

# ESCA Study of the Solid Residues of Supercritical Extraction of *Populus tremuloïdes* in Methanol

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## Synopsis

A systematic ESCA study of the solid residues of supercritical critical extraction of *Populus tremuloïdes* prepared in various conditions has been performed. Reference materials also examined by ESCA included the initial wood, Whatman no. 1 paper, and two lignins prepared by different procedures. Interest has been focused on the  $C_{1s}$  and  $O_{1s}$  spectra and on the determination of surface O/C atomic ratio. A difference between bulk O/C values measured by chemical analysis and surface O/C ratios obtained from ESCA data is considered diagnostic of a difference in chemical composition of the bulk and the surface. In the  $C_{1s}$  peaks of wood and its constitutive polymers, the usual components peaks  $C_1$ ,  $C_2$ , and  $C_3$  were observed. For the solid residues, however, a fourth peak designated as  $C_0$  appears, the importance of which increases steadily when the temperature of extraction is raised from 250 to 350°C. The component  $C_0$  was ascribed to polyaromatic constituents. Its proportion is correlated with the fraction of the carbon in the residue comprised in the recondensed material and determined independently. The  $O_{1s}$  peak shows also a complex structure with three components in the wood-derived reference materials and four in some of the solid residues. These structures have not been discussed previously in the literature and a tentative assignment for the component peaks is proposed.

## INTRODUCTION

In an earlier article,<sup>1</sup> we have reported a detailed characterization of solid residues produced by semicontinuous extraction of *Populus tremuloïdes* wood in supercritical methanol.

The present paper reports the results of an ESCA study of some of the solid samples analyzed in the previous work, in an effort to assess the usefulness of the ESCA technique in recording the chemical changes in wood samples during pyrolysis.

ESCA is a surface-sensitive technique, based on the measurement of kinetic energies of photoelectrons ejected from a given atomic energy level under the action of a monoenergetic X-ray beam. It provides quantitative information on the elemental composition as well as on the chemical environment of each atom (bonding and oxidation state).

ESCA has been extensively used in the investigation of surface structure, bonding, and reactivity of solid materials such as polymers,<sup>2-4</sup> wood fibers,<sup>5,6</sup> pulp and paper,<sup>7-10</sup> coal,<sup>11-14</sup> etc.

## EXPERIMENTAL

The ESCA spectrometer utilized was an ESCALAB MK II spectrometer fitted on a Microlab system from Vacuum Generators. It was equipped with a dual Mg-Al anode X-ray source, nonmonochromatized. Kinetic energies were measured using an hemispherical electrostatic analyzer with 150 mm radius, working in the constant pass energy (20 eV) mode. No flood gun was utilized in the experiments reported, and the vacuum was maintained in the range  $10^{-8}$ – $10^{-6}$  Torr.

The samples were introduced as small chunks or fibers pressed onto an indium disk.

Spectra were recorded at room temperature (except for the dibenzanthracene and *o*-biphenol samples which were cooled down to  $-100^{\circ}\text{C}$  during analysis), using the Mg anode at 300 W with typical accumulation times of 1000–1200 s for the carbon 1s peak and 500–1000 s for the oxygen 1s peak.

The sample designated hereafter as *Populus tremuloides* is the wood material utilized in the supercritical extraction experiments (SCE).<sup>15</sup> The sapwood of a 20-year tree was cut into cubes of 4 mm size, dried in air at  $105^{\circ}\text{C}$  for 20 h, and kept in a humidity-free container.

The Whatman no. 1 paper filter was carefully taken from the middle of a freshly opened box.

The Iotech lignin sample was kindly provided by Dr. J. Bentko from Iotech Co. It is considered to be 85% pure lignin produced by enzymatic carbohydrate hydrolysis of thermally exploded wood.

The thioglignin sample was obtained by thioglycolic acid extraction of *Populus tremuloides*. Its preparation is described in Ref. 1, where it is designated as thioglignin 2. Its dry mass was 16.5% of initial wood and C, H, O, and S mass percents are 56.5, 6.1, 29.0, and 8.5%, respectively.

The samples of SCE solid residues are also described in detail in Ref. 1. Some of the most important parameters describing the preparation and properties of these samples are reported in Table I, along with the parameters for the properties of the *Populus tremuloides* sample. The results in Table I indicate that the SCE solid residues under study are indeed of very different nature depending on the conditions of extraction. Sample MP6, for example, still contains much of the original lignin whereas MP15, although extracted at the same temperature, shows a much higher delignification and a much higher fraction of hydrolyzable material even though the glucose and xylose recovered in the hydrolyzate are in comparable amounts. Sample MP11 prepared at  $350^{\circ}\text{C}$  is almost entirely constituted of recondensed material insoluble in 72%  $\text{H}_2\text{SO}_4$ . Samples MP16, 20, and 13 show intermediate properties.

