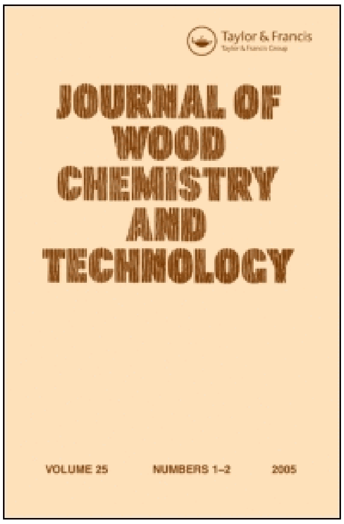

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THE GENERATION OF QUINONES FROM LIGNIN AND LIGNIN-RELATED COMPOUNDS

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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

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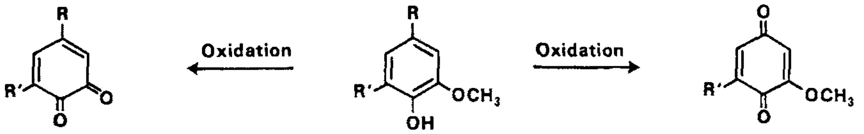
a major component of both wood and pulping liquors and contains oxygenated aromatic rings which have some similarity to AQ.

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.[1] Some of these enhanced quinones have characteristics needed to act as effective delignification catalysts.[2]

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 (1).[3] As shown in Eq. 1, oxidation of the phenolic hydroxyl group and an adjacent methoxyl group converts a lignin unit to an *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 *p*-benzoquinone (4 or 5).



2, R' = H
3, R' = OCH_3

1, R = alkyl side chain,
R' = H or OCH_3

4, R' = H
5, R' = OCH_3

A number of chemical oxidative techniques have been used to generate both *o*-quinones and *p*-quinones in lignin and lignin-related compounds. Potassium nitrosodisulfonate[4] and sodium periodate[5,6] are known to produce *o*-quinones from lignin model compounds of the substituted guaiacol type or to introduce *o*-quinone structures into various lignin preparations. Hydrogen peroxide[7-9] and peracetic acid[10-12] 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]

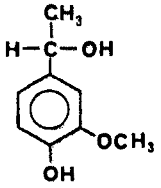
Our work described here focuses on the use of three chemical and various electrochemical oxidative techniques for the generation of specific benzoquinones. The use of these benzoquinones in catalyst production is described in the publications which follow.[1,2]

RESULTS AND DISCUSSION

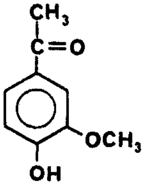
The lignin-related compounds used in the experimental work are shown below. These compounds possess common structural characteristics of lignin or may be derived from lignin; both hardwood and softwood models are represented. In addition to the simple monomeric lignin-related compounds, several lignin 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

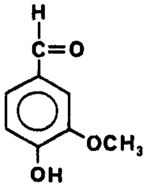
Although the use of potassium nitrosodisulfonate (Fremy's salt) often results in the generation of o-quinones,[7] recent work has shown that high yields of p-benzoquinones can be produced through the oxidation of p-hydroxybenzyl alcohols, p-hydroxybenzoic acids, and p-hydroxybenzaldehydes.[23,24]



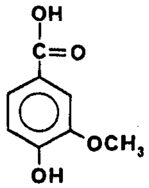
α-Methylvanillyl Alcohol



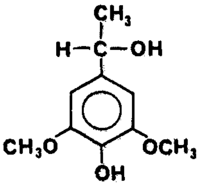
Acetovanillone



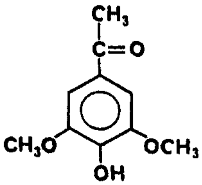
Vanillin



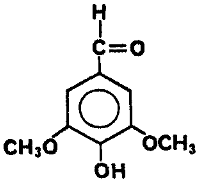
Vanillic Acid



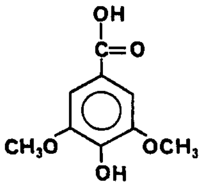
α-Methylsyringyl Alcohol



Acetosyringone



Syringaldehyde



Syringic Acid

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

Compound	Product[a]	Yield (%)
Guaiacyl Type:		
α-Methylvanillyl Alcohol	MBQ	79
Acetovanillone	--	0
Vanillin	--	0
Vanillic Acid	MBQ	77
Syringyl Type:		
α-Methylsyringyl Alcohol	DMBQ	79
Acetosyringone	DMBQ	3
Syringaldehyde	DMBQ	65
Syringic Acid	DMBQ	77

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[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.[25] The additional methoxyl group present in syringaldehyde may inhibit reactions at C_5 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.

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

TABLE 2

Fremy's salt oxidation of various lignin samples

Sample	Quinone Obtained[a]	Yield (%)
Hardwood Ethanol	DMBQ	4
LMW Ethanol 1	DMBQ	11
LMW Ethanol 2	DMBQ	16
Softwood Soda	--	0
Hardwood Kraft	DMBQ	4
Softwood Kraft	--	0
Hardwood Sulfite	DMBQ	1
Softwood Sulfite	--	0

---

[a] DMBQ = 2,6-Dimethoxy-p-benzoquinone (5).

