attempts to
oxidize this mixture with o-chloranil to get dimethyl-o-naphtho-quinones 24a and 24b (Eq. 3) were unsuccessful, yielding only a dark brown tar. Reaction with styrene (20 hr) was similarly performed; the product was not isolated, but analytical data (GC/MS) indicated that the monoadduct, 25, had formed (Eq. 4).

\[ \text{CH}_3 \ \text{O+} \ \text{X-} \ \text{°} \]

\[ \text{O} \]

\[ \text{8} \]

\[ \text{CH}_3 \]

\[ \text{25} \]

Reactions of 4-Acetyl-o-benzoquinone (9)

Benzoquinone 9 was prepared through the sodium periodate oxidation of acetovanillone. This was done in the presence of a diene so that the Diels-Alder reaction would ensue before the o-quinone was consumed by other competing reactions. Reaction of 4-acetyl-o-benzoquinone with a large excess of 2,3-dimethyl-1,3-butadiene resulted in a red-orange precipitate which was identified as the phenanthrene derivative, 26 (Eq. 5).

\[ \text{CH}_3 \]

\[ \text{C=O} \]

\[ \text{OCH}_3 \]

\[ \text{14, } R_1=\text{CH}_3 \]

\[ \text{15, } R_1=\text{H} \]

\[ \text{NaIO}_4 \]

\[ \text{R}_1=R_2=R_3=R_4=\text{CH}_3 \]

\[ \text{R}_1=R_3=\text{H}, \ R_2=R_4=\text{CH}_3 \]

\[ \text{R}_1=R_4=\text{H}, \ R_2=R_3=\text{CH}_3 \]

\[ \text{R}_2=R_3=\text{H}, \ R_1=R_4=\text{CH}_3 \]

\[ \text{R}_2=R_4=\text{H}, \ R_1=R_3=\text{CH}_3 \]

\[ \text{26, } R_1=R_2=R_3=R_4=\text{CH}_3 \]

\[ \text{27a, } R_1=R_3=\text{H}, \ R_2=R_4=\text{CH}_3 \]

\[ \text{27b, } R_1=R_4=\text{H}, \ R_2=R_3=\text{CH}_3 \]

\[ \text{27c, } R_2=R_3=\text{H}, \ R_1=R_4=\text{CH}_3 \]

\[ \text{27d, } R_2=R_4=\text{H}, \ R_1=R_3=\text{CH}_3 \]

\[ \text{29a, } R_1=R_3=\text{H}, \ R_2=R_4=\text{CH}_3 \]

\[ \text{29b, } R_1=R_4=\text{H}, \ R_2=R_3=\text{CH}_3 \]

\[ \text{29c, } R_2=R_3=\text{H}, \ R_1=R_4=\text{CH}_3 \]
The maximum yield of precipitate obtained from this reaction (using a time of 4 hr) was 29%. It is likely, however, that the yield was even higher since some of the product remained dissolved in the reaction medium. Unfortunately, the reactivity of this compound in chloroform prevented extraction to obtain additional product and determine the true yield.

Oxidation of 26 with chromic acid resulted in a 43% yield of the tetramethylphenanthrenequinone, 28. The fact that 28 was also obtained by simply adding 26 to chloroform indicates that 26 has a strong tendency to form the fully aromatized phenanthrenequinone.

The reaction of 4-acetyl-o-benzoquinone with isoprene was performed in a similar manner. The product obtained (14% yield) was identified as phenanthrenediol 27 and is most likely a mixture of the four possible isomers, 27a-27d. Oxidation of 27 with chromic acid resulted in a 70% yield of the dimethylphenanthrenequinone, 29, which is again an isomeric mixture. Isolation and analysis of the 27 isomers were hampered by their strong tendency to form fully aromatized compounds.

The formation of the phenanthrene derivatives 26-29 is significant in that these compounds can only result through elimination of the acetyl side chain. A similar side chain elimination might be expected if an analogous reaction was run using an actual oxidized lignin preparation. A possible mechanism for the side chain loss might involve loss of acetic acid from a hydration carbonyl group, as shown in Eq. 6.

\[
\begin{array}{c}
\text{R} \rightarrow \text{R}_2 \\
\text{O} \rightarrow \text{R}_1 \\
\text{OH} \rightleftharpoons \text{R}_3 \\
\text{-CH}_2\text{COH}
\end{array}
\]

An attempt was made to form the Diels-Alder adduct between 4-acetyl-o-benzoquinone and styrene by following the same procedure used for reactions with 2,3-dimethyl-1,3-butadiene and iso-
prene. The only material isolated from the reaction mixture was the starting compound, acetovanillone. Apparently styrene suppresses the formation of the quinone from acetovanillone.

Reactions of 4-(1-Hydroxyethyl)-o-benzoquinone (10)

α-Methylvanillyl alcohol was treated with sodium periodate in an attempt to prepare o-benzoquinone 10. The reaction was performed in the presence of a large excess of 2,3-dimethyl-1,3-butadiene. A mixture of products resulted, of which an o-naphthoquinone and an o-phenanthraquinone (28) indicated 10 had been produced. However, the major (14% yield) isolated product was 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16). In order to get this product, the 1-hydroxyethyl side chain must have been lost, methoxy-p-benzoquinone generated, and diene addition occurred. Side chain loss from guaiacyl compounds containing α-hydroxyl groups is possible during sodium periodate oxidation.14

The reaction of the sodium periodate-oxidized α-methylvanillyl alcohol with isoprene was performed in a similar manner. A 6% yield of an isomeric mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinone (17) was obtained. An attempt to form the Diels-Alder adduct between 4-(1-hydroxyethyl)-o-benzoquinone and styrene was unsuccessful.

Combined Oxidation/Diels-Alder Reactions

An attempt was made to combine an oxidative technique capable of generating quinones from lignin and lignin-derived compounds,2 with a Diels-Alder reaction. Oxidation to quinones in the presence of a diene might be effective in trapping shortlived quinones, such as o-quinones. The combination of two steps into one operation might also be advantageous from an economic standpoint in the industrial application of this work.

Some degree of success was achieved with the use of potassium nitrodisulfonate (Fremy's salt) as an oxidant. Appropriate reaction conditions for a combined Fremy's salt oxidation/Diel-Alder
reaction were established by first using the model compound, \( \alpha \)-methylvanillyl alcohol, together with 2,3-dimethyl-1,3-butadiene. The diene was added just prior to the addition of the Fremy's salt. After holding at room temperature for a period long enough to achieve oxidation of the alcohol to methoxy-\( p \)-benzoquinone, the mixture was heated to initiate the Diels-Alder reaction. After product isolation and chromic acid oxidation, a 26% yield of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16) was obtained.

