

ESCA Analysis of Partially Converted Lignocellulosic Materials

A. AHMED, A. ADNOT and S. KALIAGUINE, *Department of Chemical Engineering and GRAPS, Université Laval, Québec, Canada*

Synopsis

Further ESCA data of the solid residues obtained by supercritical extraction of *Populus tremuloides* are reported. The changes of the ESCA spectra with the severity of grinding are discussed. These data allow us to draw precise conclusions on the spatial distribution of carbonaceous recondensed material as thermal conversion proceeds. The C_{1s} peaks are of special interest as the distribution of the four components in these peaks bears information on the nature of the chemical compounds present on the surface of the sample.

INTRODUCTION

In a recent paper,¹ we have reported what we believe to be the first ESCA study of the solid products of a process of thermal degradation of wood. This process was the supercritical extraction (SCE) of *Populus tremuloides* in methanol.² Such studies are of interest for the detailed characterization of all lignocellulosic materials submitted to thermal treatments. They should yield informations about the mechanisms of the conversion of wood in the course of a variety of processes of wood liquefaction and gasification.

The present paper describes new ESCA data of SCE solid residues and must therefore be considered as a continuation of Ref. 1. These SCE residues are specially interesting materials for these studies, as samples were prepared in a variety of SCE conditions. Moreover, these samples were fully characterized by a series of analytical techniques including C, H, N elemental analysis, wet chemistry, thermogravimetric analysis (TGA) in flowing nitrogen, and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT).³⁻⁵

In particular, the amount of recondensed material in a given sample could be determined³ by subtracting the lignin content (established by the thioglycolic acid technique) from the content in trifluoroacetic acid insolubles. The content in TFA insolubles of a thermally converted wood chip was shown to be equivalent to the Klason residue which is actually the material insoluble in concentrated H₂SO₄. It was shown in Ref. 3 that these TFA insolubles include, besides the unreacted lignin, all the highly recondensed materials bearing polyaromatic hydrocarbons formed during thermal degradation. The content in recondensed material can therefore be determined by difference, knowing the lignin content. Moreover, the C, H, and O elemental analysis of this recondensed material was determined in addition to the C, H, and O contents of the complete sample.

In this new ESCA study the emphasis was on the evolution of the ESCA spectra with progressive grinding. This procedure is a systematic means for comparing surface and bulk compositions.

EXPERIMENTAL

The extraction conditions for samples preparation are reported in Table I along with some of the characteristics of the samples. The procedures for continuous flow extraction² and for determination of the content in recondensed material³ were described earlier. The wood conversion was defined as the percentage of weight loss after supercritical extraction, on the basis of the initial dry wood. As can be appreciated from Table I, the samples under study represent a wide range of wood conversion and content in recondensed material.

ESCA spectra were recorded using an ESCALAB MK II spectrometer fitted on a microlab system from Vacuum Generators. It was equipped with a nonmonochromatized, dual Mg-Al anode X-ray source. Kinetic energies were measured using a 150 mm radius hemispherical analyzer working in the constant pass energy (20 eV) mode. Vacuum was maintained close to 10^{-8} Torr. The spectra were recorded as the sample was maintained at low temperature ($\sim -50^{\circ}\text{C}$) using the Mg anode at 300 W, with typical accumulation times of 1000 – 1200 s for the C_{1s} peak and 500–1000 s for the O_{1s} peak.

The kinetic energy scale was referenced to the so-called O_2 component of the O_{1s} peak at 533.2 eV following the procedure described in Ref. 1.

The wood samples were 5 mm cubes before extraction, and the resulting solid residues showed no sign of heterogeneity. No difference was observed in the ESCA spectra when the material was cautiously broken up in order to expose the surface of the inner fibers. Analysis was performed either on these bundles of fibers or on the materials obtained by grinding the chips in a mortar or by a more thorough treatment using a mechanical grinder. The samples were mounted on indium disks.

