

# Improved Alkaline Oxidation Process for the Production of Aldehydes (Vanillin and Syringaldehyde) from Steam-Explosion Hardwood Lignin

Guoxiong Wu, Michele Heitz, and Esteban Chornet\*

Chemical Engineering Department, University of Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1

The production of aldehydes from a steam-explosion hardwood lignin is the main objective of this paper. It is demonstrated that the combined aldehydes yield (vanillin + syringaldehyde + hydroxybenzaldehyde) can reach 14.6 wt % of the lignin isolated from the steam-explosion process. This represents 12.2 wt % of the Klason lignin present in the initial hardwood (*Populus tremuloides*) and 2.5 wt % of the dry wood. The process steps are relatively simple: aqueous alkaline (13.5 wt % NaOH) oxidation (pure O<sub>2</sub>) of lignin in the presence of Cu<sup>2+</sup> and Fe<sup>3+</sup> as catalysts, at 170 °C and with 10 min as reaction time. The high yields of aldehydes observed in our work far exceed those obtained in the conventional alkaline air oxidation of spent sulfite liquors. Our results support the concept that biomass-derived oxyaromatic chemicals via improved process strategies may soon challenge existing petroleum-derived routes (vanillin is currently produced via the sequence benzene → cumene → phenol → guaiacol → vanillin).

## Introduction

The fractionation of lignocellulosic materials into its different polymeric constituents, cellulose, hemicellulose, and lignin, is a key objective aimed at recovering the constituents in a rather pure and usable form. Such fractionation can be carried out using steam-aqueous treatments which have the advantage of their simplicity and limited number of extractive steps (Heitz *et al.*, 1991).

The lignin derived from steam-aqueous treatments can be potentially used as feedstock for conversion into low molecular weight chemicals, such as vanillin, syringaldehyde, dimethyl sulfoxide (DMSO), phenol, and substituted phenols. Among them, only vanillin is presently manufactured at an industrial scale from lignin-containing spent sulfite liquors (SSL). A number of commercial processes have been in existence for many years (Kürschner, 1928; Lautsch *et al.*, 1941; Salvesen *et al.*, 1948; Fisher and Vincent, 1951; Marshall, 1945, 1978a,b; Van Ness, 1983;). All these processes are based on partially sulfonated lignin. To the best of our knowledge, vanillin has never been produced at a commercial scale from lignin present in kraft black liquors or other lignins.

Vanillin produced via alkaline air oxidation from spent sulfite liquors is accompanied by syringaldehyde. The quantities of syringaldehyde vary from very small in the case of lignin from softwoods to substantial in the case of lignin from hardwoods. Syringaldehyde is an interesting and useful molecule primarily as intermediate for the production of 3,4,5-trimethoxybenzaldehyde, itself an important building block for the preparation of specific drugs (Marshall and Vincent, 1978).

In the conventional production of vanillin, the lignin is present in the sulfite spent liquor at a concentration comprised between 5 and 35% solids. The ratio of alkali to lignin present in the liquor is about 0.5–3.0 parts of alkali to 1 part of lignin on a weight basis. The oxidation is carried out by flowing air through the alkaline solution at a temperature of 140–180 °C, under a pressure of about 0.3–1.4 MPa. A catalyst may be used to increase the yields of aldehydes, such catalyst consisting essentially of a salt of a redox metal. Usually such catalyst is cupric sulfate (about 5–10 wt % based on lignin). The main disadvantage

of this process is its long residence time in the reactor, usually 2.0–3.5 h. This is probably due to the use of air as oxidant, since the partial pressure of oxygen is the driving force for the mass transfer of oxygen from the gas phase into the liquid phase where oxidation takes place. Our strategy has been to increase the oxidation rate of lignin by using pure oxygen. In this case, however, a more selective catalyst has to be chosen and the reaction conditions have to be optimized to prevent excess formation of unwanted degraded oxidation products, e.g., organic acids and carbon dioxide. In our previous work (Wu *et al.*, 1992), a mixture of copper and iron salts has been found to be more effective as a catalyst than copper or iron alone. This mixture has been employed in the present work.