A hardwood lignin sample was subjected to the same set of conditions, using both dimethylbutadiene and isoprene. Reactions were conducted both with and without the chromic acid oxidation step. The solutions obtained after precipitation of the lignin were extracted with chloroform to determine if quinone structures were, in fact, being generated. In the dimethylbutadiene reactions, GC/MS analysis showed detectable levels of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16), as well as partially aromatized versions of the compound. In the isoprene reactions, the mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinones (17) was detected at very low levels.

SUMMARY AND CONCLUSIONS

The results of this investigation show that a large number of Diels-Alder reactions are possible with lignin-derived quinones. Simple \( o \)- and \( p \)-benzoquinones can be converted to naphthoquinone, anthraquinone, and phenanthrenequinone products and related derivatives. Yields from reactions using dimethylbutadiene and isoprene can be high; styrene, however, was not found to be a very effective reactant.

Reactions of the methoxy-substituted \( p \)-benzoquinones show that the unsubstituted double bond is more reactive than the methoxylated double bond, but the latter will undergo Diels-Alder reaction with subsequent elimination of methanol. The strong ten-
dency of the tetrahydronaphthoquinone product from methoxy-\(p\)-benzoquinone to aromatize to a hydroquinone structure prevents further Diels-Alder reactions. Thus, methoxy-\(p\)-benzoquinone is less desirable than 2,6-dimethoxy-\(p\)-benzoquinone if anthraquinone products are desired.

Reactions of the \(o\)-benzoquinones shows that the side chain in the 4-position may be eliminated if it contains the appropriate functional group. The loss of side chains containing \(\alpha\)-hydroxyl groups and \(\alpha\)-carbonyl groups from the lignin model quinones suggests that similar reactions could occur on quinones generated directly from lignin.

Although little attempt was made to optimize product yields, in general, better yields were observed from Diels-Alder reactions of \(p\)-benzoquinones than from \(o\)-benzoquinones. In the case of potassium nitrosodisulfonate, it was possible to combine the oxidation and Diels-Alder steps. The yield of naphthoquinone from the oxidation of \(\alpha\)-methylvanillyl alcohol, however, was only about half of what was achieved through two separate steps. The yield of higher order quinones directly from lignin samples was also quite low.

Overall, the use of Diels-Alder reactions to convert lignin or lignin-related benzoquinones to higher order quinones shows much promise. Because compounds such as anthraquinone are known to catalyze delignification reactions, this finding has important implications in the area of using lignin or lignin-derived compounds in pulping processes.\(^3\)

**EXPERIMENTAL**

Melting points were obtained using a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. NMR spectra were recorded on a Jeol FX 100 spectrometer using TMS as an internal reference. Parentheses following the signals indicate the splitting patterns (s = singlet, d = doublet, t = triplet, q =
quartet, m = multiplet, br = broad signal), integration areas, and signal assignments. Mass and NMR spectra were obtained for many compounds indicated in this section but are omitted here because the compounds are "known." The spectra were in complete accord with the assigned structures and can be found in the Ph.D. thesis of author J.C.W. Proton NMR spectra are included when observed and literature melting points differed substantially.

Gas chromatographic (GC) analyses were either done on a Hewlett-Packard 5890A GC or combined with mass spectrometric (MS) analyses and performed on a Hewlett-Packard 5985B GC/MS system. The GC/MS system employed helium (30 mL/min) as the carrier gas, a jet separator at 275°C, a source temperature of 200°C and an ionization voltage of 70 eV. On both instruments a 6-ft, 1/4-in. glass column packed with 3% silicone OV-17 on 100/120 chromosorb W-HP was used.

**Synthesis of Lignin Model Quinones**

Methoxy-p-benzoquinone, 6. The procedure of Erdtman was used; a 66% yield was obtained: m.p. 143.0-144.5°C [lit.6,15 m.p. 143-144°C, 144-145°C].

2,6-Dimethoxy-p-benzoquinone, 7. The procedure of Matsumoto and Kobayashi7 was used; a 66% yield was obtained: m.p. 253.0-254.0°C.

4-Methyl-α-benzoquinone, 8. A 14% yield was obtained through the procedure of Bailey and Dence:8 m.p. 74.5-75.5°C [lit.8 m.p. 74-76°C]. Larger, but less stable, quantities of 8 were synthesized through the procedure of Ansell, et al.;9 the yield was 64%: m.p. 72.5-74.5°C.

4-Acetyl-α-benzoquinone, 9, and 4-(1-hydroxyethyl)-α-benzoquinone, 10. The procedure of Imsgard, Falkehag and Kringstad19 was used. Appropriate reaction times were determined through GC analyses of samples which were periodically withdrawn; these indicated the complete reaction of acetovanillone and α-methylvanillyl alco-
hol in approx. 80 min and 1 min, respectively. Because of their reactivity, 9 and 10 were not isolated.

Synthesis of Diels-Alder Adducts

4a,5,8,8a-Tetrahydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone, 11. The procedure of Ansell, Nash, and Wilson\textsuperscript{11} was used except that reaction was at 45°C for 18.5 hr; a 24% yield was obtained: m.p. 133.5-134.5°C [lit.\textsuperscript{11} m.p. 140.0-141.5°C]; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \delta 1.62 (s, 6, 6- and 7-CH\textsubscript{3}), 2.0-2.5 (br, 4, 5- and 8-H\textsubscript{2}), 3.0-3.3 (br, 2, 4a- and 8a-H), 3.78 (s, 3, OCH\textsubscript{3}), 5.87 (s, 1, 3-H).

5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinol, 12. Compound 11 (0.50 g) was dissolved in approx. 2 mL of boiling glacial acetic acid. When 2 drops of concd. HCl was added, a white precipitate immediately formed. This was recrystallized from 95% ethanol to give 0.39 g (79%) of 12: m.p. 212-214°C [lit.\textsuperscript{11} m.p. 209-211°C]. Compound 12 was also obtained by the reaction of 0.20 g methoxy-p-benzoquinone and 0.41 mL of 2,3-dimethyl-1,3-butadiene, without a solvent, at 110°C for 18 hr. Recrystallization from acetic acid and washing with a little cold methanol resulted in 0.11 g (36%) of 12: m.p. 210.5-213.0°C.

5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone, 13. Through the procedure of Ansell, Nash, and Wilson,\textsuperscript{11} a 37% yield was obtained: m.p. 133.0-135.0°C [lit.\textsuperscript{11} m.p. 151-153°C]; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \delta 1.72 (s, 6, 6- and 7-CH\textsubscript{3}), 3.00 (s, 4, 5- and 8-H\textsubscript{2}), 3.81 (s, 3, 2-OCH\textsubscript{3}), 5.86 (s, 1, 3-H).