Peak synthesis was performed following the procedure described previously,¹ which makes use of products of Gaussian and Lorentzian functions ($G/L = 60\text{--}70\%$) and FWMH of 2 eV. The O/C atomic ratio was calculated

TABLE I
Conditions for SCE extraction

Sample designation	Extraction conditions			Wood conversion (wt %)	Recondensed material (wt %)
	Temp. ($^{\circ}\text{C}$)	Methanol Pressure (psi)	flow rate (L/h)		
MP-22	250	500	1.5	25.2	11.8
MP-6	250	1500	0.5	44.6	8.2
MP-15	250	2500	1.5	31.6	2.1
MP-16	300	500	0.5	59.5	30.2
MP-13	300	2500	0.5	81.6	59.5
MP-20	300	500	2.5	69.0	65.8
MP-11	350	1500	0.5	81.8	88.3

from ESCA O_{1s} and C_{1s} peak areas as

$$(O/C)_{\text{ESCA}} = (1/2.85)(I_{O_{1s}}/I_{C_{1s}}) \quad (1)$$

RESULTS AND DISCUSSION

Tables II and III give the characteristic features of the C_{1s} and O_{1s} ESCA peaks of some SCE solid residues compared to the spectrum of *Populus tremuloides*. As discussed previously,¹ the spectrum of wood shows a very low $(O/C)_{\text{ESCA}}$ value compared to the bulk value, which corresponds to the fact that the surface region sensed by ESCA is actually constituted by the middle lamella between the fibers. This lamella contains extractives which include resins, resin acids, long chain aliphatic monoalcohols, and fatty acids. The high value of C_1 characteristic of all untreated wood samples is therefore ascribed to these aliphatic chains. In the O_{1s} oxygen peak the O_2 component is the one peak found in cellulose spectra.⁶ The fact that it is the dominant peak must therefore be interpreted as indicating the presence of some carbohydrates in the surface region.

The values of E_c given in Table III correspond to the correction of the binding energy scale, obtained by setting the O_2 component at 533.2 eV.

Figure 1 indicates how the $(O/C)_{\text{ESCA}}$ value is affected by the grinding process. In sample MP22, increasing the severity of the grinding procedure increases the $(O/C)_{\text{ESCA}}$ value progressively until the bulk (O/C) value is reached. In this last instance, the homogenization of the sample is sufficient for the surface region to be representative of the volume average (bulk) of the sample.

However, the interpretation of this result is complicated by the fact that a low $(O/C)_{\text{ESCA}}$ value may correspond either to the presence of extractives or of polyaromatic recondensed material on the surface.

The results presented in Figure 2 are easier to explain. The figure shows the ratio of $(C_{\text{RM}}/C_{\text{SR}})$ as a function of C_0 . C_{RM} is the carbon content of the recondensed material whereas C_{SR} is the carbon content of the solid residue. Both C_{RM} and C_{SR} were determined from elemental analysis as described in Ref. 1. C_0 is the component of the C_{1s} peak which is not present in wood spectra and which we have ascribed¹ to carbon in polyaromatic recondensed material. Therefore, looking at the results for spectra 22.1, 22.2, and 22.3, for example, indicates that at high grinding severity, the fraction of C_0 area in ESCA C_{1s} peak, which is the atomic fraction of C_0 carbon in the surface region, is identical with the fraction of the total carbon present in the sample as recondensed carbon. The high value of C_0 observed, for example, in spectrum 22.1 indicates that, in the unground sample, the recondensed material is in higher concentration in the surface region sensed by ESCA. It is therefore established that in samples prepared at 250°C (MP22 and MP6), the recondensed material is essentially located at the peripheral surface of the wood fibers.

The behavior of sample MP6 upon grinding is somewhat different. Spectrum 6.2 shows both C_0 and $(O/C)_{\text{ESCA}}$ values lower than in 6.1. As a lower C_0 means less recondensed material, a lower $(O/C)_{\text{ESCA}}$ must indicate the pres-

