

# Ozonation Products of Organosolvolytic Extracts from Vegetal Materials

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The ozonation of lignin in an organic solution was used to produce oxyaromatic compounds. Corn (*Zea mays*) stalk and poplar (*Populus deltoides*) wood lignin solutions (organosolvolytic juices) obtained from their respective autohydrolyzed materials and an organosolv lignin were treated with ozone, and the time course trend of the identified reaction products was studied. GC/MS and GC/FID were used to identify and quantify (internal standard method) the reaction products. The following acids were identified: glycolic, oxalic, malic, glyceric, *p*-hydroxybenzoic, and vanillic. In addition, *p*-hydroxybenzaldehyde, vanillin, syringaldehyde, and hydroquinone were also identified. All the oxyaromatic aldehydes reached maximum yields at short reaction times (between 1 and 8 min). These results were used to determine the ratio between the different phenylpropane units of their constitutive lignins. The ratio of *p*-hydroxyphenyl:guaiacyl:syringyl units for corn stalk, poplar wood, and organosolv lignins was 5.3:2:1, 0.1:1:1.1, and 0:1:1.1, respectively.

**Keywords:** Ozonation; corn (*Zea mays*) stalks; poplar (*Populus deltoides*) wood; lignocellulose; lignin

## INTRODUCTION

One way of making use of lignocellulosic wastes is to oxidize them, either pretreated or untreated. From among the different possible oxidants, ozone is an attractive alternative for a number of reasons. It does not leave strongly acidic, basic, or toxic residues in the treated material, and since it is an unstable compound, it can be decomposed back to oxygen by a simple catalyst bed or by raising the temperature, meaning that the residual ozone in any gaseous effluent can be readily removed (Neely *et al.*, 1975). In this way, environmental problems are avoided. Ozone can be generated on-site as and when needed, thereby avoiding chemical supply problems in isolated areas. Finally, most ozonation reactions take place at near-ambient temperatures and pressures.

The conventional industrial chemical pulping processes (kraft and sulfite) involve the solubilization of previously depolymerized lignin along with hemicelluloses by using strong bases or sulfonation reagents. One promising alternative approach involves the pretreatment of lignocellulosic materials by fractionating them without adding external chemical reagents. This makes it possible to obtain each lignocellulosic polymer (hemicelluloses, lignin, cellulose) separately and in a less degraded form than in the conventional treatments. The plant material is first submitted to a thermomechanical–chemical process of steam or aqueous autohydrolysis, which leads to the solubilization of the hemicelluloses (Heitz *et al.*, 1991; Tortosa *et al.*, 1992) and leaves a solid material composed almost entirely of lignin and cellulose. In a second step, this solid is submitted to

organosolvolytic, during which the lignin is solubilized in organic solvents (Beltrame *et al.*, 1992; Thring *et al.*, 1993a).

Ozonation has been widely used to reduce the lignin content of both agricultural and forestry wastes. Many of the oxidation products (vanillin, syringaldehyde, catechol, guaiacol, etc.) of lignin are interesting in pharmacology and agrochemistry as well as for the cosmetic and food industries. These compounds may be used directly or after transformation into products of a greater added value (heliotropine, dopamine, papaverine, adrenaline, etc.) (Flandroy, 1992). Vanillin, which is widely used in the food industry as a flavoring, is used to synthesize L-DOPA (for the treatment of Parkinson's disease) and vanillic acid (in turn, a base for non-toxic fungicides and medicaments for controlling blood pressure) (Garcia *et al.*, 1984). In an earlier work (Quesada *et al.*, 1997a), only very small amounts of oxyaromatic compounds were detected during ozonation of lignin in the wet solid state (both *in situ* and isolated). In most previous studies, ozonation had been performed in aqueous organic solvents (Balousek *et al.*, 1981; Kaneko *et al.*, 1983). Therefore, corn (*Zea mays*) stalk and poplar (*Populus deltoides*) wood lignin solutions obtained from hemicellulose-free materials were ozonated to produce oxyaromatics. In addition, an organosolv hardwood lignin solution was also ozone-treated for comparison purposes.

