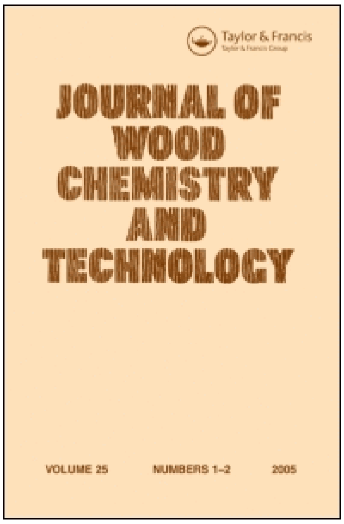

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John C. Wozniak[a]; Donald R. Dimmel[a]; Earl W. Malcolm[a]
[a] Institute of Paper Science and Technology, Atlanta, GA

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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 dimethylanthraquinone 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.[1]

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.[2] It was hoped that lignin-derived

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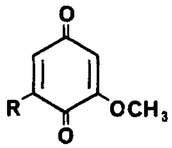
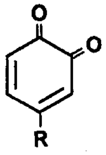
*Address inquiries to this author.



1, R = H
2, R = OCH_3



3, R = CH_3
4, R = $COCH_3$
5, R = $CH(OH)CH_3$

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.[3] 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 1*M* 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

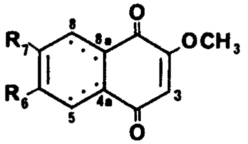
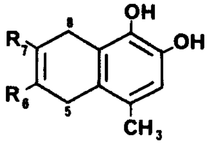
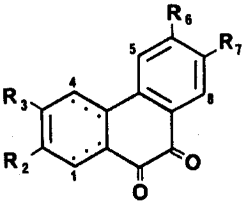
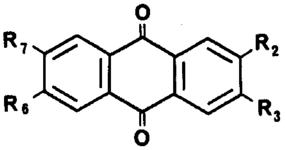
The effectiveness of the synthesized compounds as delignification promoters was determined through laboratory soda pulping of southern pine. The effects of the additives on yield and kappa number were compared to corresponding effects of AQ.

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.

Compound	Type[a]	R_2	R_3	R_6	R_7	Hydro[b]
p-Naphthoquinones:						
6	Q	--	--	Me	Me	4a,5,8,8a
7	HQ	--	--	Me	Me	5,8
8	Q	--	--	Me	Me	--
9[c]	Q	--	--	(H)	(Me)	--
o-Naphthohydroquinones:						
10	HQ	--	--	Me	Me	5,8
11[c]	HQ	--	--	(H)	(Me)	5,8
Phenanthrene-9,10-quinones:						
12	HQ	Me	Me	Me	Me	1,4
13	Q	Me	Me	Me	Me	--
14[c]	HQ	(H)	(Me)	(H)	(Me)	1,4
15[c]	Q	(H)	(Me)	(H)	(Me)	--
Anthraquinones:						
16[c]	Q	(H)	(Me)	(H)	(Me)	--
AQ	Q	H	H	H	H	--

---

[a] Q = Quinone; HQ = Hydroquinone (the reduced, aromatic version of the quinone) [b] Hydro refers to saturated carbon positions - all other ring carbons are unsaturated. [c] 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 promotors. 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.

	Anthraquinone		No Additive	
	Kappa No.	Yield (%)	Kappa No.	Yield (%)
			83.5	49.8
			79.1	48.2
	37.1	45.4	86.4	48.2
	36.5	46.0	75.3	48.8
	38.5	45.7	83.4	49.4
	36.2	45.9	83.4	50.5
Mean	37.1	45.8	81.9	49.2
Std. Dev.	1.0	0.3	4.0	0.9

TABLE 3

Evaluation of compounds as pulping additives.[a]

Compound[b]		Addition Level (%)	Kappa No.[c]	Yield (%)[d] Lignin	Carbohydrate	Total
None		--	81.9	6.0	43.2	49.2
NQs	6	0.2	72.7	5.2	42.7	47.9
	7	0.2	67.4	4.8	42.7	47.5
	8	0.2	70.3	5.0	42.8	47.8
	9	0.2	69.0	5.0	43.2	48.2
	10	0.2	77.0	5.6	42.6	48.2
	11	0.2	72.5	5.2	42.8	48.0
PQs	12	0.1	66.5	4.6	42.0	46.6
	13	0.1	68.3	4.8	42.5	47.3
	14	0.1	73.5	5.2	42.3	47.5
	15	0.1	74.8	5.4	42.6	48.0
AQs	16	0.1	31.6	2.2	43.6	45.8
	AQ	0.1	37.1	2.5	43.3	45.8
	AQ	0.2	36.3	2.5	43.2	45.7

---

[a] Addition levels and yields are based on oven-dry wood in the pulping reaction; data values are mean values of all data acquired. [b] Compound types are indicated by: NQs = Naphthoquinones, AQs = Anthraquinones, and PQs = Phenanthrenequinones. [c] Estimated error in kappa number is 4-5%. [d] Estimated error in total yield is 1-2%; Lignin yield = 0.0015(Kappa No.)(Total Yield);[4] Carbohydrate Yield = Total Yield - Lignin Yield.

TABLE 4

Evaluation of 8 and 9 at various addition levels.[a]

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

---

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

low, compounds 6 and 7 were not further evaluated. Naphthoquinones 8 and 9, which were more readily available,[2] 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.

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,[2] these compounds could potentially be produced from lignin. The low yields observed in their generation,[2] 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.[13] 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

Evaluation of **16** at various addition levels.[a]

Compound - Level (%)	Kappa No.	Yield (%)[b] Lignin	Carbohydrate	Total
AQ - .05	41.2	2.9	43.5	46.4
16 .05	35.2	2.5	44.0	46.5
AQ - .10	36.2	2.5	43.4	45.9
16 .10	31.2	2.2	44.6	46.8
AQ - .15	33.3	2.3	43.9	46.2
16 .15	28.9	2.0	44.7	46.7
None	83.4	6.3	44.2	50.5

---

[a] Addition levels and yields are based on oven-dry wood in the pulping reaction. [b] Lignin 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;[5] addition of this demethylated lignin to a pulping reaction has a small beneficial impact on both yield and kappa number.[6,7] 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,[8,9] 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 6

Laboratory pulping using oxidized lignin.[a]

Sample	Kappa number	Yield (%)[b]
Thiophenoxide Lignin	74.6	48.1
No Additive[c]	81.9	49.2
Soda Lignin	80.8	48.4

---

[a] Additive level was 1%, based on oven-dry wood. [b] Yields are based on oven-dry wood in the pulping reaction. [c] 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.[10] 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.[2] 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 dimethylanthraquinone, can be lignin itself.[1,2] 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.[2] The lignin-derived additives have the potential of becoming inexpensive alternatives for anthraquinone.[11]

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 $CHCl_3$, 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 Na_2O, % on wood)	18
Liquor Ratio (cm^3/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.[1] This lignin was oxidized with potassium thiophenoxide[8,9] 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 H_2SO_3 (prepared by bubbling SO_2 through water until saturated) was added and allowed to react for 10 min. The precipitated lignin was isolated by centrifugation, washed with H_2SO_3 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}.[12]

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