TABLE II
ESCA Results of SCE Solid Residues^a

Sample designation	Spectrum	O/C ratio		C _{1s} peak															
		Bulk	ESCA	Area (%)			Binding energy (eV)												
				C ₀	C ₁	C ₂	C ₃	C ₀	C ₁	C ₂	C ₃								
<i>Populus tremulooides</i>																			
MP-22	PT	0.77	0.24	—	72	22	6	—	285.3	287.1	289.0								
u.g.	22.1	0.66	0.38	51	34	11	4	284.3	285.9	287.2	288.9								
m.g.	22.2		0.46	35	24	35	6	284.0	285.5	286.6	288.7								
mech. g.	22.3		0.65	12	24	57	7	283.8	285.1	286.7	288.6								
MP-6		0.57																	
u.g.	6.1		0.50	25	24	45	6	283.9	285.2	287.6	288.8								
m.g.	6.2		0.43	4	45	39	12	282.9	284.7	286.4	287.8								
mech. g.	6.3		0.56	11	31	51	7	283.4	284.9	286.6	288.6								
MP-16		0.33																	
u.g.	16.1		0.24	51	36	9	4	284.3	285.3	287.2	288.7								
m.g.	16.2		0.19	73	18	7	2	283.7	285.4	287.0	288.5								
mech. g.	16.3		0.223	34	46	15	5	283.8	285.0	286.7	288.6								
MP-13		0.34																	
m.g.	13		0.29	52	28	16	4	284.2	285.2	286.7	288.2								
MP-20		0.18																	
m.g.	20		0.17	73	21	4	2	284.4	285.7	287.2	288.7								
MP-11		0.10																	
u.g.	11.1		0.15	73	18	6	3	283.9	285.0	286.9	288.5								
m.g.	11.2		0.13	85	8.5	6.5	—	284.1	285.0	286.6	—								

^a u.g. = unground; m.g. = mortar ground; mech. g. = ground in mechanical grinder.

TABLE III
ESCA Results for SCE Solid Residues^a

Sample designation	Spectrum	E_c (eV)	O_{1s} peaks							
			Area (%)				Binding energy (eV)			
			O_0	O_1	O_2	O_3	O_0	O_1	O_2	O_3
<i>Populus tremuloides</i>	PT	2.0	—	17	74	9	—	532.0	533.2	534.1
MP-22										
u.g.	22.1	1.0	15	29	56	—	531.1	532.3	533.2	—
m.g.	22.2	1.0	11	22	67	—	531.3	532.4	533.2	—
mech. g.	22.3	0.7	6	22	72	—	530.5	532.0	533.2	—
MP-6										
u.g.	6.1	1.2	3	16	81	—	530.1	531.6	533.2	—
m.g.	6.2	2.6	6	25	69	—	530.6	532.2	533.2	—
mech. g.	6.3	0.8	8	24	68	—	530.5	532.0	533.2	—
MP-16										
u.g.	16.1	0.4	6	25	69	—	530.2	531.8	533.2	—
m.g.	16.2	0	16	43	41	—	530.2	532.0	533.2	—
mech. g.	16.3	1.5	17	39	44	—	530.3	531.9	533.2	—
MP-13										
m.g.	13	2.1	8	34	58	—	530.2	532.0	533.2	—
MP-20										
m.g.	20	1.3	5.5	21.5	56	17	529.9	531.7	533.2	534.7
MP-11										
u.g.	11.1	0.5	17	46	37	—	530.5	531.8	533.2	—
m.g.	11.2	0.9	22	53	25	—	530.6	532.1	533.2	—

^aSee footnote to Table II.

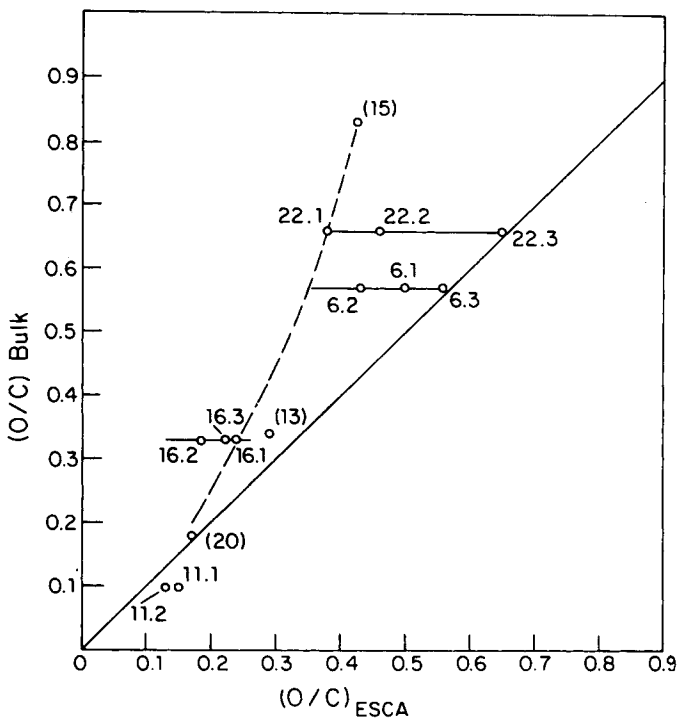


Fig. 1. Comparison of O/C ratio measured by elemental analysis and ESCA.