The chemical structure of lignin is an irregular arrangement of the three precursor monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols (Sarkanen and Ludwig, 1971). It is characterized by the nature of the aromatic (phenylpropane) monomers and the types of linkages between them. The phenylpropane units are usually determined by alkaline nitrobenzene or permanganate oxidation (Garland *et al.*, 1986), in which low molecular weight degradation products are gener-

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**Table 1. Yield of Compounds Identified in OSJs (g/100 g Dissolved Matter in OSJ)**

	corn stalk OSJ	poplar OSJ
glycolic acid	0.20	0.12
oxalic acid	0.24	0.10
malonic acid	trace	trace
glyoxylic acid	trace	trace
<i>p</i> -hydroxybenzaldehyde	0.15	0.02
<i>p</i> -hydroxybenzoic acid	0.07	0.35
hydroquinone	0.14	0.01
vanillin	0.38	0.45
vanillic acid	0.15	0.17
syringaldehyde	0.26	1.79

ated from a small portion of lignin. Ozone has also been used under mild conditions to clarify the nature of the aromatic monomers (Tanahashi *et al.*, 1975). The results obtained during ozonation of the different lignin solutions were used to determine the ratio between the different phenylpropane units of the lignin molecules.

## MATERIALS AND METHODS

**Materials.** *Corn Stalk and Poplar Organosolvolytic Extracts.* Raw dried and ground corn stalks from Abarán-Cieza (Murcia, Spain) were sieved to a particle size of 0.2–0.5 mm and extracted with a 7/3 (v/v) ethanol/toluene mixture and then with water. Poplar wood from Brockville (Ontario, Canada) was debarked and milled to chips of 0.5 cm particle size diameter. Both samples were steam explosion autohydrolyzed at 220 °C for 3 min in the pilot unit of the Chemical Engineering Department at Sherbrooke University (Québec, Canada) to eliminate the hemicellulosic fraction. The treated materials were extracted with 1 L of hot water. The pentosan content of the autohydrolyzed corn stalks and poplar wood was determined to be 4.0 and 3.1%, respectively. The autohydrolyzed materials were extracted at 210 °C for 45 min with a 75/25 (v/v) acetone/water mixture (8 g of material in 150 mL of mixture) (Quesada *et al.*, 1997b). The solid and liquid phases were separated by filtration, and the solid was washed with the solvent mixture. The liquid phase together with the wash liquid was denominated, organosolvolytic juice (OSJ). The degree of delignification reached with the autohydrolyzed corn stalk and poplar wood was 63.9 and 81.6%, respectively, giving OSJs with lignin and organic matter concentrations of 6.78 and 7.81 g/L and of 8.68 and 8.72 g/L, respectively. Chromatographic analysis of the juices (as indicated below) showed the existence of small quantities of organic acids and phenolic derivatives (Table 1) formed by cleavage of  $\beta$ -O-4 type  $\beta$ -aryl ether linkages (Barnet *et al.*, 1989), indicating the partly degraded character of the solubilized lignins.

*Corn Stalk Organosolvolytic Lignin Solution.* In order to investigate the ozonation of lignin in water-free solvents, 100 mL of corn stalk OSJ was evaporated to dryness, and the organosolvolytic lignin (OSL) obtained was redissolved in 100 mL of acetone.

*Organosolv Lignin Solution.* A 8.7 g/L hardwood organosolv lignin (COL) (Aldrich-Sigma, St. Louis, MO) solution in a 75/25 (v/v) acetone/water mixture was obtained.

**Experimental Ozonation Conditions.** Oxygen with an ozone concentration of 40 g/m<sup>3</sup> was bubbled into 100 mL of the different lignin solutions at a flow rate of 45 L/h at room temperature as described by Quesada *et al.* (1997a). Samples (6 mL) were taken at different reaction times and exposed to a stream of nitrogen to remove dissolved ozone. The samples were evaporated to dryness, silylated, and analyzed by gas chromatography.

**Analytical Methods.** Silylation of the ozonation products was carried out by adding 200  $\mu$ L of a pyridine solution containing 5 mg/mL palmitic acid (internal standard), 1 mL of bis(trimethylsilyl)trifluoroacetamide (BSTFA), and 50  $\mu$ L of trimethylchlorosilane (TMCS). The mixture was stirred continuously at 60 °C for 30 min, and a 1.5  $\mu$ L sample was analyzed by gas chromatography. Helium was used as carrier

gas at a constant flow rate of 1 mL/min. The temperature programming was as follows: 10 min at 90 °C, 5 °C/min to 205 °C, 8 °C/min to 250 °C, and 15 min at 250 °C. The injector temperature was 250 °C, and that of the detector was 275 °C. The equipment was a Hewlett Packard 5890 Series II coupled to a 5972 quadrupole mass spectrometer of 70 e.v. equipped with a HP-5 capillary column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film); splitless mode injection; the NIST database was used to identify compounds; a Konik KNK-3000-HRGC with flame ionization detector (FID) fitted with an OV-101 capillary column (25 m  $\times$  0.33 mm o.d., 0.25  $\mu$ m film); split mode injection (25/1 ratio). Compounds were considered to be positively identified when their mass spectra and GC retention times agreed with those of authentic samples. The error in the determination of all the compounds was  $\pm$  3.1%.

