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Characterization and comparison of two ligno-cellulosic substrates by ^{13}C CP/MAS NMR, XPS, conventional pyrolysis and thermochemolysis

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Abstract Ligno-cellulosic substrates (LCSs) isolated from wheat straw and bran exhibit high complexing capacities and may have important applications for metal removal from industrial effluents. These two LCSs were examined in the present work by spectroscopic and pyrolytic methods (solid state cross polarization magic angle spinning (CP/MAS) ^{13}C NMR, XPS, conventional Curie pyrolysis (Cupy)/GC/MS, and TMAH thermochemolysis/GC/MS). This combined study highlighted the limitation of some of the above methods when applied to ligno-cellulosic materials and the resulting biases and the usefulness of TMAH thermochemolysis. A large difference in composition was observed between bran- and straw-LCS due to a much higher contribution of alkyl moieties in the former. These moieties correspond to fatty acids esterified to the ligno-cellulosic macromolecular structure and such carboxylic functions should play an important role for metal complexation.

Keywords Ligno-cellulosic materials · Wheat Straw · Wheat Bran · Solid state CP/MAS ^{13}C NMR · XPS · CuPy/GC/MS · TMAH pyrolysis, thermochemolysis

Introduction

The retention properties of ligno-cellulosic substrates (LCSs) towards metal ions have been examined in several studies [1, 2, 3, 4] due to their importance for many environmental and health applications, such as the removal of metal ions from industrial effluents [1, 2, 3] and from the digestive track by sorption [4]. For the former type of application, agricultural and forest by-products (e.g. pine bark) have been studied to develop adsorption processes used as alternatives or complements to usual techniques such as precipitation or flotation [5]. Wheat bran, because of its abundance and low cost, may also represent an interesting ligno-cellulosic material for the removal of heavy metals from industrial effluents.

The interactions of metal ions with lignin and LCSs have received much less attention than humic substances [6], and the corresponding studies were chiefly concerned with the determination of sorption capacities. Furthermore, detailed information is required on the constitutive moieties and on the abundance of the functional groups involved in the complexation reactions, to better understand the sorption of metal ions on these natural organic matters.

The interactions between LCSs from wheat bran and wheat straw with several metals ions were previously examined [7, 8]. These LCSs are prepared by treatments of bran and straw with, successively, acid and alkali solutions, in order to remove starch, hemicellulose and proteins. Carboxylic and phenolic moieties were thus identified as the main functional groups in both materials. The quantification of these groups was performed by potentiometric titrations in non-aqueous medium and by Ca-acetate method for carboxylic acidity [7, 9]. It was also possible to correlate the sorption capacity of straw- and bran-LCSs towards metal copper ions with the relative abundance of their functional groups. It appeared that the total exchange capacities for protons and copper ions are of 1.0 and 0.3 mmol g^{-1} for the bran-LCS and of 0.5 and 0.1 mmol g^{-1} for the straw-LCS, respectively.

The present paper deals with the characterization and comparison of bran- and straw-LCSs. A combination of studies by CP/MAS ^{13}C NMR, XPS and Py-GC-MS was used to derive information on their molecular composition. The pyrolysis experiments were performed in the absence (conventional pyrolysis) and the presence of tetra-

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methylammonium hydroxide (TMAH thermochemolysis). The latter method, when compared to conventional pyrolysis, affords a more efficient cleavage of the macromolecular structures and a more efficient detection of some polar products through methylation. The results from the pyrolysis experiments were also compared to those previously obtained on pure cellulose and lignin samples under the same conditions[10].

Materials and methods

For characterization, all the reagents used were of highest available purity (Aldrich and Fluka). For sample preparation, all reagents used were at least of purum grade.

Sample preparation

Agro Industrie Recherche Développements (ARD) provided the wheat bran used in this study. The air-dried, coarsely powdered wheat bran (30 g) was subjected to two successive treatments without light protection: (i) acidic hydrolysis by 2 M H_2SO_4 (1/1 wt/wt of dry matter, at 100 °C for 30 min) to remove the starch, proteins, and sugars, and (ii) alkali treatment by 0.01 M NaOH (ratio bran/sodium hydroxide 10, stirring for 4 days at room temperature) to remove the low molecular weight lignin compounds by filtration. The solid was then stirred with 0.04 M HNO_3 for 4 h, washed with deionized water until the pH reached a constant value close to neutrality. LCS was isolated from straw as previously described [7]. In short, two successive treatments were applied to straw ground to coarse powder: (1) acid hydrolysis, using a straw concentration of 20 g L^{-1}, at first for 24 h at 70 °C in buffered acetic medium (pH 4.5), followed by treatment with 2 M H_2SO_4 for 0.5 h at 100 °C and (2) alkaline treatment, using a concentration of acid-treated material of 20 g L^{-1}, with 4×10^{-2} M KOH for 24 h at room temperature. After these treatments, the two LCSs were dried under vacuum, ground to a powder, and sieved at 100 μm.

