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Production of Oxychemicals from Precipitated Hardwood Lignin

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Abstract

Lignin is a major byproduct in the biomass-to-ethanol process. The lignin produced from acid treatment of biomass has characteristics suitable for further conversion to organic chemicals. It is free of contaminants and has a relatively low molecular weight. In this study, catalytic oxidative conversion of the acid-soluble lignin precipitated from acid hydrolysates of hardwood was investigated. The process is based on aqueous alkaline oxidation of lignin with dissolved O_2 in the presence of Fe^{3+} and Cu^{2+} catalysts at moderate reaction temperatures (160–180°C). Aromatic aldehydes, ketones, and organic acids are found to be the primary products identifiable on extraction with ether. The combined weight yield of the total ether extractable products is about 20–25% of the initial lignin. The yield of the aldehydes (vanillin + syringaldehyde) is in the vicinity of 15% with an additional 3 to 4% of aromatic ketones. The yields of aldehydes plus ketones observed in this work far exceeded those obtainable from the conventional alkaline air oxidation of spent sulfite liquors. This article also provides comprehensive batch reaction data on conversion and product distribution.

Index Entries: Lignin; oxidation; degradation; oxygen.

Introduction

Saccharification of cellulosic biomass by dilute acid has a much longer history than the enzymatic process. A number of saccharification processes are currently being developed solely on the basis of acid catalysis. They include the total hydrolysis process of the National Renewable Energy Laboratory (NREL) *(1)*, the ethanol plant of BC International (Jennings, LA), and the Arkenol Process (Mission Viejo, CA). The acid-based hydrolysis processes are potential sources of a special grade of lignin. In the acid processes, a large fraction of the lignin is solubilized into the hot acidic medium, as high as 70% in the case of the NREL total hydrolysis process.

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About one-third to one-half of this lignin is precipitated after cooling of the hydrolysate and becomes easily recoverable. This precipitated hardwood lignin (PHL) is relatively pure, free of sulfur or other contaminants. It has a low molecular weight, high solubility in various solvents, and high reactivity. It is amenable to further conversion into chemicals and fuels. Because lignin is a major byproduct in the biomass-to-ethanol process, enhancing its value would have a significant impact on the economics of the overall process.

Oxidation in alkaline medium is an established process for the depolymerization of lignins and lignosulfonates. Vanillin, other aromatic aldehydes, and acids are the principal products *(2)*. Among them, only vanillin is presently manufactured on an industrial scale. It is produced from spent sulfite liquors in which the yield is only 5–10% *(3)*. The industrial production of vanillin by direct oxidation of sulfite-spent liquor was practiced in the United States as early as 1936. It has since been replaced by the eugenol-based route. In other countries, especially in Europe, the lignin-based processes are still being employed *(4)*.

Vanillin is one of widely accepted flavor chemicals used in the food industry. It has a broad market for various other applications, such as a ripening agent, an antifoaming agent in lubrication oils, a brightener in zinc-coating baths, an attracting material for insecticides, intermediates for pharmaceuticals such as Aldomet (Merck) and L-Dopa (Monsanto), herbicides, a vulcanization inhibitor, and disinfectants. In addition, it shows bacteriostatic properties *(3)*. Because angiosperm lignin comprises both guaiacylpropane and syringylpropane units, vanillin produced via alkaline oxidation from hardwood lignin is accompanied by substantial quantities of syringaldehyde. Syringaldehyde has a chemical structure and properties similar to those of vanillin and, therefore, has similar applications. Pharmaceutical uses of syringaldehyde have been recently proposed for synthesis of drugs for cancer treatment *(5,6)*.

The overall goal of the present investigation was to assess the technical feasibility of converting the PHL to high-value chemicals through alkaline oxidation by molecular oxygen. Identification of the products and determination of the yields of main products (vanillin, syringaldehyde) are of prime interest. The extent of conversion, its relationship with the reaction severity, and refinement of the reaction conditions were also within the scope of this work.