## RESULTS

The kinetic energy of photoelectrons ( $E_k$ ), as measured with respect to the vacuum level, is expressed as

$$E_k = E_X - (E_B + \phi + E_c) \quad (1)$$

where  $E_X$  is the energy of the incident photon,  $E_B$  is the binding energy of the electron on its original level,  $\phi$  is the work function of the spectrometer,

TABLE I  
Preparation Conditions and Properties of SCE Solid Residues

Sample designation	SCE Conditions			Wt % based on mass of initial dry wood									
	Temp (°C)	Pressure (psi)	Methanol flow rate (L/h)	O/C	H/C	SCE residue	Preextractive	Thioglycolic acid lignin	Recondensed material	Glucose in hydrolyzate	Xylose in hydrolyzate	Acid soluble converted carbohydrate	
<i>Populus tremuloïdes</i>													
MP6	250	1500	0.5	0.77	1.69	55.4	4.4	15.6	4.5	47.6	27.2	3.8	
MP15	250	2500	1.5	0.57	1.18	68.4	3.5	12.30	1.4	21.1	7.1	7.3	
MP16	300	500	0.5	0.83	1.89	40.5	2.2	3.70	12.3	18.4	8.4	35.2	
MP20	300	500	2.5	0.33	1.08	31.0	4.1	4.9	20.4	10.5	3.2	5.1	
MP13	300	2500	0.5	0.18	0.81	18.4	2.55	3.8	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	ND <sup>a</sup>	
MP11	350	1500	0.5	0.34	1.01	18.2	1.9	1.1	10.9	1.9	0.6	2.5	
				0.10	0.70		0.7	0.7	16.1	0	0	0.15	

<sup>a</sup> Not determined.

and  $E_c$  is the energy lost in counteracting the potential associated with the steady charging of the surface.  $\phi$  and  $E_c$  are essentially corrections.  $\phi$  depends on the spectrometer and is not liable to be modified between experiments.  $E_c$  is high on low conductivity samples and can be made lower by the use of a flood gun.

Raw data are reported as uncorrected binding energies defined as:

$$E_B + E_c = E_X - E_k - \phi \quad (2)$$

and the use of a known reference is necessary to obtain an absolute scale of binding energies.

The atomic ratio of two elements in the surface region analyzed by ESCA can be estimated from the ratio of their peak intensity. For example,

$$\frac{O}{C} = \frac{\sigma_C D_C \lambda_C I_O}{\sigma_O D_O \lambda_O I_C} \quad (3)$$

where the  $\sigma$ 's are the cross section for photoelectrons generation, the  $\lambda$ 's are the mean free paths of photoelectrons which depend on their kinetic energy, the  $D$ 's are spectrometer transmissions, and the  $I$ 's are the integrated intensity of ESCA peaks. Using Scofield's cross sections<sup>16</sup> for the  $O_{1s}$  and  $C_{1s}$  peaks, the following relation can be derived from eq. (3):

$$\frac{O}{C} = \frac{1}{2.85} \frac{I_{O_{1s}}}{I_{C_{1s}}} \quad (4)$$

## REFERENCE MATERIALS

Figure 1 shows  $C_{1s}$  peaks obtained for the samples of *Populus tremuloïdes*, Whatman filter, Iotech lignin, and thiolignin as well as the resolved components of these peaks. Peak synthesis was performed using a product of Gaussian and Lorentzian functions<sup>17</sup> with a ratio  $G/L$  of 60–70%. In these conditions a good fit can be obtained with full widths at half maximum close to 2 eV for the three components of the  $C_{1s}$  peak. Tables IIA and IIB give the details of these results compared with corresponding literature data. The O/C atomic ratios obtained from chemical analysis<sup>1</sup> and by ESCA using eq. (4), are also reported along with  $C_{1s}$  results for two solids used as model compounds, namely, *o*-biphenol and dibenz (*a, h*) anthracene.

Corresponding  $O_{1s}$  data are shown in Figure 2 and Table IIB. Only for Whatman filter is the  $O_{1s}$  band described in the literature. In that case only one  $O_{1s}$  peak is reported, and we also find one. For *Populus tremuloïdes*, Iotech lignin, and thiolignin, however, we find a more complex structure involving three components.

## SCE Solid Residues

Corresponding data for SCE solid residues are reported in Figure 3 and Table IIIA for the  $C_{1s}$  bands and in Figure 4 and Table IIIB for the  $O_{1s}$  data.

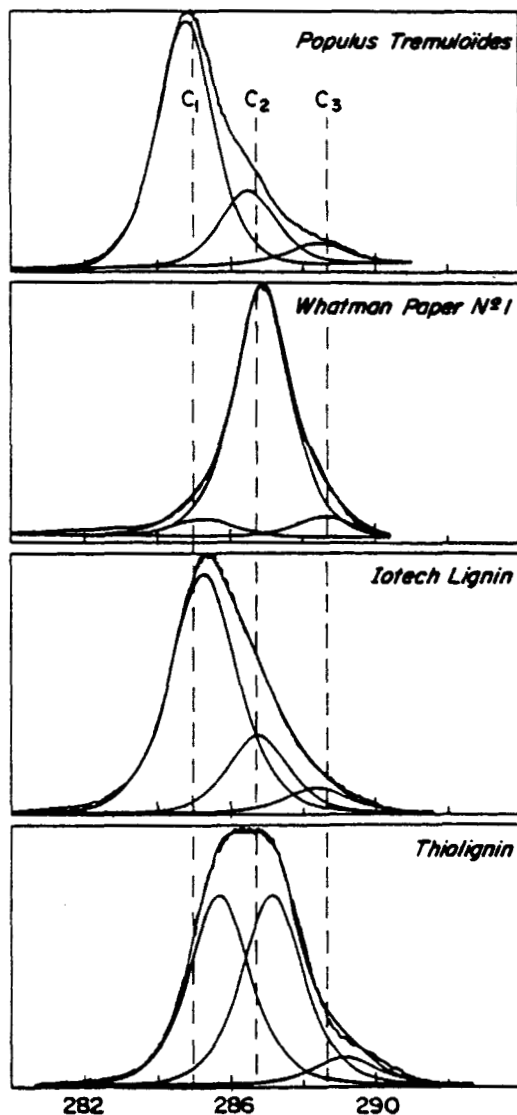


Fig. 1. ESCA spectra for reference materials ( $C_{1s}$  peaks).