Spectroscopic techniques

Solid state ^{13}C NMR spectra were obtained using the cross-polarization technique (CP) with magic angle spinning (MAS) on a Bruker MSL 400 spectrometer operating at a frequency of 75 MHz for ^{13}C, at a spinning rate of 4 kHz, with contact times ranging from 0.1 to 5 ms and a 5 s pulse delay.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry of the LCSs. Information was thus obtained on the elemental composition and the functional groups of the surface to a depth of about 0.1–1 nm. XPS spectra were recorded on a VSM-hemispheric spectrometer, with a Mg K incident X-ray beam. The X-ray source was run at 100 W and the spectra were recorded at 15 kV. The analyzer chamber pressure was in the 10^{-10} to 10^{-8} Ton range. The powdered samples were mounted on double-sided carbon tapes Binding energies were calibrated by assuming 284.6 eV for the C-C component of the C_{1s} line. Elemental composition was estimated using the area of C_{1s} and O_{1s} peaks corrected with their sensitivity factors given in a Scofield table.

Pyrolitic methods

For conventional pyrolysis (without TMAH) and TMAH thermochemolysis, the samples were loaded in small hollow ferromagnetic cylinders with a Curie temperature of 650 °C, either alone or wetted with a large excess of TMAH (25% wt./v in methanol). The sample-bearing cylinders were inductively heated to their Curie temperature in 0.15 s (10 s hold time). A Curie-point high-frequency generator was used to produce the magnetic field and the pyrolysis unit (Fisher 0316 M) was directly coupled to the GC/MS system (Hewlett Packard HP-5890 gas chromatograph and Hewlett Packard HP-5989A mass spectrometer; electron energy 70 eV; ion source temperature 250 °C; scanning from 40–650 amu; 0.7 scan s^{-1}). The partial separation of the products was achieved by a 30 m fused silica capillary column coated with chemically bound Restek RTX-5MS (0.25 mm i.d., film thickness 0.50 μm stationary phase: 5% biphenyl-95% dimethyl polysiloxane). Helium was used as carrier gas. Firstly, a stage at 50 °C for 10 min was maintained to obtain a better separation of the most volatile pyrolysis products. Secondly, the temperature of the GC oven was programmed to rise from 50 to 100 °C at a rate of 2 °C min^{-1} then from 100 to 300 °C at 4 °C min^{-1}. Compounds were identified by matching retention time and comparing the recorded mass spectra with mass spectra library (provided by HP) and mass spectra published in the literature [11, 12].

Results and discussion

Nuclear magnetic resonance spectroscopy

Solid-state CP/MAS ^{13}C NMR spectra of the two LCSs are presented in Fig. 1. The spectrum of the bran-LCS (Fig. 1a) shows several sharp resonance lines, which are characteristic of crystalline cellulose [13]. The chemical shifts of crystalline cellulose are assigned as follows: C-6 to the resonance at 65 ppm; C-2, C-3, and C-5 to the intense doublet centered at 73 ppm; C-4 to the asymmetric doublet centered at 85 ppm, and the anomeric carbon, C-1, to the sharp resonance at 105 ppm. The presence of an intense signal centered at 30 ppm is indicative of alkyl carbons [14], whereas weak peaks in the 170 ppm region should correspond to carboxylic carbon in ester and/or amides. The weak signals between 110 and 150 ppm (aro-

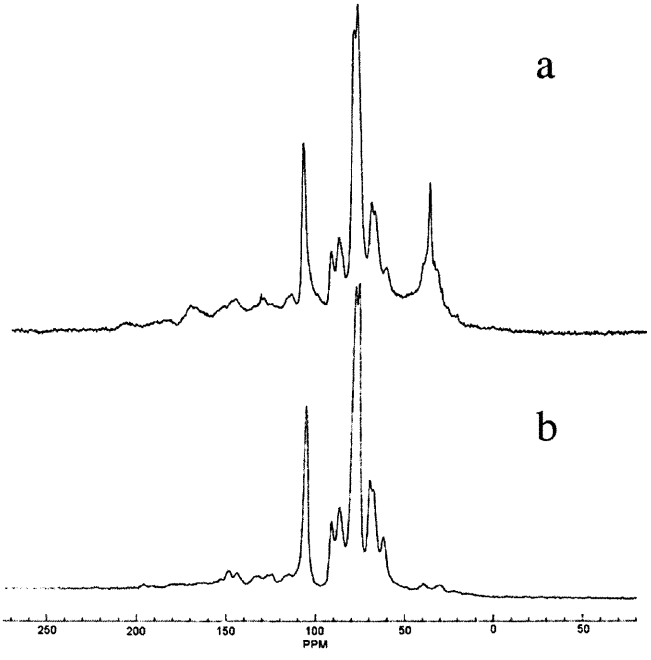

Fig. 1a, b Solid state CP/MAS ^{13}C NMR spectra of bran-LCS (**a**), and straw-LCS (**b**)

matic carbon) and the weak resonance at 56 ppm (methoxy carbon linked to aromatic structures) can be attributed to lignin. The straw-LCS spectrum (Fig. 1b) partly recalls the one of bran-LCS with a predominance of cellulose signals. Contrary to the spectrum of bran-LCS, only very weak signals are detected for alkyl carbons in the 14–54 ppm range. The contribution of lignin is only reflected by the presence of weak peaks at 56 ppm and around 150 ppm, which correspond to the main peaks of the lignin spectrum [15].