2-Methoxy-6,7-dimethyl-1,4-naphthoquinone, 16. This and several of the following procedures are adaptations of the procedure of Fieser;\textsuperscript{12} glacial acetic acid was used as the reaction medium, and aromatization was achieved through chromic acid oxidation. Methoxy-p-benzoquinone (0.50 g) and 2,3-dimethyl-1,3-butadiene (0.63 mL) were added to 23.0 mL of glacial acetic acid and heated at 45°C for 18.5 hr. A chromic acid solution consisting of 1.85 g of Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}.2H\textsubscript{2}O and 0.093 mL of H\textsubscript{2}SO\textsubscript{4} in 1.16 mL of H\textsubscript{2}O was then added, and the temperature was kept at approx. 67°C for 1 hr.
Upon addition of this mixture to approx. 100 mL of a 50% ice/water mixture, the product precipitated; it was washed several times with cold water and then dried over P$_2$O$_5$ to give 0.56 g (71%) of 16: m.p. 166.7-167.0°C [lit. 16 m.p. 167-168°C]. Compound 16 was also obtained through the reaction of 0.20 g 2,6-dimethoxy-p-benzoquinone and 0.20 mL of 2,3-dimethyl-1,3-butadiene in 3.0 mL of glacial acetic acid at 115°C for 17.5 hr, followed by chromic acid oxidation.

2-Methoxy-6- and 7-methyl-1,4-naphthoquinone, 17a and 17b. Methoxy-p-benzoquinone (0.50 g) and isoprene (0.54 mL) were added to 23.0 mL of glacial acetic acid and heated at 100°C for 18.5 hr. Treatment with chromic acid and product isolation were identical to those used for 16. This resulted in 0.39 g (53%) of a mixture of the isomers 17a and 17b: $^1$H-NMR (CDCl$_3$) $\delta$ 2.48 (s, 3, 6- or 7-CH$_3$), 3.90 (s, 3, 2-OCH$_3$), 6.13 (s, 1, 3-H), 7.44-7.57 (m, 1, 6- or 7-H), 7.85-8.04 (m, 2, 5- & 8-H); $^{13}$C-NMR (CDCl$_3$) ppm 21.6, 21.8 (6- and 7-CH$_3$), 56.2 (2-OCH$_3$), 109.4, 109.5 (3-C), 126.0, 126.2, 126.5, 126.6 (5- and 8-C), 128.5, 129.5, 130.7, 131.6 (4a- and 8a-C), 133.6, 134.6, 144.0, 145.2 (6- and 7-C), 159.9, 160.1 (2-C), 179.3, 179.8 (1-C), 184.2, 184.5 (4-C). The isomeric mixture of compounds 17a and 17b was also obtained through the reaction of 0.20 g 2,6-dimethoxy-p-benzoquinone with 0.18 mL of isoprene in 3.0 mL of glacial acetic acid at 114°C for 18 hr.

2,3,6,7-Tetramethylanthraquinone, 18. Compound 18 was obtained as a by-product of several reactions; it was not isolated. The highest yield was obtained through the reaction of 2,6-dimethoxy-p-benzoquinone with 2,3-dimethyl-1,3-butadiene to produce 16. Evidence for 18 was obtained through GC/MS: MS, m/z (rel. intensity), 264 (M$^+$,100), 249 (38), 236 (12), 221 (27), 193 (14), 191 (13), 178 (17), 103 (10), 40 (13).
2,6- and 2,7-Dimethylanthraquinone, 19a and 19b. Compounds 19a and 19b were obtained as by-products of the reaction between 2,6-dimethoxy-p-benzoquinone and isoprene to give compounds 17a and 17b as described above. They were the only products when the same reaction was run under more severe conditions: 0.20 g of 2,6-dimethoxy-p-benzoquinone and 0.30 mL of isoprene were added to 3.0 mL of glacial acetic acid and heated at 180°C for 24 hr. This was followed by oxidation with chromic acid and precipitation of the product with ice/water as described above. The yield of this reaction was estimated at 25-30\%: \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \( \delta \) 2.52 (s, 3, 2- and 6- or 7-CH\textsubscript{3}), 7.55 (d with fine splitting, 1, J = 8 Hz, 3- and 6- or 7-H), 8.07 (s with fine splitting, 1, 1- and 5- or 8-H), 8.16 (d, 1, J = 8 Hz, 4- and 5- or 8-H); MS, m/z (rel. intensity), 236 (M\textsuperscript{+}, 100), 221 (32), 208 (26), 207 (12), 193 (14), 179 (16), 178 (26), 165 (53), 89 (27), 76 (10), 63 (15). The additional splitting observed in the \textsuperscript{1}H-NMR spectrum is taken as evidence for the formation of an isomeric mixture of compounds 19a and 19b. This was confirmed when recrystallization from methanol resulted in partial separation of the product into two sets of crystals, noticeably different in appearance and melting point.

Compounds 19a and 19b were also obtained through the reaction of the isomeric mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (compounds 17a and 17b). The naphthoquinone mixture (0.100 g) was added to 3.00 mL of acetic acid and 0.074 mL of isoprene and heated at 150°C for 24 hr. This was followed by chromic acid oxidation and resulted in a reaction yield of 0.022 g (19\%).

3-Methoxyphenanthrene-1,4-quinone, 20. The procedure of Inouye and Kakisawa\textsuperscript{17} was used to give a 5\% yield: m.p. 153-157°C [lit.\textsuperscript{16} 168-169°C]; \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \( \delta \) 3.91 (s, 3, 3-OCH\textsubscript{3}), 6.09 (s, 1, 2-H), 7.49-9.50 (6, 5-H to 10-H).

5,8-Dihydro-4,6,7-trimethylnaphthalene-1,2-diol, 21. The procedure of Ansell, et al.\textsuperscript{13} was used; the yield was 43\% (based on 4-methylcatechol): m.p. 152.5-153.5°C [lit.\textsuperscript{13} m.p. 149-151°C].
5,8-Dihydro-4,6- and 4,7-dimethylnaphthalene-1,2-diol, 22a and 22b. The same procedure that was used to produce 21 was used except that 10 mL of isoprene was used, and the reaction time was 17 hr. Crystallization was achieved from toluene and resulted in 0.92 g (32% based on 4-methylcatechol) of 22. Recrystallization from toluene resulted in light pink crystals: m.p. 149.4-149.5°C; \( ^1H\)-NMR (acetone-d\(_6\)) \( \delta \) 1.78, 1.79 (s, 3, 6- or 7-CH\(_3\)), 2.05 (s, 3, 4-CH\(_3\)), 3.0-3.3 (br, 4, 5- and 8-H\(_2\)), 5.55 (m, 1, 6- or 7-H), 6.56 (s, 1, 3-H), 7.30 (br s, 2, 1- and 2-OH); MS, 190 m/z (100% rel. intensity) indicative of the molecular ion. Several of the \(^{13}\)C-NMR signals were close together in the aromatic region and were therefore difficult to assign; signals were observed to occur in pairs, however, indicating that a mixture of isomers was produced.

