Pyrolytic alkylation–gas chromatography–mass spectrometry of model polymers

Further insights into the mechanism and scope of the technique

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Abstract

The mechanism of the high-temperature hydrolysis and alkylation with tetraalkylammonium hydroxides of bio- and geopolymers has been approached mainly by studying the behaviour of single standard compounds. In the present work, we have applied this technique to three polymers of known structure, i.e. suberin, polycitraconic acid (PCA) and a lignin dehydrogenase polymer (DHP), related respectively to natural polyesters, fulvic acids and lignins, in order to get new insight into the reaction mechanism. As further application of the technique, the case study of the lignin signature during the coalification process has been analyzed by pyrolysis–butylation of humic acids extracted from two peat and lignite samples.

Keywords: Polymers; Suberin; Polycitraconic acid; Lignin dehydrogenase polymer; Alkylation

1. Introduction

Analytical pyrolysis has been widely applied for the structural characterization of natural macromolecules of various origins. Detailed analysis of the thermal degradation products by gas chromatography–mass spectrometry enables insight into the molecular structure of polymers and natural macromolecules. However, due to the known limitations of the pyrolytic technique, the results are not always in agreement with those obtained by chemical wet methods or spectroscopic techniques. For instance, carboxylic acid moieties are highly biased as potential ‘building-blocks’ upon conventional pyrolysis, since they undergo decarboxylation under these conditions [1]. Recently, pyrolysis in the presence of tetramethylammonium hydroxide

(TMAH) [1–5] and tetrabutylammonium hydroxide (TBAH) [6] has been introduced for the release of moieties bearing carboxyl groups from different polymers and macromolecules upon pyrolytic techniques. Use of the butylating reagent avoids one of the main limitations of pyrolytic methylation — its inability to distinguish between the methoxyl groups originally present in the macromolecule and the free hydroxyl groups that become methylated after the pyrolysis. This differentiation can be of key importance in studying chemical structure of lignins and in monitoring lignin signature in the geological record, since lignins are classed by the relation of contents in phenolic units with more or fewer hydroxyl and methoxyl groups, and the changes that lignin moieties undergo during organic matter diagenesis affect mainly their methoxyl contents [7,8]. Pyrolysis in the presence of TBAH introduces a butyl moiety in the originally free hydroxyl group (forming an O-butyl

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ether) that can thus be distinguished from the original methoxyl group.

The process is considered to be a thermally assisted hydrolysis followed by alkylation, rather than a true pyrolysis followed by 'in situ' alkylation of the products [1,2,6,9]. It is therefore different to the conventional pyrolysis where the pyrolysis compounds are generated from the macromolecular substances by bond breaking induced by heat only. Pyrolysis in the presence of TMAH or TBAH avoids decarboxylation and releases the methyl or butyl esters of the carboxylic groups. In addition, the derivatization of polar moieties also overcomes the problem dealing with the adsorption of polar compounds by the common apolar chromatographic phases. A reported drawback [10] is the possible formation of some artifacts as the consequence of chemical oxidation mediated by the TMAH reagent at high temperature.

With the above considerations in mind, the present work has two different aims. The first is to apply this new pyrolytic approach to polymers of known structure having a high content of polar units in order to gain more information on the thermochemolysis reaction, since all previous conclusions on the reaction mechanism have been drawn from the behaviour of single standard compounds or the macromolecular samples themselves. The samples chosen were (i) polycitraconic acid (PCA), a laboratory-made oligomer obtained from methyl maleic anhydride, with a high content of free carboxylic groups, which is somewhat similar to polymaleic acid, proposed as a model for the chemical structure of natural fulvic acids [11]; (ii) suberin, a naturally occurring higher plant polyester, which wet chemical methods show as possessing a high content of esterified carboxylic units [12,13] and (iii) a dehydrogenation polymer (DHP) made by polymerization of coniferyl alcohol in vitro, i.e. an artificial biosynthetic lignin rich in polar groups bearing aromatic units [14].