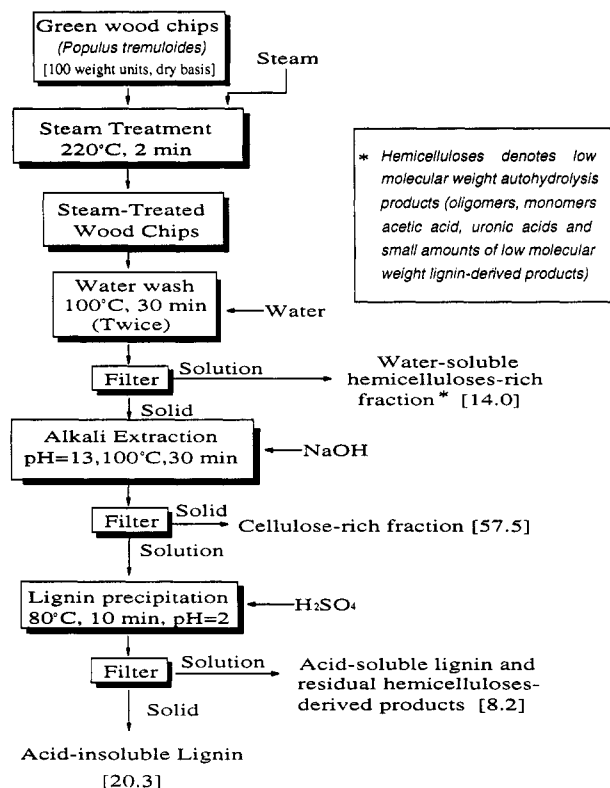
Yields of vanillin, syringaldehyde, and other degradation products are discussed in relation to the severity of the treatment. The conditions to obtain high yields of aldehydes have been determined from the experimental data. The present investigation is also concerned with the effects of the reaction parameters on the oxidation rate of lignin and with the effects of Cu<sup>2+</sup>, Fe<sup>3+</sup>, and their mixtures on the yields of aldehydes.

## Experimental Section

**Feedstock.** The wood chips used for this study were derived from *Populus tremuloides* grown in the Eastern Townships, Quebec (Canada). The compositions, determined by using the standard ASTM methods, are ethanol-toluene extractives (3.6%), pentosans (19.0%), cellulose (51.6%), Klason lignin (20.6%), and ash (0.4%). The balance to 100% is made of acid-soluble lignin and hexoses present in the hemicelluloses.

The lignin preparation and material balances are shown in Figure 1. The green wood chips were steam treated either in the 4 t/h STAKE II feeder-digester facility located in Sherbrooke (Quebec, Canada) or in a 4-L apparatus (MVC) at 220 °C for a period of 2 min, and then discharged into a receiving vessel. The discharged fibers were twice washed with hot water under the following conditions: fiber consistency, 5–6%; temperature, 75–100 °C; time, 30 min. About 65% of the initial hemicelluloses were removed and recovered in the washing steps. The residual washed fibers were then extracted with a NaOH solution under the following conditions: fibre consistency, 5%; temperature, 100 °C; time, 30 min. The pH of the suspension was controlled at 13 by adding NaOH. The alkaline filtrate was acidified to pH = 1.5–2.0 with H<sub>2</sub>SO<sub>4</sub>.

\* To whom correspondence should be addressed. Current address: National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO 80401-3393.



**Figure 1.** Lignin production flow diagram. The numbers in brackets are the yields of the different fractions referred to 100 weight units of dry chips.

at 80 °C and with 10 min as contact time. The precipitated residue, i.e., acid-insoluble lignin, was washed with water and dried.

The composition of the acid-insoluble dry lignin is as follows: Klason lignin = 84.7%; acid-soluble lignin = 3.0%; others (unknown) = 12.3%; elemental analysis = C, 64.0%, H, 6.5%, N, 0.15%; methoxyl groups = 18.7 wt % of dry lignin; hydroxyl groups = 9.2 wt % of dry lignin. The Klason lignin in the acid-insoluble dry lignin represents 83.5% of the Klason lignin initially present in the wood chips.

**Oxidation of Lignin.** Oxidation of lignin was carried out in a 500-mL magnetically stirred autoclave. In a typical experiment, 100 mL of an alkaline solution containing 10 g of lignin was placed in the autoclave. The required quantities of CuO, Fe<sub>2</sub>O<sub>3</sub>, CuSO<sub>4</sub>, and FeCl<sub>3</sub> used in the oxidations were added to the solution. The autoclave was then sealed. After purging with oxygen to remove the residual air, oxygen was introduced at a cold pressure of 1.4 MPa. The stirrer was set at 2000 rpm.

The reaction was started by immersing the bomb into a preheated salt bath, and the reaction temperature and time were recorded with a data logger. The heating rate was about 50 °C/min. After the reaction, the autoclave was rapidly cooled to room temperature by immersing the bomb in a cold water bath.