4,6,7-Trimethyl-1,2-naphthoquinone, 23. The procedure of Ansell, et al.\(^{14}\) was used; an 83% yield of orange crystals which decomposed at around 112°C was obtained: [lit.\(^{13}\) indicates decomposition at 120°C]; \( ^1H\)-NMR (CDCl\(_3\)) \( \delta \) 2.33, 2.35, 2.36 (s, 9, 4-, 6-, and 7-CH\(_3\)), 6.29 (q, 1, J = 1 Hz, 3-H), 7.24 (s, 1, 5-H), 7.87 (s, 1, 8-H).

4a,9,10,10a-Tetrahydro-4-methylphenanthrene-1,2-quinone, 25. The procedure for the preparation of 21 was employed except that 10 mL of styrene was used and the reaction time was 20 hr. Crystallization of the oil remaining after solvent evaporation was unsuccessful. Analysis of the oil by GC/MS, however, indicated that the monoadduct had formed: MS, m/z (rel. intensity), 226 (M\(^+\), 15), 171 (13), 170 (94), 156 (13), 155 (100), 154 (11), 153 (14), 128 (15), 115 (13), 92 (12), 91 (58), 77 (25), 65 (10), 51 (12).

1,4-Dihydro-2,3,6,7-tetramethylphenanthrene-9,10-diol, 26. Immediately following the addition of 0.90 g sodium periodate in 10 mL of distilled water to 0.70 g of acetovanillone dissolved in 10 mL of glacial acetic acid, 10 mL of 2,3-dimethyl-1,3-butadiene was added. The reaction vessel was kept in the dark with stirring for 38
4 hr. At that time 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The red-orange precipitate which formed was filtered and rinsed twice with cold methanol to give 0.32 g (29% based on acetovanillone) of 26. Recrystallization was achieved from methanol. Melting with some decomposition to a dark brown liquid took place at approx. 260°C.

Attempts to analyze 26 were hampered by its reactivity; $^1$H-NMR (CDCl$_3$) obtained in less than 2 min after dissolution showed $\delta$ 1.73 (s, 5, 6- and 7-CH$_3$), 2.26, 2.32 (s, d, 7, 2- and 3-CH$_3$), 2.9-3.1 (br, 4, 5- and 8-H$_2$), 7.10, 7.51 (s, 2, 9- and 10-OH), 7.72, 7.76 (s, 2, 1- and 4-H). Although the integration is not correct for the methyl groups, it is very likely that this is due to the fact that the compound had already started conversion to the fully aromatized phenanthrenequinone.

1,4-Dihydro-2,6-, 2,7-, 3,6-, and 3,7-dimethylphenanthrene-9,10-diol, 27. The procedure used to form 27 was identical to that used to produce 26 except that 10 mL of isoprene was used; raw yield was 0.14 g (14% based on acetovanillone): $^1$H-NMR (CDCl$_3$) obtained shortly after dissolution showed $\delta$ 1.83 (s, 3, 6- or 7-CH$_3$), 2.39, 2.45 (s, d, 3, 2- or 3-CH$_3$), 2.9-3.3 (br, 4, 5- and 8-H$_2$), 5.55 (m, 1, 6- or 7-H), 7.2-8.0 (m, 5, aromatic H & OH).

2,3,6,7-Tetramethylphenanthrene-9,10-quinone, 28. Compound 26 (0.10 g) was dissolved in 10 mL of glacial acetic acid and then oxidized and isolated as described above to give 0.042 g (43%) of 28: m.p. 250-254°C (with some decomposition); $^1$H-NMR (CDCl$_3$) $\delta$ 2.27 (s, 6, 2- and 7-CH$_3$) 2.35 (s, 6, 3- and 6-CH$_3$), 7.55 (s, 2, 4- and 5-H), 7.78 (s, 2, 1- and 8-H).

2,6-, 2,7-, and 3,6-Dimethylphenanthrene-9,10-quinone, 29. Compound 27 was oxidized to 29 with chromic acid by following the same procedure described above for the oxidation of 26 to 28. From 0.135 g of 27, 0.093 g (70%) of 29 was obtained: $^1$H-NMR (CDCl$_3$) $\delta$ 2.39 (s, 2, 2- and 7-CH$_3$), 2.46 (s, 4, 3- and 6-CH$_3$), 7.1-8.0 (m, 6, aromatic H).
Reaction of Compound 10 with 2,3-Dimethyl-1,3-butadiene. Immediately following the addition of 0.64 g of sodium periodate in 7 mL of distilled water to 0.50 g of α-methylvanillyl alcohol dissolved in 7 mL of glacial acetic acid, 7 mL of 2,3-dimethyl-1,3-butadiene was added. After 1 min, 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The reaction was then allowed to proceed in the dark with stirring. Reaction at room temp. for 3 hr resulted in 0.093 g of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16, 14% yield based on α-methylvanillyl alcohol). A second reaction run at 45°C for 18.5 hr. generated a brown residue; 0.034 g was filtered from the reaction mixture: m.p. 205-209°C; MS, m/z (rel. intensity), 214 (100), 199 (59), 186 (57), 171 (36), 157 (15), 143 (28), 142 (27), 141 (47), 128 (35), 115 (35), 84 (16), 77 (19), 51 (17), 44 (48). The latter compound was assumed to be 6,7-dimethyl-4-ethylene-1,2-naphthoquinone. Oxidation of the filtrate with chromic acid resulted in a mixture of compounds including the above compound, 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16), and 2,3,6,7-tetramethylphenanthrene-9,10-quinone (28).

Reaction of Compound 10 with Isoprene. The procedure used for the reaction with isoprene was identical to that used for the reaction with 2,3-dimethyl-1,3-butadiene. Reaction at room temperature for 4 hr generated 0.035 g of a mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinone (17); the yield was 6%, based on α-methylvanillyl alcohol).

Combined Oxidation/Diels-Alder Reactions

Reaction of α-methylvanillyl alcohol. A 1.00-mmole sample of α-methylvanillyl alcohol\textsuperscript{2} was dissolved in 10 mL of ethylene glycol monomethyl ether and cooled to approx. 0°C in an ice bath. Under a stream of nitrogen, potassium nitrosodisulfonate (Fremy's salt, 3.0 mmole) was added to 20.0 mL of a 0.2M KH\textsubscript{2}PO\textsubscript{4}/K\textsubscript{2}HPO\textsubscript{4} buffer solution (pH 6.0) which had also been cooled in an ice bath. The diene (2,3-dimethyl-1,3-butadiene, 1.0 mL) was then
added to the α-methylvanillyl alcohol solution, followed immedi-
diately by the dropwise addition of the Fremy's salt, using fairly
vigorous stirring and a stream of nitrogen to blanket the reac-
tion.