The  $C_{1s}$  structure has to be fitted with four component peaks. The assignment of the three which correspond to the  $C_1$ ,  $C_2$ , and  $C_3$  components defined for wood materials will be discussed later on.

The  $O_{1s}$  structure also contains a rich information with three to four different component peaks.

#### Referencing the Binding Energy Scale

Dorris and Gray<sup>9</sup> have suggested in the case of cellulose and bleached pulp and paper that the  $O_{1s}$  peak of cellulose be used as a reference at 533.2 eV. This procedure is considered equivalent to the usual procedure of using the  $C_{1s}$  peak of hydrocarbons at 285.0 eV. As shown in Table IVA, we have followed

TABLE IIA  
ESCA Analysis of Reference Materials (C<sub>1s</sub> Peaks)

Sample	O/C (chemical analysis)	O/C (ESCA)	C <sub>1s</sub> ESCA peaks									Reference
			Area (%)			Uncorrected binding energy (eV)			FWMH (eV)			
			C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	
<i>Populus tremuloides</i> (unextracted)	0.77	0.24	72	22	6	287.30	289.10	291.0	1.95	2.0	2.0	This work
Yellow poplar		0.27	64	26	10	285.0	287.0	289.5	2.1	2.3	2.2	5
Pine chips (unextr.)		0.26										6
Whatman no. 1 paper filter	0.83 <sup>a</sup>	0.73	5	89	6	288.15	289.70	291.50	2.0	1.95	1.90	This work
Whatman filter						282.8	284.2	~ 286				9
Whatman filter		0.80, 0.83, 0.79	2	81	17	281.5	283.2	~ 285				9
Whatman filter						282.5	284.6	~ 286				9
Whatman untreated filter paper		0.78	7	74	19							7
Cellulose surface		0.62	18	56	26	285.0	286.5	288.3	1.9	1.7	2.1	5
Iotech lignin	0.46	0.25	76	21	3	287.20	288.75	290.40	2.2	2.1	2.1	This work
Thiolignin	0.37	0.38	48	48	4	286.55	288.05	290.10	2.1	2.1	2.1	This work
Milled wood lignin		0.39										6
Precipitated lignin		0.40										6
Milled wood lignin		0.34	40	60	0	285.0	286.8	—	2.3	2.8	—	5
Dioxane lignin	0.36 <sup>b</sup>	0.31, 0.36	49 <sup>b</sup>	48 <sup>b</sup>	2 <sup>b</sup>							9
<i>o</i> -Biphenol	0.167 <sup>a</sup>	0.157	96	4		285.3	287.10		1.90	1.80		This work
Dibenz ( <i>a, h</i> ) anthracene			100			283.75			1.50			This work

<sup>a</sup> Calculated for cellulose and *o*-biphenol formulas

<sup>b</sup> Calculated from the Freudenberg lignin formula and reported in Ref. 9.

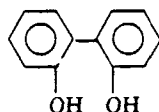
TABLE IIB  
 ESCA Analysis of Reference Materials ( $O_{1s}$  Peaks)

Sample	$O_{1s}$ peaks									Reference
	Area (%)			$E_B + E_c$ (eV)			FWMH (eV)			
	$O_1$	$O_2$	$O_3$	$O_1$	$O_2$	$O_3$	$O_1$	$O_2$	$O_3$	
<i>Populus tremuloïdes</i> (unextracted)	17	74	9	533.90	535.15	536.05	2.0	2.1	1.90	This work
Whatman no. 1 paper filter		100			536.0			1.95		This work
Whatman filter		100			530.7			—		9
Whatman filter		100			529.5			—		9
Whatman filter		100			530.9			—		9
Cellulose surface		100			—			—		5
Iotech lignin	20	70	10	533.60	535.0	536.0	2.1	2.2	2.1	This work
Thiolignin	4	24	72	532.50	534.10	534.90	2.05	2.0	2.0	This work
<i>o</i> -Biphenol	14		86	532.25		533.80	2.0		1.95	This work

Dorris and Gray's suggestion for our Whatman paper sample, which would correspond to a value of  $E_c$  of 2.8 eV. The values obtained for the binding energies of  $C_1$ ,  $C_2$ , and  $C_3$  components are in close agreement with those reported in the literature (see Table IIA).

Arbitrarily choosing the reference component designated as  $O_2$  in the  $O_{1s}$  spectra of *Populus tremuloïdes*, Iotech lignin, and thiolignin provides also close estimates of the three  $C_{1s}$  binding energies.

