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The Aerobic Oxidative Cleavage of Lignin to Produce Hydroxyaromatic Benzaldehydes and Carboxylic Acids *via* Metal/Bromide Catalysts in Acetic Acid/Water Mixtures

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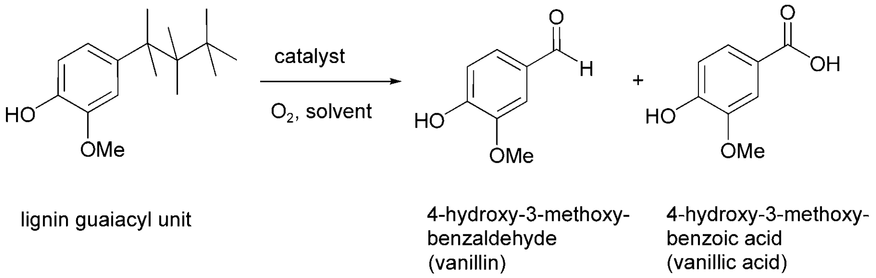
Abstract: Roughly 30% of all woody plants is composed of lignin. Five different lignin samples, from wood and bagasse, were oxidized in air with a cobalt/manganese/zirconium/bromide (Co/Mn/Zr/Br) catalyst in acetic acid as a function of time, temperature, pressure, and lignin and catalyst concentrations. 18 products were identified *via* gas chromatography-mass spectrometry (GC/MS). The most valuable products from lignin were 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 4-hydroxy-3-methoxybenzoic acid (vanillic acid), 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) and 4-hydroxy-3,5-dimethoxybenzoic acid (syringic acid). 10.9 wt% of the lignin was converted to the aromatic products. By the use of model compounds we demonstrate that 1) the presence of the phenolic functionality on an aromatic ring does inhibit the rate of reaction but that the alkyl group on the ring still does oxidize to the carboxylic acid, 2) that the masking of phenol by acetylation occurs at a reasonable rate in acetic acid, 3) that the alkyl group of the masked phenol does very readily oxidize, 4) that an acetic anhydride/acetic acid mixture is a good oxidation solvent and 5) that a two-step acetylation/oxidation to the carboxylic acid is feasible.

Keywords: autoxidation; cobalt; green chemistry; lignins; organosolv lignin; oxidation

Introduction

Lignin is a major component of woody plants, the second most abundant natural polymer (after cellulose), and is produced, largely as a waste-product, from the wood-pulp or sugar cane milling industry.[1,2] The U.S. pulp and paper industry processes approximately 108 million tons of wood annually.[3] It is most commonly used for its fuel value, i.e., its *unselective* oxidation to carbon dioxide. Lignin has a complex, polymeric structure whose exact structure is unknown and which varies depending on its source. The aromatic portion of lignin is composed of *p*-hydroxybenzene, guaiacyl (4-alkyl-2-methoxyphenol), and syringyl (4-alkyl-2,5-dimethoxyphenol) units. The most efficient and economic method for the conversion of alkylaromatic compounds to aromatic carboxylic acids is *via* the homogeneous air oxidation of these compounds using metal/bromide catalysts.[4] This led us to predict that a series of substituted aromatic acids might be produced by the aerobic oxidation of the the structural units of lignin using metal/bromide catalysts. For example, the guaiacyl unit could be oxidized as shown in Eq. (1).



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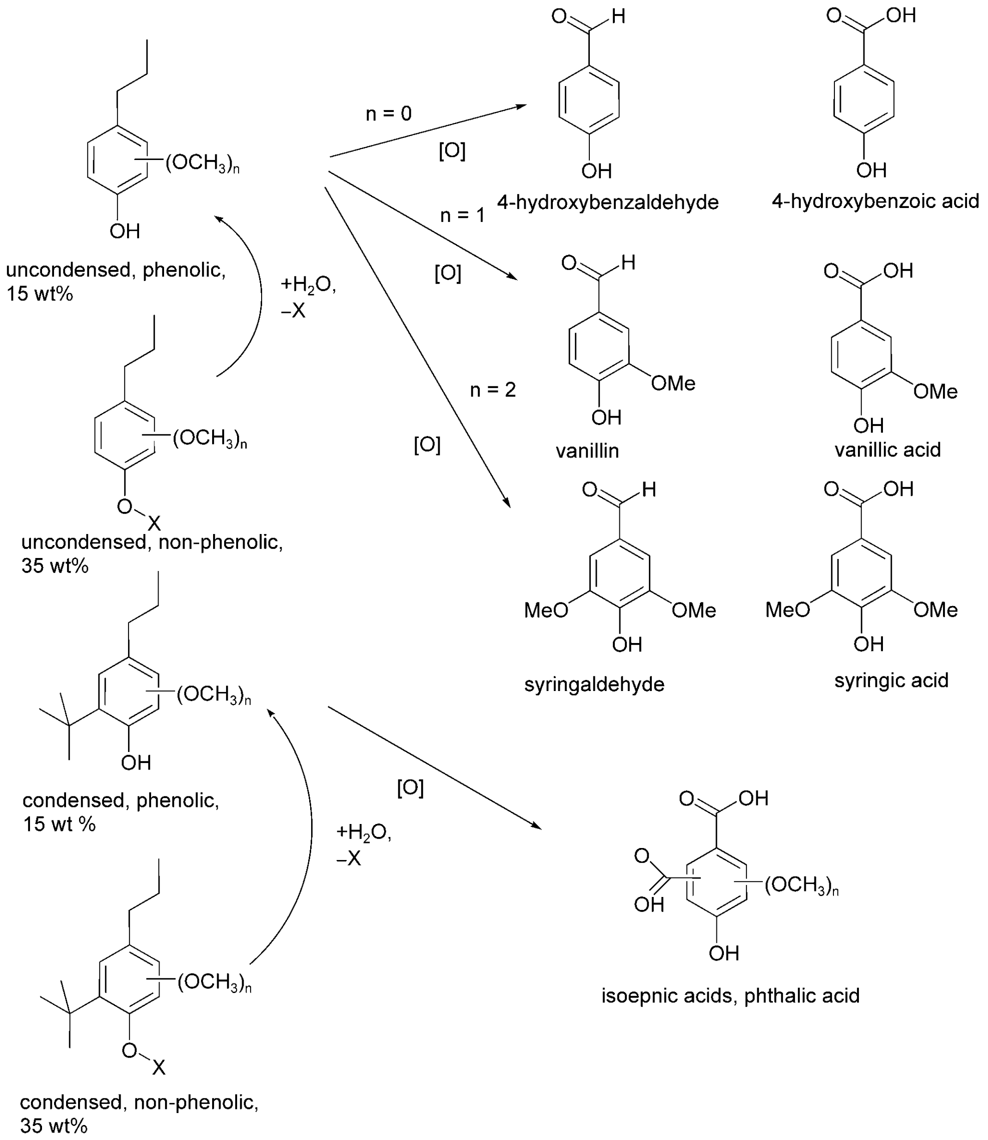
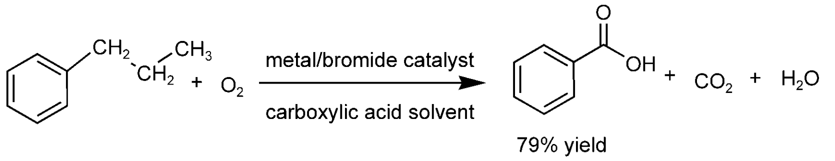


