

# $^{13}\text{C}$ Solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork

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## Abstract

The thermal decomposition of cork has been studied by Fourier transform infrared (FTIR) spectroscopy and  $^{13}\text{C}$  solid-state nuclear magnetic resonance (NMR) spectroscopy with cross-polarization and magic-angle spinning (CP-MAS), high-power  $^1\text{H}$  decoupling (HPDEC) and cross-polarization depolarization–polarization (CPDP). Waxes and other soluble components of cork begin to decompose at ca. 150°C. This is accompanied by partial decomposition of suberin, probably initiated at the points of attachment to the cell wall. The carbohydrates begin to decompose at ca. 200°C. The decomposition of lignin begins at 250–300°C, while suberin undergoes further degradation. Significant amounts of coke are formed in the process. At 400°C cork has been transformed into coke with traces of partially decomposed suberin. The thermal decomposition of cork is dependent on the calcination time, particularly in the 200–350°C range.

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## 1. Introduction

Cork, the bark of *Quercus suber* L., is a material widely used for stoppers, insulating and decorative panels, floors and walls. Cork is composed of suberin (40%), lignin (22%), polysaccharides (20%) and waxes and other extractives (15%) [1]. Thermal decomposition of cork has been studied by thermogravimetry [2], chemical methods [3], scanning electron microscopy [3] and mass spectrometry [4]. Significant mass losses begin at 200°C

and increase rapidly until ashing at ca. 450°C [2,3]. Chemical analysis indicates [3] that over 90% of the polysaccharides are degraded at ca. 250°C and completely disappear at higher temperatures. Suberin decomposes significantly only above 250°C, while lignin undergoes condensation reactions [3].

We have studied thermal degradation of cork using solid-state NMR and FTIR. NMR is a powerful and non-invasive tool to study wood and wood-related materials [5]. Although some suberin-containing materials have been investigated by NMR [6–10], this is, to our knowledge, the first  $^{13}\text{C}$  solid-state NMR study of cork and of the products of its thermal decomposition.

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## 2. Experimental

### 2.1. Samples

Portions (2 g) of cork powder were calcined in air at temperatures from room temperature to 600°C (in 50°C intervals) for 20, 60 and 120 min. Extractive-free cork powder was prepared by repeated Soxhlet extraction with dichloromethane (8 h) and ethanol (8 h).

### 2.2. Techniques

<sup>13</sup>C Solid-state NMR spectra were recorded at 100.6 MHz (9.4 T) on a Bruker MSL-400 spectrometer. The 4- and 7-mm double-bearing Bruker rotors were spun in air at 5.9–13 kHz. In all experiments the <sup>1</sup>H and <sup>13</sup>C 90° pulses were ca. 4 μs. The CP-MAS spectra were recorded with 3 s recycle delays and 1–13 ms contact times. The HPDEC spectra were recorded with 45° pulses and 1–100 s recycle delays. In the CPDP experiments dephasing delays of 50 to 90 μs were used. Liquid-state <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 75.4 MHz. Chemical shifts are quoted in ppm from external tetramethylsilane (TMS).

FTIR spectra of the same samples studied by NMR were recorded on a Nicolet Magna-IR 550 spectrometer using the conventional KBr wafer technique. To obtain the difference spectra it was necessary to use a different calcination procedure. A KBr pellet was calcined at the desired temperature for 20 min and cooled down to room temperature, and the spectrum was measured. Then the same pellet was heated up to a temperature 50°C higher and cooled down, and the spectrum was recorded again. The procedure was repeated from room temperature up to 600°C.

## 3. Results and discussion

<sup>13</sup>C CP-MAS spectra of cork are given in Figs. 1–3. Fig. 4 shows HPDEC spectra, and Table 1 gives the assignment of resonances. Since no difference was observed between the spectra of uncalcined cork and cork treated at 100°C, only the