*o*-Biphenol as the following formula:



Its ESCA spectrum shows two  $C_{1s}$  and two  $O_{1s}$  components. If the dominant  $O_{1s}$  peak corresponding to an OH on a benzene ring is considered equivalent to an OH in cellulose, then this peak would be referenced at 533.2 eV. In that case, however, the dominant  $C_{1s}$  peak, which is an aromatic carbon is assigned a rather low value at 284.7 eV. Readjusting the binding energy scale to the average  $C_1$  value for the first four samples in Table IVA, namely, 285.45 eV, shifts back  $E_c$  to 1.35 eV and the dominant  $O_{1s}$  peak to 533.95 eV. This value is in close correspondance with the  $O_3$  component which leads us to assign the phenolic OH to the  $O_3$  peak. The presence of an  $O_1$  peak at 532.4 eV must then be ascribed to some unidentified surface impurity.

Table IVB shows the binding energies attributed to the various  $C_{1s}$  and  $O_{1s}$  in the spectra of SCE solid residues, by assigning an  $O_2$  component peak referenced at 533.2 eV.

In all cases a fourth  $C_{1s}$  component is found on the low binding energy side of the spectrum, shifted from the  $C_1$  component by  $1.4 \pm 0.5$  eV. We designated this as the  $C_0$  component.

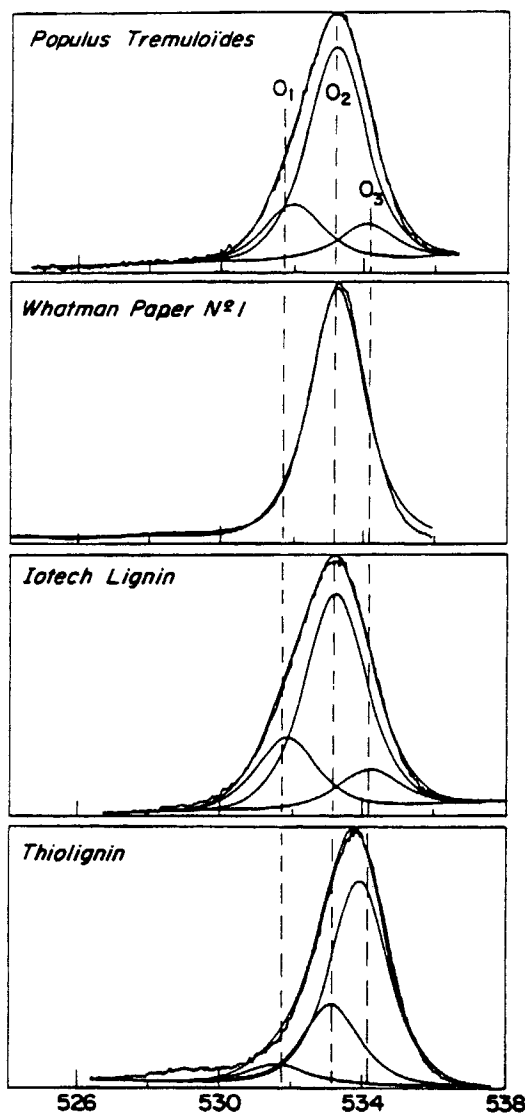


Fig. 2. ESCA spectra for reference materials ( $O_{1s}$  peaks).

It is interesting to note that the uncorrected experimental  $C_{1s}$  binding energy for dibenz (*a, h*) anthracene is very close to the binding energy for this  $C_0$  peak. As polyaromatics are electrical conductors, the charging is expected to be low and  $E_c$  close to 0. On this basis we assigned the  $C_0$  component to carbon in polyaromatics. Usually aromatic compounds show a shake up satellite located 5–7 eV above their  $C_{1s}$  peak.<sup>18,19</sup> It can be seen, however, from Figure 3 that the intensity of this satellite in dibenz (*a, h*) anthracene is considerably lower than in *o*-biphenol. Thus the satellite from  $C_0$  peak is SCE solid residues should only make a minor contribution to the overall  $C_{1s}$  band.

The binding energies are provided both as raw uncorrected data (Tables II and III) and as charge-corrected binding energies (Tables IV) to allow the



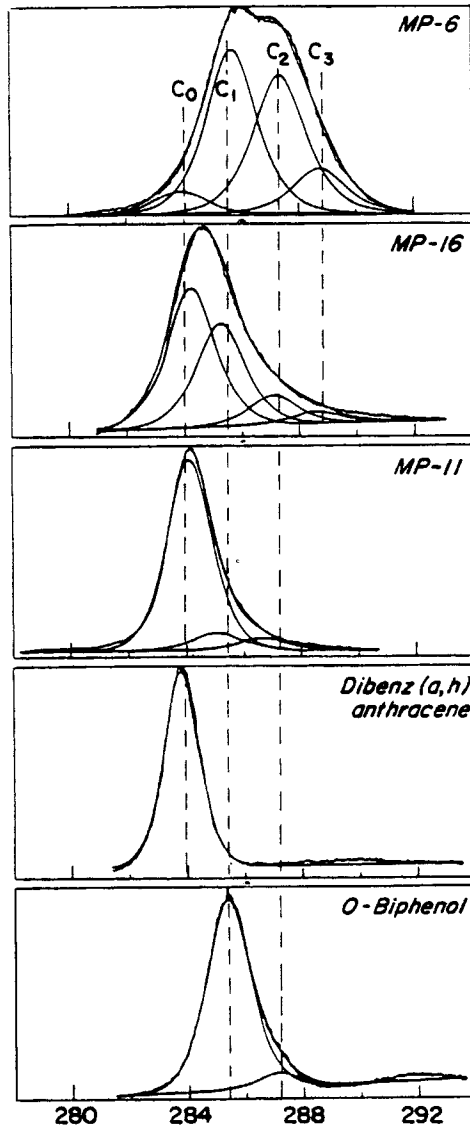


Fig. 3. ESCA spectra for SCE solid residues ( $C_{1s}$  peaks).

reader to check the original referencing method proposed in this paper for this type of materials.