When oxides of copper and iron were used in the reaction, they were removed by filtration. After that, all the reaction products were acidified at a pH ≈ 2 with a HCl solution. The precipitates were filtered, washed, and dried. Conversion of lignin to acid soluble products was calculated from these precipitates by the following equation:

$$\text{conversion} = [1 - W_R/W_1] \times 100$$

where  $W_R$  = weight of precipitated lignin and  $W_1$  = weight of Klason lignin in the initial lignin feedstock.

The filtrate obtained after acidification (about 150 mL) was divided into two parts which were extracted with diethyl ether until the ether layer appeared colorless. After removal of the ether by evaporation under nitrogen, the yield of the ether-soluble fraction was determined from one part of the filtrate. The other ether-soluble fraction was acetylated by adding 1–2 mL of acetic anhydride and 2–3 drops of pyridine to the sample and heating at 70 °C for 1 h. The acetylated product was analyzed by capillary GC (HP Model 5890A GC) using a DB-5 column (60 m × 0.25-mm diameter). The oven temperature was programmed from 65 to 140 °C at 6 °C/min, held at 140 °C for 10 min, and then heated from 140 to 220 °C at 4 °C/min and held at 220 °C for 10 min.

The quantitation of the identified compounds was done with 4-ethylresorcinol as internal standard. The relative error involved in the determination of all the compounds was ±3.2%. A chromatogram of the acetylated products from oxidized lignin solution is shown in Figure 2.

The severity factor,  $Ro = t \exp[(T - 100)/14.75]$ , where  $t$  is expressed in min and  $T$  in °C has been used to present the data in Tables 1 through 5. The  $Ro$  factor, whose units are minutes, is a marker of the severity of the reaction. A thorough discussion on the significance of  $Ro$  has been presented elsewhere (Overend and Chornet, 1990; Abatzoglou *et al.*, 1992).

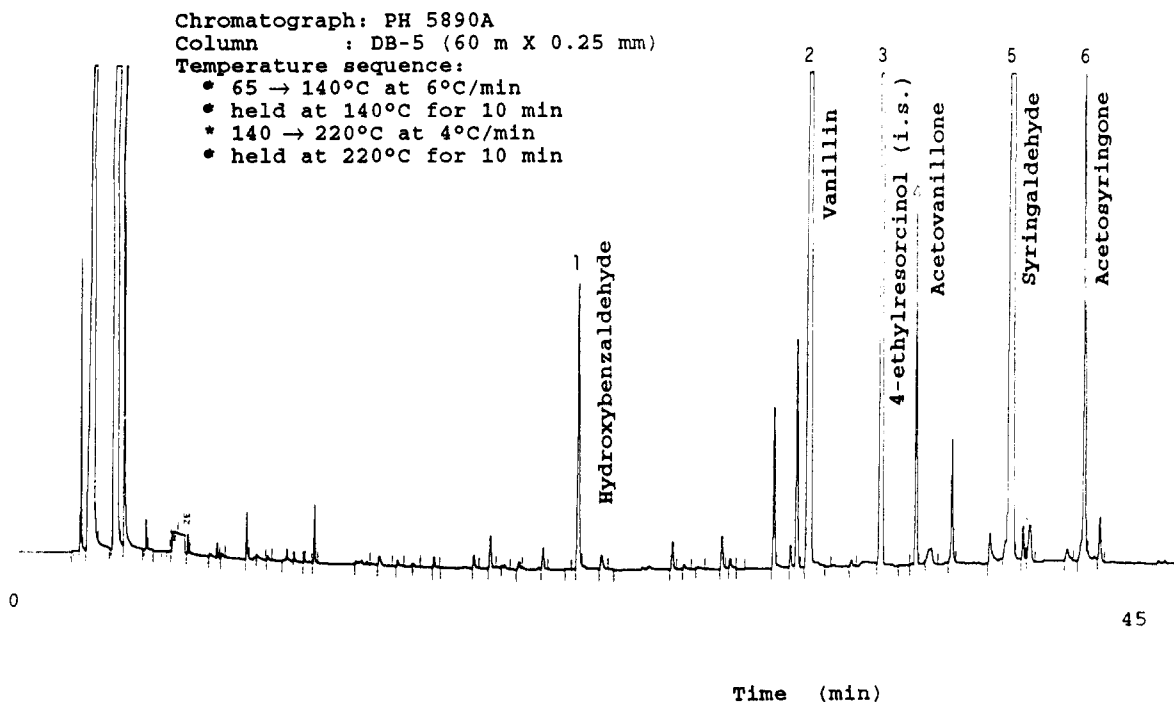
## Experimental Results and Discussion

A theoretical description of the processes involved in the alkaline oxygen degradation of lignin was discussed by Gierer (1977) based on his work on model compounds having β-aryl-ether structure. Since the reaction takes place in a strongly alkaline solution, the model compounds are dissociated to phenolate anions which are in resonance with a variety of carbanion structures.

