

Lignin Organosolvolytic from Autohydrolyzed Corn (*Zea mays*) Stalks: Ozonation of both Solvolytic Solid and Juice

J. QUESADA, M. RUBIO, D. GOMEZ

Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain

Received 27 February 1997; accepted 1 November 1997

ABSTRACT: The solubility of lignin from autohydrolyzed corn (*Zea mays*) stalks in different organic solvent–water mixtures and conditions was studied. The best lignin solvent was selected according to its lignin extraction capacity and its low reactivity to ozone. Both the organosolvolytic solid and juice obtained in optimal conditions, 75/25 (v/v) acetone–water mixture at 210°C for 45 min, and the autohydrolyzed material were treated with ozone, and the reaction products were determined by gas chromatography–mass spectrometry and gas chromatography–flame ionization detection. The concept of the solubility parameter (δ -value) was applied to explain the effect of the solvent-to-water ratio on lignin solubility. The δ -value of the lignin dissolved was 13.8 (cal/cm³)^{1/2}. The δ -value of the various solvent–water mixtures was also calculated. The experimental delignification capacity of the aqueous organic solvents clearly reflects the proximity of their δ -value to that of lignin. In other words, the closer the δ -value of the aqueous organic solvent to that of lignin, the more effective it is; the hydrogen-bonding capacity of the solvent–water mixtures was also taken into account. The following acids were identified during ozonation: glycolic, oxalic, malonic, glyoxylic, butanedioic, malic, *p*-hydroxybenzoic, vanillic, and syringic. In addition, syringaldehyde, vanillin, *p*-hydroxybenzaldehyde, and hydroquinone were identified. Ozonation of the organosolvolytic juice led to the formation of the oxyaromatic compounds, which were destroyed during treatment. This destruction was accompanied by the generation of aliphatic acids. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1867–1876, 1998

Key words: corn stalks; ozone; lignin; solubility; gas chromatography–mass spectrometry

INTRODUCTION

Plants are an important source of organic raw material due to the rich variety of products that can theoretically be obtained by different treatments. Among such treatments, the sequential fractionation of the principal lignocellulose polymers with no added chemical reagents makes it

possible to obtain different polymers selectively and in the minimum state of degradation. The first stage of fractionation consists of solubilizing the hemicelluloses in an aqueous medium (autohydrolysis) by means of thermomechanical processes to leave a solid material composed of mainly cellulose and lignin. In a second stage, the lignin is solubilized in organic solvents (organosolvolytic), leaving a solid residue almost totally composed of cellulose. Such organosolvolytic processes are currently used on an industrial scale to obtain cellulose suitable for papermaking by

Correspondence to: J. Quesada.

Journal of Applied Polymer Science, Vol. 68, 1867–1876 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/111867-10

solubilizing the lignin and hemicelluloses in one step. Autohydrolytic processes involving sudden decompression cause the material to break up, which means that the resulting cellulose cannot easily be used by the paper industry.¹ However, if the different polymers can be separated, they can be used individually, and the whole process becomes more profitable.

One of the ways of using the lignin fraction is to oxidize it to produce compounds, principally of an oxyaromatic nature, which are commercially interesting for the cosmetics and pharmaceutical industries.² Among the oxidants available, ozone is of great interest because it induces rapid reactions at ambient temperature and pressure.

Plant materials are treated with ozone for several reasons, including the following:

1. To prepare chemical paper pulps, the ozone markedly reduces the lignin content and, to a lesser extent, that of hemicelluloses, leaving the cellulose almost unaffected.³ Pulp with a high carbohydrate content (78% of the initial content) are thus obtained.
2. To obtain cattle feed, the treated material shows higher *in-vitro* digestibility values than the raw material.⁴⁻⁷
3. To produce chemicals, small doses of ozone give oxyaromatic compounds,⁸ while high doses can be used to produce low-molecular-weight carboxylic acids.⁹

In the present article, we shall first determine the optimal organosolvolytic conditions for solubilizing lignin from autohydrolyzed corn stalk, using solvents that do not react strongly with ozone. Secondly, the organosolvolytic extract is treated with ozone, and the evolution of the reaction products, especially those of an oxyaromatic nature, is observed.