## DISCUSSION

### Carbon 1s Peaks

There is a general agreement in the literature<sup>5-10</sup> on the assignment of components  $C_1$ ,  $C_2$ , and  $C_3$  in wood-derived materials. Following Siegbahn<sup>20</sup> and co-workers, three carbon 1s lines must be distinguished:  $C_1$  corresponds to carbon only linked to H or C,  $C_2$  has one link to oxygen, whereas  $C_3$  has two. In the solid phase  $C_1$  is referenced at 285.0 eV, and  $C_2$  and  $C_3$  are usually close to 287 and 289.5 eV.

TABLE IIIA  
 ESCA Analysis of SCE Solid Residues ( $C_{1s}$  Peaks)

Sample designation	O/C (chemical analysis)	O/C (ESCA)	$C_{1s}$ ESCA peaks											
			Area (%)				uncorrected binding energy (eV)				FWMH (ev)			
			$C_0$	$C_1$	$C_2$	$C_3$	$C_0$	$C_1$	$C_2$	$C_3$	$C_0$	$C_1$	$C_2$	$C_3$
MP6	0.57	0.43	4	45	39	12	285.45	287.30	289.0	290.40	2.2	2.2	2.3	2.3
MP15	0.83	0.42	2	49	41	8	285.45	287.35	288.85	290.60	2.0	2.1	2.2	2.3
MP16	0.33	0.24	51	36	9	4	284.65	285.70	287.55	289.10	2.1	2.1	2.1	2.1
MP20	0.18	0.17	73	21	4	2	285.80	287.05	288.60	290.10	2.1	2.1	2.1	2.1
MP13	0.34	0.29	52	28	16	4	286.35	287.40	288.85	290.35	2.2	1.9	2.0	2.1
MP11	0.10	0.13	85	8.5	6.5		285.0	285.90	287.50		1.85	2.0	20.5	

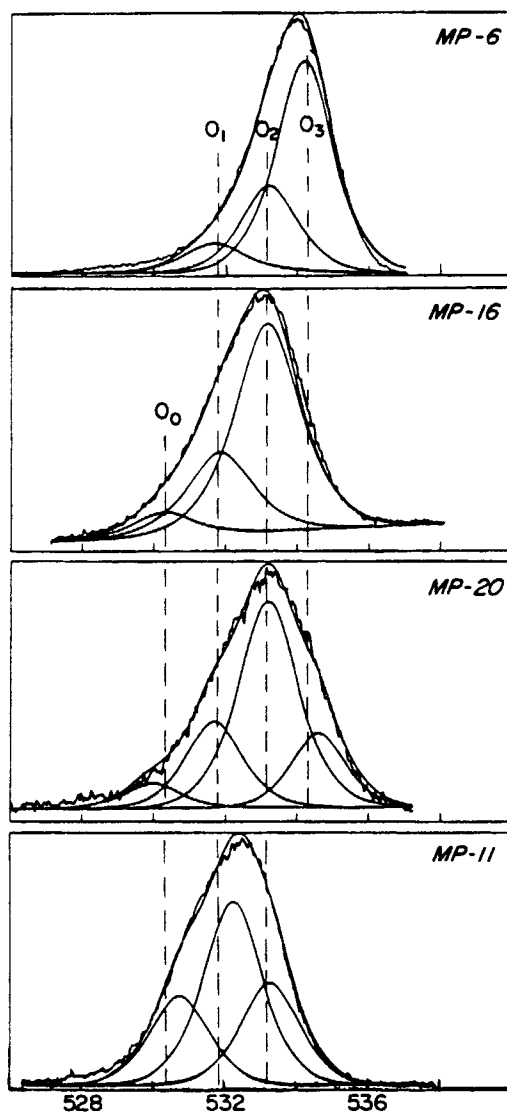

 Fig. 4. ESCA spectra for SCE solid residues ( $O_{1s}$  peaks).