latter are shown. Two main peaks at ca. 30 and 33 ppm are present in the aliphatic region along with a large number of faint lines [13]. The strong peaks at 30 and 33 ppm are due to (CH<sub>2</sub>)<sub>n</sub> suberin carbons perhaps with some small contribution from (CH<sub>2</sub>)<sub>n</sub> low-molecular-weight extractable compounds. Removal of these compounds upon solvent extraction does not change significantly the relative intensities of the two lines (Fig. 5a). However, liquid-state spectra of the extracted materials (Fig. 5b and c) do contain strong peaks at ca. 28–30 ppm. Note also that many of the faint aliphatic peaks and the sharp signals at 59.3 and 53.9 ppm are absent from the spectrum of the material after extraction. Together, CPDP (Fig. 6), CP-MAS (Fig. 3) and HPDEC (Fig. 4) spectra clearly show that the 30- and 33-ppm peaks come from different kinds of (CH<sub>2</sub>)<sub>n</sub> carbons. The 30-ppm peak is composed of at least three resonances. The suberin methylenes giving the 33-ppm peak experience strong <sup>1</sup>H–<sup>13</sup>C dipolar interactions which completely dephase the CPDP signal (Fig. 6), and are therefore motionally restricted. The 30-ppm methylene population is, comparatively, rather mobile. These results are consistent with the suggestion that some portions of the polymer chain in suberin-containing materials are closer than others to points of covalent attachment to the cell wall [7,8,10]. The methoxy peak at 55.8 ppm is given by both lignin and hemicellulose (methylglucuronoxilanes). However, cork contains a relatively small (ca. 8–10%) amount of hemicellulose [1] and, therefore, this peak can be used to monitor the transformation of lignin. On the other hand, hemicellulose gives a signal at 21.0 ppm (Fig. 3) which is indeed seen in the spectra of our cork materials calcined up to 200–250°C. This peak is always rather faint confirming that a small amount of hemicellulose is present. The lines at 71.9 and 74.3 ppm come from cellulose and hemicellulose but lignin also contributes some intensity in the range 72–75 ppm. The peaks in the range 82–90 ppm have contributions from both cellulose and lignin. To monitor the decomposition of cellulose is, hence, necessary to follow simultaneously changes in the methoxy peak at 55.8 ppm (lignin), in the lines at 71.9 and 74.3

ppm and in the range 82–90 ppm. The COO peaks at 166.5 and 172.6 ppm are from suberin and hemicellulose. They can be used to trace the decomposition of suberin. Consider the following temperature regions.

### 3.1. Room temperature to 200°C

The intensity of the 33-ppm line sharply decreases in intensity (Fig. 7). The aliphatic peaks on both sides of the 30- and 33-ppm lines disappear, but the resonances at ca. 14.5, 16.5, 41.2 and 42.7 ppm remain. Fig. 3 also shows that the sharp peaks at 59.3 and 53.9 ppm disappear. This suggests that partial decomposition of suberin occurs probably at the points of attachment to the cell wall and that the waxes and other extractives are decomposed. At 200°C, the peaks at 74 and 82 ppm decrease in intensity while the methoxy resonance at 55.8 ppm remains un-

changed. This clearly indicates that the decomposition of carbohydrates has begun.

### 3.2. From 200 to 350°C

Major changes occur in this range. At 350°C the peak at 33 ppm becomes a high-frequency shoulder on the 30-ppm signal (Fig. 2). The continuing presence of the peaks at ca. 14.5, 41.2 and 42.7 ppm indicates that they are probably not associated with waxes, but with suberin and lignin. A considerable loss in signal intensity is observed in the range 55–90 ppm, particularly at 65–105 ppm. The intensity of the COO peak at 172.6 ppm also decreases and the peak at 166.5 ppm is no longer clearly seen in the CP-MAS spectrum recorded with a 1.5-ms contact time although it is still observable in the 11-ms contact time spectrum as a rather faint signal. This shows that the carbohydrates have been decomposed and that