MATERIALS AND METHODS

Materials

Raw corn (*Zea mays*) stalks from Murcia (Spain) were dried at ambient temperature, ground in a hammer mill, and sieved to a particle size of 0.2–0.5 mm. This fraction was extracted in soxhlet with a 7/3 (v/v) ethanol–toluene mixture and then with water before being submitted to autohy-

drolisis at 220°C for 3 min in the steam explosion device of the Chemical Engineering Department at Sherbrooke University (Quebec, Canada).¹⁰ The treated material was extracted with abundant water at ambient temperature and then with 1 L of boiling water, and was denominated steam explosion autohydrolyzed material (SAM). The SAM consisted of the following: 56.7% cellulose, 4.0% pentosans, 28.1% lignin, 5.1% ash.

Equipment and Experimental Conditions

Organosolvolytic

The experimental device consists of a stainless steel cylindrical autoclave of 300 mL capacity, into which the suspension to be treated is loaded in batches. The autoclave is introduced pneumatically by a mechanical arm into a smelted salt bath, which permits the reaction mass to reach the desired temperature in less than 6 min. Meanwhile, the autoclave is continuously shaken orbitally. After the reaction time, the reactor is removed from the salt bath and introduced in a water bath to stop the reaction.¹¹

150 mL of organic suspensions containing 6% SAM by weight were prepared and left for 1 h before the process was started. The reaction was carried out by applying high temperatures and with no added acid catalysts since these cause cellulose loss and lignin condensation.¹² Nitrogen was introduced into the autoclave up to 2.5 MPa. The experimental conditions were as follows: acetone, ethanol, ethylene glycol and dioxane solvents; solvent–water ratios, 100/0, 75/25, and 50/50 v/v; temperature, 175 and 210°C; and extraction time, 15, 30, and 45 min. After treatment, the solid and liquid phases were separated by filtration, and the solid was washed with 75 mL of the solvent mixture and was denominated as organosolvolytic solid (OSS). The liquid phase and the wash liquid were mixed to make up the organosolvolytic juice (OSJ).

Ozonation

Ozone was generated by passing pure oxygen at an absolute pressure of 0.123 MPa through an air-cooled cold plasma reactor (Anseros, GMF-4). The ozonated gas was humidified to saturation by bubbling through water in a glass gas washing flask when wet solid materials were treated. The ozonation was carried out in a glass standard fixed bed semicontinuous reactor of 350 mL capacity fitted

with a sintered glass plate at the bottom, through which the ozone entered into contact with the material. The ozone in the gaseous stream was measured continuously by an ultraviolet (UV) spectrophotometric analyzer (Anseros, Ozomat GM-19). The analyzer was calibrated according to norm 001/87 (F) of the International Ozone Association. The residual ozone was destroyed catalytically before being released to the atmosphere. All the gas flows of the system were controlled automatically by means of MF Controller Ucar regulators.

6 g of solid material (7.5% moisture) were humidified to 60% moisture.¹³ The moistened material was covered and kept overnight shaded from any light source and further treated at room temperature for 20 min by applying an oxygen–ozone flow rate of 35 L/h with an ozone concentration of 40 g/m³. The compaction degree of the material in the reactor (1.4 cm high bed) and the operating pressure (0.123 MPa) were kept as constant as possible in all the experiments. After reaction, nitrogen was passed through the material to desorb the excess ozone. The treated material was extracted with 100 mL of water for 30 min at room temperature. The solid and liquid phases were separated by filtration, and the liquid was brought to 100 mL after passing through a 0.45 μm filter. 10 mL were lyophilized, silylated, and analyzed by gas chromatography (GC).

In another experiment, 100 mL OSJ, obtained in optimal conditions, were exposed at room temperature to an oxygen–ozone flow rate of 45 L/h with an ozone concentration of 40 g/m³. Samples (7 mL) were taken at different reaction times and exposed to a stream of nitrogen for several minutes to remove dissolved ozone. The samples were evaporated to dryness, silylated, and analyzed by GC.

Analytical Methods

Klason lignin, pentosan, and cellulose contents were determined by applying the ASTM D1106-56, ASTM D1787, and ASTM D1103-60 norms, respectively.

Spectrophotometric measurements of the aqueous extracts were made in an UV-160A/UV-VIS Shimadzu Recording Spectrophotometer at 254 nm, which qualitatively reflected the overall concentration in aromatic compounds.

