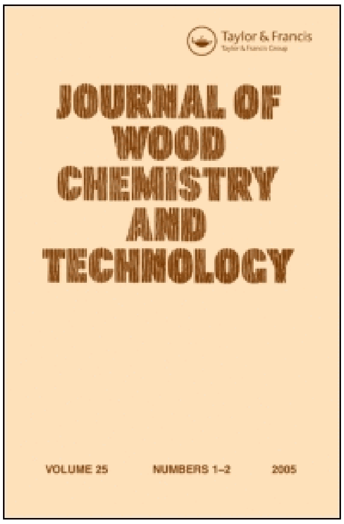

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PULPING CATALYSTS FROM LIGNIN (8). NITROGEN DIOXIDE OXIDATION OF LIGNINS TO BENZOQUINONES

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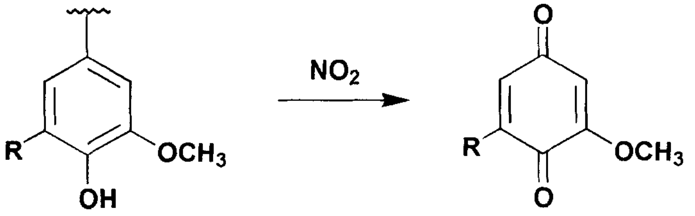
ABSTRACT

Several lignin samples have been oxidized with nitrogen dioxide (NO_2) in methanol to give low yields of benzoquinones. The yields of 2,6-dimethoxy-*p*-benzoquinone (DMBQ) from hardwood lignins were highest when the lignin was first extracted to provide a lower molecular weight lignin fraction. The yields of DMBQ were also improved by degrading the lignin to smaller fragments prior to NO_2 oxidation. One of the best pretreatments in this regards was heating with copper oxide in aqueous NaOH. Thioacidolysis analysis indicated that β-aryl ether linkages were effectively cleaved by the CuO treatment and that the product mixture contained increased levels of vanillin and syringaldehyde.

The best yields of DMBQ from a fractionated lignin and a pretreated lignin were about 10 and 15%, respectively, which corresponds to about 40-60% of the available syringyl units in the lignin. The yields were highest from organosolv lignins; such lignins are probably less condensed than kraft lignins. The yields were slightly improved when N-hydroxysuccinimide was present.

INTRODUCTION

Nitrogen dioxide (NO_2), in methanol, is an effective oxidant for generating 2,6-dimethoxy-*p*-benzoquinone (**2**, DMBQ) from many types of syringyl lignin model compounds (Eq. 1); yields are often >85%.[2] In contrast, the yields of monomethoxybenzoquinone (**1**, MMBQ) from simple guaiacyl model compounds are only 0-15%. This report provides information on the yields of benzoquinones from NO_2 oxidations of several lignin samples. The aim of the research is to generate cost-effective pulping catalysts from lignin.[3]



(Eq. 1)

R = H or OCH_3

1, R = H (MMBQ)
2, R = OCH_3 (DMBQ)

RESULTS

NO_2 Oxidations of Lignin Samples

Our initial studies involved the NO_2 oxidations of three hardwood lignin samples; N-hydroxysuccinimide (NHS) was present to enhance the yield of DMBQ.[2] Each lignin type was extracted with an organic solvent to give a soluble lignin (10-30%) and an insoluble (higher molecular weight) lignin (90-70%). The soluble lignins contained a significant fraction of material with a molecular weight <1000. For each soluble/insoluble pair tested, the soluble fraction gave roughly twice the benzoquinone yield (Table 1). Even so, the yields of DMBQ were considerably below that observed with simple syringyl model compounds. The trend in

Table 1. Oxidation of selected hardwood lignin samples by NO_2/NHS at room temperature for 24 hours.[a]

Hardwood Lignin Source	wt. % S Units[b]	wt. % G Units[b]	wt. % DMBQ[c]	wt. % MMBQ[d]
Sol. white oak extract	25	67	6.5 (9.2)	trace
Sol. aspen extract	25	66	9.8 (9.8)	5
Sol. scarlet oak extract	23	69	7.7 (7.7)	1
Insol. white oak	22	71	4.7 (5.1)	trace
Insol. aspen	23	69	4.7 (5.2)	1
Insol. scarlet oak	21	72	3.5 (3.5)	-
Kraft lignin 1[e]			5.0	trace
Kraft lignin 2[e]			7.2	trace
Ethanol lignin[f]			6.2	1

[a]50 mg lignin, 60 mg NO_2, 60 mg NHS, and 5 mL MeOH; [b]±4% as determined by FT-IR; [c]GC (HPLC) yields; [d] trace = <0.5% and - = not detected; [e]two different experimental lignins from Westvaco Corp.; [f]reference 4.

benzoquinone yields by NO_2 oxidation appears to be: lignin monomer models > low molecular weight lignin > high molecular weight lignin.

The lignins listed in Table 1 contain about 70% guaiacyl units and 25% syringyl units; the former gives MMBQ on oxidation, the latter DMBQ. For the soluble aspen lignin (the best case), the yield of each benzoquinone product based on available starting units was ~ 40% for DMBQ, but only 7% for MMBQ. The long reaction times used to oxidize the lignin samples disfavor good MMBQ yields, since MMBQ is more prone to decompose than is DMBQ.[2] The oxidation conditions could possibly be better optimized for MMBQ yield.

The NO_2/NHS system appears superior to both Fremy's salt and hydrogen peroxide for generating benzoquinones from lignin. Oxidation of the organosolv aspen lignin by Fremy's salt afforded DMBQ in 5.8% (3% less than NO_2/NHS) and no MMBQ. The hardwood ethanol lignin listed above gave a 4% DMBQ yield with Fremy's salt.[4] Hydrogen peroxide oxidations of several of the lignins described in Table 1 gave benzoquinone yields of about 1/4 that observed with NO_2/NHS.[5]

Survey of Lignin Pretreatments

Degradation of lignin into smaller fragments before performing NO_2 oxidations should result in higher yields of benzoquinones. Several pretreatments (Figure 1) were examined with a laboratory-prepared lignin that was recovered from pulping aspen in ethanol.[4] The pretreatments were selected because of anticipated lignin-lignin bond cleavage reactions and/or their practicality.