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[10] found that softwood lignin model compounds containing α-carbonyl groups were reactive when a free hydroxyl group was present in the position 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,[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.[9]

TABLE 3

Hydrogen peroxide oxidation of lignin-related compounds

Compound	Reaction Time (min)	Products	Yield[a] (%)
α-Methylvanillyl Alcohol	300	2-Methoxy-4-vinylphenol	[4]
		α-Methylvanillyl Alcohol	93
Acetovanillone	60	Methoxy-p-benzoquinone	1
		Methoxyhydroquinone	77
		Acetovanillone	15
Vanillin	10	Methoxy-p-benzoquinone	2
		Methoxyhydroquinone	95
Vanillic Acid	330	No Reaction	
α-Methylsyringyl Alcohol	300	2,6-Dimethoxy-4-vinylphenol	[12]
		α-Methylsyringyl Alcohol	59
Acetosyringone	120	2,6-Dimethoxy-p-benzoquinone	5
		2,6-Dimethoxyhydroquinone	[38]
		Acetosyringone	31
Syringaldehyde	80	2,6-Dimethoxy-p-benzoquinone	24
		2,6-Dimethoxyhydroquinone	[72]
Syringic Acid	330	Unidentified Compound	[7]
		Syringic Acid	29

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[a] 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.[10,11] In some cases, however, good yields of quinones or hydroquinones have been obtained from lignin-related compounds.[11,12] 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.[13-15] 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 4

Peracetic acid oxidation of lignin-related compounds

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

---

[a] Yields 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;[12] 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 α-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

Peracetic acid oxidation of lignin samples

Sample	Quinone Obtained[a]	Yield (%)
Hardwood Ethanol	DMBQ	1
LMW Ethanol	DMBQ	2
Hardwood Kraft	DMBQ	2
Hardwood Sulfite	DMBQ	trace

[a] DMBQ = 2,6-Dimethoxy-p-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.[18] They found that α-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.[16-18] 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.[28]

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

Experiment Number	Anode,[a] Potential[b]	Conditions[c]	Quinone[d] Yield (%)
Oxidations of α-Methylvanillyl Alcohol:			
1	Pb, 1.8V	CH_3CN/1.0M H_2SO_4 (7/1), 3°C	MBQ - 7
2	Pb, 1.8V	p-Dioxane/0.67M H_2SO_4 (7/3), 28°C	MBQ - 7
Oxidations of α-Methylsyringyl Alcohol:			
3	Pb, 1.8V	CH_3CN/1.0M H_2SO_4 (7/1), 3°C	DMBQ - 21
4	Pb, 1.8V	p-Dioxane/0.67M H_2SO_4 (7/3), 28°C	DMBQ - 30
5	Pb, 1.6V	DMSO/1.0M H_2SO_4 (7/3), 35°C	DMBQ - 16
6	Pb, 1.7V	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - 39
Oxidations of Syringic Acid:			
7	C, 1.5-2.3V	0.1N NaOH, 27°C	DMBQ - 10
8	C, 2.0V	0.1N NaOH, pH 7, 25°C	DMBQ - 5
Oxidation of Syringaldehyde:			
9	C, 2.0V	0.1N NaOH, pH 7, 25°C	DMBQ - 2
Oxidation of Ethanol Lignin:			
10	Pb, 2.0V	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - trace
Oxidation of LMW Ethanol Lignin:			
11	Pb, 2.0V	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - 1

---

[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.[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

Sample	Vanillin Yield (%)	Syringaldehyde Yield (%)	Total Yield (%)
Oxidations at 140°C:			
HW Ethanol	5.0	12.9	17.9
SW Soda	10.1	trace	10.1
HW Kraft	3.4	4.8	8.2
SW Kraft	7.9	0.4	8.3
HW Sulfite	5.1	8.9	14.0
SW Sulfite	12.1	trace	12.1
Oxidations at 159°C:			
HW Ethanol	5.8	14.6	20.4
SW Soda	12.9	trace	12.9
HW Kraft	4.6	6.5	11.1
SW Kraft	9.9	0.4	10.3
HW Sulfite	5.6	9.5	15.1
SW Sulfite	15.5	trace	15.5
Oxidations at 179°C:			
HW Ethanol	6.7	17.0	23.7
SW Soda	15.2	trace	15.2
HW Kraft	5.3	7.9	13.2
SW Kraft	13.1	0.6	13.7
HW Sulfite	6.1	10.1	16.2
SW Sulfite	16.5	trace	16.5
Oxidation at 178°C:			
LMW Ethanol	3.7	16.7	20.3

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 benzylic 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[11] and had melting points in agreement with literature[8,31] 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 H_2SO_4. 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 P_2O_5. 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 0.025$\underline{M}$ 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 $CHCl_3$ (8 x 50 mL); the extract was washed with 50 mL of distilled water, dried over anhydrous Na_2SO_4, and then evaporated. The LMW sample was then dried over P_2O_5 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.

Sample	Source
Hardwood Kraft	Westvaco RLX 4713-3A, Charleston Research Center, North Charleston, SC
Softwood Kraft	Isolated in the thesis work of Furman[32]
Hardwood Sulfite	Reed Lignin D-312-13, Rothschild, WI
Softwood Sulfite	Reed Lignin D-300-2

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 $NaHCO_3$ solution to attain a pH of approx. 3 and extracted with $CHCl_3$. The extract was dried over anhydrous Na_2SO_4 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 0.2$\underline{M}$ KH_2PO_4/K_2HPO_4 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 1.00$\underline{N}$ NaOH in an 8-ml vial equipped with a small stirring bar. Hydrogen peroxide (2.50 mL of 1.00$\underline{M}$ 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.[33] 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% H_2O_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 $CHCl_3$ prior to acidification, extraction and analysis of the product mixture.

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