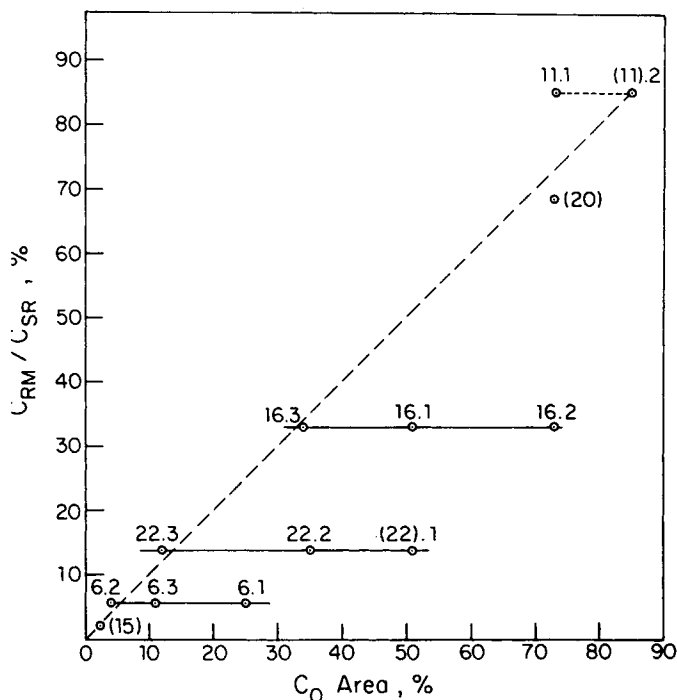


Fig. 2. Comparison of the weight fraction of the carbon residue in recondensed material and the C_0 fraction in C_{1s} ESCA spectra.

ence of more extractive on the surface of 6.2 than 6.1. Therefore, this partial grinding could have detached a superficial layer of recondensed material, exposing a yet unconverted layer of the middle lamella.

It is interesting to note from Figure 2 that the ratio C_{RM}/C_{SR} is very close to the percentage of C_0 in the total C_{1s} peak measured by ESCA, in the case of the higher severity grinding for all the samples studied. This observation confirms the previous assignment¹ for the C_0 component which appears here as identical with the carbon in highly recondensed polyaromatic material.

The behaviors of samples MP16 and MP11 upon grinding will be better understood by considering Figure 3. In this figure, the $(O/C)_{ESCA}$ ratio is plotted as a function of the C_0 percent area. Such a diagram may be considered as a ternary diagram depicting the surface composition of a given sample as a mixture of three different reference surfaces represented by points *A*, *B*, and *C* on this graph. Point *A* is the experimental point for the wood surface, which is believed to be actually the surface of middle lamellas, as already discussed. Point *C* is the hypothetical point for a surface entirely made of polyaromatic carbon namely at 100% C_0 and $(O/C)_{ESCA}$ equal to zero. Point *B* was obtained at the intersection of the experimental line joining point *C* with a series of our experimental points including those for spectra 11.2, 22.1, and 22.3. Point *B* may be viewed as corresponding to an average (O/C) value for a mixture of lignin, cellulose, and hemicellulose in a wood sample which would be completely free of extractives. The value of $(O/C) =$