Acidolysis and CuO were the most effective pretreatments for improving DMBQ yields; the yields of MMBQ were only a trace in these cases. The acidolysis treatment consisted of refluxing the lignin in a mixture of 90:10:2 dioxane/water/concentrated HCl;[6] the CuO reactions will be discussed in greater detail in the next section.

Some lignin pretreatments gave lower DMBQ yields after NO_2 oxidation than when no pretreatment was carried out, i.e., acidolysis followed by H_2O_2/NaOH. Aqueous peracetic acid pretreatments at room temperature, and under more harsh conditions, gave only 1-3% DMBQ yields after NO_2 oxidation. The combination of Na_2S/NaOH (kraft treatment, method 12) led to a low 2.9% yield after NO_2 oxidation.

Reduction of ethanol lignin by $NaBH_4$ (method 5) was carried out in order to reduce α-carbonyl groups to α-carbinol groups; the former react more rapidly during NO_2 oxidation.[2] Several reduction and work up procedures were tried; the best DMBQ yield after NO_2 oxidation was only 1.3% better than the control.

Ozone was also examined as a pretreatment; if used in limited amount, ozone might preferentially cleave olefinic units of vinyl ethers and stilbenes to give smaller lignin fragments.[7] The ethanol lignin was treated with ozone at room temperature for 90 seconds and then oxidized

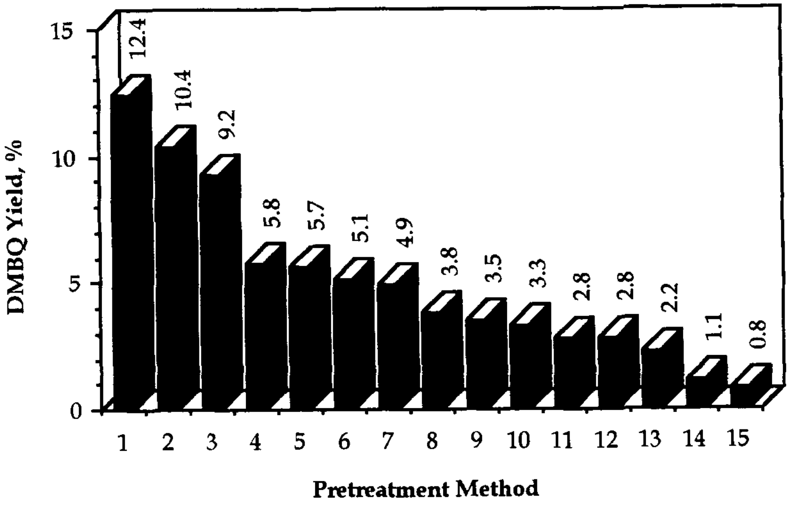


Figure 1. DMBQ yield as a function of pretreatment method for aspen ethanol lignin. Key: 1) CuO/NaOH at 170°C; 2) acidolysis + hot NO_2 treatment; 3) acidolysis; 4) MnO_2 at 170°C; 5) $NaBH_4$; 6) no pretreatment; 7) H_2O_2/NaOH; 8) aq. dioxane; 9) $Na_2S_2O_4$; 10) $NaHSO_3$; 11) peracetic acid; 12) kraft conditions; 13) alcoholic bisulfite; 14) Me_3SiI; 15) ozone.

with NO_2 to give DMBQ in only 0.5% yield. Three ozonized samples were also prepared by bubbling ozone into MeOH for 30, 60 and 120 seconds at -78°C. Upon NO_2 oxidation, these samples produced DMBQ in yields of 0.9, 0.5 and 0%, respectively. An ozone pretreatment appears to be too degradative.

Degradation of lignin into smaller fragments was expected upon heating with isopropanol-bisulfite and dioxane-water (1:1) at 165°C for 2 hr; alcohol-bisulfite cooking is reported to give fairly good yields of monomeric phenols, such as eugenol from softwoods.[8] Likewise, dioxane-water gives many low molecular weight phenols from soft- and hardwoods, and is often used for structural studies of lignin because of its mildness.[9] The lignin recovery yields after $CHCl_3$-acetone (1:2) extraction were 92% for the dioxane-water treatment and 63% for isopropanol-bisulfite treatment; the subsequent DMBQ yields after NO_2 oxidation were, however, low: 3.6% and 2.5%, respectively.

Trimethylsilyl iodide (both mild[10] and harsh[11]), sodium bisulfite,[12] sodium dithionate,[12] sodium hydroxide, and combinations of acidolysis/CuO/NaOH and acidolysis/$NaBH_4$ treatments gave lower yields than no pretreatments. Follow up experiments with acidolysis treatments routinely led to NO_2 oxidation yields of 7-8%, rather than the ~10% observed in the first reaction set; these results led us to concentrate on our best pretreatment - CuO.

CuO Lignin Pretreatment of a Hardwood Ethanol Lignin

Copper oxide at elevated temperature is known to extensively depolymerize lignin into smaller fragments.[13] Morohoshi and Glasser[14] report that CuO depolymerizes lignin better than alkaline nitrobenzene and thioacidolysis. We have performed extensive studies of CuO pretreatments to determine reaction products and to optimize DMBQ yields from aspen ethanol lignin and lignin models.

The optimization experiments involved varying the conditions of the CuO lignin pretreatments and observing the DMBQ yields from NO_2 oxidations of the products; the best DMBQ yields occurred when using one part lignin to three parts by weight of CuO in 2M aq. NaOH and heating at 176°C for 3-5 hr. Higher amounts of CuO and NaOH gave no noticeable yield improvements; in fact, yields decreased at high NaOH levels. Lower levels of CuO led to lower DMBQ yields. An example set of optimization experiments are shown in Table 2.

