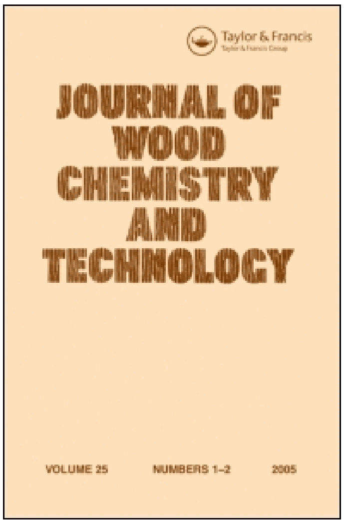

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OZONATION OF LIGNIN RICH SOLID FRACTIONS FROM CORN STALKS

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ABSTRACT

Various kinds of solid materials containing lignin were obtained by fractionation (autohydrolysis and organosolvolysis) of corn (*Zea mays*) stalks. These materials were further ozonated in order to observe the behaviour of their constituent polymers, particular attention being paid to lignin, and the evolution of the water soluble reaction products during oxidation. An optimal moisture content for these materials of 60% was found, which led to the highest degree of solubilization during ozone treatment. Results indicate that lignin is the most severely affected polymer, followed by hemicelluloses and finally by cellulose. The ozonation of autohydrolyzed material involved its gradual delignification, the elimination of lignin being more easy at the beginning of the reaction than at the end. The following acids were identified by GC/MS and injection of standards in GC/FID: glycolic, oxalic, malonic, glyoxylic, glyceric, *p*–hydroxybenzoic and malic. In addition, *p*–hydroxybenzaldehyde and vanillin were also identified. During the ozonation of lignin–containing lignocellulosic materials in moistened solid state, ozone rapidly oxidized the initially generated oxyaromatics and transformed them into short chain aliphatic carboxylic acids.

INTRODUCTION

Agroindustrial wastes are an important source of lignocellulosic materials. These materials are especially valuable if their three principal constituents (lignin, cellulose and hemicelluloses) can be separated by elimination or modification of the lignin structure.

Ozone treatment is one way of reducing the lignin content of lignocellulosic wastes. This results in an increase of the *in vitro* digestibility of the treated material,[1-6] and, unlike other chemical treatments, does not produce toxic residues, all the reaction products being easily metabolized by animals.[7] Furthermore, the fact that ozone can be easily decomposed by using a catalytic bed or increasing the temperature means that processes can be designed in order to minimize environmental pollution. Also, ozonation reactions take place at ambient temperature and pressure so that energy and investment costs are kept down.

Most ozonation experiments have been conducted in hydrated fixed bed reactors,[8,9] which, according to Vidal and Molinier,[10] lead to more effective oxidations than aqueous suspension or suspensions in 45% acetic acid.

One way of isolating the different lignocellulosic polymers so that they remain as undegraded as possible is to separate them sequentially in successive stages (fractionation) without adding chemical reagents. The first to be eliminated are the hemicelluloses by solubilization in aqueous medium (aqueous or steam explosion autohydrolysis), due to the combined effects of temperature and decompressive forces.[11] During the autohydrolysis, part of the lignin (about 20%) is solubilized and the part which remains in the solid shows a certain degree of condensation.[12] In the second stage the lignin is dissolved from the autohydrolyzed material in organic solvent (organosolvolysis) to leave a solid composed almost totally of cellulose.[13]

Lasry *et al.*[14] and Euphrosine-Moy *et al.*[15] ozonized hydrated poplar sawdust (45% moisture) and identified oxalic and formic acids as the major products in the aqueous extract of the treated material, along with glycolic, glyoxylic, succinic, glyceric, malonic, *p*-hydroxybenzoic, fumaric and propanoic acids. Morrison and Akin,[16] on the other hand, used ozone to oxidize herbaceous species moistened to 50% and identified caproic, levulinic, *p*-hydroxybenzoic, vanillic, azelaic and malonic acids, and aldehydes such as *p*-hydroxybenzaldehyde and vanillin and hydroquinone in the aqueous extract; oxalic acid was not detected.

The present paper describes the behaviour of different solid materials containing lignin, which were obtained during the different stages of corn stalk fractionation, towards ozone. The first step was to determine the optimum moisture content of the material to be treated, which could then be used in the treatment of all the materials. In the second step, the evolution of the polymers making up these materials was studied during oxidation by ozone, particular attention being paid to the lignin fraction. Finally, the content of the aqueous extract of the oxidized materials was analyzed using GC/MS and GC/FID to identify and quantify (internal standard method) the reaction products.

EXPERIMENTAL

Materials

Corn (*Zea mays*) stalks, which are widely grown in Murcia (Spain), were used as starting material. Indulin AT lignin, CF–11 cellulose and a chlorite holocellulose from corn stalks were also used. Raw corn stalks were submitted to the fractionation steps shown in Figure 1, the following materials being obtained:

Conditioned material (CM): Raw dried and ground corn stalks were sieved to a particle size of 0.2–0.5 mm and extracted in soxhlet with an 7/3 (v/v) ethanol/toluene mixture and then with water. Lastly, the material was air dried.

