Oxidative Cracking
of Precipitated Hardwood Lignin
by Hydrogen Peroxide*

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Abstract

Precipitated hardwood lignin (PHL) is a major byproduct in the biomass-to-ethanol process. Oxidative cracking of PHL by hydrogen peroxide in aqueous medium was investigated as a means to produce potentially useful chemicals. The cracking reaction takes place at moderate temperatures (80–160°C), giving mono- and dicarboxylic acids as the main products. The yields of these products are in the range of 30–50% of initial lignin. The reaction mechanism and the product distribution are dependent upon the reaction conditions, especially the pH. The reaction under strong alkaline condition proceeds well even at low reaction temperatures (80–90°C). Under acidic conditions, higher temperatures (130–160°C) are required to attain the same degrees of cracking. The reaction patterns of the oxidative cracking reaction involve the cleavage of lignin ring, aryl ether bond, or other linkages within lignin. By using the findings of this investigation and those of previous work, we have illustrated the reaction pathways for degradation of PHL under alkaline and acidic conditions. Aldehydes and aromatic acids are intermediate products in the oxidative degradation of lignin. However, they were produced only in trace amounts owing to rapid degradation induced by hydrogen peroxide.

Index Entries: Lignin; oxidation; degradation; hydrogen peroxide.

Introduction

Lignin is a nonfermentable oxygenated aromatic polymer comprising generally 10–25% of the dry wt of lignocellulosic biomass *(1)*. It is a major byproduct in the biomass-to-ethanol process. Yet, it is the least utilized

component among the three major constituent polymers of biomass. Currently, lignin from ethanol plants is viewed primarily as a source of process fuel. Enhancing the value of lignin is a factor that could significantly affect the economics of the overall process.

Lignin is produced in various phases of the biomass conversion process. During the front end of the biomass processing, the feedstock is invariably put through a pretreatment process that usually involves treatment with dilute acid. A number of saccharification processes are currently being developed, solely on the basis of an acid catalyst. They include the "total hydrolysis" process of the National Renewable Energy Laboratory (NREL) *(2)*, the ethanol plant of BC International (Jennings, LA), and the Arkenol Process (Mission Viejo, CA). All these acid-based pretreatment and saccharification processes are potential sources of a special grade of lignin. During 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 using hardwood. About one-third to one-half of this lignin is precipitated on cooling of the hydrolysate thus easily recovered. This lignin has many characteristics suitable for further conversion into various chemicals. It is a clean lignin, free of contaminants. It has low molecular weight, high solubility in various solvents, and high reactivity. Our investigation looks into the possibility of converting this lignin into low molecular weight chemicals. We focused on noncatalytic oxidative cracking of lignin in aqueous medium using H_2O_2.

Interest in reactions of hydrogen peroxide with lignin stems from the commercial use of this oxidant as a bleaching reagent in the pulp and paper industry. There has been a great deal of interest in the reactions of hydrogen peroxide with chromophoric and reactive groups in lignin. The action of hydrogen peroxide on lignin is not restricted to the interaction with chromophoric groups. It can also degrade and solubilize lignin, especially the reactive and low molecular weight lignin such as precipitated hardwood lignin (PHL). A study on the reaction of lignin with hydrogen peroxide can also reveal the characteristics of the PHL.

Hydrogen peroxide is a very weak acid that exists almost entirely in the undissociated form at pH < 9.0. At higher pH levels, hydroperoxide anions appear, and they are generally considered to be the reactive species in the oxidation reaction *(3)*. The reactions of hydrogen peroxide with lignin are controlled by the type and distribution of inorganic and organic reactive species in the reaction mixture. The two most important factors are the pH of the reaction medium and the decomposition of the hydrogen peroxide *(4)*. Depending on the pH, hydrogen peroxide acts as either a nucleophilic or an electrophilic species. It is stable under acidic conditions. Above pH = 6.0, the decomposition rate increases significantly and reaches its maximum at a pH equal to its pK_a (11.6 at 25°C) *(5)* value, with a dismutation reaction as follows:

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + HO^-$$
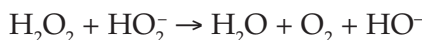
The rate of decomposition increases with temperature and pH *(6)*. It is also sensitive to traces of transition metal ions, particularly iron, copper, and manganese *(7)*. Decomposition of hydrogen peroxide forms molecular oxygen and other radical species (e.g., ·OH and ·OOH), which in turn may react with lignin in a variety of ways, thus making the total oxidation reaction mechanism extremely complicated. The scope of this investigation covers identification and quantification of the products resulting from an PHL-H_2O_2 reaction and assessment of the oxidation reaction mechanisms. The reactions were investigated under both acidic and alkaline conditions.