Figure 1. Types of aromatic functional groups in lignin and types of aromatic acids that can form as a result of oxidation of these functional groups. This figure is simplified in that biphenyl and biaryl derivatives, known to be present, are not shown. Estimated amounts from ref.[1a]

In lignin one has a propyl group, as shown in Eq. (1), which is partially oxygenated and substituted in complex ways to form the polymeric unit. The predicted acids are given in Figure 1. These 4-carboxy and 4-formyl derivatives of phenol have known commercial applications for their antibacterial, antifungal properties[5] and use in food preservation as parabens.[6] Thus aerobic oxidation of what is usually considered a waste product, could be a inexpensive green source of valuable chemicals.

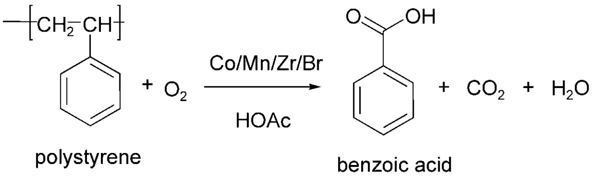
Our optimism that this could become a viable commercial source of valuable chemicals arises for the following reasons: 1) The metal/bromide catalyzed aerobic oxidation of alkylaromatic compounds in acetic acid solvent is a well-established method to produce aromatic carboxylic acids.[4] It is used industrially to produce a variety of carboxylic acids including multi-billion pound/year amounts of terephthalic acid, the major component of polyethylene terephthalate (PET). Thus, most of the engineering problems such as corrosion in bromide/acetic acid mixtures, recycling of the solvent and catalyst, and efficient mixing of the dioxygen with the acetic acid solvent have been solved. 2) The unit cell of the lignin polymer is based on propylbenzene. It is well-established that the highly active metal/bromide catalysts can convert propylbenzene derivatives to benzoic acid in high yield [Eq. (2)].[4]

Two of the carbon atoms on the propyl side-chain become oxidized to primarily carbon dioxide and



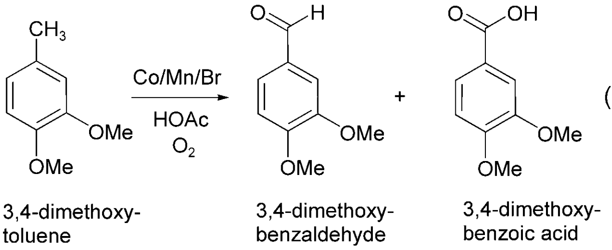
(2)

water. 3) Despite the relative insolubility of polymers in most solvents, we have demonstrated that they can be aerobically oxidized using metal/bromide homogeneous catalysts to valuable products.[7] One particularly pertinent example is the oxidation of polystyrene to benzoic acid where the aliphatic backbone is oxidized to benzoic acid in 88% yield [Eq. (3)].[7]



(3)

This demonstrates that the aliphatic backbone of the polymer can be oxidized to produce aromatic carboxylic acids. 4) One potential method to separate wood pulp from lignin uses an acetic acid/water (80:20 v/v) mixture (the organosolv method) which has little pollution and offers the possibility of total biomass recovery of the wood.[8] In this method the lignin is extracted into the solvent leaving the insoluble pulp to be further processed into paper products. Since acetic acid is the solvent of choice for metal/bromide autoxidation,[4] there is a solvent compatibility in which separation of lignin from the pulp and then oxidation of the lignin to obtain valuable acids and aldehyde can be performed. 5) Oxidation methods are one of the fundamental characterization tools to determine the structure of lignin.[2] Indeed permanganate oxidation of lignin, after methylation, does produce the acids (as their methyated derivatives) given in Figure 1. 6) We have already shown that 3,4-dimethoxytoluene,[9] a lignin model compound, can be successfully oxidized to its corresponding acid although it did have many unusual characteristics. The maximum yield was 51% to the benzaldehyde and 92% to the carboxylic acid [Eq. (4)].