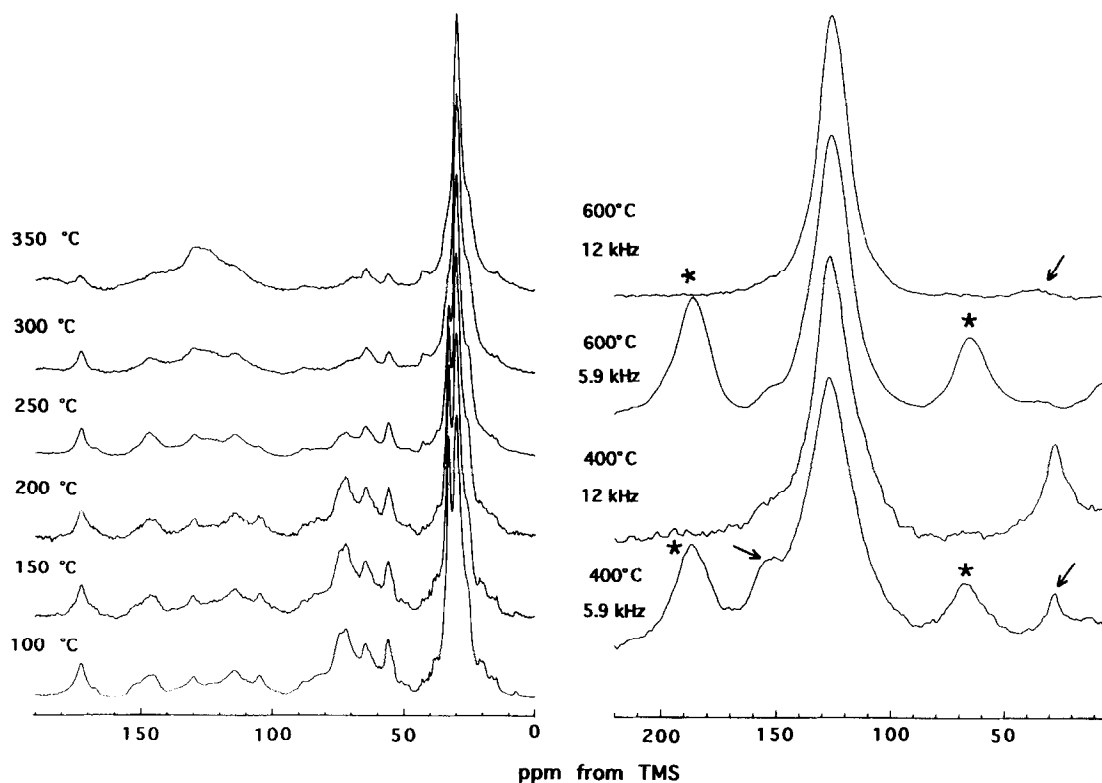


Fig. 1.  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS spectra recorded at 100.6 MHz of cork calcined in air for 20 min at the temperatures indicated. A contact time of 1.5 ms and spinning rates of 5.9 and 12 kHz (400 and 600°C) were used. Asterisks denote spinning sidebands.

the decomposition of lignin has also begun. Simultaneously, a broad signal centred at 125–130 ppm begins to grow. This peak, which is first seen at about 250°C, indicates that significant amounts of coke have formed. With MAS at 5.9 kHz spinning sidebands from this signal contribute some intensity at 70 ppm. This was confirmed by recording the spectra with a spinning rate of 13 kHz (not shown). At ca. 300°C the peaks at 151.5 ppm almost disappear. Again, this is consistent with degradation of lignin and suberin. At 350°C a broad signal begins to grow at ca. 153 ppm. This resonance is clearly seen at 400°C (in Fig. 1 the peak is marked by an arrow). We suggest it is due to some product of the lignin and suberin degradation.

### 3.3. Above 350°C

At 400°C a broad peak centred at 127 ppm, characteristic of aromatic carbon, dominates the spectra. A shoulder is also seen at ca. 153 ppm. No COO or methoxy signals are observed. The aliphatic region displays a peak at 29 ppm. This is clearly seen in the spectrum recorded with MAS at 12 kHz (Fig. 1). Since the intensity of this peak decreases with increasing temperature, this might indicate that suberin is not yet fully decomposed at 400°C (20 min).

We see that the thermal decomposition of cork depends on the experimental conditions, particularly in the range 200–350°C (see Fig. 8).