Silylation was carried out by adding 200 μL of a pyridine solution containing 5 mg/mL of palmitic acid (internal standard), 1 mL of *bis*(trimethylsi-

lyl)trifluoroacetamide (BSTFA), and 50 μL of trimethylchlorosilane (TMCS). The mixture was stirred continuously at 60°C for 30 min, and a 1.5 μL sample was analyzed by GC. The following equipment was used. (1) a Hewlett Packard 5890 Series II coupled to a Hewlett Packard 5972 quadrupole mass spectrometer of 70 eV fitted with a HP-5 capillary column (30 m \times 0.25 mm i.d., 0.25 μm film) and a splitless mode injection, and NIST database was used to identify compounds. (2) A Konik KNK-3000-HRGC with flame ionization detector (FID) equipped with an OV-101 capillary column (25 m \times 0.33 mm o.d., 0.25 μm film), and a split mode injection (25/1 ratio). Helium was used as carrier gas at a constant flow rate of 1 mL/min. The temperature programming was 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. Compounds were considered to be positively identified when their mass spectra and GC retention times agreed with those of authentic samples that were obtained from commercial sources. The error in the determination of all the compounds was $\pm 3.1\%$.

RESULTS AND DISCUSSION

Organosolvlysis

The best solvent was chosen according to its delignification capacity and according to its resistance to ozone attack.

Despite its capacity as a lignin extracting agent,¹⁴ ethylene glycol was not considered because of its high viscosity, which hinders separation of the suspension; its low vapor pressure, which makes it difficult to recover by distillation; and, principally, its high degree of reactivity with ozone. The values obtained for SAM extractability in a reflux extractor at 60°C for 2 h using an 82/18 (v/v) dioxane–water mixture¹⁵ were practically the same as those obtained with a 75/25 (v/v) acetone–water mixture,¹⁶ 15.5 y 15.4%, respectively. Furthermore, dioxane reacted strongly with the ozone, as was evident from the appearance of a great variety of reaction products, compared with those obtained with acetone, which remained practically unaffected even at long treatment times (60 min). Ethanol also reacted with ozone, although it gave rise to few reaction products. Therefore, both acetone and ethanol can

Table I Organosolvolytic Lignin with Acetone–Water Mixtures

Ac : H ₂ O		175°C			210°C		
		15 min	30 min	45 min	15 min	30 min	45 min
50 : 50	E ^a	16.7	20.0	16.2	20.8	20.0	19.7
	L ^b	17.0	18.9	16.6	16.0	15.4	14.8
	D ^c	49.3	46.1	50.5	54.6	56.1	57.4
75 : 25	E	18.9	15.0	18.6	20.7	22.9	21.7
	L	15.4	14.6	14.0	13.9	14.0	12.9
	D	55.5	55.8	59.4	60.6	61.5	63.9
100 : 0	E	8.1	9.3	8.7	7.1	6.2	9.8
	L	22.8	22.1	22.2	23.3	22.4	21.8
	D	25.1	28.2	27.7	22.6	24.9	29.9

^a E: Extractibility (g solubilized material/100 g dry initial material, %).

^b L: Klason lignin (%).

^c D: Delignification (g solubilized lignin/100 g initial lignin, %).

be used to obtain lignin solutions for subsequent ozonation. The organosolvolytic conditions were chosen according to previous unpublished work.

Tables I and II show the most relevant results obtained during organosolvolytic with acetone–water and ethanol–water mixtures, respectively. In the case of the acetone–water mixtures, a slight increase in delignification between 15 and 45 min was obtained whatever the temperature applied (Table I). The highest temperature (210°C) was more effective for the same time and acetone-to-water ratio. Moreover, the use of the 75/25 (v/v) acetone–water mixture produced the highest degree of delignification whatever the temperature and extraction time. The use of the ethanol–water mixtures increased the delignifi-

cation, which took place between 15 and 30 min, although this decreased at 45 min (Table II). This result agreed with that reported by Heitz,¹⁷ who pointed to the adverse effect of ethanol on delignification when the severity of the treatment was increased, possibly due to lignin condensation. The application of the highest temperature brought about better results for the same time and ethanol-to-water ratio. As in the above case, the use of the 75/25 (v/v) ethanol–water mixture produced the best results whatever the temperature and extraction time applied. These findings imply that during organosolvolytic pulping processes, such as cooking and washing, the optimum acetone–water and ethanol–water concentration for lignin removal is around 75/25 (v/v).