Autohydrolyzed materials (AAM and SAM): Two different autohydrolysis techniques were applied to obtain a hemicellulose free material: aqueous and steam explosion. The aqueous explosion autohydrolyzed material (AAM) was obtained by treating an CM aqueous suspension (25 g CM in 475 g water) in a cascade reactor system at 225°C for 5 min.[17] The steam explosion autohydrolyzed material (SAM) was obtained by treating CM with saturated steam at 220°C for 3 min in the pilot unit of the Chemical Engineering Department at Sherbrooke University

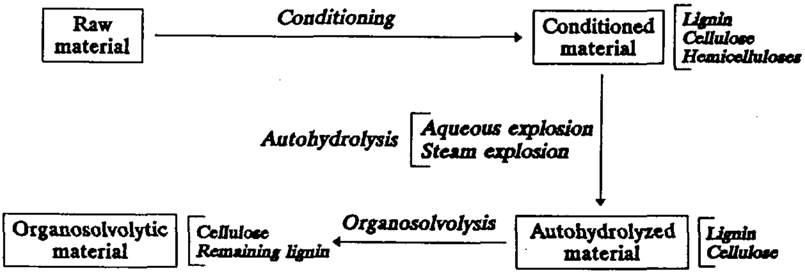

FIGURE 1. Outline of raw corn stalk fractionation.

(Québec, Canada).[18] Both AAM and SAM were extracted with boiling water and then dried at room temperature.

Organosolvolytic material (OSM): In order to prepare a material with a low lignin content, SAM was extracted at 210°C for 45 min[19] with a 75/25 (v/v) acetone/water mixture (8 g of material in 150 mL of mixture) in a stirred batch reactor. Before the reaction started, the reactor was pressurized with nitrogen up to 2.5 MPa. The suspension was prepared one hour before the process was begun. After reaction, the solid and liquid phases were separated by filtration and the solid was washed with the solvent mixture before being dried at 45°C.

Table 1 shows the composition of the following materials: CM, AAM, SAM and OSM.

Indulin AT lignin: This is a highly purified lignin (99% lignin) distributed by Aldrich–Sigma which comes from the alkaline black liquors generated in the kraft pulping process from southern pine softwood. It is a dark brown powder with a range of molecular weights between 3000 and 100000 (maximum at 7000).

Cellulose CF–11: This cellulose, supplied by Whatman, is a white powder with a fibrous structure.

Holocellulose: Obtained from CM by solubilization of the lignin fraction with sodium chlorite in the form of water soluble chlorolignins.[20] The holocellulose thus obtained is then air dried to avoid reactivity losses. It exhibits a yellowish–white fibrous structure.

TABLE 1
Characterization of the Solid Fractions

	CM	AAM	SAM	OSM
Cellulose (%)	38.7	65.0	–	–
Pentosans (%)	28.4	3.7	4.0	0.5
Klason lignin (%)	17.6	25.8	28.1	12.9
Ash (%)	7.1	4.0	5.1	3.8

Ozonation Equipment

A schematic diagram of the experimental device appears in Figure 2. The ozone is generated by passing pure oxygen at 0.123 MPa through an air-cooled cold plasma reactor (Anseros, GMF-4). The process gas containing ozone was bubbled to saturation through water in a glass gas washing flask.

The ozonation reaction was carried out in a standard semicontinuous fixed bed reactor of 350 mL capacity fitted with a sintered glass plate at the bottom, through which the ozone entered into contact with the material. A probe measured the temperature of the reacting material.

The ozone was continuously measured by a UV spectrophotometer (Anseros, Ozomat GM-19) which can analyze flow rates between 20 and 40 L/h in a range of 0 to 200 g/m^3. The analyzer was calibrated according to the 001/87 (F) norm of the International Ozone Association Standardisation Committee-Europe. Residual ozone was catalytically destroyed before release into the atmosphere. All the gas flows were automatically controlled by means of MF controller type Ucar regulators.

Ozonation Experimental Conditions

Optimal moisture content determination: Euphrosine-Moy *et al.*[15] and Vidal and Molinier[10] found that, of all the parameters investigated, the water content of the sample to be ozonized was the one which had the greatest influence on poplar