Materials and Methods

Preparation of Lignin

Yellow poplar wood chips (*Liriodendron tulipifera*) provided by NREL were used as the feedstock for the generation of PHL. The hydrolysis of this lignocellulosic biomass was conducted in a percolation reactor using extremely dilute acid (0.07% sulfuric acid) at 210–220°C. About 70% of the lignin was rendered soluble in the hydrolysate. On cooling, the PHL was precipitated out. It was filtered and dried for oxidation experiments. The details of lignin generation procedures and the characteristics of PHL are described elsewhere *(7)*.

Oxidation of Lignin

Oxidation of lignin was carried out in a 55-mL tubing bomb reactor (SS-316 tubing capped with Swagelok end fitting) connected to a pressurized oxygen source (200 psi). In a typical experiment, 20 mL of an alkaline solution (2 *N*) was placed into the reactor with 0.8 g of lignin and the required quantity of catalysts ($CuSO_4$ and $FeCl_3$). The reactor was Swagelok-sealed, vacuumed, and filled with oxygen to a desired pressure. The reaction was initiated by immersing the reactor into a preheated sand bath. The heating rate was about 110°C/min. After the reaction, the reactor was quenched in a cold-water bath. When catalysts were used in the reaction, they were removed by filtration from the reaction mixture. The liquid in the reactor was first acidified to pH $\approx$ 2.0 with an H_2SO_4 solution. The unreacted solid lignin was filtered, washed, and dried. Conversion of lignin to acid-soluble products was calculated by the weight difference.

Severity Factor

When it is deemed appropriate, the experimental conditions are converted into the severity factor, defined as $R_o = t \exp[(T - 100)/14.75]$, in which t is expressed in minutes and T in degrees Celsius *(8,9)*.

Analytical Methods

Liquid samples (the filtrate obtained after acidification) were first analyzed by high-performance liquid chromatography (HPLC). The remainder of each sample was then divided into two parts. The first part was extracted with diethyl ether until the ether layer appeared colorless. After removal of the ether by evaporation over anhydrous sodium sulfate, the yield of the ether-soluble fraction was determined from one part of the filtrate. Internal standard solution was added to the other part of the filtrate, and extraction and evaporation were ensued. The second part was subjected to gas chromatography (GC) or GC-mass spectrometry (GC-MS) analysis.

HPLC Analysis

The filtrate samples were analyzed for organic acids content by HPLC (Water Associates) equipped with a Bio-Rad Aminex HPX-87H column, a refractive index (RI) and ultraviolet (UV) detectors. The conditions used were as follows: detection, RI and UV (205 nm); eluent, 0.005 *M* H_2SO_4; flow rate, 0.6 mL/min; column temperature, 65°C.

The organic acids in the oxidized lignin solutions were identified by their retention time. Identification of the acids was confirmed by comparing the retention times with those of pure acids using a second effluent, 10% $CH_3CN/0.01\ N\ H_2SO_4$. External standards were used for quantification.

GC/GC-MS Analysis

The ether extracts were analyzed with a Varian model 3700 GC equipped with a capillary column (DB-5, 30 m × 0.25 mm × 0.25 µm) and flume ionization detector. Helium was used as the carrier gas. Injector and detector temperatures were 200 and 280°C, respectively. The temperature program was set to reach 250°C at a rate of 8°C/min starting from 50°C, with an initial time delay of 2 min and holding at 250°C for 15 min. For quantitative analysis, 4-ethylresorcinol was used as an internal standard. The ether extracts were also analyzed with a GC-MS (VG70E) equipped with an Opus V3.1 and DEC 3000 Alpha Station data system for component identification.

Results and Discussion

PHL produced both vanillin and syringaldehyde on oxidation with oxygen. This is in agreement with chemotaxonomy of plants. Lignins in wood of angiosperms consist of both guaiacyl units and syringyl units derived, respectively, from enzyme-induced dehydrogenative polymerization of coniferyl alcohol and sinapyl alcohol. Because α- and β-aryl ether linkages are the dominant types of linkages in both softwood and hardwood lignins, the cleavage of these bonds is the primary reaction in lignin degradation.