NMR spectroscopy therefore showed a pronounced difference between the two samples due to the higher abundance of the alkyl structures in the bran-LCS. In addition, these spectra point to marked predominance of cellulose relative to lignin in both cases. However, caution should be exercised in deriving quantitative information from solid state CP/MAS ^{13}C NMR spectroscopy since this method is based on polarization transfer from protons to carbon atoms and the efficiency of this transfer decreases with the sixth power of the carbon to proton distance. As a result, carbon atoms too far from protons are hardly detected and it is well documented that aromatic moieties in complex mixtures can be markedly underestimated via solid-state CP/MAS ^{13}C NMR spectroscopy [16, 17, 18]. Similarly, as recently illustrated by studies on synthetic humic substances [18], carbon atoms in highly cross-linked structures are markedly underestimated as well. Accordingly, due to the aromatic and cross-linked nature of lignin, its contribution to the LCSs must be underestimated relative to cellulose. Moreover, in the present case, lignin underestimation was favored because only the most cross-linked fraction was retained following the alkaline treatment. Therefore, although cellulose clearly predominates over lignin in the two LCSs, the relative abundance of the latter should be substantially higher than suggested by the relative intensities of the lignin and cellulose resonances in the ^{13}C NMR spectra. Indeed a previous NMR study, performed on cellulose and lignin standards and a 50:50 cellulose:lignin mixture along with straw-LCS [10], showed a lignin/cellulose ratio of around 1/6 for the latter. The relative intensities of the NMR peaks of lignin and cellulose indicate a similar ratio in the case of bran-LCS but a precise assessment is difficult.

X-ray photoelectron spectroscopy

The XPS survey spectrum of the bran-lignocellulosic substrate consists of two major elements: carbon and oxygen. The C_{1s} peak has been deconvoluted considering three components and a constant half-width peak at 2.0 eV. Due to similarities of the O_{1s} chemical shifts, which brought up difficulties in estimating their relative intensities, the discussion in this section will be focused on the relative intensities of C_{1s} peak components, as well as on the O/C ratio (Table 1).

The three components of C_{1s} peak can be assigned to three different classes of carbon atoms present in cellulose and lignin: The C_1 peak corresponds to a carbon bound to hydrogen or to another carbon, C-H or C-C bonds; the C_2 peak corresponds to a carbon singly bound to an oxygen, C-O, and the C_3 peak to a carbon doubly bound to an oxygen, C=O, or two oxygens, O-C-O [19].

By comparison with XPS spectra of lignin and cellulose, the surface content of C_1 carbon is unexpectedly high since it is close to the one of pure lignin [20]. A markedly higher intensity of the C1 peak (70%) compared to the C2 peak (ca. 25%) is also observed for bran-LCS. In contrast, the C1 and C2 peaks exhibit similar intensities (ca. 47%) for straw-LCS. These data are in accordance with the presence of an intense band at 30 ppm in the bran-LCS NMR spectrum that was attributed to non-substituted alkyl (e.g. lipids). Moreover, the relatively low value of C2 in bran-LCS compared to the value in straw-LCS seems to indicate a smaller amount of cellulose moieties $(C_6H_{12}O_5)_n$ in the former. Thanks to these results, we could assign the C3 peak of bran-LCS (4.9%) to carbon doubly bounded to oxygen (carboxylic groups) whereas the peak in straw-LCS (5.8%) could be attributed essentially to an ether bond.

The lower value of O/C ratio for bran ligno-cellulosic material indicates that the sample is rich in aliphatic and aromatic carbons close to the surface. The O/C ratio of straw-LCS is equal to 0.63, which is intermediate between the theoretical values for lignin (0.33) and cellulose (0.83) [20].

Table 1 XPS parameters of the two LCS

Peak	Straw-LCS				Bran-LCS			
	Total elemental percentage	BE[a] (eV)	Fwhm[b] (eV)	Area (%)	Total elemental percentage	BE[a] (eV)	Fwhm[b] (eV)	Area (%)
C_1		284.6	1.76	47.0		284.6	1.90	70.4
C_2	60.9%	286.2	1.58	47.2	72.6%	286.3	1.90	24.7
C_3		288.2	1.84	5.8		288.1	1.90	4.9
O_1		531.2	1.96	11.9		529.8	1.97	10.7
O_2	38.1%	532.7	1.88	83.9	25.9%	531.6	1.97	28.6
O_3		534.1	1.94	4.2		532.8	197	60.7
N_{1s}	1.0%	400.0	–	–	<1%	399.4	–	–
Na_{1s}	–	–	–	–	<1%	1072.5	–	–
S_{2p}	–	–	–	–	<1%	165.8	–	–
O/C			0.63				0.36	