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There are a number of reports where oxidation methods have been used to prepare valuable aldehyde, acids, and phenols from lignin.[10–13] There are two reports of lignin being oxidized by the Co/Mn/Br catalyst in acetic acid. Organosolv lignins have been oxidized using a Co/Mn/Br catalyst in acetic acid at 210 °C to give vanillin and vanillic acid in 1.9 and 3.0 wt% yield, respectively.[14] The same catalyst and solvent was used to measure the rates and activation energies of lignins from agricultural wastes.[15] The research in this paper gives a much more detailed report on the products found when lignins are oxidized with metal/bromide oxidations in acetic acid over a wide range of the experimental variables time, temperature, pressure, water concentration, and concentration of lignin.

This is a brief report from a biomass project that was pursued at DuPont Central Research. Unfortunately, not all of the planned avenues of research were completed, especially those in which the lignin phenolic groups were masked by the acetate group, but a number of positive scientific and technological results were obtained and are reported here.

Results and Discussion

The Use of Model Compounds to Determine the Effectiveness of Metal/Bromide Catalysts to Oxidize Lignin

We designed a series of experiments on model compounds to understand the influence of phenols on autoxidation and to determine if acetylation of the phenolic group would improve the yields to the aromatic acids. The oxidation of lignin will generate hydroxyaromatic acids through the oxidation of the aliphatic propyl group to the benzaldehyde and then to the carboxylic acid [Figure 2, Eq. (1) and Eq. (2)]. The phenolic functionality on the ring (the hydroxy group) is known to strongly retard autoxidations, i.e., they are potent anti-oxidants. Also phenols are known to oxidize at a faster rate than alkylbenzenes to give initially quinones which are subsequently degraded to carbon dioxide.[16] Thus one can anticipate a significant yield loss to the aromatic carboxylic acid *via* phenol oxidation. A known method to avoid phenol oxidation is to first 'mask' the phenolic group by reacting it with acetic anhydride to form the acetate, [Figure 2, Eq. (3)].[4,17]. Below we will demonstrate

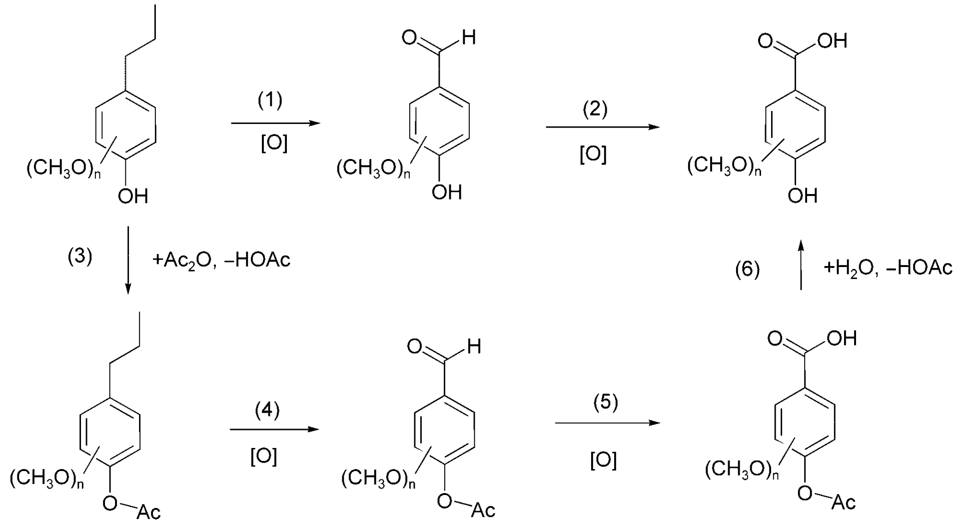
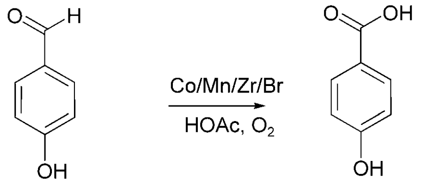


Figure 2. Oxidation/acetylation of the aromatic portion of lignin.

that 1) the presence of the phenolic functionality does inhibit the rate of reaction but that the reaction still does proceed to the carboxylic acid, 2) that acetylation of a phenol occurs at a reasonable rate in acetic acid, 3) that the resultant phenolic acetate does readily oxidize, 4) that an acetic anhydride/acetic acid mixture is a good oxidation solvent and 5) that a two-step acetylation/oxidation is feasible.

4-Hydroxybenzaldehyde was oxidized because it contains the highly reactive benzaldehyde functional group simultaneously with the 4-hydroxy (phenolic) group [Eq. (5)]. The initial conditions and results are given in Table 1. The reaction exhibited autocatalytic behavior in which no oxygen uptake occurred in the first hour. At 1.8 h a weak rate of oxygen uptake was observed along with a sizable rate of carbon dioxide formation (0.31 mL/min; 0.0124 mmol min^{-1}). The reaction was continued for 4.2 h at which the conversion was 22% with an acid yield of of 4-hydroxybenzoic acid of 12% Assuming all of the carbon dioxide came from complete oxidation of 4-hydroxybenzaldehyde, then 4% of the 4-hydroxybenzaldehyde was lost as CO_2.

Vanillin acetate was oxidized, see Eq. (6), to contrast its behavior to that of 4-hydroxybenzaldehyde discussed above. The compounds are structurally simi-



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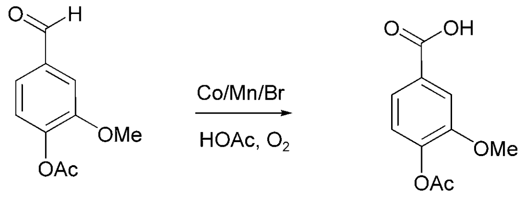
4-hydroxybenzaldehyde 4-hydroxybenzoic acid



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4-acetoxy-3-methoxy-benzaldehyde (vanillin acetate)

4-acetoxy-3-methoxy-benzoic acid

Table 1. Summary of reactions of lignin model compounds.[a]