## RESULTS AND DISCUSSION

In the ozonation process, all the lignin solutions gradually lost color, changing from dark amber to pale yellow. The volume of liquid in the reactor decreased during ozonation because solvent was carried away by the gas and because samples were taken. This decrease, as well as the quantity of each reaction product removed during sampling, was taken into account in the calculation of the reaction product yields.

During ozonation of the OSJs, sugars such as D-galactose, D-glucose, and D-mannose were tentatively identified by their mass spectra. These sugars arise from the cleavage of glycosidic linkages in the polysaccharide molecules (Katai and Schuerch, 1966) extracted during organosolvolytic. These sugars persisted in the medium for up to 20 min. The compounds indicated in Table 2 were identified chromatographically. During ozonation of the organosolv lignin, traces of *p*-hydroxybenzaldehyde were detected.

The ozone consumed during oxidation of the OSJs, of corn stalk OSL dissolved in pure acetone, and of COL dissolved in 75/25 (v/v) acetone/water mixture was practically the same (Figure 1), indicating that all the oxidized lignins have similar reactivities. However, a slightly higher amount of ozone was consumed during the ozonation of COL, perhaps due to its lower degree of condensation. Autohydrolysis induces a certain degree of condensation in lignin (Hayashi *et al.*, 1989).

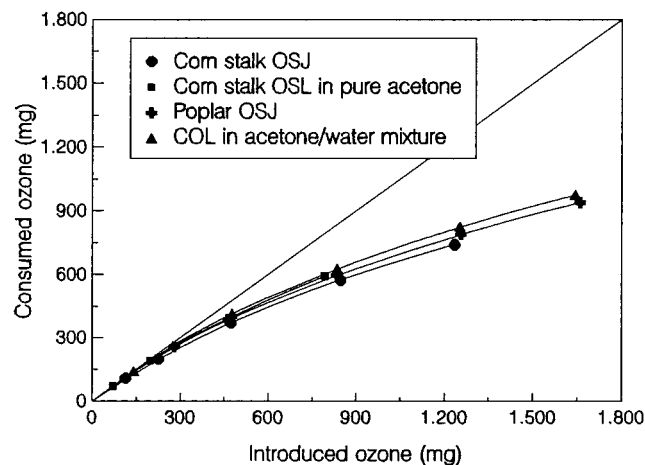
**Ozonation of Corn Stalk OSJ.** During the first minutes of the reaction, short-chain aliphatic carboxylic acids (glycolic and oxalic acids) were generated, the amounts of which increased as the reaction progressed (Figure 2). Oxalic acid was the major reaction product. The glycolic acid could arise from the oxidation of glycolaldehyde, which results from ozone attack on the double bond in substituted cinnamic alcohol type side chains, of a vanillyl alcohol type structure, or of erythronic and threonic acids, which are formed from  $\beta$ -aryl ether type structures. Oxalic acid is produced by extensive oxidation of aromatic rings in lignin (Matsumoto *et al.*, 1986). Glyceric acid, which was present in trace amounts, could have arisen from the oxidation of erythronic and threonic acids.

All the identified oxyaromatic compounds passed through a production maximum during the reaction (Figure 3). In the first few minutes (between 1 and 8 min, depending on the compound), the production of aromatic aldehydes reached its maximum in the following descending order: *p*-hydroxybenzaldehyde (3.45 g/100 g dissolved matter in the OSJ), vanillin (1.67 g/100 g dissolved matter), and syringaldehyde (1.01 g/100 g dissolved matter). This indicates that corn stalk lignin