[a]Binding energy
[b]Full width at half maximum

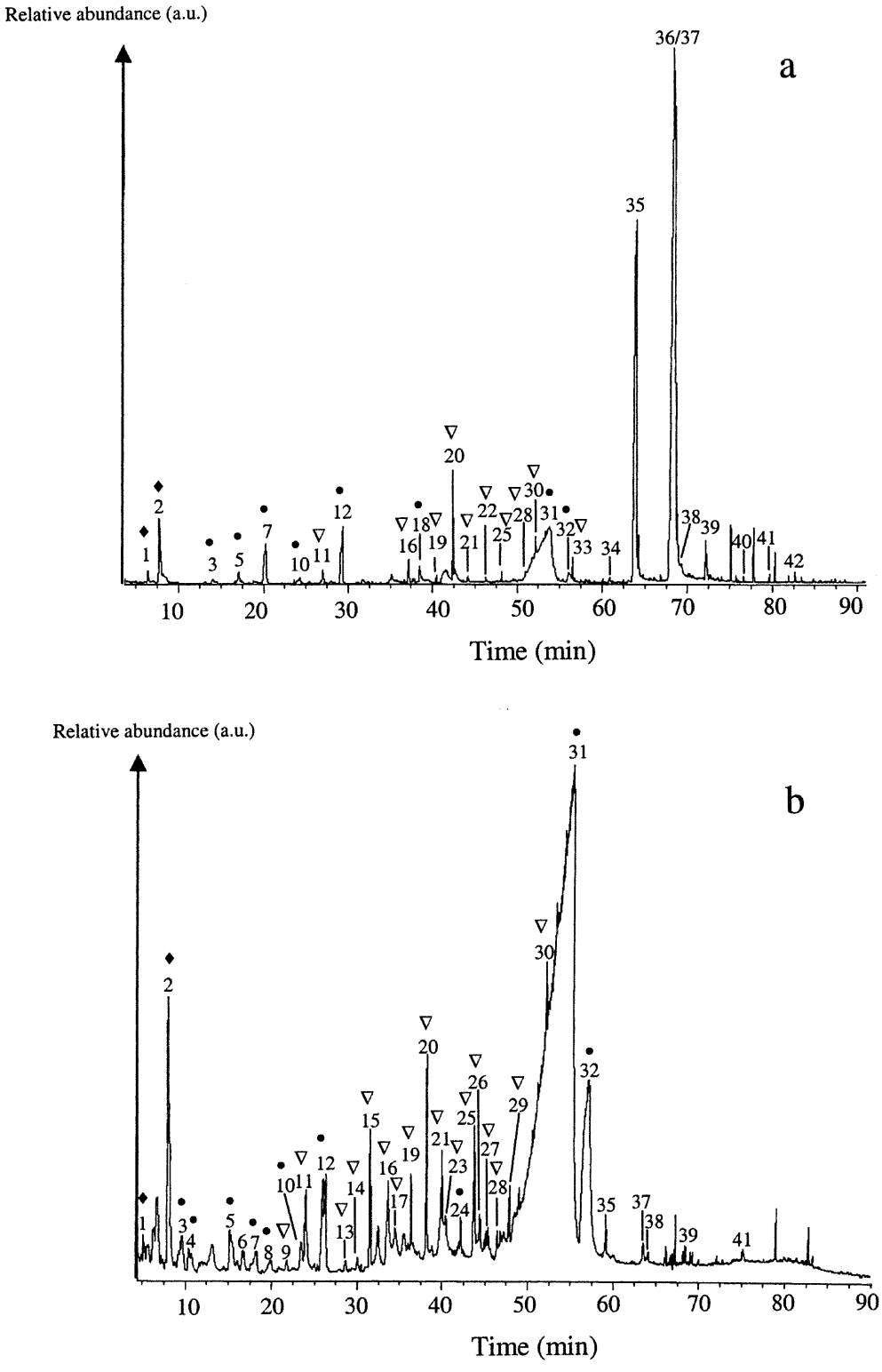

Fig. 2a, b Total ion current (TIC) trace of the 650 °C Curie point pyrolysates obtained by conventional Py-GC-MS from bran-LCS (**a**), and straw-LCS (**b**). Products derived from lignin (*triangles*), cellulose (*circles*), or both compounds (*diamonds*)

Pyrolysis without TMAH

Figure 2 shows the total ion current (TIC) traces of the conventional pyrolysates of bran-LCS and straw-LCS obtained at 650 °C. The compounds identified are listed in Table 2. The chromatogram of the bran-LCS (Fig. 2a) is dominated by long chain saturated and unsaturated fatty acids: octadecadienoic acid (36), oleic acid (37), and hexadecanoic acid (35). These fatty acids probably originate from the thermal cleavage of fatty esters. The presence of such moieties was reflected, in the ^{13}C NMR spectrum of the bran-LCS, by the resonances attributed to

Table 2 Structure of the compounds identified in the 650 °C conventional pyrolysates with indication of their relative amounts

Peak	Compounds	Structure	Straw	Bran
1	Toluene		+	+
2	Furfural		++	++
3	2,3-Dihydro-5-methylfuran-2-one		+	+
4	2-Methyl-2-cyclopenten-1-one		+	–
5	5-Methyl-2-furfuraldehyde		+	+
6	Phenol	P	+	–
7	4-Hydroxy-5,6-dihydro-(2*H*)-pyran-2-one		+	++
8	4-Hydroxy-2-methyl-cyclo-penten-1-one		+	–
9	2-Methylphenol	P-C	+	–
10	2-(Propan-2-one) tetrahydrofuran		+	+
11	Guaiacol	G	++	+
12	Levoglucenose		++	++
13	2,4-Dimethyl-phenol		+	–
14	2,3,6-Trimethylphenol		+	–
15	Methylguaiacol	G-C	++	–
16	4-Vinylphenol	P-C=C	+	+
17	4-Ethyl-3-methylphenol		+	–
18	4-Hydroxy-3-methyl-furan-carboxyaldehyde	+	+	
19	4-Ethylguaiacol	G-C-C	+	+
20	4-Vinylguaiacol	G-C=C	++	++
21	Syringol	S	+	+
22	Vanillin	G-CO	–	+
23	4-Propylguaiacol	G-C-C-C	+	–
24	Cis-isoeugenol	G-C=C-C	+	+
25	Methylsyringol	*S*-C	++	+
26	Trans-isoeugenol	G-C=C-C	+	–
27	Homovanillin	G-C-CO	+	–
28	Guaiacylacetone	G-C-C*O*-C	+	+
29	4-Vinylsyringol	*S*-C=C	+	–
30	4-Allylsyringol	*S*-C-C=C	++	+
31	Levoglucosan		+++++	+++
32	Anhydro-β-D-glucofuranose		++	+
33	4-Propenylsyringol	*S*-C=C-C	–	+
34	Pentadecanoic acid	C15:0 FA	–	+
35	Hexadecanoic acid	C16:0 FA	+	+++
36	Octadecadienoic acid	C18:2 FA	+	+++
37	Octadecenoic acid (Oleic)	C18:1 FA	+	+++
38	Octadecanoic acid	C18:0 FA	+	+
39	Eicosane		+	+
40	Eicosanoic acid	C20:0 FA	–	+
41	Tetracosane		+	+
42	Hexacosane		–	+