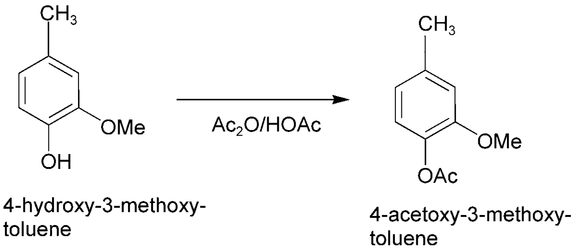
Reaction	Reagent, initial conc.	T [°C]	Catalyst[c]	Type of reaction	Rate [$s^{-1} \times 10^5$][b]	$t_{1/2}$ [h]
1	4-hydroxybenzaldehyde, 0.41 M	80	Co/Mn/Zr/Br	Oxidn	–	–
2	3-methoxy-4-acetoxybenzaldehyde, 0.52 M	80	Co/Mn/Br	Oxidn	81 (16)	0.23
3	4-methoxytoluene, 0.82 M	80	Co/Mn/Br	Oxidn	27 (1.3)	0.71
4	3-methoxy-4-hydroxytoluene, 0.37 M	95	None	Acetylaction	4.54 (0.45)	4.2
5	3-methoxy-4-acetoxytoluene, 0.37 M	95	Co/Mn/Br/Zr	Oxidn	7.2 (0.62)	2.8

[a] Reactions 1 and 2 are in acetic acid; reactions 3–5 in a acetic anhydride/acetic acid mixture.
[b] Rate of disappearance of the reagent. Standard deviation in parenthesis.
[c] Concentration of catalyst components in reaction 1 is 0.02/0.02/0.0005/0.04 M, in reactions 2, 3 it is 0.01/0.01/0.02 M, and in entry 5 0.01/0.01/0.005/0.02 M.

lar except that in vanillin acetate the phenolic group has been 'masked' by the acetate group. The 3-methoxy group only slightly deactivates the oxidation of benzaldehyde so the comparison of vanillin acetate with 4-hydroxybenzoic acid is valid.[9] The oxidation of vanillin acetate is not autocatalytic as the reaction immediately initiated. Also the rate of reaction of vanillin acetate is much faster than that of 4-hydroxybenzaldehyde. The rate of disappearance of the reagent has a half-life of only 0.23 h in contrast to a 22% conversion of 4-hydroxytoluene in 4.2 h, see Table 1. The reaction of 4-acetoxy-3-methoxybenzaldehyde was complete in two hours. A 90% isolated yield of the 4-acetoxy-3-methoxybenzoic acid was obtained by evaporation of the reactor effluent and water-washing the product.

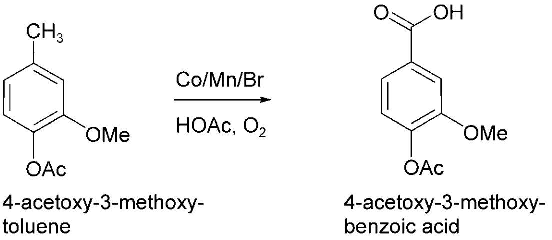
4-Methoxytoluene is a model compound of similar reactivity to the guaiacyl and syringyl groups in lignin. It was oxidized in a 30% Ac_2O/HOAc mixture to determine if this was a viable oxidation solvent, see example 3 of Table 1. A rapid oxidation of this substrate occurred with a half-life of 0.71 h confirming that indeed it is a good oxidation solvent. The rate constant for the disappearance of 3,4-dimethoxytoluene in acetic acid, as reported by us, is $1.6\times10^{-4}\,s^{-1}$ ($t_{1/2}=$ 1.2 h).[9] The reactivity of 4-methoxytoluene is about 16% higher than that of 3,4-dimethoxytoluene.[9] Thus, in an acetic anhydride/acetic acid mixture it is at least as active, if not more so, than in acetic acid alone.

The following reactions demonstrate that one can first acetylate a phenol and then oxidize it to its carboxylic acid. The rate of acetylation of 4-hydroxy-3-methoxytoluene, see Eq. (7), in 20% Ac_2O/HOAc and that of 4-hydroxytoluene was determined, see example 4 in Table 1. The acetic anhydride/reagent ratio is 5.4 mol/mol. The half-life was 4.2 h at 95 °C. The reaction was continued at 95 °C for 7 h and then cooled to room temperature overnight.



(7)

The GC analysis of the material in the Ac_2O/HOAc indicated that the reaction was 94.3% complete that is, there was 5.7% unreacted 4-hydroxy-3-methoxytoluene. This mixture was oxidized with a Co/Mn/Zr/Br catalyst at 95 °C, see Eq. (8) and example 5 of Table 1. The reaction was autocatalytic because of the residual 4-hydroxy-3-methoxytoluene in the mixture. The half-life of 4-hydroxy-3-methoxytoluene was 2.8 h after the reaction initiated. This rate at 95 °C is slower than that of 3,4-dimethoxytoluene, a compound of similar reactivity, at 80 °C which has a half-life of 1.3 h. Thus the reaction is being inhibited by the presence of the residual phenol as expected.



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Selection and Characterization of the of Lignins Used in this Study

The lignins were used as received from Aldrich Chemical.

1) Lignin, organosolv was isolated from a commercial pulp mill using mixed hardwood (50% maple, 35% birch, 15% poplar). Analysis of the sample gave 18.9 wt% methoxy groups, <0.5 wt% sugars, <1 wt% ash. ^{1}H NMR analysis indicates almost equal amounts of phenolic and aliphatic hydroxy groups.[18] This lignin was selected because one of the organosolv pulping methods uses 80% acetic acid/20% water which is the same solvent system used in this work.

2) Lignin, organosolv, acetate – this is a derivative of organosolv lignin, (see 1 above) prepared by dissolving the lignin in acetic acid and reacting it with acetic anhydride using sodium acetate as the catalyst. This procedure acetylates the phenol groups. Prior to isolation, it was partially bleached with hydrogen peroxide. ^{1}H NMR analysis indicates almost equal amounts of aromatic and aliphatic acetoxy groups.[18] This lignin was chosen because the acetylation procedure 'masks' the phenolic groups, see above.