TABLE IIIB  
 ESCA Analysis of SCE Solid Residues ( $O_{1s}$  Peaks)

Sample designation	$O_{1s}$ ESCA peaks											
	Area (%)				Uncorrected binding energy (eV)				FWMH (eV)			
	$O_0$	$O_1$	$O_2$	$O_3$	$O_0$	$O_1$	$O_2$	$O_3$	$O_0$	$O_1$	$O_2$	$O_3$
MP6		6	25	69		533.20	534.80	535.80		2.2	2.0	2.0
MP15		18	47	35		533.50	534.85	535.70		2.1	1.9	1.9
MP16	6	25	69		530.60	532.25	533.60		2.1	2.3	2.3	
MP20	5.5	21.5	56	17	531.20	533.0	534.55	536.00	1.90	2.1	2.0	2.0
MP13	8	34	58		532.40	534.20	535.35		2.1	2.1	2.1	
MP11	22	53	25		531.50	533.00	534.05		2.0	2.05	2.0	

 TABLE IVA  
 Binding Energies of  $C_{1s}$  and  $O_{1s}$  Levels in Reference Materials

Sample	$E_c$ (eV)	Binding energy (eV)					
		$C_1$	$C_2$	$C_3$	$O_1$	$O_2$	$O_3$
<i>Populus tremuloïdes</i> (unextracted) Whatman no. 1 paper filter	1.95	285.35	287.15	289.05	531.95	533.2	534.10
Iotech lignin	2.8	285.35	286.90	288.70	—	533.2	—
Thiolignin	1.8	285.40	286.95	288.60	531.80	533.2	534.20
$\alpha$ -Biphenol	0.90	285.65	287.15	289.20	531.60	533.2	534.0
	{ 0.6	284.70	286.50	—	531.65	533.2	—
	{ 1.35	285.45	287.25	—	532.40	—	533.95

 TABLE IVB  
 Binding Energies of  $C_{1s}$  and  $O_{1s}$  Levels in SCE Solid Residues

Sample	$E_c$ (eV)	Binding energy (eV)							
		$C_0$	$C_1$	$C_2$	$C_3$	$O_0$	$O_1$	$O_2$	$O_3$
MP6	1.60	283.85	285.70	287.40	288.80		531.60	533.2	534.20
MP15	1.65	283.80	285.70	287.20	288.95		531.85	533.2	534.05
MP16	0.40	284.25	285.30	287.15	288.70	530.20	531.85	533.2	
MP20	1.35	284.45	285.70	287.25	288.75	529.85	531.65	533.2	534.65
MP13	2.15	284.20	285.25	286.70	288.20	530.25	532.05	533.2	
MP11	0.85	284.15	285.05	286.65		530.65	532.15	533.2	
Dibenz ( $\alpha$ , $h$ ) anthracene	0	283.75							

The fact that the ESCA value of the O/C atomic ratio in *Populus tremuloïdes* is found much lower than the bulk value (see Table IIA) indicates a difference between the composition of the surface region sensed by ESCA and the one of the bulk.

Such a difference has been discussed by Mjöberg,<sup>6</sup> who considers that this indicates a preferential splitting in lignin-rich middle lamella<sup>21</sup> during the

chipping operation. As our O/C value of 0.24 is clearly below the 0.31–0.40 values given in the literature for lignin, it is assumed that the wood fiber surface also contains some extractives most of which have O/C ratios below 0.2. Our  $C_{1s}$  data indicate accordingly a high  $C_1$  proportion, in qualitative agreement with reported data for unextracted wood.<sup>5</sup>

The values calculated from the cellulose formula for O/C is 0.83 and for  $C_1$ ,  $C_2$ , and  $C_3$  atomic proportions 0, 0.83, and 0.17, respectively. Our Whatman paper data are thus in poorer agreement with these predictions than those reported by Dorris and Gray.<sup>9</sup>

The Iotech lignin sample also shows a difference between its surface and bulk O/C values. The most interesting result, however, about this sample is its close resemblance to the wood sample. Not only are the O/C ESCA values very close but the distribution of  $C_1$ ,  $C_2$ , and  $C_3$  peaks are also very similar. This resemblance is also reflected in the  $O_1$ ,  $O_2$ , and  $O_3$  distribution (see Table IIB) and in the value of  $E_c$  (Table IVA). Such results indicate quite clearly that in the Iotech lignin preparation the initial surface state of the middle lamella is preserved. One can indeed conjecture that the thermal explosion process would create passages for the enzymes to reach the polysaccharides in the fiber walls and for hydrolysis to be completed while the middle lamella is kept chemically unchanged.

The thioglignin sample shows almost equal bulk and surface O/C values in close agreement with literature data (Table IIA). Dorris and Gray<sup>9</sup> have calculated theoretical O/C,  $C_1$ ,  $C_2$ , and  $C_3$  proportions from the Freudenberg empirical formula for spruce lignin. These values are reported in Table IIA. They are very close from our experimental data for thioglignin. This agreement is, however, surprising since thioglignin is a thioglycolic acid derivative of lignin. It contains therefore acid groups in rather high proportion which should contribute to  $C_3$  and even shift this components towards higher binding energies.

Ortho biphenol yields an ESCA derived O/C ratio in good agreement with the calculated value. The proportions of  $C_1$  and  $C_2$ , however, do not correspond to the 12/2 theoretical distribution, the dominating  $C_1$  peak being too intense.

The data in Table IIIA show progressive changes in O/C and  $C_0$ ,  $C_1$ ,  $C_2$ , and  $C_3$  ratios with the severity of the pyrolysis treatment. As the temperature of extraction is increased from 250 to 350°C, O/C ESCA ratio is decreased, as well as its deviation from the bulk value. The  $C_0$  component increases continuously whereas the general trend of  $C_1$ ,  $C_2$ , and  $C_3$  components is a continuous decrease.