(–): not detected
(+), (++), (+++), low, medium and high amounts, respectively
C: Alkyl groups
CO: Carbonyl groups
P: Phenol
G: Guaiacol
S: Syringol
FA: Fatty acids
For example vanillin: G-CO means carbonyl bound to guaiacol units

alkyl carbon (centered at 30 ppm) and to carboxylic carbons in esters and/or amides (around 170 ppm). The formation of these acids upon pyrolysis therefore reflects the occurrence in the bran-LCS of fatty acids esterified with some hydroxy groups of the ligno-cellulosic material. Such ester functions survived the acid and base treatments used for LCS isolation. In fact, they would be sterically protected against hydrolytic cleavage within the three-dimensional macromolecular structure of this material, as previously observed for other biomacromolecules like the algaenans found in the cell walls of some microalgae [21, 22]. This chromatogram does not reflect the large contribution of cellulose to the bran-LCS observed by ^{13}C NMR spectroscopy. In fact, only the presence of relatively weak peaks corresponding to typical pyrolysis products of cellulose was noted, including furfural (2), levoglucenose (12), and levoglucosan (31), the predominant compound observed in the pyrolysate of pure cellulose. Several typical pyrolysis products of lignin were detected (guaiacol and syringol derivative units) but vinylguaiacol (20) is the only relatively intense peak representative of lignin contribution.

The trace of the pyrolysate of straw-LCS (Fig. 2b) is dominated by cellulose- and lignin-derived products. This chromatogram shows levoglucosan (31) as the major compound, followed by furfural (2), anhydro-glucofuranose (32), and 4-vinylguaiacol (20). Other relatively intense peaks corresponding to pyrolysis products of cellulose (levoglucenose, 12) and lignin (like guaiacol, 11; methylguaicaol, 15; methylsyringol, 25, and *trans*-isoeugenol, 26) are also observed. Contrary to the bran-LCS, the fatty acids (35, 36, and 37) now only appear as minor peaks on the chromatogram. The latter feature is in agreement with the lack of substantial resonances corresponding to alkyl carbons (around 30 ppm) and to carboxylic carbons in esters (around 170 ppm) in the ^{13}C NMR spectrum of the straw-LCS. Accordingly, only very low amounts of fatty acids are esterified to the ligno-cellulosic moieties in the latter LCS.

As previously observed, based on the study of mixtures of standards, conventional Py/GC/MS markedly underestimates the contribution of cellulose and lignin relative to alkyl moieties [10]. This is due to differences in the yields of volatile pyrolysis products but also in the molecular weight and/or polarity of these products and, hence, in the efficiency of their detection by GC/MS. In addition, when cellulose and lignin are compared, it appears that the former is still more underestimated due to intense charring upon pyrolysis. Such biases encountered upon conventional pyrolysis therefore account for (i) the predominance of the fatty acid peaks in the chromatogram of the bran-LCS pyrolysate, in spite of the high contribution of cellulose to this material evidenced by NMR spectroscopy and (ii) the relatively high intensity of the pyrolysis products derived from lignin when compared to those originating from cellulose, in spite of the higher contribution of the latter to both LCS.

Previous experiments have been performed on cellulose and lignin standards and 50:50 cellulose:lignin mix-