The lignin was recovered after the CuO oxidation by acidification and chloroform-dioxane extraction. Exhaustive extraction of the concentrated water layer with $CHCl_3$/acetone improved the overall lignin recovery to >90%; however, the additional extracted material produced only a small amount (~1%) of DMBQ on NO_2 oxidation. The water layer apparently does not contain many good DMBQ precursors; thus, the sec-

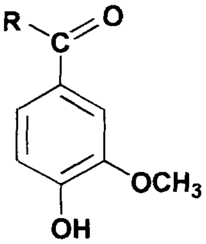
Table 2. Effect of CuO pretreatment time and temperature on DMBQ yield after NO_2 oxidation[a] of aspen ethanol lignin.

		DMBQ weight % yield[b]			
Time (hr)	90-95°C	140°C	170°C	176°C	190°C
1	-	4.1 (6.2)	6.2 (10.5)	11.8 (14.0)	11.6 (13.4)
3	-	4.9 (7.9)	9.5 (9.8)	12.4 (13.6)	11.3 (13.4)
5	-	6.2 (8.5)	9.4 (11.6)	11.7 (16.4)	9.0 (12.2)
8	-	6.2 (12.7)	9.4 (14.9)	10.9 (14.4)	10.0 (12.2)

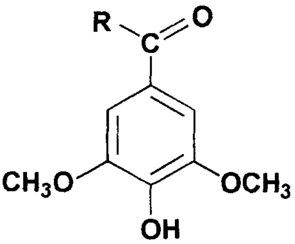
[a]the weight ratios of NO_2/NHS/lignin = 1:1:1; [b]GC yields (HPLC yields).

ond extraction was not generally performed. The data in Table 2 and other tables do not include DMBQ yields from added extractions.

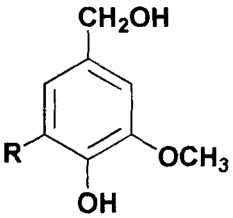
Table 3 shows the copper oxide oxidation products from aspen ethanol lignin and the effects of the treatment temperature on the yields. The identification and quantification of the main oxidation products was carried out by GC. The sum of the GC areas of vanillin, acetoguaiacone, vanillic acid, syringaldehyde, acetosyringone and syringic acid generally corresponded to >90% of the total signal areas for the conditions selected. [Acidolysis pretreatment did not give similar low molecular weight products detectable by GC.]



3, R = H
4, R = CH_3
5, R = OH



6, R = H
7, R = CH_3
8, R = OH



9, R = H
10, R = OCH_3

Table 3. Yields of CuO/NaOH[a] oxidation products from lignin.

		Yield (Wt. %)					
Temp.	hr	3	4	5	6	7	8
170°C	1	1.8	0.3	-	6.9	1.2	-
	3	3.3	0.6	1.0	9.7	2.2	2.8
	5	3.2	0.6	0.8	9.4	2.2	2.4
	8	3.2	0.7	0.5	9.2	2.2	2.1
176°C	1	3.0	0.5	0.5	9.0	1.8	0.9
	3	3.3	0.6	0.7	9.2	2.2	0.6
	5	3.0	0.6	-	8.5	1.8	-
	8	3.1	0.6	0.5	8.6	2.0	-
190°C	1	3.2	0.6	0.6	9.2	2.0	0.6
	3	2.9	0.6	0.3	8.3	1.8	0.5
	5	2.9	0.6	0.1	8.0	1.8	0.3
	8	2.6	0.5	-	6.6	1.6	-

[a] 100 mg of CuO, 35 mg of aspen ethanol lignin, 3 mL of 2M NaOH

The two major products in all cases were vanillin (**3**) and syringaldehyde (**6**). From the viewpoint of maximum product yields, the optimum temperature for the CuO oxidation was the lowest temperature, 170°C. However, in spite of the lower yield of syringaldehyde, the higher temperature CuO treatments gave more DMBQ after NO_2 oxidation than low temperature treatments (Table 2). If syringaldehyde were the only component in the CuO product mixture to give DMBQ, one can calculate the expected DMBQ based on the near quantitative conversion of syringaldehyde to DMBQ upon NO_2 oxidation.[2] For example, in the 190°C treatments, theoretical weight % yields of DMBQ from syringaldehyde in the 1, 3, 5 and 8-hr samples are 8.5, 7.7, 7.4 and 6.1%, respectively. The actual DMBQ yields were about 3% higher: 11.6, 11.3, 9.0 and 10.0%, respectively (Table 2).

These yield differences may be due to NO_2 oxidation of other syringyl products in the samples. Disyringylmethane, which is the princi-

Table 4. Conversion of α-carbinol groups during 170°C CuO treatment.

Time (hr)	Conversion - weight % yield vanillyl alcohol (**9**) to vanillin (**3**)	 syringyl alcohol (**10**) to syringaldehyde (**6**)
1	26	38
3	30	39
5	29	41
8	29	35

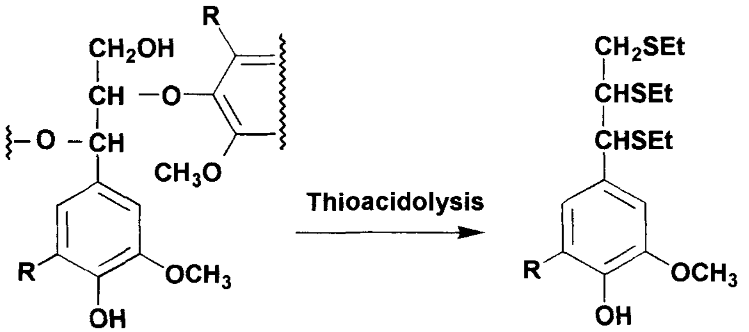
pal alkaline condensation product from syringyl alcohol, gives a good DMBQ yield upon NO_2 oxidation; ~85% of each syringyl ring is converted to DMBQ.[2] The difference between the actual and theoretical DMBQ yield based on syringaldehyde oxidation in the 3-hr 170°C CuO sample is only 0.5%. Apparently, a lower temperature treatment is less effective in converting the lignin into structures that are sensitive to NO_2 oxidation. Increasing the harshness of the CuO treatment from 170°C (3 hr) to 190°C (8 hr) causes a drop in aldehyde yields: syringaldehyde from 9.7% to 6.6% and vanillin from 3.3% to 2.6%.