3) Lignosulfonic acid, sodium salt, acetate – this is prepared by reacting the sodium salt of lignosulfonic acid with acetic anhydride in acetic acid. The lignin is believed to be derived from Norway spruce. It contains 11.6 wt% sodium, 2.6 wt% sulfur, 6.5 wt% methoxy groups, and 15.8 wt% carboxyl groups. The molecular weight is 174,400 (MW) and 16,000 (MN).[18]

4) Lignin, hydrolytic – this is a polymeric autohydrolysis lignin material isolated from a commercial hydrolysis pilot plant using predominatly sugar cane bagasse as raw material. 9–11 wt% of the sample is methoxy groups. ^{1}H NMR analysis indicates a predominance of phenolic over aliphatic hydroxy groups and shows evidence of methyl groups.[18]

5) Lignin, hydrolytic, hydroxymethyl – prepared from lignin, hydrolytic (see 4 above) by treating lignin in a homogeneous aqueous alkali solution with formaldehyde. ^{1}H NMR analysis indicates that a significant increase in aliphatic hydroxy groups occurred during hydroxymethylation.[18]

The elemental analyses of the lignin samples used are given in Table 2. This was done to ascertain the amount of nitrogen and sulfur in the samples since often compounds containing these elements are strong antioxidants. Except for the expected high sulfur in the lignosulfonic acid salt, the samples did not contain significant amounts of sulfur or nitrogen. Sulfonic acids themselves are not antioxidants.[4]

Table 2. Elemental analysis of lignin compounds evaluated in this work.

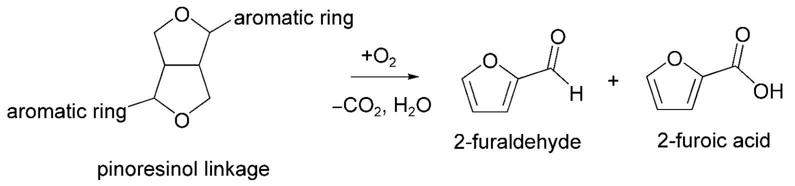
Description	C %	H %	N %	S %
lignin hydrolytic	57.73	5.54	0.54	< 0.20
lignin hydrolytic – hydroxymethyl derivative	57.64	5.66	0.41	< 0.20
lignosulfonic acid, sodium salt acetate	48.70	4.86	3.54	4.87
lignin organosolv	66.05	5.67	0.17	< 0.20
lignin organosolv acetate	62.84	5.49	0.11	< 0.20

Table 3. Results from GC/MS and silation GC/MS analysis from the products of the autoxidation of Aldrich 'lignin organosolv'.

Product(s)	Probable origin
Methyl bromide, glycolic acid, acetoxyacetic acid, maleic acid, fumaric acid	From acetic acid solvent. By-products normally found in metal/bromide oxidation in acetic acid
Methyl formate, methyl acetate, formic acid	Products expected from oxidation of acetic acid and lignin
Propionic acid	Impurity in the acetic acid solvent
Acetone, ethyl acetate, 2-furaldehyde, 2-furoic acid	From lignin oxidation
p-Hydroxybenzoic acid	Expected product from autoxidation of *p*-hydroxylphenyl units in lignin
Vanillin, vanillic acid	Expected product from autoxidation of guaiacyl units in lignin
Syringaldehyde, syringic acid	Expected product from autoxidation of syringyl units in lignin

Product Characterization by GC/MS and Silation GC/MS Analysis

Characterization of products from the aerobic oxidation of Aldrich 'lignin organosolv' for 2 h at 150 °C and 70 bar catalyzed by a Co/Mn/Zr/Br catalyst in acetic acid is given in Table 3. Four compounds of high intensity corresponded to vanillin, vanillic acid, syringaldehyde, and syringic acid. 4-Hydroxybenzoic acid was also detected but was much less intense. These are indicated in the table along with a number of other minor components associated with lignin and acetic acid oxidation. It is significant that no ring brominated products were detected considering the high electron density of the phenolic-methoxylated rings. Ring bromination would convert the active ionic bromide in an inactive catalytic form and hence reduce the activity of the catalyst. The 2-furoic acid and 2-furaldehyde probably come from oxidation of the pinoresinol linkages which constitute 8–14% of hardwood lignin,[19] see Eq. (9).



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Formic acid has been shown to come from the oxidation of the aliphatic alcohol on the propyl side chain.[1,2] Products observed during the oxidation of hydrocarbons in acetic acid form from both the oxidation of the hydrocarbon and the solvent.[7,9,20] The same by-products associated with the oxidation of the acetic acid solvent (methyl acetate, methyl bromide, glycolic acid, maleic acid) have been detected during lignin autoxidation, see Table 3. The amount of ethyl acetate varied widely from the same sample which may suggest the the samples were non-uniform in character, i.e., truly representative samples were not always obtained.

Expected Products based on Lignin Structure

Figure 1 has been adapted from the structure of lignin given in ref.[1a] If the metal/bromide catalysts can successfully oxidize the 'uncondensed phenolic lignin', then approximately 15 wt% of the lignin will be converted to aromatic benzaldehydes and acids, see Figure 1. The products differ only in the number of methoxy groups on the aromatic ring that is, $n=0$, 1, 2 in Figure 1. The 'uncondensed, non-phenolic lignin' can be converted to 'uncondensed, phenolic lignin' by hydrolysis of the Ph–O–X ether bond which would then give the same products as the former. Solvolysis of the O–X bond has been extensively studied.[2,21,22] The aromatic acids from uncondensed lignin will be different from those from condensed lignin since the condensed lignin has an additional carbon atom that can be oxidized to a carboxylic acid to produce isopenic and *ortho*-phthalic acids. The GC/MS analysis of the organosolv lignin gives products characteristic of only uncondensed phenolic compounds, that is, hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, and syringic acid.