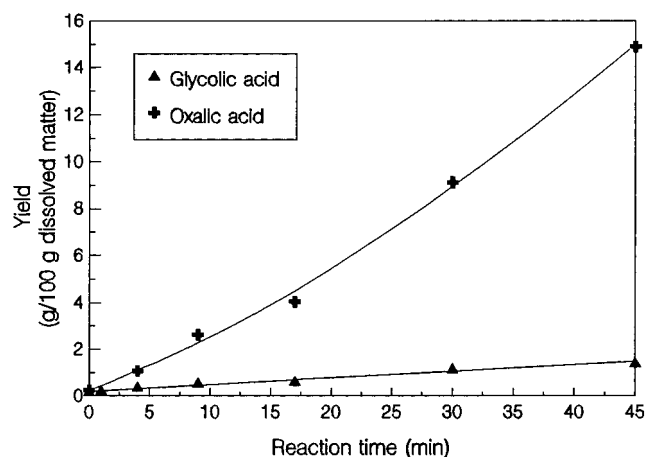
**Table 2. Reaction Products Identified during Ozonation of Various Lignin Solutions**

corn stalk OSJ	corn stalk OSL dissolved in pure acetone	poplar OSJ	COL dissolved in 75/25 (v/v) acetone/water mixture
glycolic acid, oxalic acid, malic acid (trace), <i>p</i> -hydroxybenzaldehyde, <i>p</i> -hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, glyceric acid (trace)	glyceric acid (trace)	glyceric acid (trace), butanedioic acid* (trace), 3,4-dihydroxybenzoic acid* (trace)	

\*, Identified by mass spectrum. \*\*, Identified by standard injection.



**Figure 1.** Ozone consumption during ozonation of the different lignin solutions.

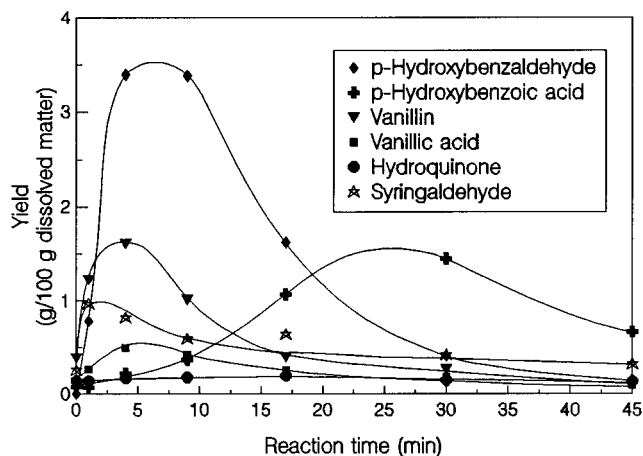


**Figure 2.** Quantification of the main aliphatic acids produced during ozonation of corn stalk OSJ.

is rich in *p*-hydroxyphenyl type phenylpropane units. These aromatic aldehydes result from oxidation of the aliphatic carbon-carbon double bonds in substituted cinnamic structures, which are the most reactive lignin linkages to the ozone attack (Eriksson and Gierer, 1985).

The fall in the yield of *p*-hydroxybenzaldehyde after 6 min was accompanied by an increase in that of *p*-hydroxybenzoic acid, suggesting that this acid basically arises from oxidation of the aldehyde group. The production of vanillic acid reached a maximum at the same reaction time as that of vanillin, suggesting that a part of this acid may arise from the oxidation of phenylcoumarone type structures (Tanahashi *et al.*, 1975).

**Ozonation of Corn Stalk OSL Dissolved in Pure Acetone.** Chromatographic analysis showed the same reaction products as were obtained from corn stalk OSJ. The production trend of the aliphatic acids was the same as that observed with corn stalk OSJ, although the yields were about 23% lower. Oxyaromatic compounds



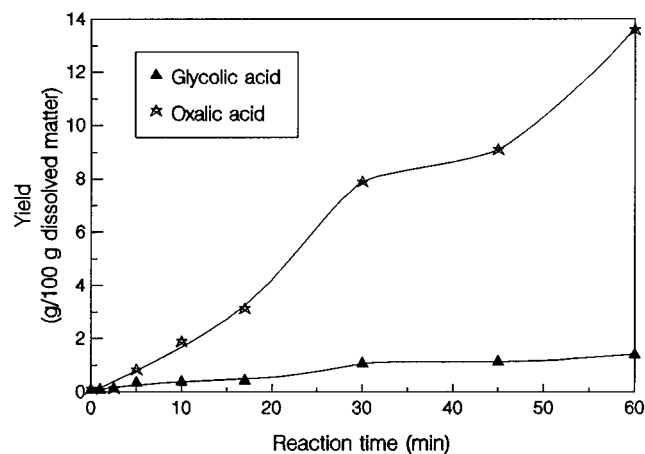
**Figure 3.** Quantification of the main aromatic compounds produced during ozonation of corn stalk OSJ.