After the addition of the Fremy's salt, the reaction mixture
was removed from the ice bath and allowed to come to room temper-
ature. After 2 hr, the reaction residue was suction filtered
through a fine sintered-glass Buchner funnel and rinsed with 25 mL
of glacial acetic acid. An additional 1 mL of diene was added to
the filtrate, and the temperature was raised to 45°C for 18 hr.
The mixture was then added to ice/water to precipitate the Diels-
Alder addition product. This material was washed with cold water
and transferred to a flask with 10 mL of glacial acetic acid for
chromic acid oxidation. The addition of the oxidized solution to
ice/water caused the precipitation of the final product; 0.26
mmole (26% yield) of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone
(16) was obtained.

Reaction of lignin. The above procedure was repeated with a lig-
nin sample isolated from the acid-catalyzed pulping of aspen with
ethanol; however, the mixture obtained after the 2-hr Fremy's
salt oxidation was not filtered, and the additional 1 mL of diene
was not added. Both dimethylbutadiene and isoprene were used with
400 mg of lignin. Lignin products obtained both with and without
chromic acid oxidation were isolated through the use of centrifu-
gation and freeze dried.

The liquid obtained after precipitation of the lignin was ex-
tracted with CHCl₃ (4 X 40 mL), and the extract was washed with
saturated NaHCO₃ solution (2 X 40 mL) and water (3 X 40 mL), and
dried over anhydrous Na₂SO₄; in a few cases the entire reaction
mixture was extracted. The extract was then evaporated under re-
duced pressure and analyzed by GC/MS.

Analyses of the CHCl₃ extracts of the dimethylbutadiene
reactions both before and after chromic acid oxidation gave
evidence of the production of 2,6-dimethoxy-p-benzoquinone (7)
and 2-methoxy-6,7-dimethyl-1,4-napthoquinone (16). Analyses of the CHCl₃ extracts of the isoprene reactions before and after chromic acid oxidation also gave evidence of the generation of 2,6-dimethoxy-p-benzoquinone as well as 2-methoxy-6- and 7methyl-1,4-naphthoquinone (17). One compound, appearing to have a molecular weight of 238, could indicate the formation of the isoprene diadduct; MS, m/z (rel. intensity), 238 (43), 183 (100), 182 (58), 167 (20), 139 (15), 123 (10), 69 (14). This compound appeared as a reaction product before chromic acid oxidation after both 112 and 185°C reactions but was much more predominant at the higher temperature.

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REFERENCES

LIGNIN-DERIVED QUINONES AS PULPING ADDITIVES

John C. Wozniak, Donald R. Dimmel,* and Earl W. Malcolm
Institute of Paper Science and Technology
Atlanta, GA 30318

ABSTRACT

Quinones, which may be generated from lignin and lignin-related materials, and their Diels-Alder derivatives were evaluated as delignification promoters. Compared to anthraquinone at a 0.1% addition level, benzoquinones and oxidized lignin showed little or no effect. However, some naphthoquinones were found effective at higher addition levels, and a mixture of dimethyl-anthraquinone isomers was found to be superior to anthraquinone. The substituted anthraquinones, phenanthrenequinones, and fully aromatized naphthoquinones appear to function in a reduction/oxidation cycle such as that proposed for anthraquinone.

INTRODUCTION

Quinone pulping additives, such as anthraquinone (AQ), can be used to increase pulping rates, improve selectivity, and save energy. The demand for these additives would increase if they could be obtained at low costs, such as from inexpensive lignin. Various oxidative techniques have been used to generate o- and p-quinone structures from lignin and lignin-derived materials.  

The simple p-benzoquinones 1 and 2 and lignin model o-benzoquinones 3-5 can be converted (via Diels-Alder reactions) to higher order quinones, such as naphthoquinones, anthraquinones, and phenanthrene-9,10-quinones.  

*Address inquiries to this author.
quinones and Diels-Alder enhanced derivatives of these quinones would be effective pulping additives.

The lignin-derived quinones and Diels-Alder homologs described herein generally have not been tested for pulping activity. These compounds are substituted with a methoxyl group and/or several methyl groups. They were evaluated in two ways: (a) a brief study was made to try to determine if the compounds function through a redox cycle such as that proposed for AQ, and (b) the effectiveness of the compounds as delignification promoters was determined from pulping experiments. Also tested were samples of directly oxidized lignin which should contain O- and p-quinone structures attached to the polymer.

RESULTS AND DISCUSSION

Redox Behavior

Quinone pulping additives generally operate through a redox cycle. For anthraquinone in alkali, this means cycling from the light yellow oxidized AQ form to the deep red reduced anthrahydroquinone dianion (AHQ\(^{-2}\)) form. The oxidizing agent and reducing agent during pulping are carbohydrates and lignin. Exposing AHQ\(^{-2}\) solutions to air (oxygen) causes oxidation back to AQ.

The lignin-related quinones, 1-3, and Diels-Alder homologs 6-16 (see Table 1) were taken through two cycles of heating in 1M NaOH with glucose and air exposure, and color changes were noted. Also, gas chromatography was used to try to detect the starting compound after the two reduction/oxidation cycles.
The test results from p-benzoquinones 1 and 2, and o-benzoquinone 3 were inconclusive. Because of their high reactivity in alkali, o-benzoquinones 4 and 5 could not be evaluated. However, p-naphthoquinone derivatives, 6-9, and o-naphthoquinone derivatives, 10 and 11, all displayed definite color changes when taken through the redox cycle test. Only in the cases of compounds 8 and 9 were the starting compounds detected after cycling.

Phenanthrenequinone derivatives 12-15 showed definite color cycles. GC analysis, however, showed that compound 13 was obtained after starting with both 12 and 13 and that 15 was obtained after starting with both 14 and 15. The ready conversion of phenanthrenediols 12 and 14 to fully aromatized phenanthrenequinones 13 and 15, respectively, was noted in the isolation of these compounds.2

When the isomeric mixture of dimethylanthraquinones (16) was tested, a definite color cycle was observed. The starting compounds were found to be the major components of a chloroform extract analyzed by GC.

In summary, color changes indicate that a redox cycle does operate for naphthoquinone compounds. Both color changes and GC analyses indicate that phenanthrenequinone and anthraquinone compounds operate in a redox cycle like AQ. It is likely, however, that the fully aromatized phenanthrenequinones rather than their partially hydrogenated diol derivatives actually cycle between reduced and oxidized forms.

**Evaluation of Compounds as Pulping Additives**

The effectiveness of the synthesized compounds as delignification promoters was determined through laboratory soda pulping of southern pine. The effects of the additives on yield and kappa number were compared to corresponding effects of AQ.