Materials and Methods

Preparation of Lignin

The wood chips of yellow poplar (*Liriodendron tulipifera*) provided by NREL were used as the initial feedstock for generation of PHL. The hydrolysis of this lignocellulosic biomass was conducted in a percolation reactor using extremely dilute acid (0.078% H_2SO_4) at 210–220°C. In a typical run, 120 g of yellow poplar were loaded into a 900-mL percolation reactor. The reactor was filled with solid feed soaked with 0.078% H_2SO_4. The reactor assembly was then heated to 210°C in an electric oven. Approximately 2000 mL of dilute acid solution were pumped through the reactor for 1 h. During the hydrolysis, up to 70% of the lignin was rendered soluble in the hydrolysate. The liquor was stored in a refrigerator (4°C) overnight, yielding the precipitated lignin (PHL). The PHL was separated by filter and dried at 50°C.

Oxidation of Lignin

Oxidation of lignin was carried out in an 18-mL tubing bomb reactor (SS-316). For oxidation under base conditions, approx 0.3 g of lignin and 1.1 g of 50% H_2O_2 solution were loaded into 10 g of 4% NaOH solution. For oxidation under acidic or neutral conditions, 0.2 g of lignin and 12 g of 5% H_2O_2 were added. Tables 1 and 2 present the details of the experimental conditions. The pH was adjusted with H_2SO_4. Reaction was initiated by immersing the reactor into a preheated sand bath. After the reaction, the reactor was quenched in a cold water bath, and gas samples were taken by opening the valve connected to the reactor.

The reaction products were first acidified to pH ≈ 2 with H_2SO_4. The precipitated lignin was filtered, washed, and dried. Conversion of lignin to acid-soluble products was calculated by the weight difference.

Severity Factor

The experimental results are analyzed in terms of 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)*.

Table 1
Oxidation of PHL Under Alkaline Conditions

	Reaction no.						
	1	2	3	4	5	6	7
Log (R_o/min)	0.4	0.4	0.4	0.7	0.7	1.3	1.6
Temperature (°C)	80.0	80.0	90.0	90.0	90.0	120.0	120.0
Time (min)	10.0	10.0	5.0	10.0	10.0	5.0	10.0
Input: aqueous solution (mL)	11.0	12.0	11.0	11.0	12.0	11.0	11.0
Containing lignin (g)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Containing H_2O_2 (g)	0.56	1.12	0.56	0.56	1.12	0.56	0.56
Containing NaOH (g)	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Conversion[a] (%)	84.6	90.3	90.0	92.5	92.3	98.0	97.8
Product[b]							
Oxalic acid (%)	13.4	13.6	17.1	17.4	16.6	17.2	18.6
Formic acid (%)	13.6	14.7	15.2	15.8	14.7	16.1	18.2
Acetic acid (%)	1.7	1.9	2.0	2.1	2.0	2.9	3.1
Malonic acid (%)	2.9	3.0	3.1	3.0	3.0	3.1	3.5
Succinic acid (%)	0.7	0.8	0.8	0.8	0.8	0.9	0.9
Other acid (%)	11.1	12.1	11.7	10.2	12.1	11.2	12.0
Total acids (%)	43.4	46.1	49.9	49.3	49.2	51.4	56.3
Ether-soluble fraction (%)	8.7	8.0	9.1	9.8	8.3	7.3	7.5

[a]Conversion refers to fraction of total lignin solubilized into aqueous phase.
[b]Numbers indicate wt% based on the initial lignin.