FTIR supports the conclusions drawn from

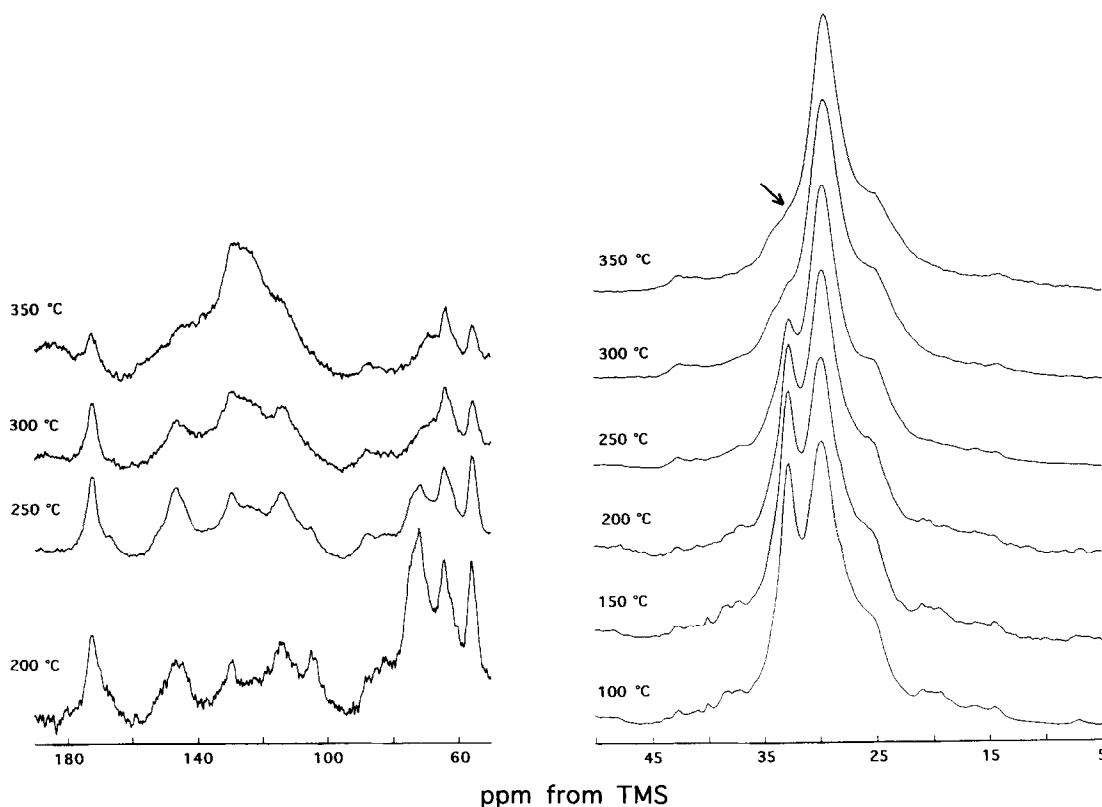


Fig. 2. Selected regions of the  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS spectra recorded at 100.6 MHz (with 11 ms contact time and a spinning rate of 5.9 kHz) of cork calcined in air for 20 min at the temperatures indicated. In both spectral regions the peak heights were normalized to the intensity of the 30-ppm peak.

solid-state NMR. The extensive overlap of bands in the room temperature FTIR spectrum of cork (see Fig. 9) reflects the complex nature of the material. Table 2 summarizes the assignments of some of the bands in the FTIR spectrum. The broad OH stretching band at  $3425\text{ cm}^{-1}$  comes from water and the carbohydrate hydroxyls. The

two sharp peaks in the CH stretch region accommodate signals from suberin, lignin, carbohydrates and extractives. The strong CO stretch band at  $1747\text{ cm}^{-1}$  is characteristic of ester groups and should thus originate mainly from suberin. A weaker shoulder at  $1719\text{ cm}^{-1}$  is due to a lower quantity of acidic groups. The aromatic region