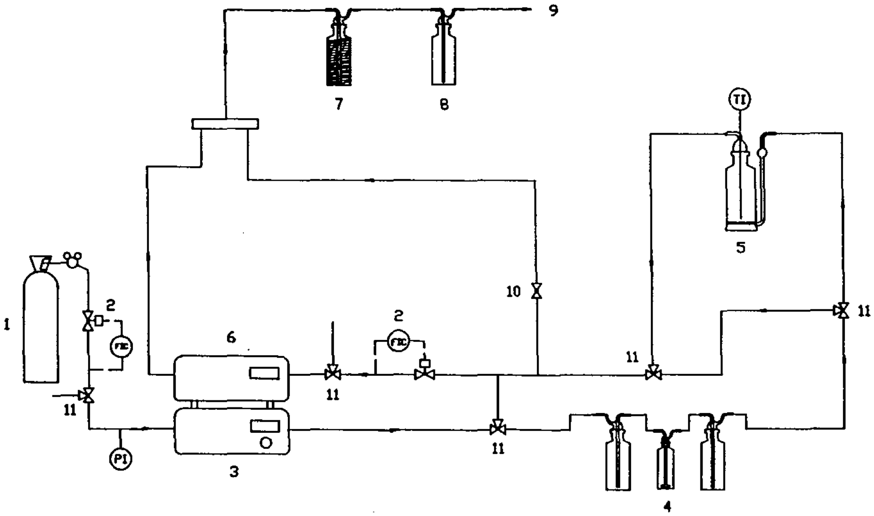

FIGURE 2. Experimental ozonation set up. (1) Oxygen cylinder. (2) Automatic gas flow control valve. (3) Ozone generator. (4) Process gas humidifier. (5) Reactor. (6) Ozone UV spectrophotometer. (7) Ozone catalytic destroyer. (8) Iodide trap to test catalyst efficiency. (9) Vent. (10) Pressure regulation valve. (11) Three way valve.

lignin and sawdust oxidation, respectively. Therefore, 10 g of CM were moistened by adding a known quantity of water, homogenized, and kept covered and shaded from light overnight. Moisture was calculated as the ratio between the water weight and the total weight (expressed as a percentage). The moistened material was slightly compressed in the reactor to obtain in all cases a bed height of about 3.5 cm and treated for 1 and 2 h at a flow rate of 10 L/h with an ozone concentration of 30 g/m^3. The ozonated material was then extracted in a fritted-glass crucible with different portions of distilled water, by stirring every time for 3–4 min, until 1 L aqueous extract was obtained.

CM: Oxidation consisted of submitting 10 g of CM, which had been moistened to its optimal value, to a flow rate of 35 L/h and an ozone concentration of 45 g/m^3 for 40 and 90 min. The bed height was also maintained at 3.5 cm.

AAM: A series of experiments was conducted to ascertain the influence of the flow rate and ozonation time on the composition of the solid residues and aqueous extracts of the treated material. Flow rates of 35, 55 and 65 L/h were used for 5, 10, 15 and 20 min. In all cases the ozone concentration was 40 g/m^3. In all the assays 6 g of AAM, which had been moistened to the optimal value, were used and a bed height of 1.4 cm was kept.

SAM and OSM: 6 g of material, brought to its optimal degree of moisture, were exposed for 20 min to the oxygen/ozone gas mixture at a flow rate of 35 L/h with an ozone concentration of 40 g/m^3.

Indulin AT lignin, CF-11 cellulose and holocellulose: 3.6 g of each material, brought to the optimal moisture level, were exposed for 25 min to a flow rate of 35 L/h with an ozone concentration of 47 g/m^3.

In all cases, the ozonated materials were extracted at room temperature by stirring in 150 mL of water for 30 min, bringing the aqueous extracts up to 150 mL. These aqueous extracts were passed through 0.45 µm filters before analysis. All the solids obtained after extraction were dried in an oven at 45°C and weighed.

Analytical Methods

Klason lignin, pentosans and cellulose contents were determined according to ASTM D1106-56, ASTM D1787 and ASTM D1103-60 norms, respectively.

The optical density of the aqueous extracts was measured at 254 nm in an UV-160A/UV-VIS Shimadzu Recording Spectrophotometer. This measurement reflects the overall concentration of aromatic compounds in the medium.

The Total Organic Carbon (TOC) content of the aqueous extracts was measured with an Ionics 1270M TOD/TOC/TC analyzer by infrared detection of the carbon dioxide produced by catalytic combustion of the organic matter at 900°C.

Silylation prior to GC was carried out on 10 mL of lyophilized aqueous extract by adding 200 µL of a pyridine solution containing 5 mg/mL of palmitic acid (internal standard), 1 mL of N,O–bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 50 μL of trimethylchlorosilane (TMCS). The mixture was stirred continuously for 30 min at 60°C and a 1.5 μL sample was analyzed by GC. Helium (1 mL/min) was used as carrier gas. 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 275°C. The equipment was a Hewlett Packard 5890 Series II coupled to a HP 5972 quadrupole mass spectrometer of 70 e.v. equipped with a HP–5 capillary column (30 m x 0.25 mm i.d., 0.25 μm film); 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 x 0.33 mm o.d., 0.25 μm film); split ratio of 25/1. 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 ± 3.1%.