A mixture of vanillyl and syringyl alcohols in a ratio roughly equal to the G/S unit ratio in the aspen ethanol lignin was treated with CuO/NaOH at 170°C. Gas chromatograms of the product mixture at different times all showed only vanillin and syringaldehyde and an absence of the alcohol starting materials (Table 4). The data showed α-carbinols are readily oxidized by CuO, but the conversion to aldehyde groups is low; once formed, the aldehydes are relatively stable. More than half of the CuO products were not detectable by GC, the guaiacyl model conversion being worse than syringyl model conversion.

Assuming that all syringyl units are oxidized with a conversion similar to that of syringyl alcohol (40%, Table 4), we predict that CuO treated aspen lignin, containing ~25% syringyl units, would produce syringaldehyde in ~10 weight % yield. Our best observed yield was 9.7% (Table 3). Our best *DMBQ yield* for this lignin, 12.4% (Table 2), corresponds to 50% of the theoretical DMBQ yield from available syringyl structures in the sample. Much less vanillin was observed over that predicted.

Thioacidolysis Characterization of CuO Treated Lignin

To better understand structural changes resulting from CuO treatments, we conducted thioacidolysis analyses of a lignin before and after treatment. The lignin chosen for study was a poplar-O_2-organosolv lignin (Table 9); this lignin showed a large increase in DMBQ yield after CuO treatment. Thioacidolysis is a chemical degradation technique that depolymerizes lignin by selective cleavage of ether linkages.[15,16] Equation 2 shows the main monomeric products derived from noncondensed β-O-4 linked guaiacyl or syringyl units in lignin.[17]



(Eq. 2)

guaiacyl unit, R = H
syringyl unit, R = OCH_3

11e/t, R = H, erythro/threo
12e/t, R = OCH_3, erythro/threo

The gas chromatographic separation of the products is shown in Figure 2. Table 5 gives results of the yield of main monomeric products recovered from thioacidolysis of the lignin investigated; vanillin and syringaldehyde are converted to the corresponding thioacetals, **13** and **14**,

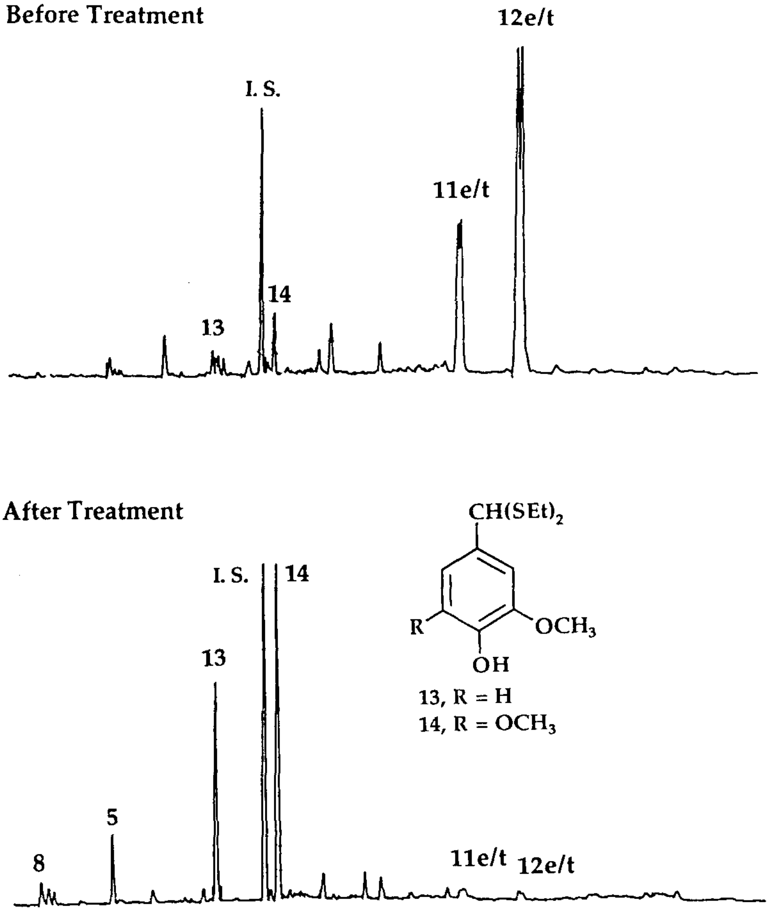


Figure 2. Gas chromatograms of thioacidolysis (trimethylsilated) products from a poplar-O_2-organosolv lignin before and after CuO treatment. The numbers correspond to text compound numbers; the internal standard (I.S.) was docosane.

during thioacidolysis. The data of Figure 2 and Table 5 clearly indicate that the lignin sample before CuO treatment contained β-O-4 structures, but that the treatment led to extensive fragmentation; almost no β-O-4 linked guaiacyl and syringyl units remained. Large amounts of vanillin,

Table 5. Yield of the main thioacidolysis monomeric products from a poplar-O_2-organosolv lignin before and after CuO treatment.

Product	Yield (μmol/g lignin) Before treatment	 After treatment
β-O-4 linked guaiacyl unit (**11**)	326	15
β-O-4 linked syringyl unit (**12**)	762	7
Vanillin (**13**)	29	157
Syringaldehyde (**14**)	58	320
Vanillic acid (**7**)	-	36
Syringic acid (**8**)	-	70

syringaldehyde, vanillic acid and syringic acid formed, presumably by oxidative cleavage of C_α-C_β bonds. The ratio of vanillin + vanillic acid/syringaldehyde + syringic acid observed were similar to the ratio of β-O-4 linked guaiacyl/syringyl units in the starting material in this case.