Gierer and Imsgard *(10)* theorized the step-by-step processes involved in the alkaline oxygen degradation of lignin based on their work on model compounds having a β-aryl ether structure. According to them, lignin oxidation in alkaline condition occurs in three main steps. First is the formation of hydroperoxide intermediates through either an electrophilic attack directly by molecular oxygen or nucleophilic addition of hydroperoxide anions to carbonyl and conjugated carbonyl structures. Then the hydroperoxide intermediates undergo several types of reactions, i.e., rearrangement reactions, conversion into quinols, and dehydration or other elimination reactions. Finally, these hydroperoxides or other derivatives are further oxidized and degraded into a series of low molecular weight compounds, such as aldehydes and organic acids.

A series of preliminary experiments were carried out to obtain the profiles of the oxidation reaction. The conditions were varied with different oxygen partial pressures (with system closed or open to constant pressured oxygen source), temperatures, reaction times, and catalysts. Efforts were made to optimize the conditions to raise the yields of identifiable low molecular weight degradation products. Table 1 summarizes the results of the typical preliminary experiments. The data include the amounts of identifiable phenolic aldehydes (vanillin and syringaldehyde) and ketones (acetovanillone and acetosyringone) at various conditions. The amounts produced are expressed as a percentage of the original lignin.

Table 1
Preliminary Study of PHL Oxidation by Oxygen

	Reaction no.							
	1	2	3	4	7	8	9	10
Reaction system	Oxygen fed-batch	Oxygen fed-batch	Closed batch	Closed batch	Closed batch	Closed batch	Closed batch	Closed batch
Oxygen partial pressure	Constant	Constant	Reducing	Reducing	Reducing	Reducing	Reducing	Reducing
Temperature (°C)	170	170	170	170	170	170	170	170
Time (min)	5	10	5	10	10	10	10	20
$\mathrm{Log}(R_o/\mathrm{min})$	2.76	3.06	2.76	3.06	3.06	3.06	3.06	3.36
Input: aqueous solution (mL)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Contains:								
Lignin (g)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
$CuSO_4$ (g)	None	None	None	None	0.04	None	0.04	0.04
$FeCl_3$ (g)	None	None	None	None	None	0.004	0.004	0.004
O_2 (g)	>0.65	>0.65	0.65	0.65	0.65	0.65	0.65	0.65
Conversion (%)[a]	58.3	69.2	46.5	53.4	62.7	58.9	64.3	70.3
Vanillin (%)	2.1	2.2	1.8	2.8	3.5	3.6	3.9	4.7
Syringaldehyde (%)	3.7	1.6	3.4	5.1	6.8	5.3	7.2	8.8
Total aldehyde (%)	5.8	3.8	5.2	7.9	10.3	8.9	11.1	13.5
Acetovanillone (%)	0.4	0.4	0.3	0.6	0.7	0.6	0.7	0.7
Acetosyringone (%)	0.7	0.6	0.7	1.5	2.8	2.2	2.5	2
Total ketones (%)	1.1	1.0	1.0	2.1	3.5	2.8	3.2	2.7

[a] All percentages refer to total lignin (Klason + acid-soluble lignin), which represents 99.7% of the dry brut lignin used.

To study the effect of O_2 partial pressure or the oxidation process, a parallel reaction system was designed. This unit has an open connection to the oxygen tank that allows the lignin to react with oxygen under a constant level of O_2 partial pressure (data represented by reactions no. 1 and 2 in Table 1). By contrast, a normal batch reactor system was initially filled with oxygen to a certain level and closed. The O_2 partial pressure in this unit steadily decreases as the reaction proceeds. The data from these runs are represented by reactions no. 3 and 4 in Table 1. A higher O_2 partial pressure brings about a higher rate of oxygen transfer from the gas phase into the liquid phase and, consequently, a higher dissolved concentration of oxygen in the solution. This results in a higher total conversion of PHL. However, the yields of aldehydes and ketones decreased with time. We think it is because these phenolic compounds easily degrade under a high oxygen pressure. A previous kinetics study on vanillin oxidation *(11)* notes that the reaction rate is first order in dissolved oxygen concentration at pH > 12.0. Under the conditions used in the alkaline oxygen oxidation of lignin, the syringyl structure in lignin is more sensitive to oxygen pressure and more reactive than guaiacyl structure *(12,13)*. To obtain high yields of the phenolic products, it is preferable to keep an initial high pressure of oxygen to rapidly break down the lignin and then gradually lower the oxygen pressure to continue the oxidation of the lignin fragments and reaction intermediates but prevent further degradation of the phenolic products. The normal batch process is therefore a better reactions scheme for our purpose than the oxygen fed-batch process.