Table 1  
 $^{13}\text{C}$  NMR assignments of cork components

Chemical shift		Assignment	Ref.
This work	Literature		
7.2–19.6	–	Extractives	–
21.0	22	$\text{CH}_3\text{-COO-}$ , hemicellulose	[12]
25–28	–	Extractives	–
29.9	30	$-(\text{CH}_2)_n-$ , suberin	[8], [10]
32.8	33	$-(\text{CH}_2)_n-$ , suberin	[8], [10]
37.2–53.9	–	Extractives	–
55.8	56	Ar-OCH <sub>3</sub> , lignin	[5], [12]
		-OCH <sub>3</sub> , hemicellulose	[11]
		-OCH <sub>3</sub> , suberin	[8], [10]
59.3	–	Extractives	–
61–62	63 (sh.)	C $\gamma$ -OH, C $\beta$ -OAr, lignin	[5]
	62	C6, cellulose	[12], [11]
	62	C6, carbohydrate attached to suberin	[8]
64.4	66	C6, cellulose	[12], [11]
71.9	72.6	C2, C3, C5, cellulose + hemicellulose	[12], [11]
	72	C2, C3, C5, carbohydrate attached to suberin	[8]
74.3	75.3	C2, C3, C5 cellulose + hemicellulose	[12], [11]
	72–75	C $\gamma$ -OR, C $\beta$ -OR, lignin	[5]
82.0	83	C4, carbohydrate attached to suberin	[8]
	84 (sh.)	C4, cellulose	[12], [11]
88.0	89	C4, cellulose	[12], [11]
	84–90	C $\beta$ -OR, C $\alpha$ -OR, lignin	[5]
104.7	101	C1, carbohydrate attached to suberin	[8], [10]
	103 (sh.)	C1, carbohydrates	[12], [11]
	105	C1, cellulose	[12], [11]
	105	-CH = CH-, suberin	[8]
	102–106	G2, S2, S6, lignin	[5]
114	113–116	G5, lignin	[5]
	115	-CH-, aliphatic and aromatic, suberin	[8]
122–126	123–125	G6, C $\beta$ , lignin	[5], [11]
129.5	127	Quaternary C, aromatic, suberin	[8]
	130	C $\alpha$ , lignin	[5]
146	148	G4, S4, lignin	[5]
151–152	150	Quaternary C, aromatic, suberin	[8]
	154	G3, S3, S5, lignin	[5]
166.5	(168)	(Ester group in intact cutin)	[6]
172.6	172	-COO-, suberin	[8], [10]
	(173)	(Ester group in intact cutin)	[6]
	174	$\text{CH}_3\text{-COO-}$ , hemicellulose	[12]
		-COOH, hemicellulose (uronic acids)	[12]

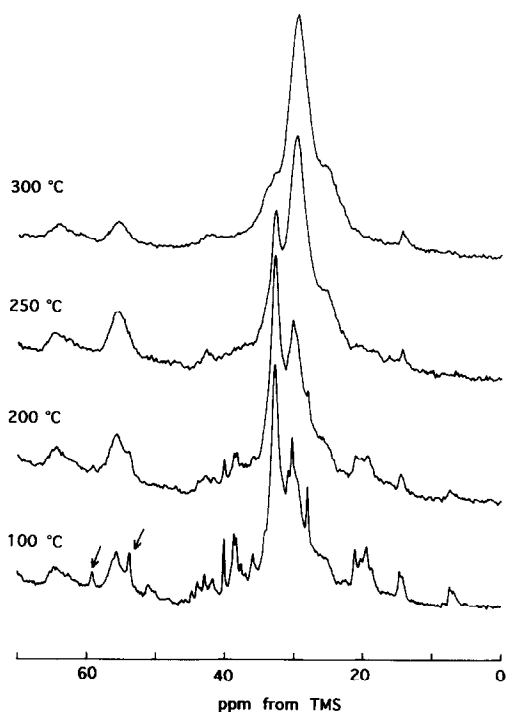


Fig. 3. Region of the  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS spectra recorded at 100.6 MHz (with 11 ms contact time and a spinning rate of 5.9 kHz) of cork calcined in air for 20 min at the temperatures indicated.

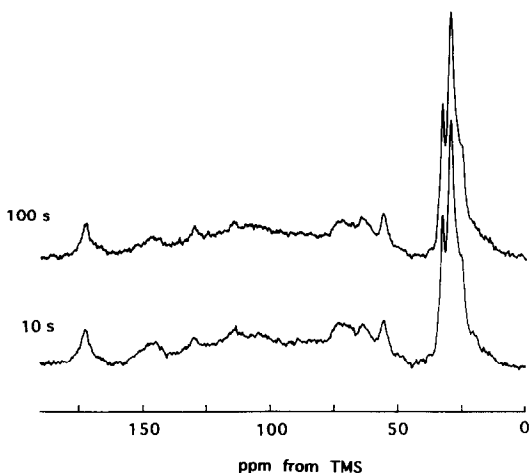


Fig. 4.  $^{13}\text{C}$  MAS spectra recorded at 100.6 MHz with high-power  $^1\text{H}$  decoupling. The recycle delays used are indicated. The spinning rate was 5.9 kHz.