Table II Organosolvolytic Lignin with Ethanol–Water Mixtures

EtOH : H ₂ O		175°C			210°C		
		15 min	30 min	45 min	15 min	30 min	45 min
50 : 50	E ^a	13.2	14.4	14.6	16.1	18.4	19.6
	L ^b	21.1	19.8	20.3	21.2	19.8	18.7
	D ^c	34.6	39.4	38.1	36.4	42.2	46.1
75 : 25	E	15.9	16.8	16.3	19.4	22.8	22.1
	L	18.0	17.2	17.8	14.7	14.5	15.9
	D	46.0	49.0	46.7	57.6	59.9	55.8
100 : 0	E	12.0	20.9	11.5	11.6	12.4	12.9
	L	22.0	21.8	21.1	20.4	20.6	20.1
	D	30.9	38.4	33.1	35.4	35.7	37.3

^a E: Extractibility (g solubilized material/100 g dry initial material, %).

^b L: Klason lignin (%).

^c D: Delignification (g solubilized lignin/100 g initial lignin, %).

The effect of the solvent-to-water ratio on SAM lignin solubility can be explained by the theory of solubility parameters (δ -value); that is, maximum solubility occurs when the δ -value of the solvent is close to that of lignin and when the hydrogen-bonding capacity of the solvent increases as it is in an optimal δ -value. Therefore, to apply these concepts, the δ -value of the lignin dissolved, and those of the different solvent–water mixtures were determined.

The δ -Value of the Lignin Dissolved

The solution of a network polymer like lignin requires fragmentation by chemical reaction or organosolvolytic treatment. Fragments obtained by random cleavage would be expected to be of various sizes and chemically heterogeneous. The lignin fragments solubilized from SAM, whose δ -value was determined, were obtained at 210°C for 45 min using the 75/25 (v/v) acetone–water mixture. These conditions led to the maximum degree of lignin solubilization observed (63.9%) and produced an OSJ with a concentration in organic matter of 7.8 g/L, composed of 87% lignin and 13% hemicelluloses (equivalent to 92.5% of their solubilization). The fact that a low delignification degree (63.9% as maximum) was reached could be explained because of the condensation of lignin during autohydrolysis.¹⁸ Chromatographic analysis of this juice revealed the presence of small quantities of organic acids and phenolic derivatives produced by cleavage of the β —O—4 type β —arylether linkages,¹⁹ indicating the partially degraded nature of the solubilized lignin. The following quantities refer to the compounds identified in the OSJ, expressed in g/100 g of matter in the OSJ: glycolic acid, 0.20; oxalic acid, 0.24; malonic acid, trace; glyoxylic acid, trace; *p*-hydroxybenzoic acid, 0.07; vanillic acid, 0.15; *p*-hydroxybenzaldehyde, 0.15; vanillin, 0.38; syringaldehyde, 0.25; and hydroquinone, 0.14.

One of the methods proposed in the literature for estimating the δ -value of a polymer is based on the atomic and functional group contribution when the structure of the repeating unit of the polymer is known. Data concerning the atomic and functional group contribution to the heat of vaporization and the molar volume are available.²⁰ This method is based on the assumption that

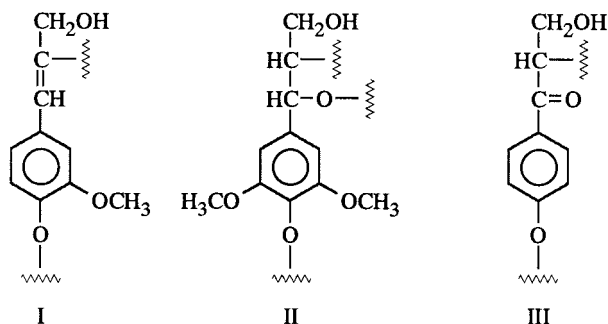


Figure 1 Typical phenylpropane units of lignin.

$$E = \sum \Delta e_i$$

and

$$V = \sum \Delta v_i$$

where the Δe_i and Δv_i are the additive atomic and functional group contribution for the energy of vaporization (E) and molar volume (V), respectively. The δ -value is then calculated by the following equation:²¹

$$\delta = (E/V)^{1/2}$$

To calculate the δ -value of the lignin dissolved, the structural elements and functional groups of this lignin need to be known. Lignin is largely made up of three repeating units, structures I, II, and III (Fig. 1), representing the guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) type phenylpropane units, respectively. A molar ratio for G:S:H of 2:1:5.3 was obtained for our lignin, as indicated below during the ozonation experiments.

The δ -values for structures I, II, and III are then calculated, as shown in Table III. Δv_o is a correction factor for divergence in the V values, which for lignin is 18 cm³/mol.²² The δ -values thus obtained are 13.5, 12.9, and 14.1 (cal/cm³)^{1/2}, respectively. The average solubility parameter for the lignin dissolved from SAM is therefore 13.8 (cal/cm³)^{1/2}, in consideration of its molar ratio.