Results from the Aerobic Oxidation of Various Lignins

Initial attempts to oxidize lignin were made in a glass autoclave at ambient pressure and 95 °C as previous described.[9,16,20] The reaction did not initiate probably because of the presence of phenolic compounds which were extracted from the lignin into the solvent which made the reactions autocatalytic (see above). To go to higher temperatures and to maintain the system in the liquid phase, small vials were used at elevated pressures to keep the acetic acid in the liquid phase. The experiments were performed on batch in which the contents of the vials were analyzed after cooling to room temperature. This same technique has been successfully used previously to oxidize a number of selected reagents including *p*-xylene and 4-hydroxylmethylfurfural[27] to the expected products in high yield. The experiments are designed so there is sufficient O_2 in the vials to oxidize the reagents.

The experimental variables studied were 1) temperature (100–220 °C), 2) time (1–10 h), lignin concentration (3.8–38 wt% in solvent), catalyst concentration (6.9–30 mM Co), concentration of water in acetic acid (0, 8, 20 wt%), type of catalyst (Co/Mn/Zr/Br, HBr) and pressure (69, 136 bar). Only a selected number of these experiments are reported in Table 4 and Table 5. The Co/Mn/Zr/Br catalyst was chosen because it is one of the most active and selective metal/bromide catalysts known.[4,9,20] HBr was chosen because it is an active and selective catalyst [23], but also provides acidity which may aid hydrolysis of the lignin. Increasing the catalyst concentration increases activity but also selectivity in alkylaromatic aerobic

Table 4. Initial conditions for the aerobic oxidation of selected lignins.

Entry	Name of lignin	Catalyst type,[a] [Co] mM	H_2O [wt%]	*T* [°C]	Time [h]	*P* [bar]	[lignin] wt%
1	organosolv	1, 6.9	8.00	180	2.00	138	8.00
2	organosolv	1, 6.9	8.00	140	8.00	138	8.00
3	organosolv	1, 6.9	8.00	140	2.00	69	8.00
4	organosolv	1, 6.9	8.00	140	2.00	69	8.00
5	organosolv	1, 6.9	8.00	140	2.00	69	8.00
6	organosolv	1, 6.9	8.00	140	2.00	69	8.00
7	organosolv	1, 6.9	0.00	140	2.00	69	8.00
8	organosolv	1, 6.9	0.00	140	2.00	69	8.00
9	organosolv	1, 6.9	20.00	140	2.00	69	8.00
10	organosolv	1, 6.9	20.00	140	2.00	69	8.00
11	organosolv	1, 6.9	8.00	140	2.00	138	8.00
12	organosolv	1, 30	0.00	140	2.00	69	8.00
13	organosolv	1, 6.9	8.00	220	2.00	138	8.00
14	organosolv	1, 6.9	8.00	140	2.00	69	4.00
15	organosolv	1, 6.9	8.00	140	2.00	69	16.00
16	organosolv	1, 6.9	8.00	140	2.00	69	24.00
17	organosolv	2, 55	0.00	140	10.00	69	8.00
18	hydrolytic	1, 30	0.00	140	2.00	69	8.00
19	hydrolytic	1, 6.9	8.00	140	2.00	138	8.00
20	hydrolytic	1, 6.9	8.00	100	2.00	138	8.00
21	organosolv acetate	1, 30	0.00	140	2.00	69	8.00
22	organosolv acetate	1, 6.9	8.00	140	8.00	138	8.00
23	organosolv acetate	1, 6.9	8.00	180	2.00	138	8.00
24	organosolv acetate	1, 6.9	8.00	140	2.00	138	8.00
25	hydrolyic hydroxymethyl	1,30	0.00	140	2.00	69	8.00
26	sulfonic acid, sodium salt, acetate	1, 30	0.00	140	2.00	69	8.00

[a] Catalyst type 1 is a Co/Mn/Zr/Br mixture at a ratio of 1.00/1.00/0.10/2.00 mol/mol. Catalyst type 2 is HBr.

Table 5. Aromatic benzaldehydes and benzoic acids from the autoxidation of lignin.

Entry	Hydroxybenzaldehyde [wt%]	Hydroxybenzoic acid [wt%]	Vanillin, [wt%]	Vanillic acid [wt%]	Syringaldehyde [wt%]	Syringic acid [wt%]	Total	Syringic/vanillic acid [mol/mol]
1	0	0	0.99	2.91	2.52	4.51	10.9	1.80
2	0	0	1.12	2.34	2.86	4.4	10.7	2.10
3	0	0	0.98	2.35	3.24	3.63	10.2	2.06
4	0	0	0.88	1.05	1.83	2.84	6.61	2.42
5	0	0	0.83	1.46	1.41	2.84	6.53	1.86
6	0	0	0.39	0.96	0.75	2.31	4.41	2.27
7	0	0	0.73	1.58	2.36	2.99	7.65	2.32
8	0	0	0.70	1.20	2.34	3.03	7.27	2.83
9	0	0	1.36	1.13	3.48	3.39	9.35	2.76
10	0	0	1.17	0.96	3.19	3.10	8.43	2.95
11	0	0	0.92	1.82	2.36	3.83	8.93	2.26
12	0	0	0.63	1.03	0.13	2.73	4.52	1.72
13	0.84	0	0.0	0.0	0.0	0.0	0.84	–
14	0	0	1.02	1.04	3.03	2.85	7.94	2.85
15	0	0	0.79	0.95	2.66	2.39	6.79	2.90
16	0	0	0.79	0.26	2.63	0.65	4.33	3.12
17	0	0	0.51	1.09	0.95	2.11	4.67	1.91
18	0	1.22	1.12	1.35	2.33	1.51	7.53	1.55
19	0	0	1.45	N.M.[a]	1.73	N.M.	–	1.19
20	0	0	0.62	N.M.	0.61	N.M.	–	0.98
21	0	0	0.37	0.84	0	1.01	2.22	0.83
22	0	0	1.27	N.M.	3.24	N.M.	–	2.55
23	0	0	1.02	N.M.	2.79	N.M.	–	2.74
24	0	0	1.01	N.M.	2.51	N.M.	–	2.49
25	0	0	0	0	0.64	0.28	0.92	–
26	0	0	0.15	0.05	0	0	0.2	0.00