For the poplar lignin, whether untreated or treated, syringyl units were the major monomeric products. This is probably because syringyl units have no C_5-sites available for condensation with other lignin building units; condensed, higher molecular weight materials are not observed in this test. Interestingly, the untreated lignin was similar to that of a poplar milled wood lignin studied by another group.[16] Both the yield of non-condensed guaiacyl and syringyl units and the ratio of guaiacyl/syringyl are comparable. This implies that condensation reactions were not very prevalent during the O_2-organosolv pulping process and, thus, much of the original lignin structure was retained.

DMBQ Yield Optimum Based on Aldehyde Content

Several optimization studies were performed to maximize benzoquinone yields from a mixture of vanillin and syringaldehyde, the principal products of the CuO pretreatments. For the experiments reported in Table 6, the NO_2 amount was held constant and at a high level and the

Table 6. Effect of NHS dose on DMBQ yield from a 3:1 mixture of vanillin to syringaldehyde.[a]

Entry	NHS equivalents[b] vanillin	syringaldehyde	Mol % yield DMBQ
1	0	0	75
2	6	2	89
3	12	4	96
4	22	8	97
5	33	12	94
6	78	29	93

[a] NO_2 dose was 31 equiv. to vanillin and 12 equiv. to syringaldehyde; oxidation time was 3 hr. [b] The different NHS equivalents relates to the fact there was 3 times less vanillin in the mixture.

ratio of vanillin to syringaldehyde (1:3) was set to approximate that observed from the CuO pretreatments. No benzoquinone (MMBQ) was observed from oxidation of the vanillin. The yield reduction in the absence of NHS was a little larger in the case of syringaldehyde, relative to that observed for syringyl alcohol.[6] Increasing the NHS dose had a small, negative impact on DMBQ yield.

Table 7 shows the effects of NO_2 amount on DMBQ yield; the optimum dose was 12 equiv. This is a large excess compared with the 5.5 equivalents used when syringaldehyde is oxidized alone and gives an 87% DMBQ yield.[2] The large excess needed for the mixture may be related to extensive losses of NO_2 in vanillin/NO_2 reactions.[2] The optimum time for reaction appears to be 3 hr (Table 8).

CuO Treatment of Various Lignins

The conditions, workup, and reagent quantities that worked best for the aspen ethanol lignin were applied to the pretreatment and oxidation

Table 7. Effect of NO_2 amount on DMBQ yield from an aldehyde mixture for a 3 hr reaction. [a]

	NO_2 equivalents[b]		Mol % yield	
Entry	syringaldehyde	vanillin	DMBQ	MMBQ
1	4	11	77	-
2	12	31	94	-
3	33	88	91	-
4	64	170	81	-

[a] NHS dose was 33 equiv. to vanillin and 12.4 equiv. to syringaldehyde. [b] The different NO_2 equivalents relates to the fact there was 3 times less vanillin in the mixture.

Table 8. Effects of time on the DMBQ yield for the oxidation of syringaldehyde with 12 equiv. of NO_2 and 4.3 equiv. of NHS.

Time (hr)	DMBQ yield (mol%)
0.5	76
1	81
2	87
3	96
5	95

of several lignin samples. The sequential copper oxide/NO_2 oxidations had two goals: (1) to learn the general effectiveness of CuO treatments for different lignins and (2) to confirm that the DMBQ yield can be predicted from the syringaldehyde content in the treated lignin. Conditions were not optimized for each of the different lignins.

The reaction mixtures from treatment of the lignin samples with CuO/NaOH were separated into two portions. The first portion was analyzed for the relative amounts of monomeric compounds present

Table 9. Yields of Products from Treating Various Hardwood Lignins with Copper Oxide at 176°C for 3 hr.

	Weight % Yield[a]					
Lignin	3	4	5	6	7	8
1. Lab. Ethanol Organosolv[b]	3.26	0.61	0.70	9.21	2.17	0.64
2. White Oak Organosolv Ext.[c]	2.81	0.50	-	8.08	2.14	-
3. White Oak Organosolv Insol.[c]	2.43	-	-	8.33	1.76	-
4. Aspen Organosolv Ext.[c]	2.03	0.40	-	7.15	1.53	1.16
5. Aspen Organosolv Insol.[c]	2.36	0.52	-	7.10	1.66	-
6. Scarlet Oak Organosolv Ext.[c]	2.27	0.51	-	5.96	1.80	-
7. Scarlet Oak Organosolv Insol.[c]	2.01	0.50	0.22	5.26	1.25	0.21
8. Alcell Lignin[d]	0.76	0.20	-	4.02	1.29	trace
9. Birch O_2-Organosolv[e]	3.08	trace	-	10.54	2.19	-
10. Aspen O_2-Organosolv[e]	3.86	0.62	-	11.14	2.86	-
11. Poplar O_2-Organosolv[e]	4.04	0.90	1.01	7.98	1.69	0.45
12. Hardwood Lignosulfonate[f]	3.42	0.75	-	6.00	2.40	-
13. White Oak Organosolv Ext.[g]	2.65	0.49	-	7.53	2.12	-
14. Kraft Hardwood[h]	1.79	0.57	-	3.41	1.62	-
15. Hardwood Organosolv[g]	4.48	0.68	-	12.58	2.84	-
16. Organosolv Aspen[g]	2.98	0.47	-	10.73	2.13	-
17. Organosolv Aspen[g]	2.59	0.52	-	7.54	1.92	0.35

[a] see text structures. [b] ref. 4. [c] same sample as that reported in Table 1. [d] Repap Corp.; wood source has 43% syringyl and 57% guaiacyl units.[18] [e] from a laboratory in St. Petersburg, Russia.[19] [f] from Reed Lignin, Wisconsin. [g] Sample prepared differently (i.e., no acid catalyst) than that listed in footnote c. [h] Westvaco Corp. experimental lignin.

(Table 9). The second portion was oxidized with NO_2/NHS; the DMBQ yields were determined (based on the amount of lignin used in the CuO experiments) and compared to yields obtained from direct oxidation of untreated lignins (Table 10). The amount of syringaldehyde found from analysis of the first portion was used to calculate an expected DMBQ yield from oxidation of the second portion.