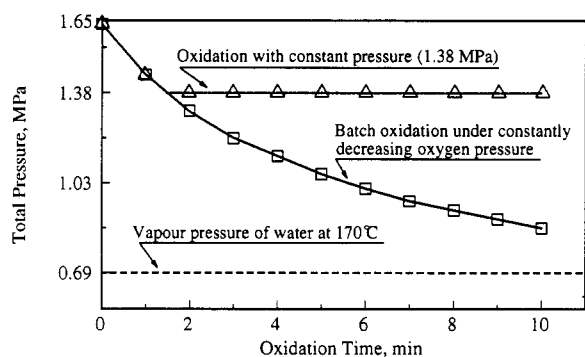
After ionization of the phenolic structure, the hydroperoxide structure forms via two different reaction pathways: (1) an electrophilic attack directly by molecular oxygen, i.e., ionic pathway; (2) two consecutive one-electron transfers, i.e., radical pathway, in which the phenoxy radical is the intermediate. Once formed, this hydroperoxide structure undergoes an alkali-induced rearrangement and oxidative degradation into a series of low molecular weight compounds, such as aldehydes and organic acids.

**Effect of O<sub>2</sub> Partial Pressure.** When the oxidation reaction of lignin is carried out in a conventional batch reactor, total pressure, which is essentially the sum of O<sub>2</sub> partial pressure and water vapor pressure, increases from 1.38 MPa to the maximum (up to 1.65 MPa for our reaction conditions) during the heating-up period, and then declines constantly due to the consumption of oxygen inside the reactor (Figure 3). To demonstrate the importance of oxygen partial pressure, two series of experiments were designed. Under the conditions reported in Table 1, the total pressure was kept at 1.38 MPa during the reaction by introducing oxygen into the autoclave continuously. This allowed lignin to react with oxygen under a constant high O<sub>2</sub> partial pressure rather than under a regularly decreasing O<sub>2</sub> partial pressure as in normal batch processes (conditions reported in Table 2). The course of the reaction was monitored by measuring the values of lignin conversion and the yields of aldehydes. The results are shown in Figure 4.

If the O<sub>2</sub> pressure is maintained constant, a higher rate of oxygen transfer from the gas phase into the liquid phase takes place. This results in a faster rate of the ionic



**Figure 2.** Chromatogram of acetylated phenolic products from alkaline oxidation of lignin at 170 °C and 5 min in the presence of 0.5% FeCl<sub>3</sub> and 5% CuSO<sub>4</sub>. 1, Hydroxybenzaldehyde; 2, vanillin; 3, 4-ethylresorcinol (internal standard); 4, acetovanillone; 5, syringaldehyde; 6, acetosyringone.



**Figure 3.** Oxygen consumption during oxidation (reactant loadings are shown in Table 2).

**Table 1. Conditions and Input Materials Used for Alkaline O<sub>2</sub> Oxidation with FeCl<sub>3</sub> at Constant O<sub>2</sub> Pressure (1.38 MPa)**

	170	170	170
temperature, °C	170	170	170
time, min	2	3	5
log( <i>R</i> <sub>0</sub> /min)	2.56	2.71	2.83
aqueous solution, mL	100	100	100
Klason lignin, g	10.0	10.0	10.0
NaOH, g	12.5	15.5	16.5
FeCl <sub>3</sub> , g	0.05	0.05	0.05

pathway. The conversion and the yields of aldehydes increase sharply in a very short time (Figure 4).

Syringaldehyde is more sensitive than vanillin to oxygen pressure. It forms quickly but it readily degrades under a high oxygen pressure. Under the conditions used in the alkaline oxygen oxidation of lignin, the reactivity of the syringyl structure in lignin is higher than that of the guaiacyl structure. The results from Sultanov and Wallis (1991) showed a similar trend. Figure 4 shows that the amount of syringaldehyde reaches the maximum (6.4%) at 3 min and then decreases rapidly. The results indicate that, in order to obtain high yields of syringaldehyde, it is preferable to keep an initial high pressure of oxygen to rapidly break down the lignin and then lower the oxygen pressure to continue the oxidation of the lignin fragments but prevent the degradation of the syringaldehyde.