RESULTS AND DISCUSSION

Determination of Optimum Water Content

In all cases, ozonation brought about a gradual blanching of the solid bed from the bottom upwards. Figure 3 shows the TOC values of the aqueous extracts obtained for different degrees of moisture. The curves obtained for both 1 and 2 h of treatment showed maxima at between 50 and 70% water content. The quantity of organic carbon dissolved in the medium increased with longer reaction times, while the material solubilization rate decreased. This rate reached a maximum at the optimal moisture level.

The above behaviour might be explained by the stationary film theory, according to which ozone first diffuses through the aqueous film surrounding the particles of the solid before reacting with them. After this reaction, the

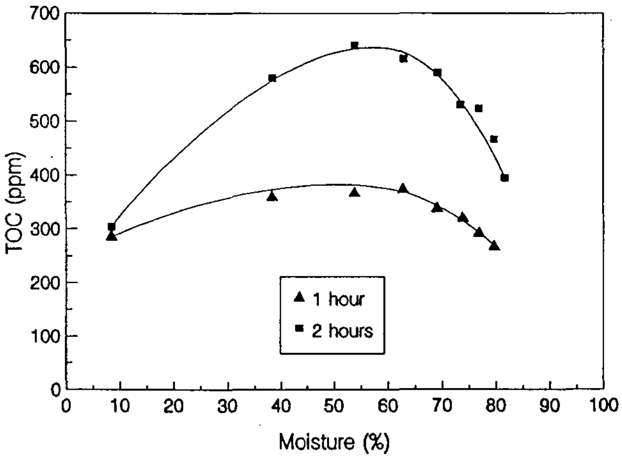

FIGURE 3. Optimal moisture content.

hydrosoluble products pass to the aqueous layer, where they can react with the ozone (secondary reactions). If the thickness of the aqueous layer is greater than that corresponding to the optimal moisture level (moisture higher than the optimal), the ozone will take longer to diffuse towards the particle and react with all the solubilized products, the material solubilization rate thus decreasing. If, on the other hand, the thickness is less (moisture lower than the optimal) the ozone will hardly react with the material because its physical structure will remain slightly swollen and hinder ozone penetration. The above explains why an optimal moisture content exists, at which secondary oxidation reactions are minimized and which favours the penetration of ozone into the material.

Ozonation is accompanied by acidification of the aqueous extract. The pH decreases slightly with increased moisture, reaching a minimum at about 70%. In addition, longer reaction times result in lower pH values; therefore, for a moisture content of 70%, pH is 3.1 after 1 h and 2.6 after 2 h. This pH diminution may be explained by the appearance of increasingly oxidized species, the final reaction products basically being aliphatic carboxylic acids.[2,21]

Based on the above, the optimal moisture content was fixed at 60%, which coincides with that obtained by Ferron[22] who also used conditioned corn stalk.

Ozonation of CM

Table 2 shows the changes undergone by the lignocellulosic matrix of CM. Lignin, hemicelluloses and cellulose contents decrease as treatment progresses, lignin being the most severely affected polymer, followed by hemicelluloses and finally by cellulose. However, the obtained cellulose values are perhaps not totally reliable since the cellulose content rises slightly at 40 min and then falls sharply at 90 min. The unreliability of determining cellulose in ozone treated materials according to the ASTM D1103–60 norm has been mentioned by several authors.[22]

The higher the amount of the applied ozone, the higher the quantity of material solubilized in the aqueous extract. During the first minutes of reaction all the introduced ozone is consumed and trace amounts only begin to appear at the reactor outlet after 20 min. At 40 min the ozone consumption was 97.1%, representing 0.101 g consumed ozone/g dry initial material and 1.07 g solubilized lignin/g consumed ozone.

To ascertain whether the quantity of ozone consumed per unit of treated material can be used as independent variable to follow the ozonation process, 3.25 g of dry CM brought to 60% moisture content were exposed for 25 min to the oxygen/ozone gas mixture at a flow rate of 35 L/h with an ozone concentration of 50 g/m^3.

In these conditions 0.106 g consumed ozone/g dry initial material were obtained, very close to those obtained at 40 min. Solid solubilization was found to be 20.4% with a delignification of 60.2%. In addition, 0.9 g solubilized lignin/g consumed ozone and an aqueous extract pH of 1.85 were also obtained. All these values were very similar to those obtained after ozonation lasting 40 min. Furthermore, as shown in Table 3, during the ozonation of AAM, when similar quantities of ozone were consumed (always the same quantity of material was treated), the values of g solubilized lignin/g consumed ozone were also similar

TABLE 2
Time Course Changes of the Principal CM Polymers During Ozonation

	Ozonation time (min)		
	0	40	90
Klason lignin (g)	1.61	0.65	0.40
Holocellulose (g)	7.76	6.26	4.94
Cellulose (g)	3.54	3.62	2.81
Delignification (%)	0	59.6	75.1
Hemicelluloses elimination* (%)	0	37.4	49.5
Cellulose elimination (%)	0	0	20.6
Solid solubilization (%)	0	19.2	31.2
Concentration of soluble matter in the aqueous extract (g/l)	0	8.4	11.6

*: *Hemicelluloses* are taken to be *holocellulose – cellulose*

independently of the flow rate and reaction time. For this reason, the quantity of ozone consumed per unit of treated material seems to be a valid parameter to follow the attack of ozone on the lignocellulosic matrix and may be used as an independent variable.