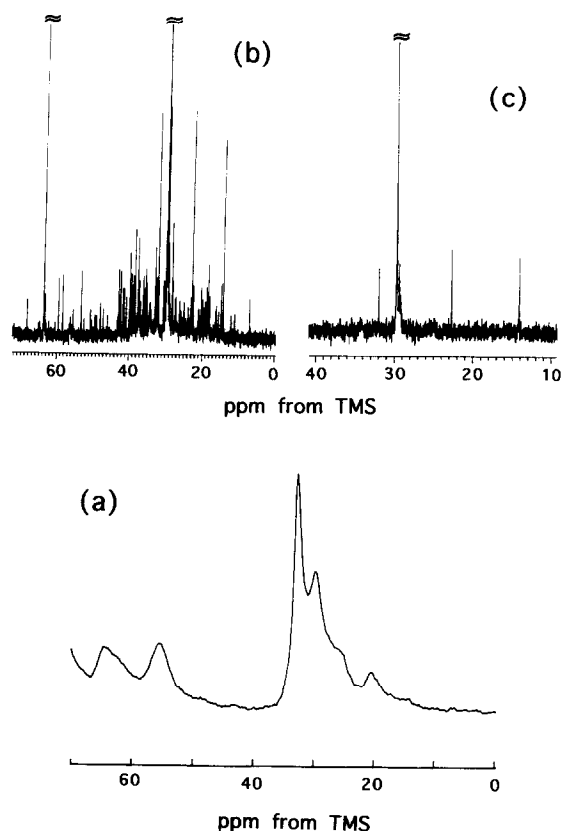


Fig. 5. (a) Solid-state  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS spectrum recorded at 100.6 MHz (with 11 ms contact time and a spinning rate of 5.9 kHz) after treating cork with dichloromethane and ethanol. Liquid-state spectra recorded at 75.4 MHz of the materials extracted from cork after treatment with (b) dichloromethane and (c) ethanol.

( $1600$ – $1500\text{ cm}^{-1}$ ) has contributions from lignin, suberin and minor components such as tannins and other extractives. The peak at  $1513\text{ cm}^{-1}$  has been used to monitor structural changes in the extracted lignin fractions [16]. Suberin may, however, have a significant contribution to this peak. In the fingerprint region ( $1200$ – $900\text{ cm}^{-1}$ ) suberin ester groups should contribute to the absorbance at  $1263$  and  $1164\text{ cm}^{-1}$  (Table 2). The latter band includes contribution of lignin methoxy groups, and cellulose and hemicellulose also absorb strongly in this region.

Upon heating the cork to  $150^\circ\text{C}$  slight intensity reductions are seen in the fingerprint region of

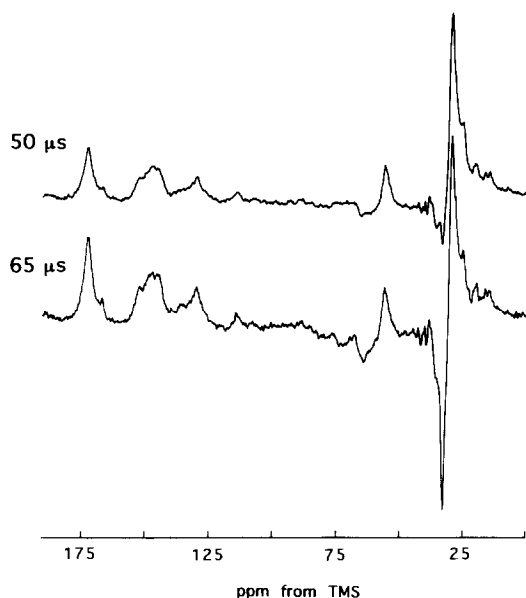


Fig. 6. Cross-polarization depolarization–polarization  $^{13}\text{C}$  spectra recorded at 100.6 MHz (using the dephasing delays depicted) of cork.

the spectrum (not shown). The corresponding difference spectrum confirmed that these changes reflect the early loss of extractives. In addition, a shift to lower wave numbers of the  $1747\text{ cm}^{-1}$  band is visible at  $150^\circ\text{C}$ . By heating up to  $250^\circ\text{C}$  the intensities of the peaks at  $1100$  and  $1036\text{ cm}^{-1}$  decrease relatively to the peaks at  $1164$  and  $1263\text{ cm}^{-1}$ . This shows that carbohydrate degradation is occurring prior to degradation of lignin and suberin, since both of these components have