**Effect of pH.** Table 3 demonstrates the importance of the pH on the conversion of lignin and the yields of aldehydes. The pH has an obvious impact on the oxidation process in the presence of catalysts, especially when a mixture of CuSO<sub>4</sub> and FeCl<sub>3</sub> is used. In order to obtain a high yield of aldehydes, the pH of the oxidation medium has to be controlled between 10.5 and 12.0. Results from previous studies (Landucci, 1978; Gierer and Nilvebrant, 1986) also show that the oxidative degradation of lignin and formation of vanillin are dependent upon the hydroxide ion concentration used. The oxidation takes place only after the phenylpropane units have been ionized to phenolate anions. The observed increase of the oxidation rate with the pH can be interpreted in terms of increased ionization of the hydroxyl groups in the lignin structure.

**Effect of Catalyst.** CuSO<sub>4</sub> has been used in the commercial production of vanillin via air oxidation of lignosulfonates. The results obtained in our experiments confirmed that CuSO<sub>4</sub> is an effective catalyst for the conversion of lignin into aldehydes. The yields are higher than those obtained in the case of the control experiments without catalyst (Table 4). For example, the use of Cu<sup>2+</sup> increases the yield of total aldehydes from 8.5% to 12.1% and the conversion from 58.0% to 71.8% at 170 °C and 10 min. To try to improve our yields, another catalyst, FeCl<sub>3</sub>, and a mixture of CuSO<sub>4</sub> and FeCl<sub>3</sub> were also used in the oxidation.

Comparing the data obtained in the presence of Cu<sup>2+</sup> and Fe<sup>3+</sup>, it is clear that these metal ions influence the oxidation in different ways. Cu<sup>2+</sup> displays a strong catalytic effect on the formation of aldehydes even at low severity. At log(*R*<sub>0</sub>) = 2.5–2.7, the yield of total aldehydes increases from 6.7% (the control) to 8.8%, and formation of aldehydes reaches the maximum at log(*R*<sub>0</sub>) = 3.1 with a total yield of 10.3%.

As previously discussed, two reaction routes, ionic and radical reactions, coexist in the reacting system. Cu<sup>2+</sup> is a well-known electron acceptor in radical reactions, even at low temperatures (80 °C), and can accelerate the radical reaction (Landucci, 1978). The low lignin oxidation ability of Cu<sup>2+</sup> and the acceleration of the radical reaction are in

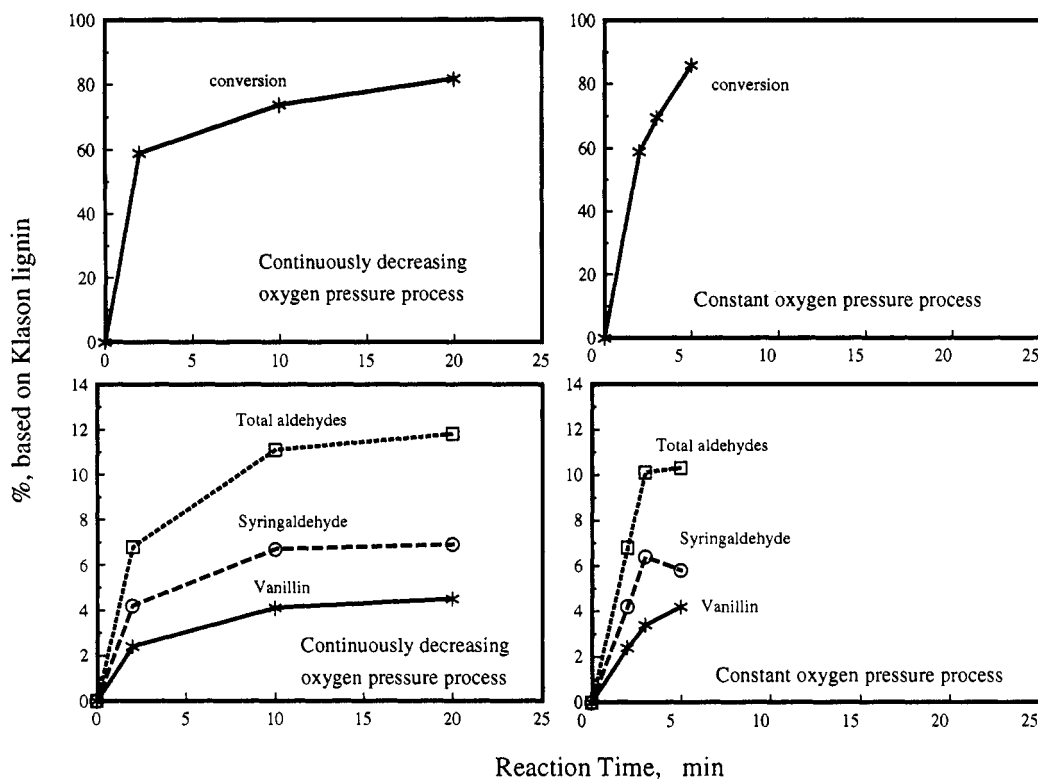


Figure 4. Effect of oxygen pressure at 170 °C (reactant loadings are shown in Tables 1 and 2).