The preliminary experiments also addressed the effects of Cu^{2+}, Fe^{3+}, and their mixture on the yields of aldehydes. With no catalysts, selectivity toward aldehydes and ketones was very poor. In commercial production of vanillin via air oxidation of lignosulfonates, $CuSO_4$ is used as the catalyst. The results of our preliminary studies indeed confirmed that $CuSO_4$ is an extremely effective catalyst for the oxidation of PHL. We also found that Fe^{3+} enhances the selectivity for aldehydes. A combination of Cu^{2+} and Fe^{3+}, however, was far more effective in improving the selectivity toward the oxidation reactions. For example, the data in Table 1 show that the use of both Cu^{2+} and Fe^{3+} increases the yield of total aldehydes from 7.9 to 11.1% and the conversion from 53.4 to 64.3% at 170°C and 10 min, in direct comparison with the control experiment without catalyst. It has been suggested *(14)* that Cu^{2+} acts as an electron acceptor accelerating the formation of the phenoxy radical and that Fe^3 can form a new reaction intermediate, O_2-Fe^{3+}-lignin complex, which acts as an oxygen carrier and can attack lignin to form degradation products, thus enhancing the oxidation reaction.

The data also indicate that the optimal conditions are in the range of 160–180°C and 10–30 min in the batch reactor system with combined Cu^{2+}/Fe^{3+}. A series of comprehensive oxidation experiments were therefore conducted near the optimal conditions; Table 2 summarizes the results. Figure 1 shows lignin conversion profiles during the oxidation reaction of

Table 2
Data of PHL Oxidation Near Optimal Oxidation Conditions

	Temperature												
	180°C				170°C					160°C			
Time (min)	5	10	20	30	5	10	20	30	60	10	20	30	60
Log(R_o/min)	3.05	3.36	3.66	3.83	2.76	3.06	3.36	3.54	3.84	2.77	3.07	3.24	3.54
Input: aqueous solution (mL)	20	20	20	20	20	20	20	20	20	20	20	20	20
Contains:													
Lignin (g)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
NaOH (g)	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
$CuSO_4$ (g)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
$FeCl_3$ (g)	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
O_2 (g)	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Conversion (%)[a]	63.2	71.5	77.8	81.2	56.2	64.3	70.3	75.8	81.4	55.7	62.9	68.5	74.6
Vanillin (%)	3.3	4.6	4.3	3.9	3.1	3.8	4.7	4.1	3.8	2.9	3.7	5.1	4.5
Syringaldehyde (%)	6.7	9.8	8.4	7.1	6.3	7.2	8.8	8.2	5.8	6.9	7.7	8.6	7.5
Total aldehyde (%)	10.0	14.4	12.7	11.0	9.4	11.0	13.5	12.3	9.6	9.8	11.4	13.7	12.0
Acetovanillone (%)	0.5	0.7	0.8	0.4	0.3	0.5	0.7	0.7	0.3	0.3	0.5	0.6	0.6
Acetosyringone (%)	2.4	2.6	2.6	1.8	1.5	2.3	2.5	2.6	1.6	1.9	2.4	2.7	1.8
Total ketones (%)	2.9	3.3	3.4	2.2	1.8	2.8	3.2	3.3	1.9	2.2	2.9	3.3	2.4
Oxalic acid (%)	8.4	12.5	16.3	15.4	7.2	8.6	14.1	16.2	16.0	6.7	9.4	13.4	15.3
Formic acid (%)	5.6	6.2	10.3	13.4	4.2	5.2	6.7	9.3	12.5	4.1	6.1	7.2	10.1
Acetic acid (%)	10.7	15.6	27.4	28.6	10.3	12.6	18.5	26.1	31.7	11.4	14.2	19.5	27.5
Malonic acid (%)	1.3	1.6	1.5	1.5	0.8	1.2	1.6	1.6	1.2	0.7	1.1	1.5	1.2
Succinic acid (%)	0.4	0.4	0.5	0.4	0.1	0.2	0.4	0.3	0.3	0.1	0.3	0.3	0.4
Vanillic acid (%)	1.2	1.7	2.0	2.4	0.8	1.1	1.6	2.3	1.9	0.9	1.8	2.4	2.3
Syringic acid (%)	2.8	3.5	3.9	3.8	2.1	2.5	4.2	3.7	2.9	2.2	3.4	3.7	3.7
Total acids (%)	30.4	41.5	61.9	65.5	25.5	31.4	47.1	59.5	66.5	26.1	36.3	48.0	60.5