[a] N.M. = not measured.

oxidations.[16,20a] The water concentration was varied to enhance possible hydrolysis reactions, see Figure 1. It is known that increasing water concentration decreases the activity of the catalyst.[4,16]

One does not measure the oxygen uptake or carbon dioxide formation from the oxidation experiments given in Table 4 and Table 5 which represents the usual evidence that aerobic oxidation is occurring. However, direct evidence that oxidation is occurring is from the expected products of oxidation, see Table 3, and from the changes in methyl acetate formation. Methyl acetate is a characteristic by-product of aerobic oxidation which, just like carbon dioxide, originates from the catalytic decarboxylation of acetic acid.[24] Figure 3 illustrates the expected increase in rate of formation of methyl acetate as a function of temperature. It also increased with reaction time during lignin oxidation. For example, when organosolv acetate was oxidized at 150 °C for 1, 2 and 5 h the yields of methyl acetate were 0.98, 1.8, 2.2 wt%, respectively. One cannot preclude the possibility that methyl acetate is also forming from the lignin by oxidation of its aliphatic methyl groups.

The mechanism of air oxidation of hydrocarbons using homogeneous metal/bromide catalysts in acetic acid is a catalyst-modified free radical chain mechanism, commonly called autoxidation.[16,25] The rate of autoxidation is often idiosyncratic[26] because it is highly sensitive to the presence of trace amounts of specific metals and organic compounds such as phenols and amines.[4] The presence of these substances can make the reactions autocatalytic with varying induction times which can make reproducibility in yield difficult. This was observed occasionally in this work.

Results from Oxidation of Organosolv Lignin

The yields to hydroxybenzaldehyde, hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde and syringic acid are given on Table 5. The yields are given in weight percent because the exact composition of these aromatic moieties in the lignin are unknown. Organosolv lignin gave the highest yields of aromatic compounds with a total of 10.9 wt% at 2 h at 180 °C with 8% water, see example 1 of Table 4 and Table 5. This yield could be closely duplicated by going to lower temperatures (140 °C) and longer reaction time (8 h), see example 2. The reproducibility in examples 7 and 8 and 9 and 10 was good but is quite poor in ex-

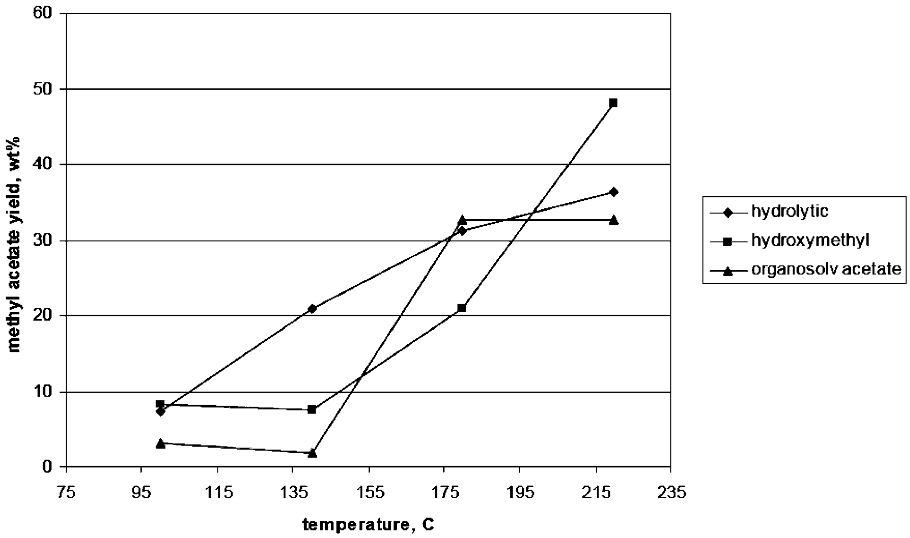

Figure 3. Methyl acetate formation as a function of temperature using different lignins. All data using 8.0 wt% lignin in 8% water/acetic acid for 8 h.

amples 3–6 where the total yield to aromatic benzaldehydes and acids varied from 4.4 to 10.2 wt% with an average value of 6.9%. Increasing the water concentration at 140 °C for 2 h from 0 to 8% increased the yield from 7.4% (examples 7 and 8) to 10.2% (example 3) but slightly decreased the yield to 8.8 at 20% water (examples 9 and 10). Slower reaction rates are normally observed with increasing water concentration in metal/bromide oxidations[16] hence the decrease in yield in example 10 may be because the reaction was incomplete. Unusually low acid/aldehyde ratios probably means that the reactions were not driven to completion since benzaldehydes are very reactive intermediates in autoxidation reactions.[20a] The unusually low acid/aldehyde ratio in examples 9 and 10 could therefore give significantly higher yields if the reaction time was increased. Doubling the pressure did not improve the yields (examples 3 and 11) nor did increasing the catalyst concentration (compare examples 7 and 8 to 12). Increasing temperatures at 2 h to 140, 180 and 220 °C gave yields of 8.9, 10.9 and 0.84% (examples 11, 1, 13) respectively. The low yield at 220 °C is not surprising considering the high reactivity of these compounds which will result in extensive decarboxylation and subsequent degredation of the products. Increasing lignin concentrations of 4, 8, 16, 24 wt% gave yields of 7.9, 10.2, 6.8 and 4.3 wt% when oxidized for 2 h at 140 °C (compare examples 14, 3, 15, 16). This suggests that an optimum lignin concentration may exist. This optimum may exist because the concentration of phenols in solution increase from 0.016 to 0.055 M which will decrease the rate of reaction. The acid/aldehyde ratios are unusually low for examples 15 and 16 suggesting that longer reaction times may give a higher yield. The HBr catalyst gave an inferior yield of 4.7% yield, see example 17 in Table 4.