Table 2. Conditions and Input Materials Used for Alkaline O<sub>2</sub> Oxidation with FeCl<sub>3</sub> under Constantly Decreasing O<sub>2</sub> Pressure (1.38 MPa as Initial Pressure)

temperature, °C	160	160	160	170	170	170	180	180	180
time, min	2	10	20	2	10	20	2	10	20
log( <i>R<sub>o</sub></i> /min)	2.23	2.81	3.1	2.65	3.08	3.34	2.81	3.31	3.64
aqueous solution, mL	100	100	100	100	100	100	100	100	100
Klason lignin, g	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
NaOH, g	9.5	15.3	16.2	10.2	16.0	17.0	11.5	16.5	17.5
FeCl <sub>3</sub> , g	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
O <sub>2</sub> , g	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5

Table 3. Effect of pH on Alkaline O<sub>2</sub> Oxidation with Different Catalysts at 160 °C and 10 min<sup>a</sup>

	catalyst													
	CuSO <sub>4</sub> /FeCl <sub>3</sub> (0.5 g/0.05 g)				CuO/Fe <sub>2</sub> O <sub>3</sub> (0.5 g/0.05 g)				none					
aqueous solution, mL	100	100	100	100	100	100	100	100	100	100	100	100	100	100
lignin, g	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
NaOH, g	8.0	8.2	10.0	11.2	12.0	12.5	13.0	6.0	7.2	11.5	12.5	6.8	8.9	11.8
O <sub>2</sub> , g	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
pH	8.7	8.9	9.0	9.3	10.2	11.0	12.9	8.0	8.4	10.1	12.7	7.9	9.9	13.0
conversion, %	53.3	55.8	56.7	59.8	66.8	65.9	67.2	53.5	59.1	61.6	61.1	53.9	55.2	57.8
ether-soluble fraction, %	12.8	12.6	15.5	16.3	17.7	17.6	17.4	6.8	10.5	17.3	17.6	10.9	13.2	17.6
hydroxybenzaldehyde, %	0.3	0.3	0.3	0.4	0.4	0.3	0.3	0.2	0.5	0.3	0.2	0.1	0.2	0.2
vanillin, %	2.8	3.0	3.5	3.4	4.5	4.0	4.0	1.2	2.3	3.7	2.8	1.2	2.1	2.5
syringaldehyde, %	3.6	4.3	3.6	5.5	7.4	7.7	6.9	1.5	3.1	7.2	6.7	2.8	3.2	4.5
acetovanillone + acetosyringone, %	0.3	0.4	0.2	1.2	0.8	0.8	0.6	0.3	0.9	1.1	0.8	1.0	0.7	0.8
total aldehydes, %	6.7	7.6	7.4	9.3	12.3	12.0	11.2	2.9	5.9	11.2	9.7	4.1	5.5	7.2

<sup>a</sup> % refers to Klason lignin, which represents 84.7% of the dry brut lignin used.

agreement with the low conversion of lignin and the high yields of aldehydes observed. In the oxidation process, the dissolved oxygen may be not only used to oxidize lignin and its derivatives, but also used to reoxidize the formed monovalent copper, since the reduced forms of copper are readily oxidized by molecular oxygen dissolved in the alkaline solution (Landucci, 1978). This process speeds up the redox catalytic cycle and increases the concentration of Cu<sup>2+</sup> species in solution, thus increasing the rate of the radical pathway. Since both reaction routes, ionic and radical reactions, coexist, the overall rate of lignin oxidation is higher than in the case of the control without catalyst. As compared with the control without catalyst, the

conversion of lignin increases by 3–10% and the yield of total aldehydes increases by 1–4%.