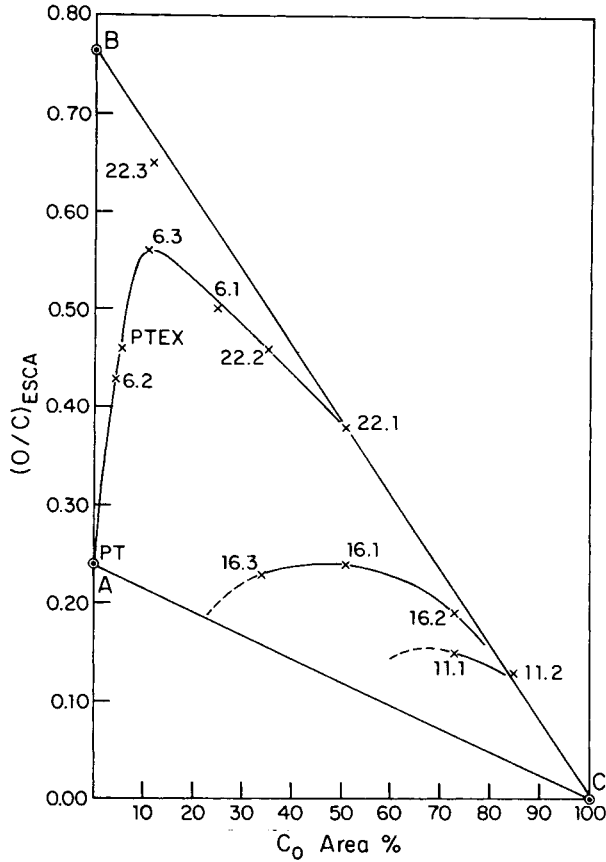


Fig. 3. Diagram showing (O/C) as a function of C₀ from ESCA spectra.

0.76 found from the graph is indeed very close to the bulk value of 0.77 of wood.

Therefore, on such a graph, a surface sample represented on the *BC* line is considered free of extractives. As the three points 22.1, 22.2, and 22.3 lie almost on this line it may be concluded that sample MP22 has been entirely freed from any extractives.

Point 6.1, which corresponds to the composition of the peripheral surface of the fibers in sample MP6, shows a rather high polyaromatic content (high C₀) and a low extractives content (proximity to the *BC* line), suggestive of a partial extraction of these extractives. Indeed the 6.2 point shows, as discussed previously, a much lower C₀ content and a higher extractive content, indicating that the surface exposed by this mild grinding is still closer from the composition of middle lamellas than the surface of the fibers before grinding.

As a matter of fact we have placed in Figure 3 the point representative of a wood sample having been submitted to benzene-alcohol extraction (PTEX). A common line may be drawn joining point A, 6.2, PTEX, and 6.3, suggesting that surface compositions represented by points 6.2 and 6.3 may be obtained from a middle lamella surface submitted to extraction. One may wonder why

the extraction process generates some C_0 as indicated by point PTEx. Although this has not yet been explained, a similar result with a nonzero C_0 has been observed for solvent extracted cotton linters.⁶

Thus samples MP22 and MP6, although they have both been prepared at 250°C, show different kinds of heterogeneity probably associated with their different extraction histories, sample MP22 being much more free of extractives.

The curves representative of samples MP16 and MP11 show that both spectra 16.1 and 11.1 are reminiscent of the extractives in middle lamella. A mild grinding, which in the case of sample MP11 is sufficient to produce a very thin powder, exposes a surface containing more recondensed polyaromatic material. Curiously the thorough grinding of sample MP16 exposes a surface (16.3) closer to the AC line, indicating the presence in the bulk of material derived from extractives. The small distance between points representing samples 11.1 and 11.2 indicates that the solid carbonaceous residue produced at 350°C is much more homogeneous than samples prepared at lower temperatures.

Figures 4 and 5 underline yet another aspect of ESCA analysis, namely the ability to characterize the functionality of the element detected. Figure 4 for example is a ternary diagram of the variables C_0 , C_1 , and $C_2 + C_3$. C_0 as mentioned before, is the carbon in recondensed material, C_1 is the carbon in