The second aim is to prove the potential advantages of pyrolysis–butylation over pyrolysis–methylation for monitoring diagenetic changes of lignin moieties by analyzing the behaviour of two humic acids (HA) extracted from low-rank coals at different coalification stage (where the lignin moieties should

present different degree of alteration) against the high temperature hydrolytic butylation reaction.

2. Experimental

2.1. Materials

Polycitraconic acid (PCA) was prepared from citraconic anhydride (Merck) following the same method used by Brawn and Pomakis to prepare polymaleic acid [15]. Suberin was obtained from potato tubers by enzymatic hydrolysis [16]. The DHP synthetic polymer was obtained by in vitro free radical polymerization of coniferyl alcohol induced by horseradish peroxidase and hydrogen peroxide [17].

The humic acids (HA) were extracted from two low-rank coal deposits in Padul (Granada, South Spain) and Pontes de Garcia Rodriguez (La Coruña, North Spain). Chemical, geochemical and geological data of the deposits, the extraction procedure of the HAs, and their analytical characteristics were published elsewhere [18–20].

2.2. Pyrolysis–gas chromatography–mass spectrometry

All the samples were pyrolyzed under the same conditions with and without alkylating reagents. In the first case, the samples were first dissolved in the minimum amount of TMAH or TBAH in 25% aqueous solutions (Aldrich) and dried in an air-evacuated desiccator overnight. The syrups were placed on the ribbon foil of the CDS pyroprobe and heated to 500°C for 10 s. The on-line coupling pyroprobe–GC was realized through a resistively heated special device previously described [21]. The pyrolysis products were separated by a fused silica column (SE-52, J and W Scientific) of 25 m length, 0.2 mm I.D. and 0.25 μm film-thickness. The gas chromatograph (Hewlett-Packard HP-5890) was programmed from 40 to 300°C at a rate of 6 °C/min. Helium (1 ml/min flow-rate) was used as carrier gas. The mass spectrometer (HP 5988 A) was set at 70 eV. Identification was achieved by mass fragmentography, library search and comparison with literature

data. When possible, the identifications were confirmed by comparison with authentic standards.

3. Results

Fig. 1. shows the total ion chromatograms (TICs) of the products obtained after pyrolysis of the PCA and suberin samples in the absence and in the presence of TMAH.

The main pyrolysis products released after conventional pyrolysis of PCA were series of aromatic compounds, not directly related to the original monomer, and several furandione derivatives. However, pyrolysis of PCA in the presence of TMAH (Fig. 1b) released some significative pyrolysis products, such as the dimethyl ester of methyl butanedioic acid (peak 1), as well as the methyl esters of methyl butenedioic acid (peak 2) and pentenedioic acid (peak 3), arising from the direct breakdown of the polymeric chain.

The conventional pyrolysis of suberin (Fig. 1c) and its pyrolysis in the presence of TMAH (Fig. 1d)

Fig. 1. Pyrograms of PCA (a) without and (b) with TMAH, and of suberin (c) without and (d) with TMAH. In (b) peak 1: dimethyl ester of methyl butanedioic acid, peak 2: methyl esters of methyl butenedioic acid, and peak 3: pentenedioic acid. Numbers in (d) refer to fatty acids homologous series.

also show a great discrepancy, as previously observed for PCA and cutin [2], a closely related polyester. Thus, whereas the former released predominantly a series of alkenes and/or alkanols, and minor amounts of alkadienoic acids, pyrolysis in the presence of TMAH yielded the methyl derivatives of the alcohols and fatty acids arising from hydrolysis of the esters in the macromolecule. A peak arising from the esterified *p*-ferulic acid present in the suberin structure was also detected.

Fig. 2 shows the pyrograms of the DHP polymer without any alkylating reagent (Fig. 2a), and in the presence of TMAH (Fig. 2b) and TBAH (Fig. 2c). The identity of the pyrolysis products is shown in Table 1. The original pyrolysis products that become methylated and butylated are marked on the corresponding peaks in Fig. 2b and c.