The results from our previous work (Wu *et al.*, 1992) have revealed that Fe<sup>3+</sup> cannot serve as oxidant in the absence of oxygen, since it does not act readily as an electron acceptor to accelerate the radical reaction. Fe<sup>3+</sup> influences, however, the conversion of lignin at high severity (Table 4). Using Fe<sup>3+</sup>, the observed conversions are about 10–15% higher than those obtained in the control experiment (no catalyst) and 5–10% higher than those using Cu<sup>2+</sup>. At low severity, Fe<sup>3+</sup> does not seem to affect the formation of aldehydes. A high severity, log(*R<sub>o</sub>*) = 3.0, is needed for Fe<sup>3+</sup> to act. Although the mechanism

**Table 4. Comparison of Results from O<sub>2</sub> Oxidation with CuSO<sub>4</sub> and Those of Control Experiments in the Absence of Catalyst<sup>a</sup>**

	alkaline O <sub>2</sub> oxidation				control	
	150	160	170	170	150	170
temperature, °C	150	160	170	170	150	170
time, min	10	10	10	20	10	10
log( <i>R</i> <sub>0</sub> /min)	2.57	2.85	3.09	3.39	2.53	3.12
aqueous solution, mL	100	100	100	100	100	100
Klason lignin, g	10.0	10.0	10.0	10.0	10.0	10.0
NaOH, g	12.3	13.5	14.6	15.8	10.9	12.2
CuSO <sub>4</sub> , g	0.5	0.5	0.5	0.5	none	none
O <sub>2</sub> , g	7.5	7.5	7.5	7.5	7.5	7.5
conversion, %	53.7	59.7	71.8	69.8	50.4	58.0
ether-soluble fraction, %	17.2	17.8	20.9	23.6	15.3	18.0
hydroxybenzaldehyde, %	0.3	0.4	0.3	0.3	0.3	0.4
vanillin, %	3.3	3.7	3.9	3.5	3.2	3.4
syringaldehyde, %	5.2	7.6	7.9	6.5	3.2	4.7
acetovanillone + acetosyringone, %	1.2	1.2	1.7	1.9	0.7	0.5
total aldehydes, %	8.8	11.7	12.1	10.3	6.7	8.5

<sup>a</sup> % refers to Klason lignin, which represents 84.7% of the dry brut lignin used.

**Table 5. Effects of CuSO<sub>4</sub> Quantity and FeCl<sub>3</sub> Quantity at 170 °C for 10 min<sup>a</sup>**

	100	100	100	100	100	100
aqueous solution, mL	100	100	100	100	100	100
Klason lignin, g	10.0	10.0	10.0	10.0	10.0	10.0
NaOH, g	16.0	13.5	16.2	14.6	15.8	16.3
CuSO <sub>4</sub> , g	0.0	0.5	1.0	0.5	0.5	0.5
FeCl <sub>3</sub> , g	0.05	0.05	0.05	0.0	0.1	0.2
O <sub>2</sub> , g	7.5	7.5	7.5	7.5	7.5	7.5
conversion, %	73.7	73.0	72.0	71.8	75.2	74.2
ether-soluble fraction, %	21.9	22.2	22.4	20.9	21.2	22.0
hydroxybenzaldehyde, %	0.3	0.4	0.3	0.3	0.3	0.3
vanillin, %	4.1	4.7	4.1	3.9	4.4	4.2
syringaldehyde, %	6.7	9.5	8.8	7.9	8.6	8.1
acetovanillone + acetosyringone, %	1.1	1.3	1.3	1.7	1.3	1.4
total aldehydes, %	11.1	14.6	13.2	11.9	13.3	12.6

<sup>a</sup> % refers to Klason lignin, which represents 84.7% of the dry brut lignin used.

is still unclear, previous work (Riffer, 1984) suggests that Fe<sup>3+</sup> complexes are formed with phenolic compounds and act as oxygen carriers in the oxidation process, thus accelerating the ionic reaction. This accounts for the observed catalytic effect of Fe<sup>3+</sup>.

Among the catalysts used, the mixture of CuSO<sub>4</sub> and FeCl<sub>3</sub> proved to be the most effective one. The highest yield of aldehydes was obtained using this mixture. The results obtained indicate that, in a mixture of CuSO<sub>4</sub> and FeCl<sub>3</sub>, the ratio of these two compounds has an obvious impact on the yields of aldehydes (Table 5). The best result was obtained when 5% CuSO<sub>4</sub> and 0.5% FeCl<sub>3</sub>

(percentages based on Klason lignin) were used. Using this mixture, the oxidation under 170 °C for the period of 10 min accounts for 14.6% as total aldehydes (vanillin, 4.7%; syringaldehyde, 9.5%; and *p*-hydroxybenzaldehyde, 0.4%), which is at least 3% more than in the cases using other catalysts. We propose that a higher oxygen concentration in solution related to the in-situ formation of Fe<sup>3+</sup>-lignin complexes favors the ionic pathway as well as the redox cycle of copper. The latter is responsible for the radical reaction. Hence the overall reaction rate is higher than that observed when only Fe<sup>3+</sup> or Cu<sup>2+</sup> is used.