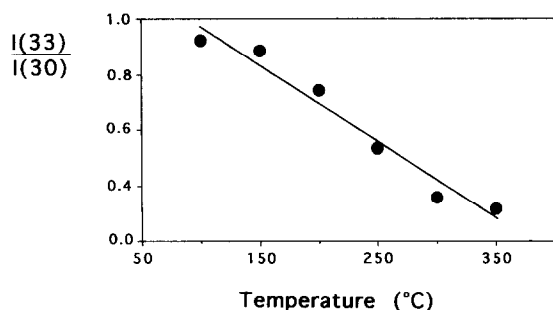


Fig. 7. Plot of the height ratios of the  $^{13}\text{C}$  CP-MAS peaks at 33 and 30 ppm as a function of temperature revealing a linear dependence (correlation 0.96).

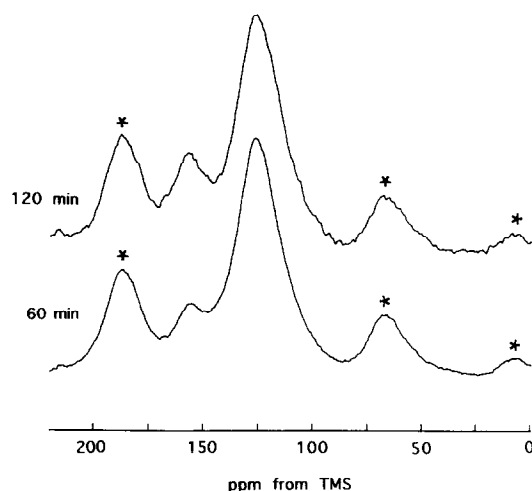


Fig. 8.  $^1\text{H}$ – $^{13}\text{C}$  CP-MAS spectra recorded at 100.6 MHz (with 1.5 ms contact time and a spinning rate of 5.9 kHz) of cork calcined in air for 60 and 120 min at  $350^\circ\text{C}$ . Asterisks denote spinning sidebands.

strong contributions to the latter peaks. The less marked intensity decrease of the lines at  $1513$  and  $1740\text{ cm}^{-1}$  confirm that lignin and suberin remain more resistant to thermal degradation than the carbohydrates. At  $250^\circ\text{C}$  the intensity decrease at  $1513\text{ cm}^{-1}$  is accompanied by a de-

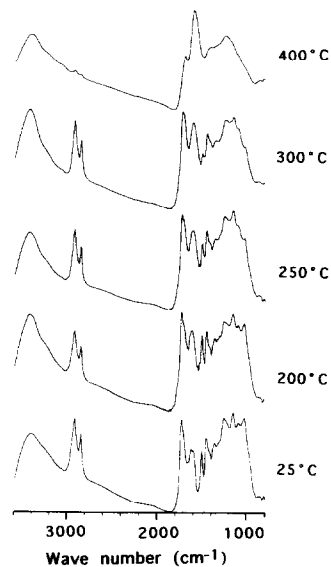


Fig. 9. FTIR spectra of cork calcined in air for 20 min at the temperatures indicated.

Table 2  
Infrared assignments of cork components

Wavenumber (cm <sup>-1</sup> )	Description	Assignment
3425	OH stretch	Water, hemicellulose [14], cellulose [14]
2919	CH aliph. stretch	Extractives, suberin, hemicellulose, cellulose, lignin [14]
2849	CH aliph. stretch	Extractives, suberin, hemicellulose, cellulose, lignin [14]
1747	C = O stretch	Extractives, suberin, hemicellulose, cellulose, lignin [14]
1719	C = O stretch	Hemicellulose, cellulose, extractives
1635	C = C stretch	Suberin, extractives
1607	C = C stretch	Extractives [15], suberin, lignin [14]
1513	C = C stretch	Extractives [15], suberin, lignin [14]
1466	CH asym. deformation	Extractives, suberin, hemicellulose, cellulose, lignin [14]
1366	CH sym. deformation	Extractives, suberin, hemicellulose, cellulose, lignin [14]
1263	CO stretch	Suberin, hemicellulose [4], cellulose [4], lignin [14]
1164	CO asym. stretch	Suberin, hemicellulose [15], cellulose [15], lignin [14]
1101	CH, CO deformation	Hemicellulose [15], cellulose [15], lignin [14]
1036	CH, CO deformation	Hemicellulose [14,15], cellulose [14,15], lignin [14]