**Variability in Experimental Results**

It should be pointed out that it was not a goal of this study to establish error limits using a strict statistically designed
### TABLE 1

Diels-Alder homologs of lignin-related quinones.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type&lt;sup&gt;a&lt;/sup&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;</th>
<th>R&lt;sub&gt;6&lt;/sub&gt;</th>
<th>R&lt;sub&gt;7&lt;/sub&gt;</th>
<th>Hydro&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Naphthoquinones:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Q</td>
<td>--</td>
<td>--</td>
<td>Me</td>
<td>Me</td>
<td>4a,5,8,8a</td>
</tr>
<tr>
<td>7</td>
<td>HQ</td>
<td>--</td>
<td>--</td>
<td>Me</td>
<td>Me</td>
<td>5,8</td>
</tr>
<tr>
<td>8</td>
<td>Q</td>
<td>--</td>
<td>--</td>
<td>Me</td>
<td>Me</td>
<td>--</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Q</td>
<td>--</td>
<td>--</td>
<td>(H)</td>
<td>(Me)</td>
<td>--</td>
</tr>
<tr>
<td>o-Naphthohydroquinones:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>HQ</td>
<td>--</td>
<td>--</td>
<td>Me</td>
<td>Me</td>
<td>5,8</td>
</tr>
<tr>
<td>11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>HQ</td>
<td>--</td>
<td>--</td>
<td>(H)</td>
<td>(Me)</td>
<td>5,8</td>
</tr>
<tr>
<td>Phenanthrene-9,10-quinones:</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>HQ</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>1,4</td>
</tr>
<tr>
<td>13</td>
<td>Q</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>--</td>
</tr>
<tr>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>HQ</td>
<td>(H)</td>
<td>(Me)</td>
<td>(H)</td>
<td>(Me)</td>
<td>1,4</td>
</tr>
<tr>
<td>15&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Q</td>
<td>(H)</td>
<td>(Me)</td>
<td>(H)</td>
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</tr>
<tr>
<td>Anthraquinones:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Q</td>
<td>(H)</td>
<td>(Me)</td>
<td>(H)</td>
<td>(Me)</td>
<td>--</td>
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<tr>
<td>AQ</td>
<td>Q</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>--</td>
</tr>
</tbody>
</table>

<sup>a</sup>Q = Quinone; HQ = Hydroquinone (the reduced, aromatic version of the quinone)  
<sup>b</sup>Hydro refers to saturated carbon positions - all other ring carbons are unsaturated.  
<sup>c</sup>Parentheses indicate isomers; substituents could be reversed.
set of experiments. Compound evaluation was of a screening nature to identify those compounds which might act as pulping promoters. Once potentially good materials were identified, more detailed experiments were carried out.

However, it was possible to estimate the variation involved in the laboratory pulping experiments which were repeated several times. Table 2 shows the kappa numbers and yields obtained when AQ was used at the 0.1% addition level in four separate experiments and when no additive was used in six experiments. Included in the table are the mean values and standard deviations for each set of data.

These data indicate that, at the 95% confidence level, AQ at the 0.1% addition level produces a kappa number of 37.1 ± 1.6 and a pulp yield of 45.8 ± 0.5; with no additive, a kappa number of 81.9 ± 4.2 and a pulp yield of 49.2 ± 0.9 is obtained. Similar ranges (4-5% in kappa number, 1-2% in yield) might be expected with other additives and when these additives are compared to each other as a group.

Compound Evaluation

The results obtained in laboratory pulping are presented in Table 3. The total fiber yield was separated into its lignin and carbohydrate components. The effect of the additives on kappa number generally is clear; the effect on carbohydrate yield is not as apparent.

The benzoquinone compounds are not shown in the table, but samples 1 and 2 were tested and were found to be ineffective promoters of delignification. The highly reactive 4-acetyl- and 4-(1-hydroxyethyl)-o-benzoquinone compounds (4 and 5) could not be evaluated. Of course, their high reactivity rules out their possible use as pulping promoters.

Some activity, indicated by a decrease in kappa number, was demonstrated by p-naphthoquinone-related compounds 6-9. Because pulping activities were not outstanding and synthetic yields were
**TABLE 2**

Standard deviation of kappa number and % yield in several pulping experiments.

<table>
<thead>
<tr>
<th>Anthraquinone</th>
<th>No Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa No.</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>Mean</td>
<td>37.1</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td></td>
<td>Std. Dev.</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
</tr>
</tbody>
</table>

**TABLE 3**

Evaluation of compounds as pulping additives.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Addition Level (%)</th>
<th>Kappa No.</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>--</td>
<td>81.9</td>
<td>43.2</td>
</tr>
<tr>
<td>NQs 6</td>
<td>0.2</td>
<td>72.7</td>
<td>42.7</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>67.4</td>
<td>42.7</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>70.3</td>
<td>42.8</td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>69.0</td>
<td>43.2</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>77.0</td>
<td>42.6</td>
</tr>
<tr>
<td>11</td>
<td>0.2</td>
<td>72.5</td>
<td>42.8</td>
</tr>
<tr>
<td>PQs 12</td>
<td>0.1</td>
<td>66.5</td>
<td>42.0</td>
</tr>
<tr>
<td>13</td>
<td>0.1</td>
<td>68.3</td>
<td>42.5</td>
</tr>
<tr>
<td>14</td>
<td>0.1</td>
<td>73.5</td>
<td>42.3</td>
</tr>
<tr>
<td>15</td>
<td>0.1</td>
<td>74.8</td>
<td>42.6</td>
</tr>
<tr>
<td>AQs 16</td>
<td>0.1</td>
<td>31.6</td>
<td>43.6</td>
</tr>
<tr>
<td>AQ</td>
<td>0.1</td>
<td>37.1</td>
<td>43.3</td>
</tr>
<tr>
<td>AQ</td>
<td>0.2</td>
<td>36.3</td>
<td>43.2</td>
</tr>
</tbody>
</table>

*Addition levels and yields are based on oven-dry wood in the pulping reaction; data values are mean values of all data acquired. bCompound types are indicated by: NQs = Naphthoquinones, AQs = Anthraquinones, and PQs = Phenanthrenequinones. cEstimated error in kappa number is 4-5%. dEstimated error in total yield is 1-2%; Lignin yield = 0.0015(Kappa No.)(Total Yield); eCarbohydrate Yield = Total Yield - Lignin Yield.*

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low, compounds 6 and 7 were not further evaluated. Naphthoquinones 8 and 9, which were more readily available, were selected for more detailed evaluation, using higher levels of addition in a second pulping study. The results obtained (Table 4) show that 8 and 9 are somewhat effective catalysts at higher addition levels.