Table 10. Effects of Copper Oxide Oxidation (176°C/3 hr) on DMBQ Yields from NO_2 Oxidation of Selected Lignins.

	Weight % Yield[a]		
Lignin	No Treatment	CuO Treatment	Δ%
1. Laboratory Ethanol Organosolv[b]	5.1 (3.3)	12.4 (8.5)	+ 7.3
2. White Oak Organosolv Ext.[c]	4.4 (5.0)	8.5 (7.5)	+ 4.1
3. White Oak Organosolv Insol.[c]	3.9 (3.5)	9.0 (7.7)	+ 5.1
4. Aspen Organosolv Ext.[c]	7.8 (7.3)	8.3, 7.4 (6.6)	+ 0.5
5. Aspen Organosolv Insol.[c]	3.6 (3.5)	6.1 (6.6)	+ 2.5
6. Scarlet Oak Organosolv Ext.[c]	6.1 (5.4)	7.9 (5.5)	+ 1.8
7. Scarlet Oak Organosolv Insol.[c]	3.5	6.8 (4.9)	+ 3.3
8. Alcell Lignin[d]	7.6 (6.7)	7.7 (3.7)	+ 0.1
9. Birch O_2-Organosolv[e]	2.1	14.3 (9.7)	+12.2
10. Aspen O_2-Organosolv[e]	2.3	15.1 (10.3)	+12.8
11. Poplar O_2-Organosolv[e]	2.1	14.4 (7.4)	+12.3
12. Hardwood Lignosulfonate[f]	1.7	5.6 (5.5)	+ 3.9
13. White Oak Organosolv Ext.[g]	6.9	9.4 (7.0)	+ 2.5
14. Kraft Hardwood[h]	5.7 (5.3)	6.0, 5.5 (3.1)	+ 0.3
15. Hardwood Organosolv[g]	7.3	12.0 (11.6)	+ 4.7
16. Organosolv Aspen[g]	7.3	10.8 (9.9)	+ 3.5
17. Organosolv Aspen[g]	6.0 (5.9)	8.8 (7.0)	+ 2.8

[a] NO_2 oxidations were for 3 hr in methanol and employed a lignin/NO_2/NHS weight ratio of 3/1/3; the yields were determined by direct GC; numbers in parentheses are theoretical yields calculated from syringaldehyde yields given in Table 9. [b-h] see Table 9 footnotes.

Many CuO oxidized samples showed comparatively large differences between their actual and theoretical DMBQ yields; better agreement was observed for the untreated samples. In most cases, higher yields of DMBQ than predicted were observed. Even so, the amount of syringaldehyde present after copper oxide treatment is a useful indicator of possible DMBQ yields; other monomeric substrates can also be converted to DMBQ upon NO_2 oxidation.[2]

Six lignin samples gave >10% yields of DMBQ. All CuO treated lignins produced DMBQ in higher yields than untreated lignins; the three pretreated O_2-organosolv lignins were more than six times higher than untreated samples. The observed 15.1% yield with aspen O_2-organosolv lignin corresponds to oxidation of roughly 60% of the available syringyl units (assuming 25% syringyl units present). Other than the aspen ethanol lignin, the reactant ratios and conditions were not optimized for any of the lignins.

The yields of oxidized fragments (**3-8**) from CuO treatment of pairs of extracted and insoluble lignins (entries 2/3, 4/5, and 6/7, Table 9) were fairly similar. The same was true for DMBQ yields after NO_2 oxidation (Table 10). In essence, the CuO treatment degraded the higher (insoluble) and lower (extracted) molecular weight lignin to the same mixture of components and, thus, the same DMBQ yields upon NO_2 treatment. A greater DMBQ yield improvement occurred with insoluble lignins since these lignins gave low DMBQ yields before CuO treatment.

Entries 2-7 in Table 10 correspond to the lignins reported earlier in Table 1. The DMBQ yield *trends* for untreated lignins (column 1, Table 10) are similar to that reported in Table 1, but the absolute amounts differ, since reactant ratios and times differed. The DMBQ yields were greater in the earlier studies, where three times more NO_2/lignin was used. The experiments reported in Table 10 used less NO_2 - amounts that would be more in line in with prospective commercialization.

The question as to fate of the excess NO_2 in our lignin oxidations was answered by performing elemental analyses of an organosolv hardwood lignin before and after treatment with an excess (8.6 equivalents/lignin monomer unit) of NO_2. The untreated lignin had a molecular formula of $C_{10}H_{13.1}N_{0.06}O_{4.7}$; the treated lignin had a formula of $C_{10}H_{12.9}N_{0.46}O_{6.8}$. The data indicate that ~50% of the aromatic rings on the residual lignin had been nitrated in this case. The nitration probably occurred primarily on the guaiacyl rings.[2]

Product Analysis

The yields of DMBQ varied as a function of isolation procedure. Two methods were examined to recover DMBQ from reaction mixtures. These methods were developed by studying the recovery of DMBQ from a *model* mixture containing known amounts of ethanol organosolv lignin, DMBQ, and AQ in $CHCl_3/CH_3OH$ solution. The homogeneous mixture was evaporated and the DMBQ was separated from the residue by extraction with refluxing $CHCl_3$ or by column chromatography over Al_2O_3 using $CHCl_3$ as the eluent. Both methods showed excellent DMBQ recovery (100%).

If water was added to the model homogeneous mixture, a gummy precipitate formed. Evaporation of the solvent and work up as above resulted in DMBQ recoveries of ~70%. The AQ recovery was unaffected by the water addition; it was 100% in all cases. [An internal standard, benzophenone, was used to measure the recoveries.] Identical trends were observed for an NO_2-treated ethanol lignin: the DMBQ yield was 5.1% for direct hot $CHCl_3$ extraction or column chromatography, but dropped to 3.3% when water was added prior to extraction or chromatography. These effects are probably due to DMBQ incorporation into the lignin polymeric structure during precipitation by water.