also showed the same behavior as that indicated above. Their maximum yields were the same except that of vanillin, which was slightly greater (2.25 g/100 g dissolved matter), while *p*-hydroxybenzaldehyde was lower (2.54 g/100 g dissolved matter) as was *p*-hydroxybenzoic acid (0.97 g/100 g dissolved matter). All these maxima appeared at shorter reaction times than in the case of corn stalk OSJ, except that of syringaldehyde, which appeared at the same time. Furthermore, the aromatic aldehydes initially generated were destroyed more rapidly during the reaction. This different behavior can be explained by the fact that the redissolution of corn stalk OSL in pure acetone is not total (suspended solids remain) and, since a solid/gas reaction is less effective than a liquid/gas reaction, the ozone reacts more readily on the initially dissolved lignin molecules and on the initial reaction products than on the suspended solid particles.

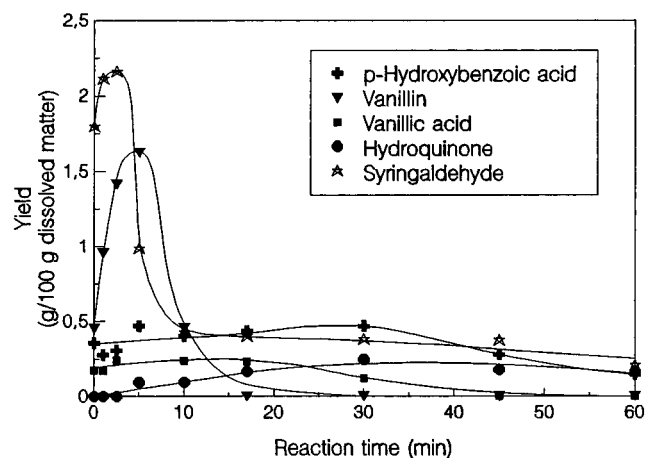
**Ozonation of Poplar OSJ.** To understand the influence of ozone on another type of lignin, poplar OSJ was used. The time course trend of the glycolic and oxalic acid yields was very similar to that observed with corn stalk OSJ up to 30 min of treatment, but thereafter between 30 and 45 min the production of these acids inexplicably levelled off, only to rise again later until 60 min had passed (Figure 4).

The main aromatic aldehyde generated was syringaldehyde, followed by vanillin (maxima of 2.21 and 1.63 g/100 g dissolved matter, respectively) (Figure 5). *p*-Hydroxybenzaldehyde was obtained in very small amounts (maximum of 0.14 g/100 g dissolved matter). This confirms that poplar lignin has a typical hardwood composition.

The destruction of vanillin and syringaldehyde did not lead to any significant increase in the corresponding acids, which means that these acids were oxidized rapidly. The fact that greater amounts of *p*-hydroxybenzoic acid than of *p*-hydroxybenzaldehyde were detected means that the acid could arise from oxidation



**Figure 4.** Quantification of the main aliphatic acids produced during ozonation of poplar OSJ.



**Figure 5.** Quantification of the main aromatic compounds produced during ozonation of poplar OSJ.

of phenylcoumarone type structures (Tanahashi *et al.*, 1975) or from the demethoxylation of other aromatic acids (Haluk and Metche, 1986).

Hydroquinone was generated in very small quantities during treatment and reached a maximum at 30 min (0.4 g/100 g dissolved matter). This compound could arise from the oxidation and rearrangement of ester-linked *p*-coumaric acid (Morrison and Akin, 1990).

**Ozonation of COL Dissolved in a 75/25 (v/v) Acetone/Water Mixture.** The time course trend of the oxalic acid was the same as that shown during poplar OSJ ozonation. However, in this case, yields of about 9% higher were obtained for any reaction time. Glycolic acid also showed a similar behavior. *p*-Hydroxybenzaldehyde was not detected among the oxyaromatic reaction products. However, small quantities of its corresponding acid were measured, which reached a maximum of 0.14 g/100 g dissolved matter at 15 min. The rest of the aromatic compounds showed the same trend as that observed with poplar OSJ. However, the maximum produced quantities of vanillin and syringaldehyde were slightly lower (1.28 and 1.76 g/100 g dissolved matter, respectively).