[a] All percentages refer to total lignin (Klason + acid-soluble lignin), which represents 99.7% of the dry brut lignin used.

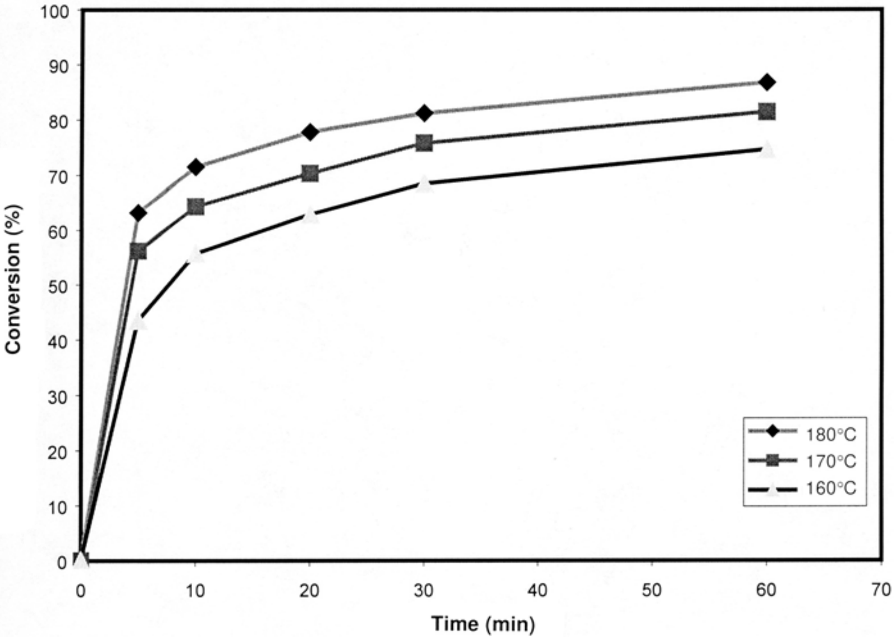

Fig. 1. PHL conversion profiles near the optimal oxidation conditions.

PHL. At a severity index (SI) above 3.36, the PHL conversion reaches above 70%. Even at a lower SI region, more than 50% of lignin conversion is attainable. This indicates that PHL undergoes a rapid initial degradation into liquid products by alkaline oxidation. More severe conditions, although providing higher conversion, did not improve the yields of aldehydes and ketones. Figures 2 and 3 show the yield profiles of aldehydes and ketones under the optimized oxidation conditions. In the best case, the yields reach 14.4% for aldehydes and 3.4% for ketones, which it occurred within the time span of 10–20 min and the SI range of 3.36–3.66. About 5% of aromatic acid (vanillic acid and syringic acid) and a larger amount of low molecular organic acids (mainly acetic, oxalic, and formic acids) were also produced as byproducts. The total yields of acids were in the range of 30–65%.

Conclusion

Degradation of PHL with alkaline oxidation by molecular oxygen was investigated as a means of producing value-added oxychemicals. PHL is readily depolymerized and solubilized by alkaline oxidation to produce aromatic aldehydes, ketones, and organic acids under moderate reaction conditions with the SI in the range of 3.0–3.8. Catalysts can enhance the reaction selectivity toward useful products. A combination of Cu^{2+} and Fe^{3+} catalysts was most effective in raising the yield of ketones and aldehydes. With the implementation of catalysts, the yields of aldehydes and ketones