**TABLE 4**

<table>
<thead>
<tr>
<th>Compound - Addition Level</th>
<th>Kappa No.</th>
<th>Lignin</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbohydrate</td>
<td></td>
</tr>
<tr>
<td>8 - 0.1</td>
<td>76.5</td>
<td>5.6</td>
<td>42.8</td>
<td>48.4</td>
</tr>
<tr>
<td>0.2</td>
<td>74.9</td>
<td>5.4</td>
<td>43.0</td>
<td>48.4</td>
</tr>
<tr>
<td>0.4</td>
<td>71.8</td>
<td>5.2</td>
<td>43.1</td>
<td>48.3</td>
</tr>
<tr>
<td>0.8</td>
<td>58.1</td>
<td>4.2</td>
<td>43.8</td>
<td>48.0</td>
</tr>
<tr>
<td>None</td>
<td>86.4</td>
<td>6.2</td>
<td>42.0</td>
<td>48.2</td>
</tr>
<tr>
<td>AQ - 0.1</td>
<td>37.1</td>
<td>2.5</td>
<td>42.9</td>
<td>45.4</td>
</tr>
<tr>
<td>9 - 0.1</td>
<td>68.6</td>
<td>4.9</td>
<td>43.2</td>
<td>48.1</td>
</tr>
<tr>
<td>0.2</td>
<td>68.9</td>
<td>5.0</td>
<td>43.8</td>
<td>48.8</td>
</tr>
<tr>
<td>0.4</td>
<td>68.8</td>
<td>5.0</td>
<td>43.4</td>
<td>48.4</td>
</tr>
<tr>
<td>0.8</td>
<td>62.5</td>
<td>4.6</td>
<td>44.4</td>
<td>49.0</td>
</tr>
<tr>
<td>None</td>
<td>75.3</td>
<td>5.5</td>
<td>43.3</td>
<td>48.8</td>
</tr>
<tr>
<td>AQ - 0.1</td>
<td>36.5</td>
<td>2.5</td>
<td>43.5</td>
<td>46.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Addition levels and yields are based on oven-dry wood in the pulping reaction. <sup>b</sup>Lignin and carbohydrate yields are based on kappa number - see Table 3.

The o-naphthoquinones 10 and 11 were generated from lignin model quinones rather than from quinones which could actually be produced from lignin. They were tested to determine if quinones of this type had any potential pulping activity. Table 3 shows that o-naphthoquinone 10 is relatively poor as an additive. Although the use of 11 lowers the kappa number to 72.5, the effect is far below that resulting from the use of AQ.

Phenanthrenequinone derivatives 12-15 demonstrated effects similar to naphthoquinones 8 and 9. Because the mechanism of formation involves side chain elimination, these compounds could potentially be produced from lignin. The low yields observed in their generation, however, probably precludes their use as pulping
additives. It is interesting to note the similarity in results obtained for 12 and 14 and for 13 and 15. As discussed earlier, it is quite likely that pulping conditions are such that diols 12 and 14 are converted into the fully aromatized phenanthrenequinones 13 and 15, respectively, early in the pulping process.

The data in Table 3 indicate that the isomeric mixture of 2,6- and 2,7-dimethylanthraquinone (16) may be an outstanding pulping promoter. The mixture was further studied in a head-to-head comparison with AQ at three levels of addition; the results are presented in Table 5.

The data indicate that the dimethylanthraquinone mixture (DMAQ) is superior to AQ at all levels tested. In fact, better results were obtained with DMAQ at the 0.05% addition level than were obtained with AQ at the 0.10% level. Although the data obtained are not sufficient to be able to show that DMAQ is twice as effective as AQ on a sound statistical basis, indications are that DMAQ is superior to AQ. It should be pointed out that the individual isomers of DMAQ have been previously evaluated as pulping additives but have been shown to be slightly inferior to AQ. The experimental conditions used in that study, however, were such that the additives were tested at a much higher level; the effectiveness at very low levels apparently was not observed.

**TABLE 5**

<table>
<thead>
<tr>
<th>Compound Level (%)</th>
<th>Kappa No.</th>
<th>Lignin</th>
<th>Carbohydrate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQ - .05</td>
<td>41.2</td>
<td>2.9</td>
<td>43.5</td>
<td>46.4</td>
</tr>
<tr>
<td>16 .05</td>
<td>35.2</td>
<td>2.5</td>
<td>44.0</td>
<td>46.5</td>
</tr>
<tr>
<td>AQ - .10</td>
<td>36.2</td>
<td>2.5</td>
<td>43.4</td>
<td>45.9</td>
</tr>
<tr>
<td>16 .10</td>
<td>31.2</td>
<td>2.2</td>
<td>44.6</td>
<td>46.8</td>
</tr>
<tr>
<td>AQ - .15</td>
<td>33.3</td>
<td>2.3</td>
<td>43.9</td>
<td>46.2</td>
</tr>
<tr>
<td>16 .15</td>
<td>28.9</td>
<td>2.0</td>
<td>44.7</td>
<td>46.7</td>
</tr>
<tr>
<td>None</td>
<td>83.4</td>
<td>6.3</td>
<td>44.2</td>
<td>50.5</td>
</tr>
</tbody>
</table>

^aAddition levels and yields are based on oven-dry wood in the pulping reaction. ^bLignin and carbohydrate yields are based on kappa number — see Table 3.
Direct Oxidation and Testing of Lignin

Quinone and catechol structures are produced when kraft lignin is heated in white liquor at 240-320°C; addition of this demethylated lignin to a pulping reaction has a small beneficial impact on both yield and kappa number. We, too, have briefly examined the direct oxidation/demethylation of lignin and the activity of the resulting products as pulping catalysts. The lignin used in this phase of the work was isolated from the black liquor resulting from a soda cook of loblolly pine.

The lignin was treated with potassium thiophenoxide, according to the method of Francis and Reeve, to give a demethylated lignin; the methoxyl content decreased from 13.6% to 2.8% following oxidation. The lignin was also found to have increased in weight by approx. 13%, indicating some take up of thiophenol.

The demethylated sample was tested for possible delignification activity through laboratory pulping using an additive level of 1%. Kappa numbers and pulp yields were compared to those obtained when no additive was used and when unoxidized soda lignin was used as an additive. The results obtained are presented in Table 6.

The thiophenoxide-demethylated lignin had a slight beneficial effect on delignification; however, additional experiments would have to be carried out in order to determine if the effect is statistically significant. In any case, it is clear that any difference which may exist is much less than that obtainable with AQ.

<table>
<thead>
<tr>
<th>Table 6</th>
</tr>
</thead>
</table>
| **Laboratory pulping using oxidized lignin.**
| Sample          | Kappa number | Yield (%) |
| Thiophenoxide Lignin | 74.6         | 48.1       |
| No Additive      | 81.9         | 49.2       |
| Soda Lignin      | 80.8         | 48.4       |

---

Additive level was 1%, based on oven-dry wood. Yields are based on oven-dry wood in the pulping reaction. Data values are mean values of all data acquired during the course of the experimental work; see Tables 2 and 3.
Similar experiments were conducted with lignin which had been electrochemically oxidized (see Experimental). Infrared (IR) analysis of the oxidized lignin indicated a general trend of increasing carbonyl content with increasing severity of oxidation. However, IR spectra of the oxidized samples lacked the strong absorption band at 1660-1690 cm\(^{-1}\) which is characteristic of the quinone carbonyl group. Laboratory pulping indicated no beneficial effect when the electrochemically-oxidized lignin samples were used as pulping additives at the 1% level.