The pH of the aqueous extract of the oxidized material falls sharply during the first minutes of the reaction. This diminution was practically annuled between 40 and 90 min, at which values of 2.1 and 1.8 were reached, respectively. Chromatographic analysis of the aqueous extracts pointed to the existence of glycolic, oxalic, malonic, glyoxylic, glyceric and malic acids. In addition, an 1,4–lactonized derivative of the 2,3,4,5–tetrahydroxypenthanoic acid was identified by its mass spectra (perhaps D–xylonic acid or D–arabinonic acid). This acid presumably arises from hemicelluloses degradation. No oxyaromatic compounds were detected. The generated carboxylic acids which provoke the pH diminution arise principally from extensive lignin degradation.

Ozonation of AAM

Since this material is practically devoid of hemicelluloses and basically contains lignin and cellulose, presenting a more open and accessible structure than

CM,[23] and since the lignin fraction is the most reactive to ozone, AAM was oxidized in order to produce oxyaromatic compounds during lignin degradation. Temperatures of 50–60°C were usually reached after 6 min of treatment, although they later fall slightly.

Figure 4 shows that, for the same quantity of introduced ozone, the consumption of ozone falls as the flow rate increases. At the same time, for the same reaction time, the quantity of consumed ozone is increased if the flow rate increases. Therefore, the higher the flow rate, the more ozone is introduced into the reactor during the same reaction time, and despite the fact that a higher quantity of ozone escapes without reacting at higher flow rates (for the same overall quantity of ozone introduced), ozone consumption increases although not proportionally with the flow rate.

After oxidation, the amount of material solubilized during extraction increases continuously (Figure 5) and, moreover, the amount solubilized per unit of consumed ozone remains practically constant throughout and even falls slightly. Ozonation is accompanied by a gradual diminution of the lignin content of the material (Figure 6). Lignin is degraded more easily at the beginning of the reaction and it becomes increasingly difficult to eliminate residual lignin remaining in the solid. This may be because part of the lignin has a chemical structure condensed by formation of new carbon–carbon bonds as a result of the autohydrolytic process suffered,[12,24] making it more resistant to ozone attack. In addition, this lignin has undergone substantial cleavage of the major (β–O–4) interunit linkage.[25]

The most important results relating to lignin degradation during ozonation are resumed in Table 3, where it can be seen that, for the same flow rate, the quantity of lignin solubilized per unit of consumed ozone decreases as time elapses. This means that the ozone not only oxidizes lignin but also the initial degradation products of the lignin. Moreover, when the flow rate is increased the quantity of lignin solubilized per unit of consumed ozone falls for the same reaction time, probably for the same reason (secondary reactions).

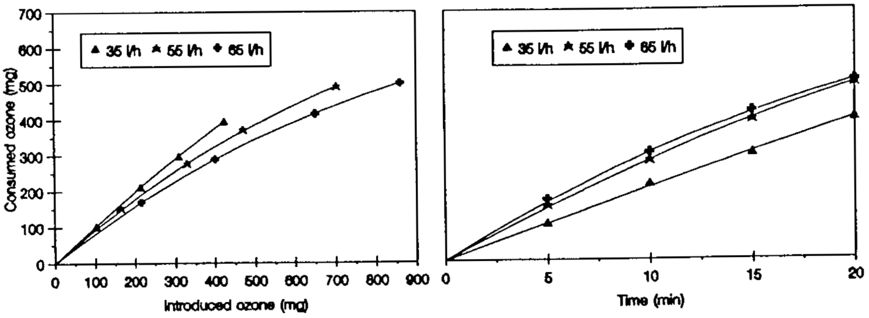

FIGURE 4. Ozone involved in the process during AAM treatment.

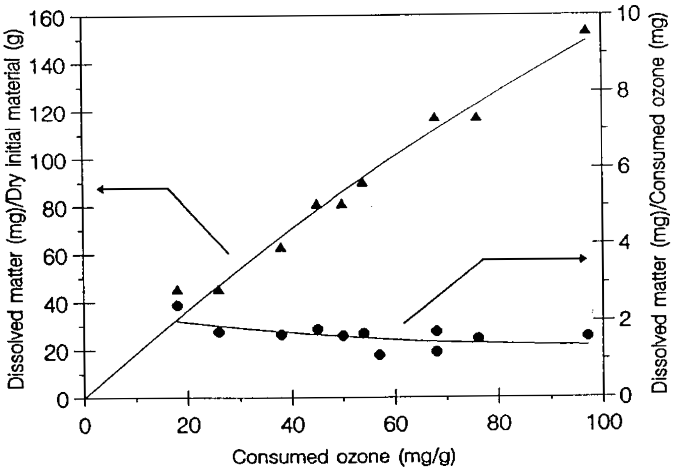

FIGURE 5. Quantity of material solubilized during AAM oxidation.