The δ -Value for the Solvent–Water Mixtures

According to Schuerch,²³ the δ -value for low-molecular-weight liquids can be calculated as

$$\delta = [(\Delta H - RT) \cdot \rho / M_w]^{1/2}$$

Table III Solubility Parameter (δ -Value) of the Lignin Dissolved

Atom or Group	Δe_i (cal/mol)	Δv_i (cm ³ /mol)
Structure I		
OH	7120	10.0
CH ₂	1180	16.1
C=	1030	-5.5
CH	820	-1.0
Phenyl (trisubstituted)	7630	33.4
CH ₃	1125	33.5
2 × O	2 × 800	2 × 3.8
Δv_o		18
Total	20505	112.1
Structure II		
OH	7120	10.0
CH ₂	1180	16.1
2 × CH	2 × 820	2 × (-1.0)
Phenyl (tetrasubstituted)	7630	14.4
2 × CH ₃	2 × 1125	2 × 33.5
4 × O	4 × 800	4 × 3.8
Δv_o		18
Total	23020	138.7
Structure III		
OH	7120	10.0
CH ₂	1180	16.1
CH	820	-1.0
C=	1030	-5.5
Phenylene (<i>p</i>)	7630	52.4
2 × O	2 × 800	2 × 3.8
Δv_o		18
Total	19380	97.6

where ΔH is the vaporization heat in cal/mol, T is the boiling point in K , ρ is the density in g/cm³, and M_w is the molecular weight in g g⁻¹ mol⁻¹.

The required data concerning vaporization heat, boiling point, and density were obtained from Perry et al.²⁴ The results are resumed in Table IV. It shows that the δ -value of the acetone-

water and ethanol-water mixtures increases as their water content increases.

In the case of the ethanol-water mixtures, Coccia et al.²⁵ found that the hydrogen-bonding capacity hardly changes as an increasing amount of ethanol is added to water. As regards the acetone-water mixtures, Schuerch²³ found that when water [hydrogen-bonding capacity, $\delta_H = 19.7$ (cal/cm³)^{1/2}] is mixed with acetone [$\delta_H = 5.3$, δ -value = 9.4 (cal/cm³)^{1/2}], a solvent which has a δ_H lower than that of water and a δ -value of 9 or greater, the solubility of lignin is greater in the mixture than in either solvent alone. The hydrogen-bonding capacity of the acetone-water mixtures is greater than that of one individual solvent.²³

Based on the δ -value theory, the lignin shows maximum solubility when the δ -value of an acetone-water and ethanol-water mixture is close to its own. Therefore, one would expect that the lignin fragments [δ -value = 13.8 (cal/cm³)^{1/2}] generated would show the maximum solubility when the δ -value of an acetone-water and ethanol-water mixture is around 13.8 (cal/cm³)^{1/2}. The maximum solubility of the lignin observed in this study corresponded to acetone-water and ethanol-water mixtures of 75/25 (v/v) whose δ -values were indeed the closest to that of lignin. These conditions mean that both low- and high-molecular-weight lignin fractions dissolve in these solvents because of their good hydrogen-bonding capacity.

Moreover, the further the δ -value of the solvent used is from that of lignin, the less capacity it should have to solubilize lignin. Thus, of the acetone mixtures used, the 75/25 (v/v) mixture (δ -value, 13.56) was better than the 50/50 (v/v) mixture (δ -value, 16.70), while the pure acetone (δ -value, 9.40) which showed the δ -value furthest from lignin produced the worst results. The same occurs with ethanol, the 75/25 (v/v) mixture (δ -value, 14.18), being followed by the 50/50 (v/v)

Table IV Solubility Parameters (δ -Values) of the Different Solvent Mixtures

	EtOH Pure	EtOH-H ₂ O (75/25, v/v)	EtOH-H ₂ O (50/50, v/v)	Ac Pure	Ac-H ₂ O (75/25, v/v)	Ac-H ₂ O (50/50, v/v)
ΔH (cal/mol)	9214	8032	6948	7200	8071	8450
T (°K)	351.0	352.0	354.8	329.25	333.45	337.08
ρ (g/cm ³)	0.7851	0.8634	0.9230	0.7840	0.8681	0.9274
M_w (g g ⁻¹ mol ⁻¹)	46.069	31.500	24.640	58.08	34.977	25.882
δ (cal/cm ³) ^{1/2}	12.05	14.18	15.30	9.40	13.56	16.70

Table V Ozonation of SAM and OSS

	SAM	OSS
Ozone consumption (%)	99.3	66.4
Consumed ozone (mg)	415	276
Solid conversion (%)	11.8	7.3
Delignification (%)	49.0	59.2
PH of aqueous extract	1.85	2.05
Optical density (254 nm) (dilution, 1 : 25)	1.44	0.69
g Solubilized lignin per g consumed ozone	1.88	1.63

(δ -value, 15.30) and finally by the pure ethanol (δ -value, 12.05).