The most reliable yields come from a direct analysis of the reaction mixture by either HPLC (with external calibration) or GC (with AQ as an internal standard). The DMBQ yields are often 0-50% higher (0-4% in absolute amount) for the HPLC method; the reasons for this are unclear. However, the observed yield trends by GC and HPLC are in good agreement (see Tables 1 and 2). Most of our analyses employed GC, simply because it was a faster method, even though the yield determination might be somewhat lower by this method. The yields reported in the tables are by the direct GC analysis method, unless stated otherwise. Any commercial process for producing DMBQ (and MMBQ) from lignin will need to take into account the association of simple quinones with precipitated lignin and design a recovery system accordingly.

CONCLUSIONS

Direct oxidation of lignin samples by NO_2 provides relatively poor yields of benzoquinones. Yields can be improved by solvent extraction of the lignin to obtain a low molecular weight fraction prior to NO_2 oxidation. Fractionated hardwood lignin samples having molecular weights below 1000 gave yields of DMBQ of about 10%, which represented conversion of roughly 40% of the available syringyl units. The yields of MMBQ from guaiacyl lignin units are near zero.

Another way to improve DMBQ yields is to pretreat the lignin with CuO/NaOH before conducting the NO_2 oxidation. The yields can often be improved to 10-15%; the pretreatment does not require prior fractionation to obtain the improved yields. Thioacidolysis analysis of a lignin before and after CuO treatment indicated that the treatment is very effective in cleaving β-aryl ether bonds. The target benzoquinone yield appears to depend largely on the level of syringaldehyde in the CuO treated lignin.

EXPERIMENTAL

The general experimental conditions, such as NO_2 oxidation procedures and gas chromatographic (GC) analyses have been described earlier.[2] For direct GC analysis, a pre-column was used to protect the main column from lignin contamination. The high performance liquid chromatography (HPLC) analyses employed a Hewlett-Packard Model 1090 instrument with a 2.1 x 100 mm Spheri-5 RP-18 microbore column and a 2.1 x 30 mm precolumn of the same packing. The eluent was 5% acetonitrile/95% 35 mM acetic acid at a rate of 0.7 mL/min. A photo diode array detector monitored wavelengths of 256 nm for MMBQ, 290 nm for DMBQ, and 270 nm for vanillin, acetovanillin, and syringaldehyde. Quantification relied on calibrating responses for standard mixtures of each analyzed component for concentrations ranges of 0.01-3 mg/mL Test solutions were diluted to have concentrations of analyte in this calibration range. Correlation coefficients (R^2) of 0.99 were typical for the calibration table.

Lignin Samples. White oak, scarlet oak, and aspen lignins were obtained by organosolv pulping processes. A representative preparation involved heating presorted aspen chips for 2.5 hours at 165°C in a rotating autoclave with a pulping liquor that was 70% (v/v) methanol in water and contained 0.05M H_2SO_4 catalyst. The solvent to wood ratio was 4:1. The lignin was isolated from the pulping liquor by precipitation with water after removal of methanol by rotary evaporation under a mild vacuum. The precipitated lignin was isolated by filtration, washed again with water and dried at 40°C in a vacuum oven. The procedure is explained in greater depth elsewhere.[20] Sources of the other lignins studies are given in Table footnotes.

Lignin Extraction and Analysis. Several lignins were extracted to separate a low and high molecular weight fractions (the exact details are part of a proprietary process developed at the National Renewable Energy Laboratory). The ratio of syringyl to guaiacyl units in the lignins was determined by methoxyl analysis using FT-IR and partial least squares regression.[21] Molecular weights were determined by gel permeation chromatography (GPC). The lignin samples were first acetylated according to the method of Gierer and Lindeberg.[22] GPC was performed at 25 °C using a solvent flow rate of 10 mL/min of HPLC grade tetrahydrofuran through a HP 1090 instrument (diode array and refractive index detectors connected in series) using two styrene/divinyl benzene copolymer gel columns with nominal pore diameters of $1x10^{-3}$ and $1x10^{-4}$ Å connected in series. Elution of lignins, 50 μL injections of ~2 mg/mL solutions, was monitored at 260 nm with a bandwidth of 80 nm. Solvents and sample solutions were filtered through a 0.2 mm nylon membrane filter before use. Molecular weight distributions of both polymers were calculated relative to the retention times of polystyrene standards. The low molecular weight fractions eluted during GPC as a single curve (compared to the bimodal elution of the whole lignin). The weight average molecular weight of the low molecular weight lignin samples in acetone was confirmed by Huffman Labs using vapor pressure osmometry. The observed value of ~670 was in excellent agreement with that obtained using GPC.

Effect of NO_2 Age on DMBQ Yield. The age of the stored NO_2 can effect DMBQ yields. The NO_2 was generally stored in a freezer prior to use. Each time the NO_2 container was opened, and a sample removed, some hydrolysis occurred. A sample of old NO_2 contained significant contamination from HNO_3 and, therefore, less NO_2/mL. Old NO_2 was prepared by exposing fresh NO_2 to air many times. Fresh NO_2 gave generally reproducible DMBQ yields for a CuO-treated lignin: 15.4, 15.0 and 14.9%. However, older NO_2 gave significantly lower yields with the same lignin: 13.7% after 40 exposures and 12.2 after 60 exposures. In the experiments comparing DMBQ yields from various lignins (Table 10), we took great care to use fresh NO_2.

Thioacidolysis of Lignin Samples. Thioacidolysis[16] was carried out on a poplar-O_2-organosolv lignin,[19] before and after CuO treatment (176°C, 2N NaOH, 3 hr). Samples were trimethylsilylated (TMS) with N,O-bis-(trimethylsilyl)trifluoroacetamide/pyridine. The TMS derivatized monomeric products were identified by GC-MS and quantified by GC with conditions previously described,[16] except for a column temp. program of 150°C (1 min), 5°C/min to 280°C (hold), injector temp. of 250°C, detector temp. of 280°C, helium carrier gas at a flow rate of 30 mL/min. Docosane was used as internal standard. Analytical error range of duplicate tests was <5 %. The results are given in the text.