Table 2
Oxidation of PHL Under Acidic Conditions

	Reaction no.						
	1	2	3	4	5	6	7
Log (R_o/min)	1.3	1.9	2.2	2.5	2.7	2.5	2.8
Temperature (°C)	95.0	140.0	140.0	140.0	140.0	160.0	160.0
Time (min)	30.0	5.0	10.0	20.0	30.0	5.0	10.0
Input: aqueous solution (mL)	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Containing lignin (g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Containing H_2O_2 (g)	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Containing H_2SO_4 (mg)	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Initial pH	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Conversion[a] (%)	14.6	44.5	62.7	86.5	89.4	90.7	97.4
H_2O_2 residual (%)	86.5	70.2	43.0	0.3	Trace	10.8	0.6
Product[b]							
Oxalic acid (%)	0.2	0.2	0.2	0.3	0.2	0.8	0.3
Formic acid (%)	3.0	9.7	18.8	23.0	26.6	26.3	22.2
Acetic acid (%)	0.7	2.0	4.2	7.9	10.1	7.0	8.8
Malonic acid (%)	0.3	1.0	1.8	1.5	1.6	1.2	1.0
Succinic acid (%)	0.7	0.5	1.2	1.7	2.4	1.4	1.6
Other acid (%)	0.4	1.0	1.0	0.3	0.3	0.2	0.1
Total acids (%)	5.3	14.4	27.2	34.7	41.2	36.9	34.0
Ether-soluble fraction (%)	0.4	2.6	1.5	0.3	0.4	0.5	0.4

[a]Conversion refers to fraction of total lignin solubilized into aqueous phase.
[b]Numbers indicate wt% based on the initial lignin.

Analytical Methods

Liquid samples (the filtrate obtained after acidification) were first sampled for high-performance liquid chromatography (HPLC) analysis. The filtrate was then divided into two parts, which were 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 was added to the other part of the filtrate, and extraction and evaporation were ensued. The extracts from both filtrates were put through gas chromatography (GC) and/or GC-mass spectrometry (MS) analysis. Authentic samples of the identified products, when available, were used for comparison of chromatographic retention times and quantitative determination.

HPLC Analysis

The liquid products were analyzed for organic acids by HPLC equipped with a Bio-Rad Aminex HPX-87H column, an refractive index (RI), and ultraviolet detectors. 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 eluent, 10% CH_3CN/0.01 N H_2SO_4. External standards were used for quantitative analysis.

GC Analysis

The ether extracts were analyzed with a Varian model 3700 gas chromatograph equipped with an Alltech capillary column (DB-5, 30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Helium was used as 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-ethylresorcino was used as internal standard.

Mass Spectrometry

The ether extract as well as gas samples were analyzed with a VG 7070 high-resolution mass spectrometer equipped with an Opus V3.1 and DEC 3000 Alpha Station as the data system. Selected samples were analyzed with an external analytical service (Mass Spectrometry Facility, University of California, Riverside GC-MS) for further confirmation and identification of components.

Results and Discussion

Characteristics of PHL

The average composition of precipitated yellow poplar lignin was as follows: Klason lignin, 84.2%; acid-soluble lignin, 15.5%; glucan, trace; other carbohydrates, trace; and ash, 0.1%.
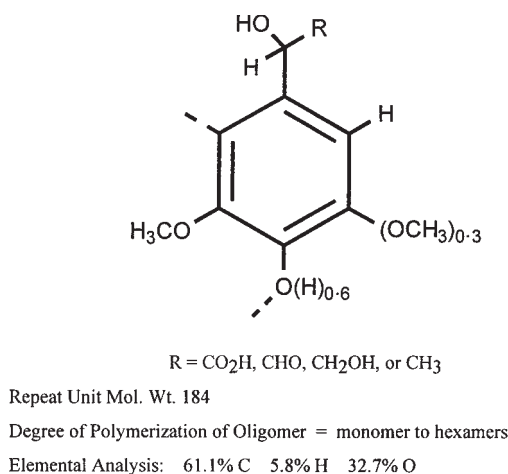
R = CO$_2$H, CHO, CH$_2$OH, or CH$_3$

Repeat Unit Mol. Wt. 184

Degree of Polymerization of Oligomer = monomer to hexamers

Elemental Analysis: 61.1% C   5.8% H   32.7% O

Fig. 1. Average structure of low molecular weight acid hydrolysis lignin.