In contrast to the above, the conventional pyrolysis of DHP released significative structural monomers, such as dihydroconiferyl alcohol (peak 20), vanillin (peak 13) and 4-hydroxy,3-methoxy-1-(2-propenyl) (peak 21), all of them with the guaiacyl nucleus (3-hydroxy, 4-methoxy) of the precursor. Some unexpected artifacts, such as anthracenecarboxylic acid (peak 22), present in relatively high abundance, and one minor carboxylic-substituted aromatic unit (peak 23), were also detected.

In the presence of TMAH, the synthetic lignin yielded mainly 3,4-dimethoxybenzenes (Fig. 2b), whereas in the presence of TBAH (Fig. 2c), the butylated counterparts were the most abundant pyrolysis products. It is interesting to note the relatively large amounts of coumaric acid (peaks 38 and 43) released after the pyrolysis in the presence of the alkylating reagents. Some other carboxylic-bearing units (peaks 33, 34, 35, 36, 38) were also detected.

The TICs of the thermal degradation products obtained after pyrolysis of the HAs in the presence of TBAH are shown in Fig. 3. The identification of the different pyrolysis products related to the lignin macromolecule is shown on the corresponding chromatographic peaks. The main diagnostic groups among the pyrolysis products of both HAs were the butyl derivatives of benzenecarboxylic acids (BC) with characteristic lignin structures (as also occurs for pyrolysis-methylation [22]).

Fig. 2. Pyrograms of the DHP polymer without alkylating reagent (a), and in the presence of TMAH (b) and TBAH (c). Marks ▲ and ● indicate the original pyrolysis products that become methylated and butylated.

The butyl-aryl ethers arising from lignin moieties are formed by butylation of free phenolic groups and by TBAH-assisted cleavage of the alkyl-aryl ether bonds. Whereas the OH group at C-4 is always released as a butyl ether, the positions at C-3 in the guaiacyl structures and C-3 and C-5 in the syringyl

Table 1

Products obtained from the DHP sample by conventional pyrolysis and in the presence of alkylating reagents

1	2,3-Dimethoxytoluene
2	2-Methoxyphenol (guaiacol)
3	2-Methoxy-4-methylphenol
4	Phenol, 4-acetyl-2-methoxy
5	Phenol, 2-methoxy-4-propyl
6	Phenol, 2-methoxy-4-(2-propenyl)
7	4-Hydroxy-3-methoxyvinylbenzene
8	Phenol, 2-methoxy-4-(1-propenyl)
9	Phenol, 2-methoxy-4-(1-propenyl) (isom?)
10	Benzaldehyde, 3,4-dimethoxy
11	Benzoic acid, 3,4-dimethoxy, methyl ester
12	Benzene, 1,3-dimethoxy
13	Benzaldehyde, 4-hydroxy,3-methoxy (vanillin)
14	Ethanone, 1-(4-hydroxy-3-methoxybenzene)
15	2-Propanone, 1-(4-hydroxy-3-methoxybenzene)
16	1,3-Benzenediol
17	1,2-Benzenediol, 3-methyl
18	2-Propenoic acid, 3-(4-hydroxybenzene)
19	1,2-Benzenediol, 3-methoxy
20	4-Hydroxy-3-methoxy cinnamyl alcohol (dihydroconiferyl alcohol)
21	Benzene, 4-hydroxy,3-methoxy-1-(2-propenyl)
22	9-Anthracenecarboxylic acid
23	Benzoic acid, 4-hydroxy-3-methoxy
24	Benzene, 1-ethyl-4-methoxy
25	Benzene, 1-ethenyl,4-methoxy
26	Benzene, 1-methoxy-4-(2-propenyl)
27	Benzaldehyde, 3-methoxy
28	Benzene, 1,2,3-trimethoxy
29	Benzaldehyde, 4-methoxy
30	Benzene, 4-ethenyl-1,2-dimethoxy
31	Benzene, 1,2,4-trimethoxy
32	Benzoic acid, 4-methoxy, methyl ester
33	Benzoic acid, 4-hydroxy-3-methoxy, methyl ester
34	Benzenedicarboxylic acid, dimethyl ester
35	Benzenedicarboxylic acid, dimethyl ester
36	Benzeneacetic acid, 3,4-dimethoxy, methyl ester
37	cis-3,4-Dimethoxybenzenepropenol, methyl ether
38	2-Propenoic acid, 3-(3,4-dimethoxybenzene), methyl ester (coumaric acid, methyl ester)
39	Benzene, 4-ethenyl-4-hydroxy-3-methoxy
40	Benzoic acid, 3,4,5-tributoxy, butyl ester
41	Benzoic acid, 4-hydroxy-3-butoxy, butyl ester
42	2-Propenoic acid, 3-(4-hydroxy-3-butoxybenzene), butyl ester (coumaric acid, butyl ester)
43	2-Propenoic acid, 3-(3,4-dibutoxybenzene), butyl ester