**Structural Features of the Lignin Molecules.** The amount of ozone needed to maximize the production of each aromatic compound can also be expressed per phenylpropane unit. When the molecular weight for a phenylpropane unit is 205 (Vidal, 1985), this optimal consumption has been found to be between 0.18 and 1.28

**Table 3.** Ratio between Phenylpropane Units of Various Lignin Molecules

	<i>p</i> -hydroxyphenyl: guaiacyl:syringyl cinnamic phenylpropane units	cinnamic:total phenylpropane units
corn stalk OSL	5.3:2:1	10:100
poplar OSL	0.1:1:1.1	5:100
COL	0:1:1.1	4:100

mol of ozone/mol of phenylpropane units, indicating that only the alkene C=C bonds are cleaved (Sarkanen *et al.*, 1992). The value of 1 mol/phenylpropane unit obtained by Vidal and Molinier (1988) for the ozonation of a suspension of a southern pine kraft softwood lignin (Indulin AT, Westvaco Co., Charleston, SC) for 3 h in 45% acetic acid falls within this range.

Therefore, considering that the aromatic aldehydes (*p*-hydroxybenzaldehyde, vanillin, and syringaldehyde) detected in the first minutes of ozonation basically arise from the corresponding substituted cinnamic structures present in the lignin molecule, assuming the error which may be introduced due to partial destruction by ozone of the initially formed aromatic aldehydes, and based on the maximum quantities of these aldehydes produced, the molar ratio between the three different types of cinnamic phenylpropane units present in the treated lignin molecules was calculated. These molar ratios together with the ratios between cinnamic and total phenylpropane units are shown in Table 3 for all the treated lignins.

The ratio of *p*-hydroxyphenyl:guaiacyl:syringyl units in corn stalk OSL (5.3:2:1) was similar to that obtained by Tanahashi *et al.* (1975) by ozonation of an acidolysis residue of bamboo milled-wood lignin (MWL) (9:3:1). Likewise, Morrison and Akin (1990) reported that during the ozonation of Coastal Bermuda grass (*Cynodon dactylon*) (also a monocotyledonous species) the main aromatic products were *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid, followed by vanillin and vanillic acid.

The molar ratio between guaiacyl and syringyl phenylpropane units (V/S) obtained during the ozonation of poplar OSL (0.88) is similar to that achieved by other authors for the alkaline nitrobenzene oxidation of poplar wood. Thus, Sarkanen and Hergert (1971), Alibert and Boudet (1979), and Thring *et al.* (1993b) obtained V/S values of 0.33, 0.56, and 0.67, respectively. Moreover, the average V/S value for woody dicotyledonous species was determined to be 0.77 (Higuchi, 1980). Wu *et al.* (1994) obtained a V/S molar ratio of 0.59 for a catalytic alkaline oxidation of an alkali lignin extracted from steam autohydrolyzed poplar.

On the basis of the relative proportions between the different phenylpropane units (C<sub>9</sub>) in poplar OSL, it can be calculated that the average number of methoxyl groups per phenylpropane unit (MeO/C<sub>9</sub>) is 1.45. This value is very close to that 1.43 obtained by Björkman and Person (1957) for MWL from poplar (*Populus tremula*) wood. Sarkanen and Hergert (1971) found a MeO/C<sub>9</sub> value of 1.38 for the lignin thioglycolic acids of poplar trunk wood. Therefore, since ozonation does not seem to produce demethoxylation of the aromatic rings (in accordance with the results reported by Tanahashi *et al.*, in 1975) at short reaction times, the higher V/S value obtained with poplar OSL could be due to the higher degradation rate of the syringyl rings in relation to that of the guaiacyl rings.

On the other hand, the time course trend of the product concentrations during lignin degradation and the residual ozone that escapes reaction coincides with that predicted by the second kinetic model of Ouederni (1984), in which the ozone intervenes every time in  $n$  successive reactions with partial orders different from the unit, which is in accordance with the depolymerization of an infinite three-dimensional gel (Vidal *et al.*, 1985).

Thus, the following reaction scheme for the ozonation of lignin in organic solutions implies

(a) Depolymerization of the lignin macromolecule accompanied by the liberation of low molecular weight oxyaromatic compounds.

(b) Degradation of the initially generated aromatic products accompanied by the formation of low molecular weight carboxylic acids.

Judging from the phenolic oxidation products and the radical entities formed during ozonation (Katuscak *et al.*, 1972), it is possible that condensation (Balousek *et al.*, 1981) or polymerization reactions might develop in the medium, which would lead to the formation of high molecular weight organic compounds that cannot be identified by GC. This would explain why the sum of all the quantities of the detected oxyaromatic compounds (the main products generated at short treatment times) only amounts to about 8% of the lignin initially present in the treated lignin solutions.

#### ABBREVIATIONS USED

OSJ, organosolvolytic juice; OSL, organosolvolytic lignin; COL, organosolv lignin.

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