The high association of alcohols frequently results in a lower solvent power than expected; and the assumption that molecules have a uniform force field around them, which is implicit in the use of the δ -value, is clearly not true for molecules with nonpolar and highly polar portions.²³ Therefore, the ethanol–water mixtures dissolve lignin to a lesser degree than expected.

Ozonation of Solid Materials (SAM and OSS)

The principal results obtained with both materials are shown in Table V. Table VI shows the compounds identified in the aqueous extracts of the ozonized SAM and OSS, together with the results of their quantification.

The values of ozone consumption, solid conversion (g solubilized matter/g dry initial material, %), g dissolved lignin/g consumed ozone, and optical density were lower in the case of OSS, while the pH was greater. This means that the reaction in which OSS was involved was less severe, probably because the least resistant lignin was eliminated in the organosolvolytic stage. This least resistant lignin is probably composed of fractions, which are produced during the organosolvolytic treatment, of lower molecular weight than those remaining in the OSS. The higher optical density of the ozonized SAM aqueous extracts suggested a greater concentration of aromatics, as was confirmed by the identification of *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, and vanillin, which were not detected with the OSS. This indicates that a portion of the lignin present in SAM has a low degree of condensation.

The only value that may at first seem surprising was the higher degree of delignification ob-

tained with OSS, which may have been simply due to the fact that a similar quantity of ozone was being applied to a material with a much lower lignin content. The quantities of glycolic and oxalic acids obtained with OSS were practically half those obtained with SAM, while the quantity of glyoxylic acid was very similar.

Ozonation of the Organosolvolytic Juice (OSJ)

In the ozonation process, the lignin solution 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 OSJ, sugars such as D-galactose, D-glucose, and D-mannose were identified by their mass spectra. These sugars, which arise from the cleavage of glycosidic linkages in the polysaccharide molecules²⁶ extracted during organosolvolytic, persisted in the medium for up to 20 min. Moreover, the following compounds were identified in the ozonized juices. Aliphatic acids were as follows: glycolic, oxalic, and malic. Monomeric oxyaromatics were as follows: *p*-hydroxybenzoic, vanillic and syringic acids, *p*-hydroxybenzaldehyde, vanillin, syringaldehyde, and hydroquinone.

During the first minutes of the reaction, short chain aliphatic carboxylic acids (glycolic and oxalic acids) were generated, the amounts of which

Table VI Yield of the Products Identified in the Aqueous Extracts of the Ozonized SAM and OSS (g/100 g dry initial material)

	SAM	OSS
Glycolic acid	0.12	0.06
Oxalic acid	1.17	0.55
Malonic acid	Trace	NP ^a
Glyoxylic acid	0.09	0.08
Butanedioic acid	Trace	NP
Malic acid	0.02	NP
<i>p</i> -Hydroxybenzoic acid	0.03	NP
<i>p</i> -Hydroxybenzaldehyde	0.07	NP
Vanillin	0.02	NP

^a NP: Not produced.

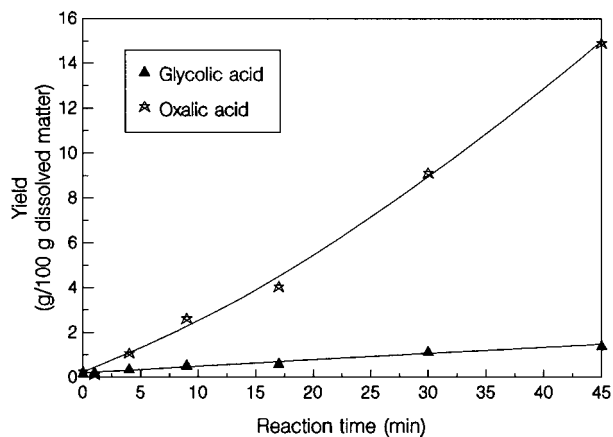


Figure 2 Quantification of the principal aliphatic acids identified.