Because of the large number of variables involved in the electrochemical oxidations, the best conditions may not have been employed.

SUMMARY AND CONCLUSIONS

The isomeric mixture of 2,6- and 2,7-dimethylanthraquinone stands out as an extremely good pulping promoter. A synthetic yield of 25-30% is also respectable and might be increased with further research to optimize reaction conditions. Benzoquinones are not effective pulping additives. Naphthoquinones with o-carbonyl groups and phenanthrenequinones are somewhat effective, but low synthetic yields probably would prevent their economical use. Fully aromatized p-naphthoquinones, 8 and 9, also exhibit some catalytic activity; this finding, together with fairly high synthetic yields, indicates that these compounds might have some potential use as delignification catalysts if they could be produced at low cost.

The starting material for several very effective delignification promoters, such as dimethylanthaquinone, can be lignin itself. Overall, it appears that best chance of success in generating an effective pulping additive from lignin lies in the initial production of p-benzoquinone starting compounds. Diels-Alder reactions can then be used to convert these materials into effective naphthoquinone and anthraquinone compounds. The lignin-derived additives have the potential of becoming inexpensive alternatives for anthraquinone.
EXPERIMENTAL

Redox Behavior of Compounds

Each additive (5.0 mg) and glucose (10.0 mg) were added to 5.0 mL of 1M NaOH in a 16-mL vial and heated under a stream of nitrogen. The color change observed was compared to that of a control sample which contained the additive in NaOH but no glucose. Following heating to approx. 85°C, the solution was allowed to cool in the open air and oxygen was bubbled through it; any color change was again noted. After the addition of another 10 mg of glucose, this procedure was repeated.

As a further test for a redox cycle, the solutions in their oxidized form were analyzed to see if the compounds initially used were still present. This was done by extracting with CHCl₃, reducing each extract to approximately one-half its original volume, and analyzing by GC. Analysis was done on a Hewlett-Packard 5890A GC using a 6-ft, 1/4-in. glass column packed with 3% silicone OV-17 on 100/200 chromosorb W-HP and the following temperature program: 1 min at 100°C, 100°C to 285°C at 10°/min, and 10 min at 285°C. Compounds were identified by spiking with a known sample and reanalyzing the extract. In some cases the solution was neutralized with dilute HCl before extraction. Those mixtures in which there was incomplete solubility of the additive were filtered through glass wool in their reduced states before cooling, oxidation, and extraction.

Laboratory Pulping

Evaluation through laboratory pulping was carried out by conducting soda cooks of southern pine in stainless-steel pressure vessels with a maximum capacity of 70 g oven-dry wood. The following pulping conditions were used:

| NaOH (as Na₂O, % on wood) | 18 |
| Liquor Ratio (cm³/g) | 4 |
| Cooking Schedule: |
| Time at 90°C (min) | 15 |
| Time from 90 to 173°C (min) | 90 |
| Time at 173°C | 94 |
| H-factor | 2100 |
Eight cooks were done simultaneously; for comparison, each batch generally contained vessels in which anthraquinone was used as an additive and in which no additive was used.

**Potassium Thiophenoxide Oxidation**

The isolation of the lignin starting material was described earlier. This lignin was oxidized with potassium thiophenoxide as described below. First, freshly distilled tetrahydrofuran (THF, 200 mL) was added to a 500-mL, 3-neck, round-bottom flask equipped with a stirring bar. Potassium (1.7 g) was cut into small pea-size pieces and added to the THF under a nitrogen atmosphere. Thiophenol (5.00 mL) was then added and the reaction was allowed to proceed with stirring for 1 hr. After reaction, unreacted potassium was scooped out, and the THF was evaporated through gentle heating.

Lignin (1.00 g) was then added along with 150 mL of 2-hydroxyethyl ether, and the temperature was raised to 200°C for 30 min. After the flask was cooled to room temperature, 200 mL of H₂SO₃ (prepared by bubbling SO₂ through water until saturated) was added and allowed to react for 10 min. The precipitated lignin was isolated by centrifugation, washed with H₂SO₃ and water, and freeze dried. The degree of oxidation was ascertained by determining change in weight and change in methoxyl content. Methoxyl analyses were performed by Chem-Lig International, Inc., Schofield, WI.

**Electrochemical Oxidation**

The electrochemical cell consisted of a hand-blown glass anode compartment of approx. 400 mL total capacity and a smaller cathode chamber constructed from a Teflon cylinder. The cell was designed so that the cathode chamber fit inside of the anode compartment. A Dupont Nafion #125 perfluorinated membrane was placed at the bottom of the cathode chamber to separate the two halves of the cell. The working electrode was constructed from a 5-cm diameter metal disk; a Beckman saturated calomel reference electrode
was used. The cell was connected in series with an EG & G Princeton Applied Research Model 371 Potentiostat-Galvanostat and an Electrosynthesis Model 640 coulometer equipped with a Model 645 shunt. A digital voltmeter was used to measure the cell potential.

After filling the cell with the electrolyte to be used (NaOH, 0.20 to 1.00M, 150 to 200 ml anolyte), inert gas was bubbled through the solution to remove most of the dissolved oxygen. The anode was then pretreated at 0.800 V for approx. 10 min. to generate an oxidized, reproducible surface. The lignin was then added (0.020 g/ml), and the electrolysis was carried out. Copper and nickel anodes were employed at both 20 and 60°C, using potentials from 0.75 to 0.80 V vs. a saturated calomel electrode. The amount of charge passed through the lignin solution was varied up to 6000 coulombs/g. Upon completion of the electrolysis, the lignin was obtained by precipitation (pH approx. 3) and dried in a vacuum oven at 45°C. For several samples, an acid-soluble lignin fraction was also isolated.

Infrared (IR) spectra were obtained of both oxidized and unoxidized lignin samples by pressing the lignin into KBr pellets (0.5% lignin). Spectra of the acid-soluble lignin samples were obtained using NaCl disks by dissolving the lignin in acetone, applying a few drops of the solution to the disk, and then evaporating the solvent under a stream of nitrogen. A Perkin Elmer 599B IR Spectrophotometer was used. The extent to which the original lignin phenyl-propane units were converted into carbonyl (possibly quinone) structures was ascertained by comparing the IR absorption due to carbonyl stretching at 1715 cm\(^{-1}\) to that due to aromatic skeletal vibration at 1510 cm\(^{-1}\).

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REFERENCES


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