As in the case of CM oxidation, organic acids are generated during ozonation due to severe lignin oxidation. These acids would be responsible for the rapid fall in pH of the aqueous extracts during the first minutes of treatment (Figure 7). Above a level of 18 mg consumed ozone/g dry initial material, pH remains practically constant and even falls slightly.

As Figure 8 shows, during treatment aromatic compounds are generated from lignin oxidation. These compounds pass to the aqueous phase during

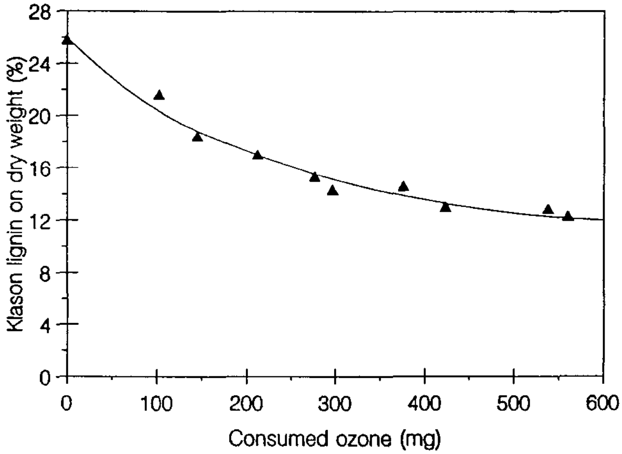

FIGURE 6. Variation of the lignin content during AAM oxidation.

TABLE 3

Influence of Oxygen/Ozone Flow Rate and Reaction Time on the Lignin Degraded during Ozonation of AAM

Flow rate (L/h)	Time (min)	Consumed ozone (mg)	Klason lignin on dry weight (%)	Delignification (%)	g solubilized lignin/ g consumed ozone
No treatment			25.8	–	–
35	5	103	21.6	19.9	2.77
35	10	212	17.0	37.2	2.51
35	15	297	14.4	49.3	2.38
35	20	423	13.1	55.3	1.87
55	10	277	15.4	45.2	2.34
55	15	371	13.9	52.6	1.83
55	20	538	12.9	57.7	1.54
65	5	145	18.4	32.5	3.14
65	10	289	16.1	43.1	2.14
65	20	560	12.7	58.0	1.48

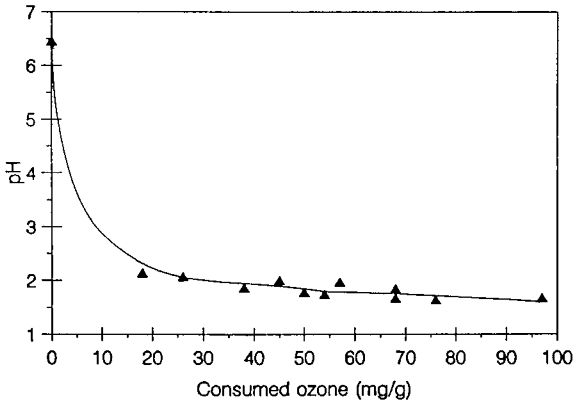

FIGURE 7. pH of the AAM aqueous extracts during ozonation.

extraction, thus increasing their overall concentration in the medium. Furthermore, the optical density (OD) values per gram of solubilized material show that as the reaction proceeds the amount of aromatics per unit of solubilized material gradually decreases, demonstrating, on the one hand, the tendency of ozone to react with the initial oxyaromatic products and, on the other, the resistance of lignin to ozone attack.

Chromatographic analysis pointed to the existence of the same reaction products as in the case of CM, together with *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid. In addition, a monosaccharide was detected which, according to its mass spectrum, is D-xylose or D-mannose; this sugar probably arises from the cleavage of glycosidic linkages in the residual hemicellulosic fraction[26] in AAM.