The elemental analysis of the PHL as determined at the NREL (pro-vided to us in conjunction with our research) led to the average structure shown in Fig. 1. The distribution of functional groups is consistent with the analyses. One would expect a considerable variation in the structure of the aromatic units in the lignin. It appears that there is a partial degradation of the original lignin during the preparation process, as evidenced by short-ening of the side chains and the appearance of carbonyl and carboxylic groups. The exact position of interunit linkages is unknown at this time. An estimate of the range of oligomers is also reported here. The monomeric fraction of the product was estimated to be in the range of 10–20 wt% of total PHL by GC. The number (M_n) and weight (M_w) of the average molecular weights of acetylated derivatives (as determined by the NREL Biofuels Research Team) are 670 and 1200, respectively.

Lignin Oxidation with Hydrogen Peroxide Under Alkaline Conditions

Table 1 summarizes the data on precipitated hardwood lignin oxi-dized by hydrogen peroxide under alkaline conditions. Even at lower severity (log R_o = 0.4), the PHL was easily degraded and solubilized by hydrogen peroxide. The high reactivity may be because PHL has a low molecular weight and relatively uniform structure. At 90°C, about 90% of overall conversion/solubility was attained within 5 min. The yield of mono- and dicarboxylic acids was about 50 wt%. Among the identified carboxylic acids were oxalic, formic, acetic, malonic, and succinic. There were a few other low molecular weight acids visible in the HPLC chromatogram. They are yet to be identified. No phenolic compounds were detected in the ether-soluble portion by mass spectra. Aromatic acids and aldehydes were present only in extremely low amounts. The level of these products were as follows: vanillic acid, 0.15%; benzenedicarboxylic acid, 0.08%; vanillin, 0.12%; syringaldehyde, 0.10%; and hydroxybenzaldehyde, 0.04%.

$$H_2O_2 + OH^- \Leftrightarrow H_2O + \underline{HOO^-}$$

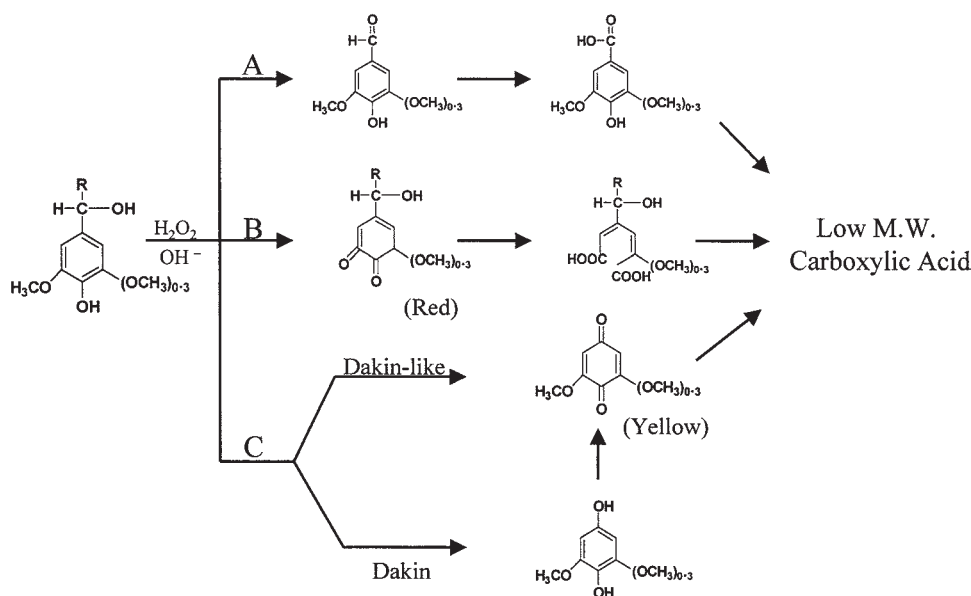$\underline{HOO^-}$: strong nucleophile species

Fig. 2. Proposed reaction sequence under alkaline conditions.

Based on the results of this work and previous studies concerning the reaction between hydrogen peroxide and lignin model compounds *(10,11)*, we propose a possible reaction sequence for oxidation of PHL by hydrogen peroxide under alkaline conditions (Fig. 2). Perhydroxyl anion (HOO–), an extremely strong nucleophile, is considered to be the active species for alkaline hydrogen peroxide oxidation. The aryl ether bonds and other linkages within precipitated lignin constituents are also broken extensively under these conditions. Lignin-derived products of commercial interest such as vanillin and syringaldehyde are produced by side-chain reaction through pathway A. It appears that they are rapidly degraded by hydrogen peroxide, resulting in a very low amount in the final products. Chromophoric groups are generated as reaction intermediates through pathways B and C. Their presence was evidenced by dark brown liquid products in our experiments. These chromophoric groups also undergo ring cleavage reaction and further degradation to form low molecular weight acids.