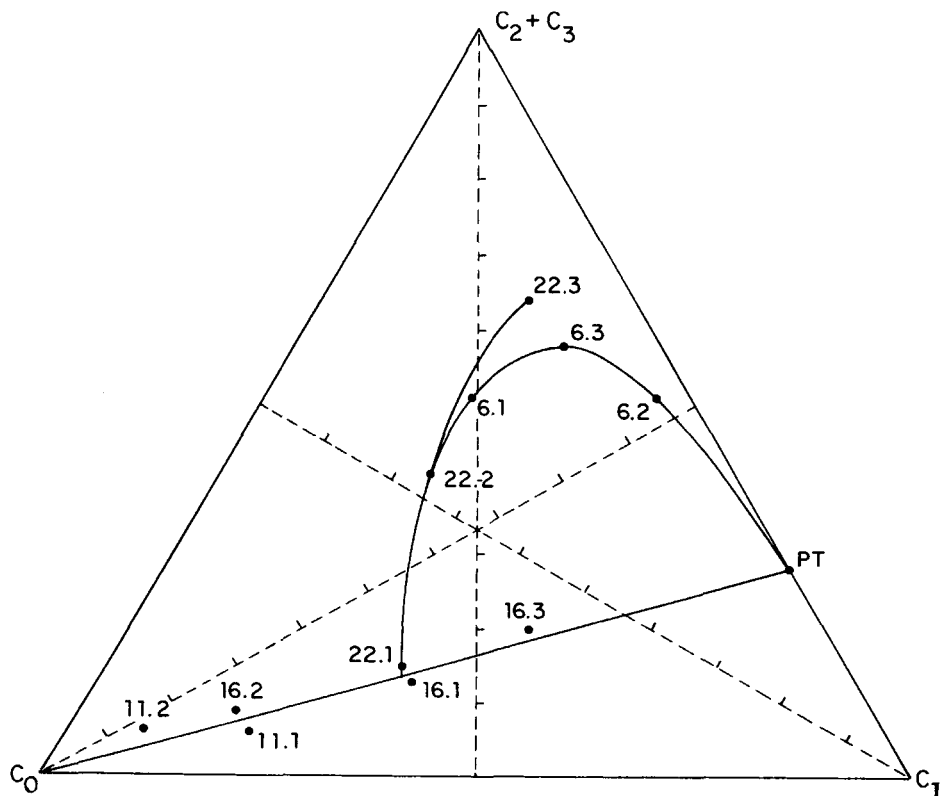


Fig. 4. Ternary diagram showing the distribution of carbon components in C_{1s} ESCA spectra.

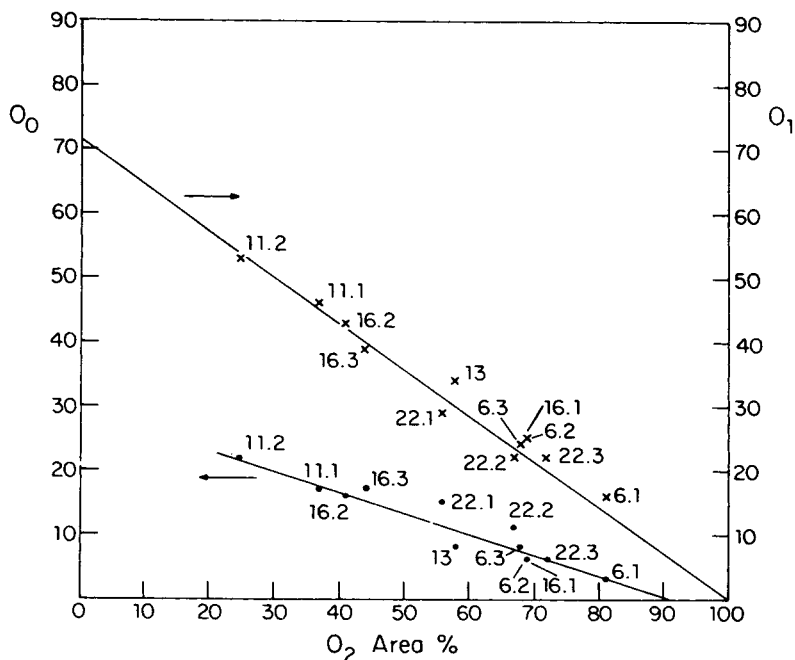


Fig. 5. Correlation between O_0 , O_1 and O_2 in O_{1s} ESCA spectra.

aliphatic and aromatic hydrocarbons whereas C_2 and C_3 are respectively carbons with one or two links to oxygen. Figure 4 shows that all the points corresponding to samples prepared at SCE temperatures of 300 and 350°C lie very close to a line joining the point PT which represents the surface of the middle lamella in wood, to the point C_0 corresponding to pure polyaromatic carbon. As suggested in the discussion of Figure 3, those materials would therefore have a surface composition close to the one of a mixture of middle lamella and recondensed material.