The principal reaction products were chromatographically quantified (GC/FID) using palmitic acid as internal standard. Figure 9 shows the trend of the compound yields as a function of the ozone consumed. The most abundant water soluble ozonation products detected were glycolic and oxalic acids, which increase in quantity as the process progresses. Oxalic acid is produced by extensive

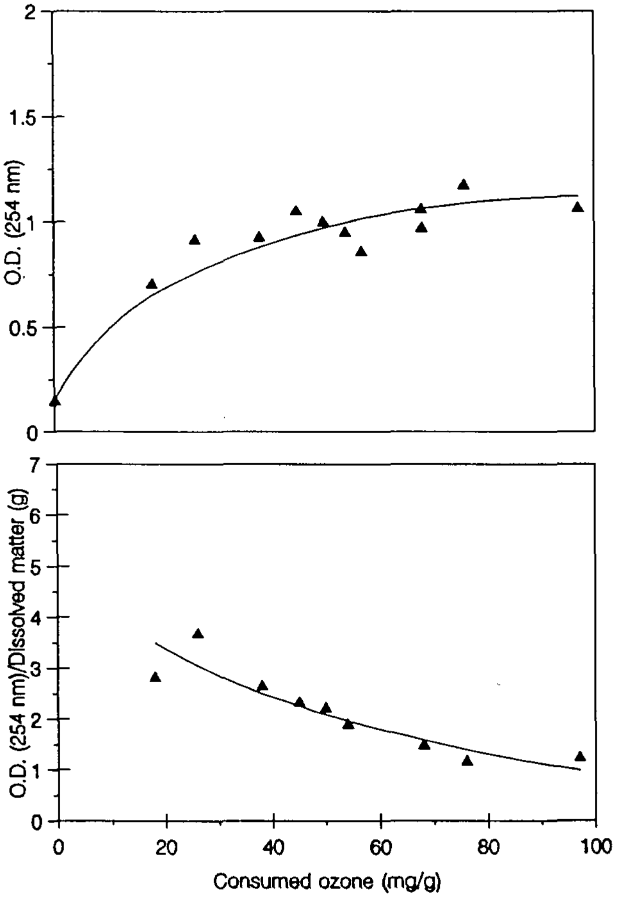

FIGURE 8. Optical density of the AAM aqueous extracts during ozonation.

oxidation of aromatic rings in lignin.[27] The other products also increase at the beginning of the treatment but after the consumption of 150 mg of ozone, their yields remain practically constants or even decrease slightly.

Ozonation of SAM and OSM

Table 4 shows the principal results obtained with both materials alongside those obtained for AAM for comparison purposes. The reaction products identified

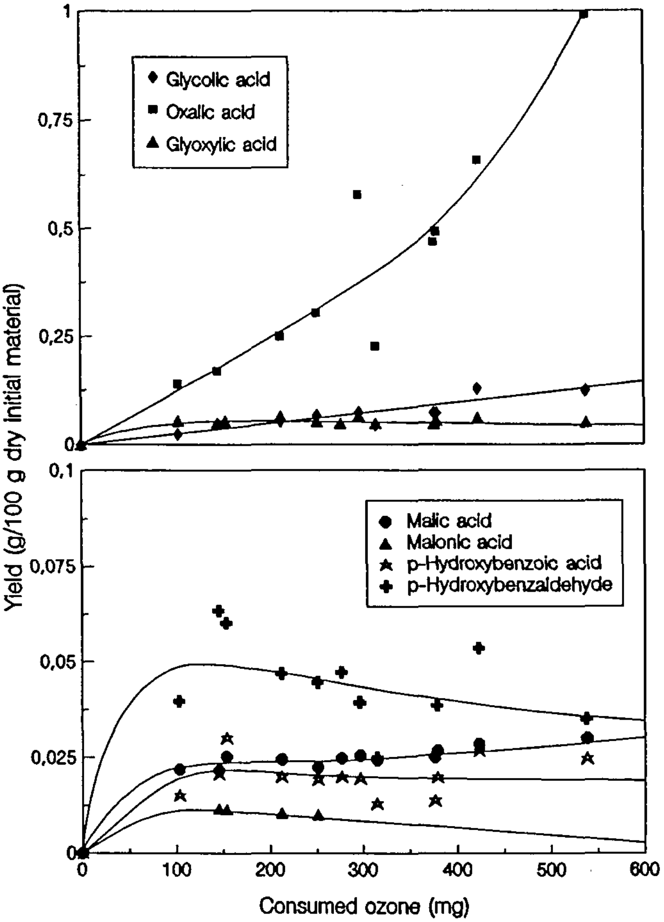

FIGURE 9. Quantification of the water soluble reaction products during AAM ozonation.

TABLE 4
Ozonation of SAM, OSM and AAM

	SAM	OSM	AAM
Ozone consumption (%)	99.3	66.4	99.8
Consumed ozone (mg)	415	276	423
Solid solubilization (%)	11.8	7.3	11.7
Delignification (%)	49.0	59.2	55.3
pH of the aqueous extract	1.85	2.05	1.76
Optical density (254 nm) (dilution, 1:25)	1.44	0.69	1.18
g solubilized lignin/g consumed ozone	1.88	1.63	1.87

TABLE 5
Yield of Products Identified in the Aqueous Extracts of Ozonized SAM, OSM and AAM (g/100 g dry initial material)