As  $C_0$  was assigned to polyaromatic carbon, its proportion should be correlated with the recondensed material. As in Ref. 1, we have proposed a method for the estimation of elemental analysis of recondensed material, we are in a position to calculate the ratio  $C_{RM}/C_{SR}$ , where  $C_{RM}$  is the mass of carbon in the recondensed material contained in a given sample and  $C_{SR}$  is the carbon content of the whole solid residue. Figure 5 shows not only that this ratio is correlated to the  $C_0$  fraction of the  $C_{1s}$  peak, but that both values are almost equal for all samples (a value for  $C_{RM}/C_{SR}$  was not obtained for sample MP-13 as elemental analysis of recondensed material was not available for this sample<sup>1</sup>).

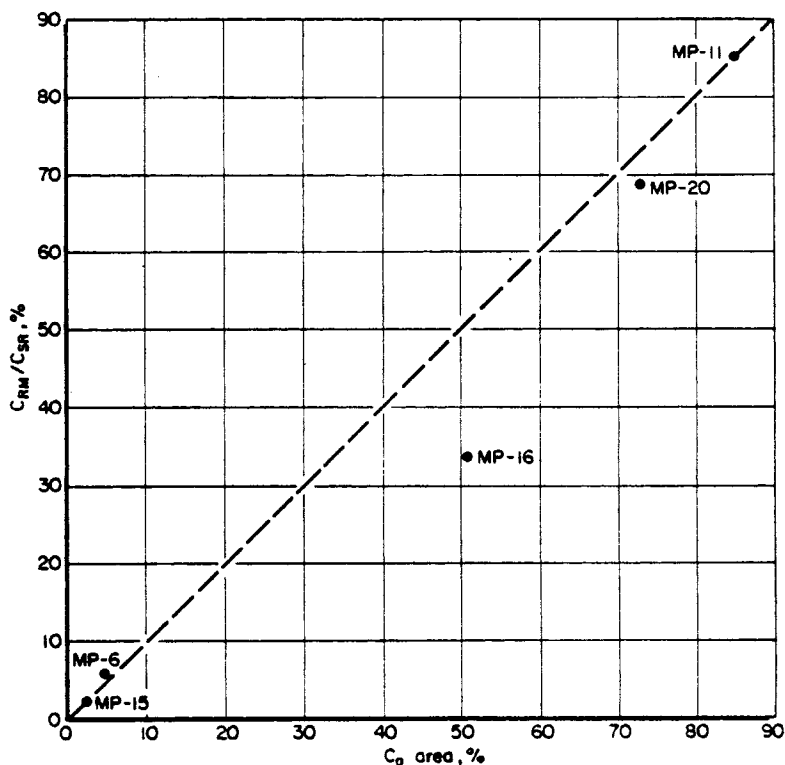


Fig. 5. Relation between carbon in recondensed material and polyaromatic carbon from ESCA  $C_{1s}$  peaks.

The stoichiometric relation between  $C_2$ ,  $C_3$ , and  $O/\dot{C}$  ratio may be written as

$$n_2 C_2 + n_3 C_3 = O/C \quad (5)$$

where  $n_2$  and  $n_3$  are the average number of oxygen atoms per  $C_2$  and  $C_3$  carbon atom, respectively. Obviously,  $0.5 \leq n_2 \leq 1$  and  $1 \leq n_3 \leq 2$ .

Assuming  $n_3 = 1$  in *Populus tremuloïdes*, Whatman filter, and Iotech lignin, eq. (5) yields reasonable values for  $n_2$ ,  $0.82 \pm 0.08$ ,  $0.75 \pm 0.02$ , and  $1.05 \pm 0.07$ , respectively. The theoretical value for  $n_2$  derived from the cellulose formula is 0.80.

The calculated curves on Figure 6 show that solutions for  $n_2$  and  $n_3$  in eq. (5) can be found only for samples MP6 and MP15. For all SCE residues produced at temperatures higher than  $250^\circ\text{C}$ , the  $O/C$ 's calculated from eq. (5) are clearly lower than the  $O/C$ 's from the ESCA intensity ratio.

This could only be explained by the presence in these samples of oxygen not bound to carbon. As no silicon 2p was detected in the ESCA spectra, we think that this cannot be assigned to oxygen in ashes. We would therefore have to assume the presence of very strongly adsorbed water. In sample MP11, for example, less than 2% of water would produce an  $O/C$  signal comparable to the one observed. We may conjecture here that in the highly carbonized samples micropores may have developed in which water molecules may be

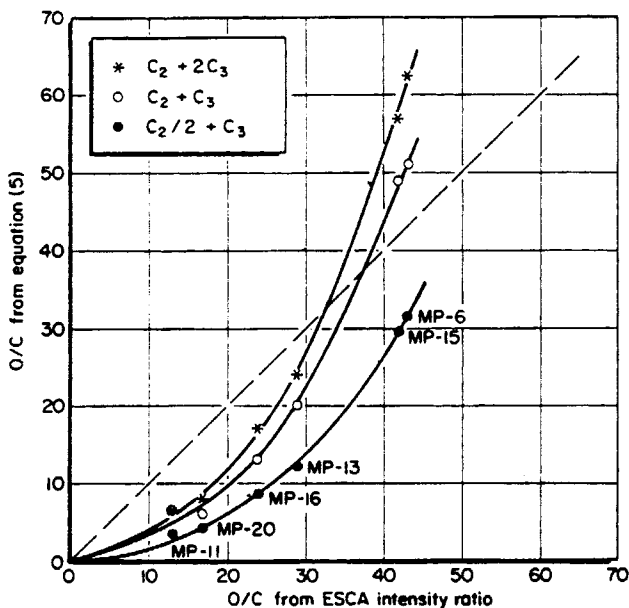


Fig. 6. Stoichiometric relation between oxygen and carbon derived from ESCA spectra.