**Optimization of Reaction Conditions.** After knowing the effects of all the variables, a series of experiments was run at the optimum pH range with the most effective catalyst combination. To optimize the reaction conditions, e.g., temperature and time, the reaction ordinate *R*<sub>0</sub> was used. The data obtained are represented in Table 6. The maximum yield of aldehydes (ca. 4.7% vanillin and 9.5% syringaldehyde) was obtained at log(*R*<sub>0</sub>/min) = 3.1.

## Conclusions

The present work on alkaline oxidation (oxygen) of a steam-explosion (*Populus tremuloides*) lignin has provided evidence that the oxidative degradation of lignin leading to aldehydes is favored by ionization of the phenylpropane units under high hydroxide ion concentration. The maximum oxidation rate was obtained at the pH range of 10.5–12.0.

Poor selectivity toward aldehydes is observed in the presence of pure O<sub>2</sub> with no catalysts. Syringaldehyde is readily degraded to acids under high O<sub>2</sub> pressures. To obtain the highest yields of syringaldehyde, the process strategy was to initiate the reaction at high O<sub>2</sub> pressure, let the O<sub>2</sub> pressure continuously decrease during the course of the oxidation reaction, and use suitable catalysts. Such strategy can be readily achieved by using a jet mixer followed by a tubular reactor operating in plug flow mode.

The results obtained have shown that the mixture of CuSO<sub>4</sub> and FeCl<sub>3</sub> is an effective catalyst combination to improve the oxidation selectivity of the process. A reaction time of 10 min, at 170 °C, has resulted in high yields of aldehydes (4.7% of vanillin and 9.5% of syringaldehyde).

It is suggested that in the reacting system, Cu<sup>2+</sup> acts as an electron acceptor accelerating the formation of the phenoxy radical. Fe<sup>3+</sup> cannot be a catalyst in the radical reaction, because it has no ability to absorb an electron from the phenolate anion. However, our results have shown that Fe<sup>3+</sup> has a significant effect on the oxidation of lignin with and without Cu<sup>2+</sup>. We propose that Fe<sup>3+</sup>-

**Table 6. Alkaline O<sub>2</sub> Oxidation with 5% CuSO<sub>4</sub> and 0.5% FeCl<sub>3</sub><sup>a</sup>**

	170 °C				160 °C				150 °C			
	5	10	20	5	10	20	30	60	10	20	30	40
time, min	5	10	20	5	10	20	30	60	10	20	30	40
log( <i>R</i> <sub>0</sub> /min)	2.81	3.08	3.35	2.56	2.78	3.06	3.25	3.57	2.52	2.78	2.94	3.07
aqueous solution, mL	100	100	100	100	100	100	100	100	100	100	100	100
lignin, g	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
CuSO <sub>4</sub> , g	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
FeCl <sub>3</sub> , g	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
NaOH, g	10.9	13.5	14.7	10.4	12.5	13.6	14.2	17.0	11.0	12.5	13.1	14.5
O <sub>2</sub> , g	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
conversion, %	64.6	73.0	79.1	57.5	65.9	71.2	75.7	85.6	57.0	68.5	73.1	75.9
ether-soluble fraction, %	17.4	22.2	24.3	17.2	17.6	20.4	21.0	22.6	17.0	17.7	18.3	20.7
hydroxybenzaldehyde, %	0.3	0.4	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.5	0.4
vanillin, %	3.0	4.7	4.0	3.1	4.0	4.6	4.2	4.3	3.6	3.8	5.5	4.8
syringaldehyde, %	5.8	9.5	7.8	6.4	7.7	8.7	8.8	5.2	5.7	6.8	7.6	7.0
acetovanillone + acetosyringone, %	0.9	1.3	0.8	0.9	0.8	0.6	0.6	0.1	0.7	0.5	0.2	0.2
total aldehydes, %	9.1	14.6	11.2	9.8	12.0	13.7	13.4	9.9	9.7	10.9	13.6	12.2

<sup>a</sup> % refers to Klason lignin, which represents 84.7% of the dry brut lignin used.

lignin complexes are formed in-situ and act as oxygen carriers which increase the oxygen concentration in the reaction medium thus helping to speed up the ionic reaction, as well as the redox catalytic cycle of copper when present. The latter, in turn, accelerates the rate of the radical reaction.

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