	SAM	OSM	AAM
Glycolic acid	0.127	0.062	0.133
Oxalic acid	1.173	0.551	0.667
Malonic acid	trace	ND	trace
Glyoxylic acid	0.092	0.086	0.065
Butanedioic acid	trace	ND	trace
Malic acid	0.025	ND	0.031
p–Hydroxybenzoic acid	0.033	ND	0.022
p–Hydroxybenzaldehyde	0.076	ND	0.053
Vanillin	0.023	ND	ND

ND: Not detected

in the aqueous extracts of the oxidized materials are shown in Table 5, in which their yields are indicated. The lowest values for ozone consumption, solid solubilization, g solubilized lignin/g consumed ozone and optical density were obtained for OSM. The autohydrolyzed materials produced similar results. The highest OD value obtained for SAM reflects the greatest concentration of aromatic compounds in its aqueous extract, as confirmed by the identification of greater quantities of *p*–hydroxybenzoic acid, *p*–hydroxybenzaldehyde and vanillin than for AAM where, indeed, vanillin was not detected. These aromatic compounds were not detected in the case of OSM, in accordance with its lower OD. The pH of the ozonated OSM aqueous extract was the highest, illustrating that the reaction it had suffered was less severe. The only value which at first might seem surprising is that of delignification, which was higher for OSM probably because a similar quantity of ozone was applied to a material with a lower lignin content. The yields of glycolic and oxalic acids obtained with OSM were practically half those obtained with SAM, the glyoxylic acid yield being similar in both cases. The amount of oxalic acid (the major product) generated with SAM was greater than that obtained with AAM.

All these results indicate that OSM is much less reactive than the autohydrolyzed materials, basically because the least resistant lignin has already been eliminated during the organosolvolysis step. Furthermore, the results obtained with the autohydrolyzed materials show overall differences of little statistical significance, so that their behaviour during ozone attack is similar. However, as regards the reaction products, SAM seems to generate a larger quantity of water soluble aromatic compounds, probably because the lignin it contains is less condensed by the autohydrolytic treatment it has undergone.

Ozonation of Indulin AT Lignin, CF-11 Cellulose and Holocellulose

The results depicted in Tables 6 and 7 show that cellulose is the least degraded polymer since it hardly consumes ozone and it is not solubilized at all. Very few reaction products are detected, and those which are detected are in very small quantities.

Holocellulose undergoes the greatest degree of solubilization, the production of oxalic and glycolic acids being less than that observed with Indulin AT. In addition, an extensive series of products were detected chromatographically which, although not positively identified, probably arise from the cleavage of glycosidic linkages in the polysaccharide matrix.[26]

In the case of Indulin AT, no aromatic compounds were detected, which suggests that during treatment of the moistened solid material, ozone degrades the

TABLE 6
Results of Ozonation of Lignocellulosic Polymers

	Indulin AT lignin	Chlorite holocellulose	CF-11 cellulose
Introduced ozone (mg)	609	695	621
Consumed ozone (mg)	183	220	41
Ozone consumption (%)	30.0	31.6	6.7
Solid solubilization (%)	14.6	28.1	0.0
pH of the aqueous extract	2.8	2.4	3.8

TABLE 7
Yield of Products Identified in the Aqueous Extracts of Oxidized Polymers (g/100 g dry initial material)

	Indulin AT lignin	Chlorite holocellulose	CF-11 cellulose
Glycolic acid	0.048	0.033	0.003
Oxalic acid	0.402	0.218	0.009
Malonic acid	trace	ND	ND
Glyoxylic acid	0.033	ND	ND
Malic acid	trace	ND	ND

ND: Not detected

oxyaromatic products initially generated, giving rise to greater quantities of aliphatic acids than in the case of holocellulose. However, the low degree of solubilization achieved with this lignin is probably due to the doughy nature of its moistened form which hinders a good contact with the reaction gas.

CONCLUSIONS

The present study demonstrates that a water content of 60% (optimal moisture level) for conditioned corn (*Zea mays*) stalks leads to the highest solubilization degree of the material during ozone treatment. Ozonation showed that lignin is the polymer most affected by ozone, followed by hemicelluloses and finally by cellulose.

Ozonation of aqueous explosion autohydrolyzed corn stalks (hemicelluloses-free material) leads to a gradual delignification, in which it is easier to eliminate the lignin at the beginning of the reaction than at the end due to condensation of part of lignin during the autohydrolytic process.

Organosolvolytic corn stalks (hemicelluloses-free and almost lignin-free) are much less reactive to ozone attack than the autohydrolyzed materials (hemicelluloses-free), which in turn show similar behaviour towards ozone attack, suggesting that their respective lignins show a very similar physical and chemical structures.

The results show that during the ozonation of lignin-containing lignocellulosic materials in moistened solid state, ozone rapidly oxidizes the initially generated oxyaromatic products and transforms them into short chain aliphatic acids. The most abundant water soluble reaction products detected were glycolic and oxalic acids, which yields increased as the reaction progressed. For this reason, the production of oxyaromatics from lignin can only be optimized by initially solubilizing the lignin and then oxidizing it while in solution.

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