crease at 1160 cm<sup>-1</sup>. The latter is seen clearly in the 250–200°C difference spectrum (not shown). This is due to degradation of one or both of the components lignin and suberin. Simultaneously, the broad band centred at 1620 cm<sup>-1</sup> begins to grow indicating the formation of coke. At 300°C the bands at 1513 and 1164 cm<sup>-1</sup> are further weakened relatively to the CO stretch ester band. This suggests that the degradation of lignin occurs preferentially to that of the remaining suberin. However, the 1740 cm<sup>-1</sup> band shifts to 1736 cm<sup>-1</sup> and decreases its intensity relative to the shoulder at 1719 cm<sup>-1</sup>, thus confirming that suberin is also undergoing thermal decomposition. At 350°C the 1513 cm<sup>-1</sup> band disappears almost completely as well as the lignin methoxy-contributed band at 1160 cm<sup>-1</sup>. At the same time, the 1735 cm<sup>-1</sup> band reduces to a weak shoulder and the centre of the CO stretch band shifts to 1705 cm<sup>-1</sup>, indicating the formation of acidic decomposition products. Above 350°C the growth of an aromatic band at 1620 cm<sup>-1</sup> and of a featureless band at 1500–1000 cm<sup>-1</sup> dominates the FTIR spectra showing the expected conversion of cork into coke.

#### 4. Conclusions

<sup>13</sup>C NMR and FTIR indicate that thermal degradation of cork components begin at temper-

atures around 150°C. Polysaccharides, waxes and other extractives are decomposed at the early stages of the process. Partial degradation of suberin begins at 150°C starting probably at points of attachment to the cell wall. The major structural modifications of cork components take place between 200 and 350°C. The decomposition of lignin begins at 250–300°C. Even at temperatures as high as 350–400°C, traces of partially decomposed suberin are present along with significant amounts of coke. This may explain why cork maintains its basic cellular structure at relatively high temperatures (ca. 350°C) [3].

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#### References

- [1] H. Pereira, *Wood Sci. Technol.*, 22 (1988) 211.
- [2] M. Emília Rosa and M.A. Amaral Fortes, *J. Mat. Sci. Lett.*, 7 (1988) 1064.
- [3] H. Pereira, *Wood Sci. Technol.*, 26 (1992) 259.
- [4] M. Filomena Bento, M. Aurea Cunha, A.M.C. Moutinho, H. Pereira and M.A. Fortes, *Int. J. Mass Spectrom. Ion Processing*, 112 (1992) 191.



- [5] G.R. Hatfield, G.E. Maciel, O. Erbatur and G. Erbatur, *Anal. Chem.*, 59 (1987) 172.
- [6] T. Zlotnik-Mazori and R.E. Stark, *Macromolecules*, 21 (1988) 2412.
- [7] R.E. Stark, T. Zlotnik-Mazori, L.M. Ferrantello and J.R. Garbow, *Am. Chem. Soc. Symp. Series*, 399 (1989) 214.
- [8] J.R. Garbow, L.M. Ferrantello and R.E. Stark, *Plant Physiol.*, 90 (1989) 783.
- [9] J.R. Garbow and R.E. Stark, *Macromolecules*, 23 (1990) 2814.
- [10] R.E. Stark and J.R. Garbow, *Macromolecules*, 25 (1992) 149.
- [11] W. Kolodziejcki, J.S. Frye and G.E. Maciel, *Anal. Chem.*, 54 (1982) 1419.
- [12] J.F. Haw, G.E. Maciel and H.A. Shroeder, *Anal. Chem.*, 56 (1984) 1323.
- [13] J. Rocha, A. Gil, C. Pascoal Neto, A.P. Esculcas and J.D. Pedrosa de Jesus, in preparation.
- [14] N. Morohoshi, in D.N.-S. Hon and N. Shiraishi (Eds.), *Wood and Cellulosic Chemistry*, Marcel Dekker, New York and Basel, 1991, p. 331.
- [15] M.C. Maccann, M. Hammouri, R. Wilson, P. Belton and K. Roberts, *Plant Physiol.*, 26 (1992) 259.
- [16] D. Stewart and I.M. Morrison, *J. Sci. Food Agric.*, 60 (1992) 431.