increased as the reaction progressed (Fig. 2). Oxalic acid was the major reaction product. The glycolic acid could arise from the oxidation of glycoaldehyde, which results from the ozone attacking 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 β -aryl ether type structures. Oxalic acid is produced by extensive oxidation of aromatic rings in lignin.²⁷

All the identified oxyaromatic compounds passed through a production maximum during the reaction (Fig. 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

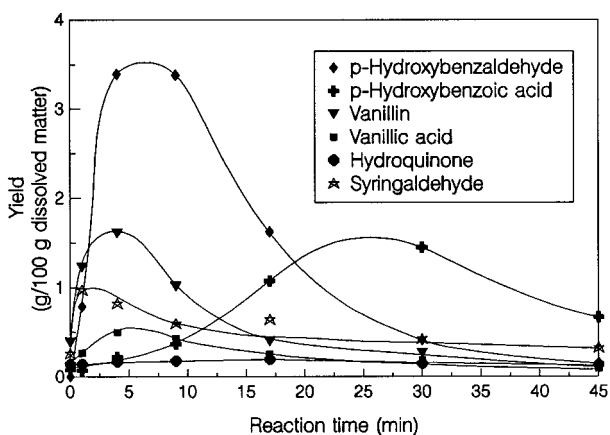


Figure 3 Quantification of the principal oxyaromatic compounds identified.

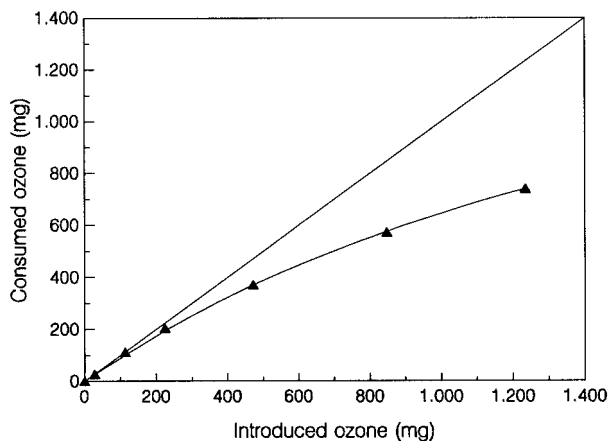


Figure 4 Ozone consumption during treatment of organosolvolytic juice.

OSJ), vanillin (1.67 g/100 g dissolved matter), and syringaldehyde (1.01 g/100 g dissolved matter). This indicates that corn stalk lignin 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.²⁸

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.²⁹

As a general conclusion, ozonation of the OSJ (lignin extracted in organic solvent from SAM) produces a greater variety and quantity of oxyaromatic compounds than the ozonation of the *in situ* lignin present in the moistened SAM.

The trend of ozone consumption is shown in Figure 4, from which it can be seen that the ozone consumed-to-ozone introduced ratio falls as the reaction progresses, indicating that the initial reaction products are less reactive than lignin.

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 205,³⁰ this optimal consumption has been found to be between 0.18 and 1.28 mol of ozone-to-mol of phenylpropane units, indicating that only the alkene C=C bonds are cleaved.³¹ The value of 1

mol/phenylpropane unit obtained by Vidal and Molinier³² 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 (vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde) 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 of guaiacyl:syringyl:*p*-hydroxyphenyl cinnamic phenylpropane units in corn stalk organosolvolytic lignin was 2:1:5.3. This ratio was similar to that obtained by Tanahashi et al.²⁹ by ozonation of an acidolysis residue of bamboo milled wood lignin (3:1:9). Likewise, Morrison and Akin³³ 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.

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,³⁴ 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.³⁵

Thus, the reaction scheme for the ozonation of lignin in organic solutions implies (1) depolymerization of the lignin macromolecule accompanied by the liberation of low-molecular-weight oxyaromatic compounds, and (2) 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,³⁶ it is possible that condensation³⁷ or polymerization reactions might develop in the medium, which would lead to the formation of high-molecular-weight organic compounds, which 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 OSJ.

The present article is abstracted from the Ph.D. thesis of J. Quesada. The authors thank Mr. E. Chornet of the University of Sherbrooke for permission to use their steam explosion device. This work was supported by a research grant of the Ministry of Education and Science (MEC) of Spain. The authors also gratefully acknowledge the financial support of Electricité de France (EDF).