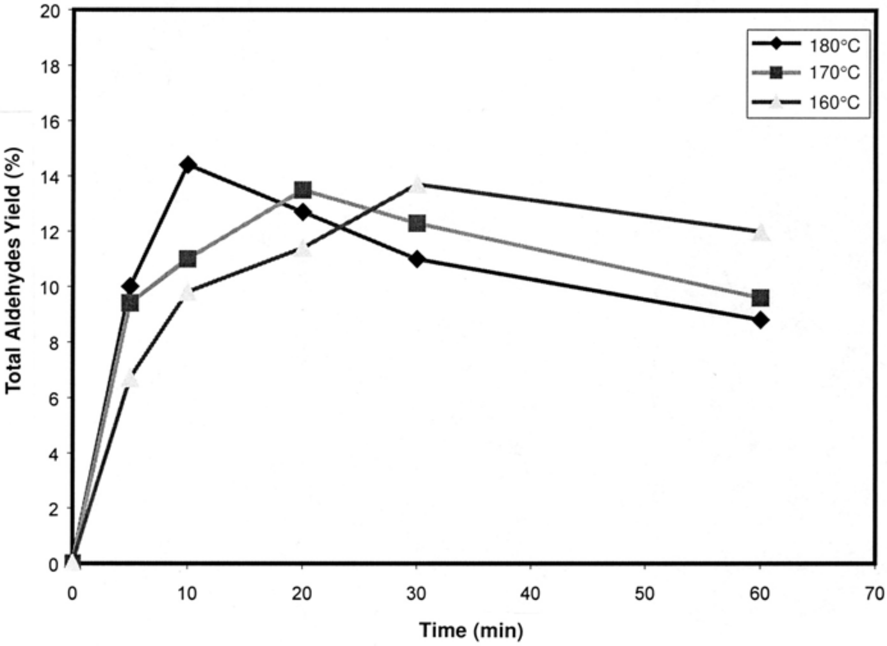

Fig. 2. Total aldehydes yield profiles near the optimal oxidation conditions.

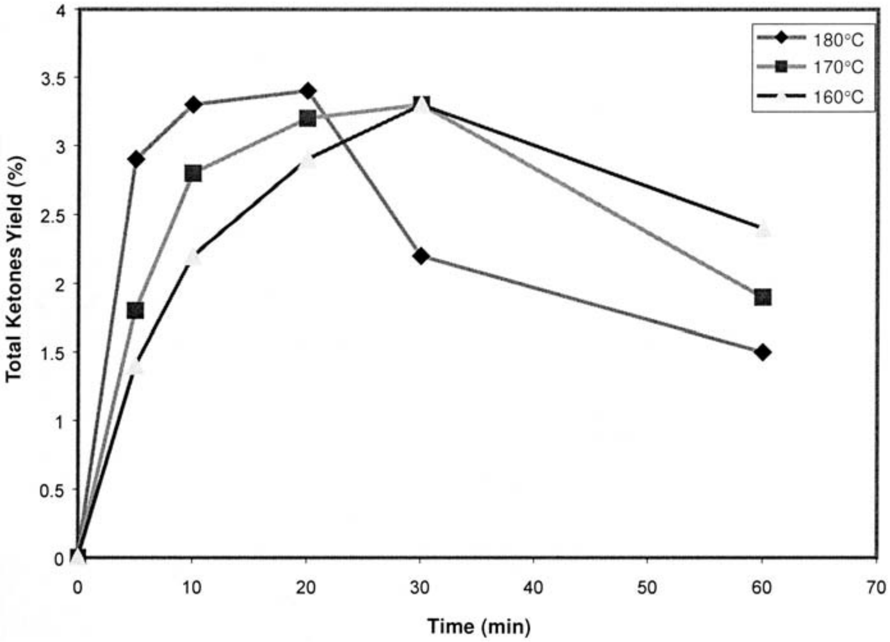

Fig. 3. Total ketones yield profiles near the optimal oxidation conditions.

are improved to the level of 4.6% for vanillin, 9.8% for syringaldehyde, 0.7% for acetovanillone, and 2.6% for acetosyringone. Organic acids are the major byproducts of the oxidation process. The aromatic products are unstable under high oxygen tension, being degraded to acids. A reaction pattern with declining O_2 further improves the yields of aldehydes and ketones.

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