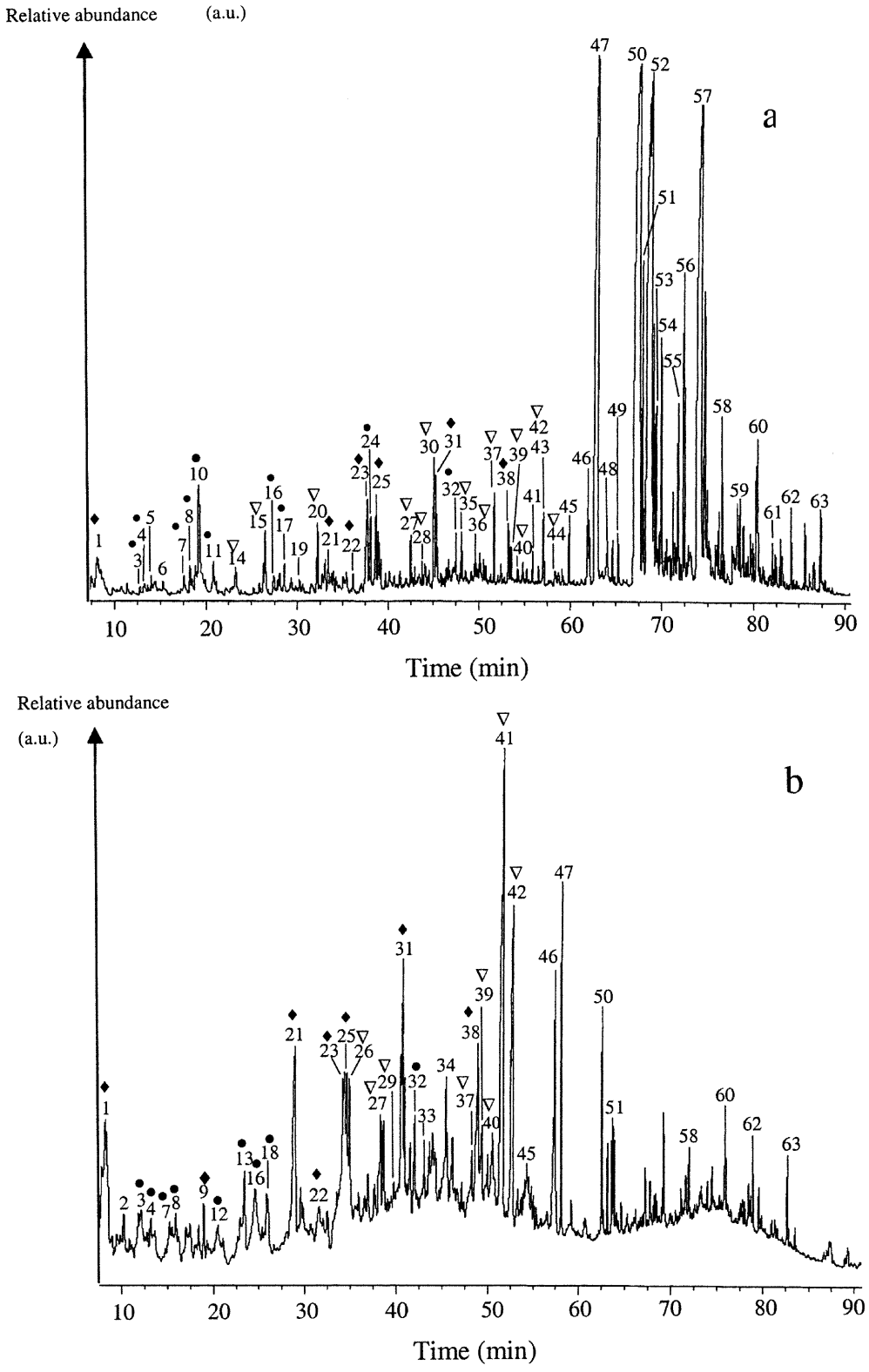

Fig. 3a, b Total ion current (TIC) trace of the 650 °C Curie point thermochemolysates obtained by TMAH/Py-GC-MS from bran-LCS (**a**), and straw-LCS (**b**). Products derived from lignin (*triangles*), cellulose (*circles*), or both compounds (*diamonds*)

ture [10]. Thus it has been demonstrated, by acid-insoluble lignin determination, that straw-LCS is approximately composed of 80% cellulose and 20% lignin [7] Moreover, in the case of the bran-LCS, and due to the importance of long chain fatty acids, the proportion of each moieties was about 50% of cellulose and 20% of lignin [8].

TMAH thermochemolysis

The TIC traces of the thermochemolysates of the two LCSs are shown in Fig. 3. The main compounds identified, together with their relative abundance, are listed in Table 3. Previous studies [23, 24, 25, 26, 27, 28, 10]

Table 3 Structure of the compounds identified in the 650°C thermochemolysates with indication of their relative amounts