REFERENCES

1. F. Carrasco, J. J. Garceau, J. F. Colom, and B. V. Kokta, *Ing. Quím.*, April, 103 (1992).
2. L. Flandroy, *Biofutur*, Sept., 49 (1992).
3. R. A. D. Mbachu and R. St. J. Manley, *J. Polym. Sci.*, **19**, 2079 (1981).
4. R. W. Tock, C. R. Richardson, I. Gancarz, J. Chang, and M. R. Owsley, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 101 (1982).
5. D. Ben-Ghedalia and G. Shefet, *Nutr. Rep. Int.*, **20**, 179 (1979).
6. D. Ben-Ghedalia and J. Miron, *Biotechnol. Bioeng.*, **23**, 823 (1981).
7. J. P. Joseleau and E. Martini, *Cell. Chem. Technol.*, **15**, 473 (1981).
8. B. Ferron, *Ph.D. thesis, University of Poitiers, France*, 1994.
9. T. Lasry, J. L. Laurent, V. Euphrosine-Moy, R. S. Bes, J. Molinier, and J. Mathieu, *Analisis*, **18**, 192 (1990).
10. F. Bouguettaya-Matejek, *Dissertation, University of Sherbrooke, Canada*, 1991.
11. J. Carrión, M. Rubio, D. Gómez, A. Miñana, and A. Soler, in *Biomass for Energy and Industry, 5th E.C. Conference*, G. Grassi, G. Gosse, and G. dos Santos, Eds., Elsevier Applied Science, New York, 1990, p. 2.45.
12. A. A. S. Curvelo, *Proceedings of the 2nd Brazilian Symposium on the Chemistry of Lignins and Others Wood Components*, N. Duran and E. Esposito, Eds., FAPESP, Sao Paulo, Brazil, Vol. III, 1992, p. 44.
13. J. Quesada, *Ph.D. thesis, University of Murcia, Spain*, 1996.
14. R. W. Thring, *Ph.D. thesis, University of Sherbrooke, Canada*, 1990.
15. J. M. Pepper and M. Siddiqueullah, *Can. J. Chem.*, **39**, 1454 (1961).
16. J. F. Tortosa, *Ph.D. thesis, University of Murcia, Spain*, 1992.
17. M. Heitz, *Ph.D. thesis, University of Nancy I, France*, 1993.
18. N. Hayashi, K. Shimizu, and S. Hosoya, *Mokuzai Gakkaishi*, **35**, 521 (1989).

19. D. Barnet, G. Excoffier, and M. Vignon, *Bull. Soc. Chim. Fr.*, **6**, 836 (1989).
20. A. F. M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1985.
21. J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Rheinhold, New York, 1950.
22. Y. Ni and Q. Hu, *J. Appl. Polym. Sci.*, **57**, 1441 (1995).
23. C. Schuerch, *J. Am. Chem. Soc.*, **74**, 5061 (1952).
24. R. H. Perry, D. W. Green, and J. O. Maloney, *Manual del Ingeniero Químico*, 6th ed., McGraw-Hill, New York, 1993.
25. A. Coccia, P. L. Indovina, F. Pado, and V. Viti, *Chem. Phys.*, **7**, 30 (1975).
26. A. A. Katai and C. Schuerch, *J. Polym. Sci., Part A-1*, **4**, 2683 (1966).
27. Y. Matsumoto, A. Ishizu, and J. Nakano, *Holzforsch.*, **40**, 81 (1986).
28. T. Eriksson and J. Gierer, *J. Wood Chem. Technol.*, **5**(1), 53 (1985).
29. M. Tanahashi, F. Nakatsubo, and T. Higuchi, *I. Wood Res.*, **58**, 1 (1975).
30. P. F. Vidal, *Ph.D. thesis, INPT*, Toulouse, France, 1985.
31. K. V. Sarkanen, A. Islam, and C. D. Anderson, in *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence, Eds., Springer-Verlag, Heidelberg, 1992, Chap. 6.
32. P. F. Vidal and J. Molinier, *Biomass*, **16**, 1 (1988).
33. W. H. Morrison and D. E. Akin, *J. Agric. Food Chem.*, **38**, 678 (1990).
34. A. Ouederni, *Ph.D. thesis, INPT*, Toulouse, France, 1984.
35. P. Vidal, J. Molinier, L. Torres, and J. Mathieu, *J. Chim. Phys.*, **82**, 963 (1985).
36. S. Katuscák, A. Hrivik, G. Katuscáková, and O. Schiessl, *Papp. och Trä*, **12**, 861 (1972).
37. P. J. Balousek, T. J. McDonough, R. D. McKelvey, and D. C. Johnson, *Svensk Papperstidn.*, **9**, R49 (1981).