Results from Oxidation of Hydrolytic Lignin

This and the other lignins discussed below were not as extensively investigated as organosolv lignin. Example 18 of Table 4 gives a total aromatic product yield of 7.6% when oxidized at 150 °C for 2 h in anhydrous acetic acid. The comparable benzaldehyde yields in examples 19 indicate an equally high yield at 140 °C for 2 h. The measured methoxy content of hydrolytic lignin is considerable less than that of organosolv lignin (10% *vs.* 15%, respectively) hence a lower weight percent yield for hydrolytic *vs.* organosolv lignin is expected.

Results from Oxidation of Organosolv Acetate

The total benzaldehyde + aromatic acid yield of organosolv acetate at 140 °C for 2 h at 0% water gives a total yield of only 2.2% (example 21). Since the phenols were acetylated in this sample and the phenolic acetates of the benzoic acids were not determined, the yields could be considerably higher. Examples 22–24 in Table 4 give benzaldehyde yields of 3.5–4.5% which suggests that substantially higher yields are possible. This Aldrich sample was partially bleached with hydrogen peroxide. There is the possibility that the bleaching may have significantly changed the structure of the lignin and destroyed some of the aromatic groups *via* oxidation also accounting for lower yields.

Results from the oxidation of hydrolytic hydroxymethyl lignin gave a total yield of only 0.9%, see example 25 in Table 4. A number of other samples were evaluated as their benzaldehydes only, and a maximum yield of only 1.1% was obtained. Only one experiment was performed using the lignosulfonic acid derivative which gave a yield of only 0.2 wt%, see example 26. The lignin sulfonic acid derivative has only 6.5 wt% methoxy groups hence a low yield is anticipated.

Absolute Yields of the Hydroxyaromatic Benzaldehydes and Acids

As discussed above the GC/MS analysis of the organosolv lignin gives products characteristic of only 'uncondensed phenolic lignin' Since roughly 15% of lignins are composed of uncondensed phenolic species and the maximum observed yield for organosolv lignin was 10.9 wt%, then one has an approximate yield of about 70% of these groups that have been successfully oxidized to the aromatic phenols. This assumes that no hydrolysis of the Ph−O−X ether bond has occurred. The organosolv lignin is reported to have 18.9 wt% of methoxy groups. Since we know the moles of methoxy groups in the oxidation products, one finds that 15.9% of the methoxy groups in entry 1 of Table 5 can be accounted for in the isolated products. This also suggests that most of the uncondensed, phenolic part of the lignin is being oxidized.

Conclusions

We have successfully isolated a number of expected products from the autoxidation of various lignins using the well-established industrial method with metal/bromide catalysts in acetic acid. We suspect that some of the 'condensed, phenolic lignin' has been oxidized to isopenic and phthalic acids but their identification requires further analytical development. Further development of this approach to optimize yields would involve a study of the initial acetylation of the phenols followed by oxidation. Also the rate of hydrolysis of the uncondensed and condensed ether linkages should be studied apart from oxidation. When the hydrolysis reaction has been optimized, then one should hydrolyze the lignins first, then acetylate them, and finally oxidize the mixture. The chemistry of lignins is very complex and one must recognize that condensation reactions are also known to occur and these must obviously be minimized.

Experimental Section

General Remarks

Aldrich cobalt(II) and Fluka manganese(II) acetate tetrahydrates, Baker hydrobromic acid, Aldrich zirconium(IV) acetate (16% solution in acetic acid/water solution) were used as received. All lignin samples were obtained from Aldrich and used as received. The catalyst used was a mixture of cobalt(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, zirconium(IV) acetate and hydrogen bromide at a 1.0/1.0/0.1/2.0 (mol/mol) ratio, respectively. The catalyst was prepared by dissolving the compounds in acetic acid. The lignins were soluble at room temperature to at least 7.6 wt%. Reported yields are in weight percent based on the amount of lignin used that is, weight product × 100/weight lignin.

Apparatus

A glass cylindrical reactor, as previously described,[27] was used for the reactions at ambient atmospheric pressure. Autoxidation at 70 bar in air were performed in 20-mL cylindrical glass reactors. The samples were analyzed after removal from the reactor.

Caution: *The use of high pressures and the use of dioxygen/nitrogen mixtures is potentially explosive and dangerous. They should be performed only with adequate barriers for protection. The source of oxygen was air which contains 20.9%* O_2

Analysis of Products using GC

After and sometimes before autoxidation, lignin samples were analyzed *via* GC by direct injection onto the column using an HP6890 gas chromatograph equipped with a 25 m HP-FFAP column and FID detector using terphenyl as the internal standard. Response factors were obtained from authentic compounds using terphenyl as the internal standard. The following compounds were analyzed by GC: methyl formate, methyl acetate, ethyl acetate, 3,3-dimethoxy-2-butanone, vanillin acetate, vanillin, syringaldehyde acetate, syringaldehyde.

The acids were analyzed using silation gas chromatography (SGC). After evaporation of the acetic acid/water at 50 °C, the samples were treated with BSTFA and analyzed on an HP5890 with an MDN-5S fused silica capilary column. Compounds analyzed were 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, vanillin, vanillin acetate, vanillic acid, syringaldehyde, and syringic acid using terphenyl as an internal standard.

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