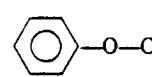
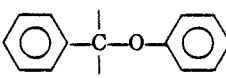
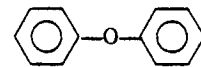
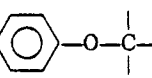
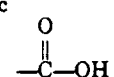
linked by double hydrogen bonds  $\cdots \text{HOH} \cdots$ . Water dissociatively chemisorbed as OH groups would likely be associated with  $\text{C}_2$  type carbons.

### Oxygen 1s Peaks

$\text{O}_{1s}$  peaks of wood-derived materials are almost not discussed in the literature. The reason for this is probably related to the predicted more complex shifting behavior of  $\text{O}_{1s}$  binding energies compared to  $\text{C}_{1s}$ .<sup>22</sup> It is not, for example, possible to discriminate easily oxygen singly and doubly bound to carbon. Assignment of  $\text{O}_{1s}$  peak components must therefore be done by comparison with known model compounds. As only one  $\text{O}_{1s}$  peak is found with Whatman paper, all oxygens in cellulose have to be ascribed to the  $\text{O}_2$  component. Those are, of course, oxygens in COH groups as well as the two C—O—C linking carbons nos. 1 and 5 as well as 1 and 4 in glucosidic bounds. As discussed with respect to the spectrum of *o*-biphenol, phenolic oxygen is ascribed to  $\text{O}_3$ .

The spectra of *Populus tremuloïdes* and Iotech lignin are of little use as it was shown earlier that they do not represent the bulk. We have therefore to utilize the thiolignin spectrum for additional assignments of oxygens. Freudenberg and Neish<sup>23</sup> have not only proposed an empirical formula for lignin, but have also suggested a model for the reaction of thioglycolic acid with this compound. He indicates that about two-thirds of the thioglycolic acid units attach by cleavage of ether bonds while the other one-third substitutes hydroxyls in lignin as  $\text{C}_2\text{H}_3\text{O}_2\text{S}$  groups. This may serve as the basis for a model of thiolignin, which can be quantified using our experimental determination of the percentage of elemental sulfur in thiolignin. From this

model we calculate the following repartition for atomic oxygen in thiolignin:

(a) phenolic OH		7.60
(b) aliphatic OH		13.30
(c) carbonyl C=O including aldehydes and ketones		4.75
(d) oxygens in lactone groups		
		0.95
(e) aliphatic ether,		4.28
(f) aliphatic aromatic ether excluding methoxyl		10.45
(g) benzyl aryl ether		4.04
(h) diaryl ether		1.43
(i) methoxy groups		21.86
(j) oxygen in thioglycolic acid		31.34



(a) has already been ascribed to  $O_3$ . (b), (c), and (e) can be ascribed to  $O_2$  as well as the two oxygens in (d). If we consider that the component  $O_1$  increases steadily with the temperature of extraction of SCE residues (see Table IIIB),  $O_1$  has to be associated with oxygen in recondensed material and in particular in groupings like (g) and (h), which are liable to be formed by dehydration of two OH groups. We may therefore decide to ascribe (g) and (h) to the component  $O_1$ .

At this point, all yet nonassigned oxygens have to be ascribed to  $O_3$  if we want to generate a distribution liable to represent the experimental distribution of oxygens in the spectrum of thiolignin (given in Table IIB), where the  $O_3$  component is dominant.

Summing up, the following assignments

$\frac{O_1}{g}$	$\frac{O_2}{b}$	$\frac{O_3}{a}$
h	c	f
	d	i
	e	j

would yield the distribution of  $O_1$ ,  $O_2$ , and  $O_3$  as 5.5, 23.3, and 71.2, respectively, which fits very well the experimental distribution (4, 24, 72).

However, this distribution is not free from criticism as, for example, the  is expected to have its  $O_{1s}$  binding energy shifted by at least 1 eV below . There should also be at least 1 eV shift between the two oxygens in the



acid group.

As arbitrary as it is, we propose this assignment as a basis for discussion, hoping that future work will shed some light on the true nature of the  $O_{1s}$  bands.

As to the  $O_0$  component peak appearing in the  $O_{1s}$  peaks of the carbonized samples (Tables IIIB and IVB), we believe it could be associated with the oxygen in strongly adsorbed water suggested by the analysis of the  $C_{1s}$  peaks of solid residues.

## CONCLUSION

The progressive changes in the chemical nature of SCE solid residues associated with changes in the conditions of extraction are reflected in the ESCA spectra of these samples. The  $C_{1s}$  peak in particular is rich in information, allowing one, for example, to measure rapidly the proportion of carbon in polyaromatics. Some even richer results may be obtained in the future from the analysis of the  $O_{1s}$  peaks as they show a very detailed structure which evolves in a continuous manner with the conversion to recondensed material. A preliminary assignment of the component peaks in this structure has been proposed, but it is felt that more experimental work is necessary before the full potential of this approach can be appreciated.

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