All samples produced at 250°C lie above the PT- C_0 line on this diagram. This is in agreement with the high content in nonconverted or mildly converted carbohydrates still present in these solids, which contain carbons linked to oxygen. The point representing sample 22.1 lies almost on the PT- C_0 line. This is fortuitous as the discussion of Figure 3 has indicated that extractive material is completely absent from sample MP22. The rather high C_1 value observed in this sample must therefore correspond either to carbon in the aromatic rings in lignin or from hydrocarbons chains arising from the conversion of polysaccharides.

Figure 5 gives the variations of the components O_0 and O_1 with the O_2 component of the O_{1s} peak.

No definite identification is available for these various oxygen peaks except for the component O_2 which is the only one found in the spectrum of cellulose. As a consequence, oxygens in alcoholic OH groups and in ether bridges are belonging to component O_2 . We have given recently¹ tentative assignments to components O_1 , O_2 , and O_3 , according to which O_1 would include benzylaryl ethers and diaryl ethers. The linear increase in O_1 as O_2 decreases is therefore

suggestive of the condensation reactions of polysaccharides (rich in O_2) yielding aryl-aryl or benzyl-aryl ether bridges (O_1). However, this assignment of O_1 is not considered very sound so that this conclusion should be made with caution.

The O_0 component of the O_{1s} peak is not really identified. It was suggested earlier¹ that this could be associated with oxygen in water strongly adsorbed on highly carbonized material. It was also reported in the literature^{7,8} that the surface of polyaromatic materials such as high rank coals having bulk (O/C) ratio of the order of 0.1 are covered with physisorbed oxygen. It is, however, hard to believe that physisorbed oxygen not chemically bound could stay on the surface in the high vacuum environment of the ESCA spectrometer.

Moreover, Figure 5 indicates a rather good correlation between O_0 and O_2 . This correlation is more suggestive of a conversion of one functional form of oxygen into the other rather than of O_0 being an adsorbed essentially randomly variable species.

The good correlations shown in Figure 5 between O_0 or O_1 and O_2 indicates that precise information regarding the composition of the sample surface would be available if a clear assignment could be made for the various components of the O_{1s} ESCA peaks.

CONCLUSIONS

This work illustrates the potential of the ESCA technique to provide information on the spatial distributions of the various components of a partially converted lignocellulosic sample. It was, for example, established that in the early stages of the SCE process the recondensed material which includes polyaromatic carbon is located at the peripheral surface of the wood fiber. This is true whether this surface has been preliminarily freed of its extractives (like in sample MP22) or if it has the same composition as middle lamella (like in sample MP6).

The distribution of the various carbon components which may be distinguished in the C_{1s} peak is specially informative, as illustrated in Figure 4. In particular the solids still containing nonconverted or mildly converted carbohydrates, and therefore still liable to yield oils by further thermal treatment, are characterized by a higher value of the $C_2 + C_3$ carbons. A highly converted sample containing more recondensed material shows higher values of the C_0 carbon.

The spectra of O_{1s} which cannot yet be completely understood are, however, showing the promise of more chemical information as they show an orderly variation of the various oxygen components which can be quantified from these spectra.

References

1. A. Ahmed, A. Adnot, and S. Kaliaguine, *J. Appl. Polym. Sci.*, **34**, 359-375 (1987).
2. M. Poirier, A. Ahmed, J. L. Grandmaison, and S. Kaliaguine, *Ind. Eng. Chem., Prod. Res. Dev.*, **26**, 1738-1743 (1987).
3. A. Ahmed, J. L. Grandmaison, and S. Kaliaguine, *J. Wood Chem. Techn.*, **6**(2), 219-248 (1986).

4. J. L. Grandmaison, J. Thibault, S. Kaliaguine, and P. D. Chantal, *Anal. Chem.*, **59**, 2153-2157 (1987).
5. J. L. Grandmaison, A. Ahmed, and S. Kaliaguine, *Am. Chem. Soc., Prepr. Fuel Div.* **32**(2), 157-166 (1987).
6. A. Ahmed, A. Adnot, J. L. Grandmaison, S. Kaliaguine, and J. Doucet, *Cell. Chem. Technol.*, to appear.
7. J. S. Mattson and H. B. Mark, Jr. in *Activated Charcoal*, Dekker, New York, 1971.
8. T. T. P. Cheung, *J. Appl. Phys.*, **53**(10), 6857-6862 (1982).

Received June 1, 1987

Accepted August 18, 1987