Under alkaline conditions, hydrogen peroxide is quickly decomposed to molecular oxygen and other radical species. Comparing reaction no. 1 with no. 2 and reaction no. 4 with no. 5 (*see* Table 1), only a minor difference was observed when hydrogen peroxide loading was doubled. This indicates that the excess hydrogen peroxide is decomposed before it reacts with lignin and other intermediate compounds. Oxygen and other radical species generated from decomposition of hydrogen peroxide will continu-

ously act as oxidative reagents. However, they are not very active at 80–90°C. With increase of temperature, these species will play a significant role in overall oxidation. This would explain the increased conversion and total yield of low molecular weight acids at higher temperatures.

Lignin Oxidation with Hydrogen Peroxide Under Acidic Conditions

In contrast to the oxidation under alkaline conditions, a much higher reaction severity is required to degrade the PHL under acidic conditions (0.01 N H_2SO_4 medium) (Fig. 3). Table 2 summarizes the reaction data under acidic conditions. At 95°C, the reaction conversion was very low and most of the hydrogen peroxide was preserved well in the medium. Obviously, higher reaction severity is needed to degrade the lignin to an appreciable extent. At 140°C for 30 min, about 89% of overall conversion was attained. A large amount of gas product was formed at the same time, but it was determined to be predominantly CO_2 by GC-MS. The yield of mono- and dicarboxylic acids was about 41 wt% of initial lignin. The main components were formic acid (26.6 wt%) and acetic acid (10.1 wt%). They account for about 90 wt% of the total acids. None of the aromatic acids, aldehydes, and phenolic compounds was detected in the ether-soluble portion. These results indicate that decomposition of these products is more strongly influenced by the reaction severity than by the lignin oxidation reaction, particularly under acidic conditions. Unlike the reaction in alkaline medium, the liquid product was transparent in all runs. This indicates that no chromophoric groups were generated under acidic conditions.

Hydrogen peroxide is protonated and functions as a cationoid oxidation species under acidic conditions *(12)*:

$$H_2O_2 + H^+ \Leftrightarrow H_2^+OOH \Leftrightarrow H_2O + OH^+$$

The cationoid species thus serves as an electrophile, the main oxidative reactant for lignin cracking. The cationoid species is electron deficient; therefore, it will react with the π electrons of the benzene ring, resulting in a typical electrophilic aromatic substitution and further ring cleavage reactions. A previous study on lignin model compounds *(13)* found that oxidation of vanillyl alcohol, vanillyl ethyl ether, acetoguaiacone, or guaiacyl methyl carbinol with hydrogen peroxide at pH 2.0 and low temperature generates vanillin, vanillic acid, and protocatechualdehyde as the final components. We postulate a possible oxidative sequence to be shown in Fig. 4 for PHL side-chain reactions. Vanillin, syringealdehyde, and other aromatic acids are potential products coming from these side-chain reactions. However, these aromatic compounds were undetectable by GC. We cite two reasons: First, PHL is an acid-insoluble lignin. The oxidation reaction between PHL and hydrogen peroxide in acidic medium is heterogeneous. Thus, the cleavage of lignin aryl ether bonds and other lignin linkage is difficult and slow. Second, the aromatic structure of these compounds is not well preserved under acidic conditions, being attacked by OH^+ and other radicals. These aromatic compounds therefore face rapid degradation to low molecular weight acids and eventually to CO_2.
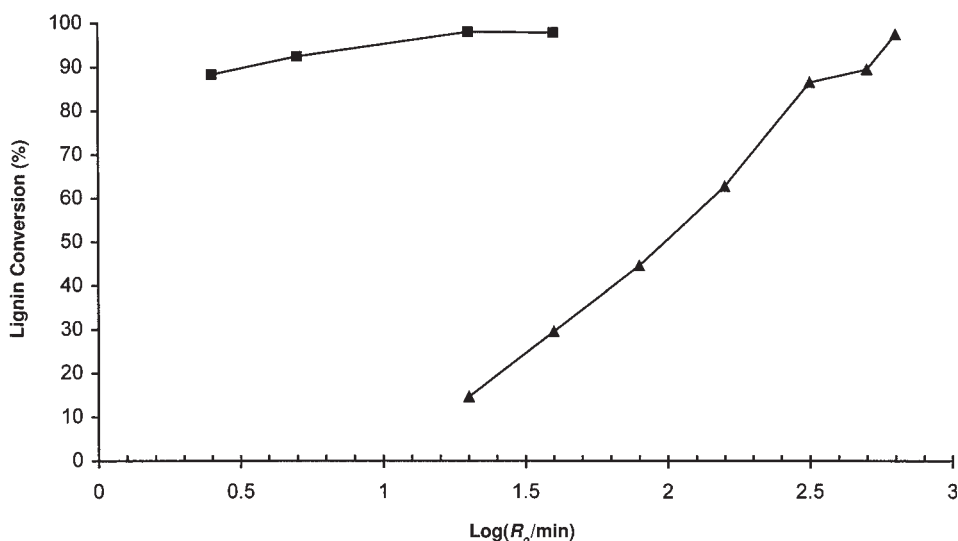
Fig. 3. Lignin conversion at different reaction severity indexes. (—■—), Alkaline condition; (—▲—), acidic condition.
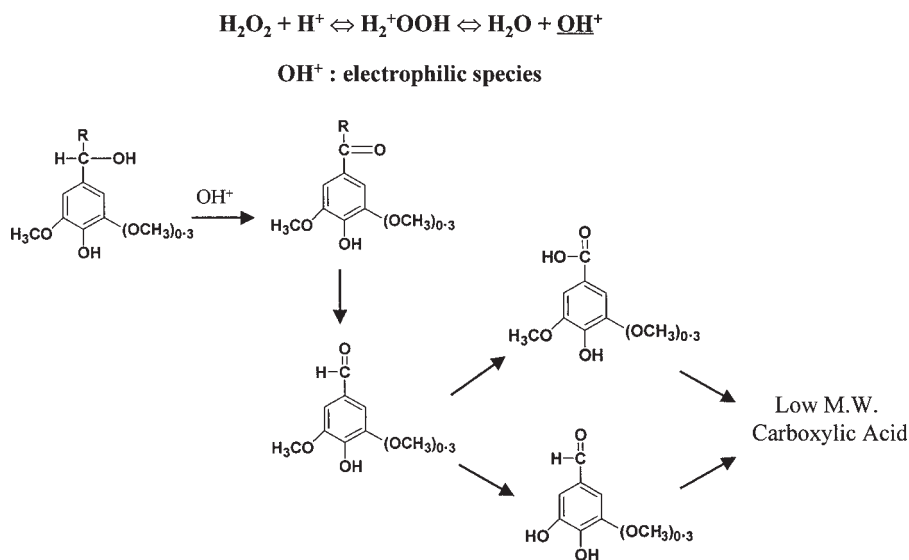
$$H_2O_2 + H^+ \Leftrightarrow H_2^+OOH \Leftrightarrow H_2O + \underline{OH^+}$$

OH^+ : electrophilic species

Fig. 4. Proposed reaction sequence under acidic conditions.

Conclusion

Degradation of PHL with hydrogen peroxide was investigated at moderate-to-high temperatures under alkaline and acidic conditions. The results indicate that PHL is easily depolymerized and solubilized by hydrogen peroxide at low and moderate reaction severity. The main degradation products are low molecular weight mono- and dicarboxylic acids

and CO_2 in both conditions. The mechanism of the oxidative cracking PHL under alkaline conditions appears to be different from that under acidic conditions. Under alkaline conditions, chromophoric groups are generated through Dakin and Dakin-like reaction pathways; this is evidenced by the color of the liquid products. However, the chromophorics are absent when the reactions are carried out under acidic conditions. Hydrogen peroxide acts as either a nucleophile or an electrophile depending on the pH. Vanillin and syringealdehyde are formed as reaction intermediates under alkaline conditions. They may be formed as reaction intermediates under acidic conditions as well. However, these aldehydes are not detected owing to its rapid degradation by hydrogen peroxide. The use of less reactive oxidants such as molecular oxygen may enhance the level of these products.

Acknowledgments

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