Peak	Compounds	Structure	Straw	Bran
1	Furfural		++	+
2	2,6-Dimethylbenzene		+	–
3	2-Methyl-2-cyclopenten-1-one		+	+
4	2-Methoxybenzene		+	+
5	Hexanoic acid methyl ester	C6:0 FAMe	–	+
6	Butanoic acid methoxy methyl ester		–	+
7	5-Methyl-2-furancarboxaldehyde		+	+
8	2-Furoic acid methyl ester		+	+
9	2-Methoxytoluene		+	–
10	4-Hydroxy-5,6-dihydro-(2*H*)-pyran-2-one		–	+
11	2-Methoxy-3-methylfuran		–	+
12	3-Methyl-1,2-cyclopentanedione		+	–
13	3-Methyl-1,2,4-cyclopentanetrione		+	–
14	Butanedioic acid dimethyl ester		–	+
15	3-Hydroxy-2-methyl-(4H)-pyran-4-one		–	+
16	Guaiacol	G	+	+
17	Benzoic acid methyl ester		–	+
18	1-Ethyl-4-methoxybenzene		+	–
19	Decanoic acid methyl ester	C8:0 FAMe	–	+
20	Methylguaiacol	G-C	–	+
21	1,4-Dimethoxybenzene		++	+
22	4-Methoxybenzaldehyde		+	+
23	2,5-Dimethoxy-3-methylfuran		++	+
24	2,5-Dimethyl-naphtalene			+
25	3,5-Dimethoxytoluene		++	+
26	1,4-Dimethoxy-2-methylbenzene		++	–
27	1,3,5-Trimethoxybenzene		+	+
28	3-Methoxy-benzoic acid methyl ester		–	+
29	3,5-Dimethoxyphenol		+	–
30	1,2-Dimethoxy-4-(1-ethenyl)-benzene		–	++
31	1,2,3-Trimethoxybenzene		++	++
32	1,2,3-Trimethoxy-5-methyl-benzene		+	+
33	Decanoic acid methyl ester	C10:0 FAMe	+	+
34	3,4-Dimethoxybenzaldehyde		++	–
35	Octanedioic acid, dimethyl ester		–	+
36	Dodecanoic acid methyl ester	C12:0 FAMe	–	+
37	1-(2,6-Dimethoxyphenyl)-ethanone		+	+
38	3,4-Dimethoxy-benzoic acid methyl ester		++	+
39	3,4,5-Trimethoxybenzaldehyde		+	+
40	3,4-Dimethoxy-benzeneacetic acid methyl ester		+	+
41	1-(3,4,5-Trimethoxyphenyl)-ethanone		+++	+
42	3,4,5-Trimethoxy-benzoic acid methyl ester		+++	+
43	Tetradecanoic acid methyl ester	C14:0 FAMe	–	+
44	3,4,5-Trimethoxy-2-methyl-benzoic acid methyl ester		–	+
45	Pentadecanoic acid, methyl ester	C15:0 FAMe	+	+
46	3-(3,4-Dimethoxyphenyl)-2-propenoic acid methyl ester		++	+
47	Hexadecanoic acid, methyl ester	C16:0 FAMe	+++	+++
48	Hexadecanoic acid	C16:0 FA	–	+
49	Heptadecanoic acid methyl ester	C17:0 FAMe	+	+
50	Octadecenoic acid, methyl ester	C18:1 FAMe	++	+++
51	Octadecanoic acid, methyl ester	C18:0 FAMe	+	++
52	Octadecadienoic acid, methyl ester	C18:2 FAMe	–	+++
53	Octadecadienoic acid, methyl ester	C18:2 FAMe	–	++
54	Nonadecanoic acid methyl ester	C19:0 FAMe	–	++
55	Eicosenoic acid, methyl ester	C20:1 FAMe	–	++
56	Eicosanoic acid methyl ester	C20:0 FAMe	–	++
57	Heneicosanoic acid methyl ester	C21:0 FAMe	–	+++
58	Docosanoic acid methyl ester	C22:0 FAMe	+	+
59	Tricosanoic acid, methyl ester	C23:0 FAMe	–	+
60	Tetracosanoic acid methyl ester	C24:0 FAMe	+	++
61	Pentacosanoic acid, methyl ester	C25:0 FAMe	–	+
62	Hexacosanoic acid methyl ester	C26:0 FAMe	+	+
63	Octacosanoic acid methyl ester	C28:0 FAMe	+	+

(–): not detected
(+), (++), (+++): low, medium and high amounts, respectively
C: Alkyl groups
G: Guaiacol
S: Syringol
FAMe: Methyl ester fatty acids

showed that TMAH thermochemolysates of lignin comprise methyl esters of aromatic carboxylic acids, in addition to the methylated counterparts of the compounds generated upon conventional pyrolyses. These thermochemolysates thus contain numerous methoxybenzenes substituted by remnants of the original C_3 side-chain of lignin units, bearing various oxygenated functions (aldehydes, ketones, methoxy and carboxylic acid methyl esters). Contrary to conventional pyrolyses, the formation of low amounts of fatty acids was also observed upon TMAH thermochemolysis of standard lignin [10]. TMAH thermochemolysis of cellulose results in the formation of a number of compounds, including di- and trimethoxybenzenes, dimethoxyphenols, and naphthalenes derivatives [29].

Thermochemolysis of the bran-LCS (Fig. 3a) produced a number of methyl esters of long chain fatty acid as major compounds. These saturated and unsaturated fatty acids are dominated by hexadecanoic acid methyl ester (47), octadecenoic acid methyl ester (50), octadecanoic acid methyl ester (51), octadecadienoic acid methyl ester (52) nonadecanoic acid methyl ester (54), eicosanoic acid methyl ester (56), and heneicosanoic acid methyl ester (57). Fatty acids esters up to C28 occur in this thermochemolysate. These fatty acid esters originate from the thermochemolysis of fatty acid moieties esterified to hy-

droxy groups of lignin and also may be of cellulose. As previously observed from standard lignin [10], the occurrence of esterified moieties is more efficiently revealed by TMAH thermochemolysis when compared to conventional pyrolysis. Indeed, a markedly wider range of fatty acid esters is generated from the bran-LCS when the former method is used. The fatty acids esterified to the macromolecular structure of the bran-LCS appears much more abundant than in the standard lignin previously examined by TMAH thermochemolysis [10] under the same experimental conditions.