Elemental Analysis of NO_2 Treated Lignin. A sample of organosolv hardwood lignin was treated with 8.6 equiv. of NO_2 in methanol under the usual procedure. At the conclusion, the reaction mixture was diluted with 15 mL of Et_2O to precipitate the residual lignin. This mixture was centrifuged and the supernatant decanted. The sediment was washed with Et_2O and the residual lignin was freeze-dried. Duplicate elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA) for the lignin before and after treatment; the agreement was good between duplicate sets.

Starting lignin: C, 57.21%; H, 6.24%; N, 0.04%; O, 36.15% (by difference)
Reacted lignin: C, 48.40%; H, 5.16%; N, 2.62%; O, 43.83% (by difference)

Copper Oxide Oxidation. The lignin sample (35 mg), 3 mL of 2 M NaOH and copper (II) hydroxide (100 mg) were added to a 4.5 mL stainless steel pressure bomb. The bomb was heated at elevated temperature for various times. The bomb was cooled and the contents filtered to remove the inorganic components; the bomb was rinsed several times with 2 M NaOH and then water. The filtrate was diluted to 25 mL with water. When necessary, 5 mL of the filtrate was removed, acidified, extracted with $CHCl_3$; the extract was analyzed by GC to determine the product composition (Table 9). The remainder of the filtrate was acidified with dilute HCl and extracted with 3-15 mL portions of 33% $CHCl_3$/dioxane. Each phase was processed and subjected to NO_2 oxidation; the organic phase provided water phase provided ~1% DMBQ. The combined $CHCl_3$/dioxane extracts was washed with water, dried (Na_2SO_4 overnight), and concentrated to dryness *in vacuo*; the residue was dried over $CaSO_4$ *in vacuo* to a constant weight and then subjected to the NO_2 oxidation. The water layer was concentrated to a small volume *in vacuo* and extracted with 3-15 mL of 33% $CHCl_3$/acetone. The combined organic extracts were washed with saturated NaCl aq. soln., dried (Na_2SO_4 overnight) and concentrated *in vacuo*. The residue was oxidized with NO_2.

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REFERENCES

1. (a) Address correspondences to this author; (b) Visiting Scientist from the Institute of Agricultural and Forest Engineering, University of

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2. D.R. Dimmel, M.R. Karim, M.C. Savidakis, and J.J. Bozell, J. Wood Chem. Technol., 16, 169 (1996).

3. D.R. Dimmel and J.J. Bozell, Tappi J., 74 (5), 239 (1991).

4. J.C. Wozniak, D.R. Dimmel, and E.W. Malcolm, J. Wood Chem. Technol., 9, 491 (1989).

5. J.J. Bozell, D.R. Dimmel, and P. Van Vreede, J. Wood Chem. Technol., Paper 10 in the series, in preparation.

6. K. Lundquist and R. Lundgren, Acta Chem. Scand., 26, 2005 (1972).

7. P.S. Bailey, Ozonation in Organic Chemistry, Vol. I, Academic Press, NY, 1978.

8. K. Sakai, S.-P. Mun, and H. Imamura, J. Wood Chem. Technol., 6, 523 (1986); K. Sakai, H. Takeuchi, S.-P. Mun, and H. Imamura, *ibid.*, 8, 29 (1988).

9. A. Sakakibara and N. Nakayama, J. Japan Wood Res. Soc., 7, 13 (1961); *ibid.*, 8, 153, 157 (1962).

10. G. Meshitsuka, T. Kondo, and J. Nakano, J. Wood Chem. Technol., 7, 161 (1987); S. Makino, G. Meshitsuka, and A. Ishizu, J. Japan Wood Res. Soc., 36, 460 (1990).

11. S.M. Shevchenko, L.G. Akim, A.V. Pranovich, and M.Ya. Zarubin, Tappi, 74(4), 257 (1991).

12. S. Hosoya, H. Hatakeyama, and J. Nakano, J. Japan Wood Res. Soc., 16, 140 (1970).

13. I.A. Pearl, J. Amer. Chem. Soc., 64, 1429 (1942); I.A. Pearl and D.L. Beyer, Tappi, 29, 171 (1956); S. Larsson, and G. E. Miksche, Acta Chem. Scand., 25, 647 (1971);J.M. Pepper and J.C. Karapally, Pulp Paper Canada, 73, T232 (1972).

14. N. Morohoshi and W.G. Glasser, Wood Sci. Technol., 13, 165 (1979).

15. C. Rolando, B. Monties, and C. Lapierre, J. Wood Chem. Technol., 5, 277 (1985).

16. C. Rolando, B. Monties, and C. Lapierre, "Thioacidolysis," in Methods in Lignin Chemistry, S.Y. Lin and C.W. Dence Editors, Springer Verlag, Berlin, 1992, p. 334-49.

17. C. Rolando, B. Monties, and C. Lapierre, Proceed. 4th Intern. Symp. Wood Pulping Chem., Paris, 1987, Vol 2, p. 431.

18. D.K. Gallagher, H.L. Hergert, M. Cronlund, and L.L. Landucci, Proceed. 5th Intern. Symp. Wood Pulping Chem., Raleigh, NC, 1989, p. 709.

19. C.P. Neto, D. Evtuguin, and A. Roberts, J. Wood Chem. Technol., 14, 383 (1994).

20. H.C. Chum, D.K. Johnson, S.K. Black, J. Baker, K. Grohmann, K.V. Sarkanen, K. Wallace, and H. A. Schroeder, Biotechnology and Engineering, 31, 643 (1988).

21. B.R. Hames, S.K. Black, F. Agblevor, R. Evans, D.K. Johnson, and H.L. Chum, Proceed. 6th Intern. Symp. Wood Pulping Chem., Melbourne, Australia, April 1991, Vol. 1, p. 535.

22. J. Gierer and O. Lindeberg, Acta Chem. Scand., B34, 161 (1980).