A number of typical pyrolysis products of lignin and cellulose were also identified but they occur in much lower relative abundance when compared to the fatty acids. The main products derived from cellulose were 4-hydroxy-5,6-dihydropyran-2-one (10), 2,5-dimethoxy-3-methylfuran (23), and 2,5-dimethylnaphthalene (24). The main products derived from lignin included guaiacol (16), 1,2-dimethoxy-4-ethenyl-benzene (30), 1-(2,6-dimethoxyphenyl)-ethanone (37), 3,4 dimethoxybenzoic acid methyl ester (38), 1-(3,4,5-trimethoxyphenyl)-ethanone (41), 3,4,5-trimethoxybenzoic acid methyl ester (42), and 3-(3,4-dimethoxyphenyl)-2-propenoic acid methyl ester (46). Some compounds, like 1,4-dimethoxybenzene (21) and 1,2,3-trimethoxybenzene (31), are generated both from cellulose and lignin. The presence of guaiacol (16) and methylguaiacol (20) in addition to their methylated counterparts (21) and (26) also of low amounts of hexadecanoic acid (48) along with hexadecanoic acid methyl ester (47) indicates that complete methylation did not take place. In spite of the more efficient production of GC-amenable products achieved via TMAH thermochemolysis for cellulose, the contribution of such products to the bran-LCS remains largely underestimated when compared to lignin in the thermochemolysate [30] and both macromolecular materials remain underestimated relative to the fatty acid moieties.

Substantial amounts of fatty acids methyl esters were identified in the thermochemolysate of the straw-LCS. These esters are dominated by hexadecanoic acid methyl ester (47), and octadecanoic acid methyl ester (50) and homologs up to C28 are detected. The low relative abundance of the fatty esters in the thermochemolysate of the straw-LCS, when compared to the bran-LCS, reflects the much lower contribution of esterified acyl moieties in the latter material. In fact, such acids were not detected in the conventional pyrolysate of this LCS (Fig. 2b). Numerous products derived from lignin and cellulose are identified in the thermochemolysate of the straw-LCS (Fig. 3b), as also observed for the bran sample. The main product originating from cellulose is 2,5-dimethoxy-3-methylfuran (23). Lignin contribution is mostly reflected by 3,4-dimethoxybenzaldehyde (34), 3,4-dimethoxybenzoic acid methyl ester (38), 3,4,5-trimethoxybenzaldehyde (39), 1-(3,4,5-trimethoxyphenyl)-ethanone (41), 3,4,5-trimethoxybenzoic acid methyl ester (42), and 3-(3,4-dimethoxyphenyl)-2-propenoic acid methyl ester (46). 1,4-dimethoxybenzene (21), 1,4-dimethoxy-2-methylbenezne (26), and 1,2,3-trimethoxybenzene (31) can originate both from cellulose and lignin. The underestimation of cellulose relative to lignin, even upon thermochemolysis, is well illustrated by this chromatogram since the predominant compounds (41) and (42) are related to lignin.

It appears that alkyl and aromatic moieties containing carboxylic groups are esterified to the macromolecular structure of the bran-LCS. Their presence is well revealed by thermochemolysis. Such moieties are much less abundant in the case of the straw-LCS. These carboxylic groups may have an important role in metal complexation by these LCSs.

Conclusions

The main conclusions of this parallel study by spectroscopic (solid state ^{13}C NMR, XPS) and pyrolytic (conventional CuPy/GC/MS, TMAH thermochemolysis/GC/MS) methods of LCSs isolated from wheat straw and bran are summarized below:

- A combination of the above methods is required to derive information on such materials since (i) solid state CP/MAS ^{13}C NMR strongly underestimates lignin versus cellulose and versus alkyl moieties due to the aromatic and highly cross-linked nature of the former, (ii) conventional pyrolysis underestimates lignin and cellulose versus alkyl moieties and such an underestimation is especially pronounced for cellulose due to intense charring upon heating, and (iii) more efficient cleavage of the macromolecular structures and detection of the generated products, including those from cellulose, is achieved through TMAH thermochemolysis; nevertheless, some underestimation of cellulose compared to lignin is still observed.
- Both LCSs are dominated by cellulose and also contain substantial amounts of lignin (lignin/cellulose ratio of around 1/6). A conspicuous difference is, however, observed due to a large contribution of alkyl moieties in bran-LCS. These moieties chiefly correspond to C_6 to C_{28} even-carbon-numbered fatty acids esterified to hydroxy groups of the ligno-cellulosic structure. The ester functions benefited from a very efficient steric protection within the three-dimensional macromolecular structure of the ligno-cellulosic material so that they survived the hydrolysis treatments applied for LCS isolation. Such fatty acyl moieties are much less abundant in straw-LCS. These carboxylic groups should play an important role for metal complexation by the LCSs and hence for the efficiency of such materials for the removal of metal ions from industrial effluents. The above difference in the abundance of these groups should be related to the higher exchange capacity of bran-LCS compared to straw-LCS.

Pyrolysis and thermochemolysis mainly produce the principal structural units, which can be recombined to create some new components, especially benzenecarboxylic acids [31]. Methylation makes a number of polar products volatile enough for gas chromatographic analysis. Thus,

contrary to their unmethylated counterparts during classic pyrolyses, these compounds are not affected by secondary decomposition before volatilization and transfer from the pyrolysis unit to the GC column. Moreover, it was demonstrated that TMAH/pyrolysis does not merely allow in situ methylation and corresponds to a thermally assisted chemolytic degradation rather than degradation simply induced by thermal bond cleavage [32, 33, 34].

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