ones can be found either with a methoxyl group or demethylated, with a free hydroxyl group that will become butylated after pyrolysis in the presence of TBAH. Thus, different benzenecarboxylic acids with guaiacyl structure having the OH groups at C-3

Fig. 3. Pyrograms of the humic acids extracted from the peat (top) and the lignite (bottom) in the presence of BTAH. BC= benzenecarboxylic units.

either methylated or butyated (compounds marked as G in the TICs) were identified in both samples. Benzenecarboxylic acids with syngyl structure, having the OH groups at C-3 and C-5 methylated or butyated (compounds marked as S in the TICs), were also found.

4. Discussion

The product discrepancy between thermochemolysis in the presence of alkylating reagents and conventional flash pyrolysis is clearly reflected in the respective patterns of pyrolysis products obtained with the aliphatic polymers studied (Fig. 1), as also observed by McKinney et al. [23] with another similar polymer. In the case of PCA and suberin, only the results obtained with the pyrolytic-alkyla-

tion procedure are well related to the known structural features of both polymers.

Thus, the thermochemolysis of PCA in the presence of TMAH allows identification of the monomeric sequence present in the oligomer $[-CH(COOH)-C(CH_3,COOH)]_n$, which, on the other hand, has not been detected in fulvic acids [1].

Likewise, under thermochemolysis conditions, suberin yielded mainly the hydroxy fatty acids and fatty acid methyl ester of varying carbon chain length, which are interesterified with fatty alcohols forming its polyester structure [13]. Nearly all of the C_{16} and C_{18} monomers identified in cutin have been reported in suberin as well. The major difference in comparison with the pyrolytic behaviour of cutin in the presence of TMAH is the occurrence in suberin of monomers with chain lengths longer than C_{18} having a lesser degree of mid-chain substitution. These longer chain monomers consist predominantly of *n*-alcohols and corresponding fatty acids ($C_{20}-C_{30}$) and ω -hydroxy fatty acids [$C_{16}-C_{24}$]. It has been suggested that suberin contains, apart from these aliphatic building-blocks, a considerable amount of esterified phenolic acids, such as the ferulic acid identified among the pyrolysis products.

Such discrepancy is much less evident in the case of the aromatic synthetic lignin, since the pyrograms obtained without and with alkylating reagents are well related with the structural make-up of the polymer. In agreement with the results reported by other authors, the pyrogram of DHP is somewhat similar to that of pine lignin (representative of softwood), composed exclusively of guaiacyl units [6]. In the presence of TMAH, its behaviour (Fig. 2b) is also similar to that of pine lignin [22]. The relatively abundant carboxylated aromatic units detected could arise from oxidation induced by the H_2O_2 used to synthesize the polymer in the case of the conventional pyrolysis, or by the alkaline reagent, as pointed out by Hatcher and Minard [10].

Regarding the behaviour of HA from low-rank coals of different rank in pyrolysis-butylation, the results obtained confirm the advantage of this procedure over pyrolysis in the presence of TMAH, i.e. the possibility of distinguishing the free phenol-groups bearing units (that form the corresponding butyl ethers), from the originally methoxylated

groups in the lignin macromolecule. In addition, previous, well documented observations [7,8] were confirmed, that during the coalification process there is a progressive demethylation of the methoxyl groups in the lignin macromolecule and the formation of the corresponding catechols. Thus, although quantitative relationships should be considered with caution when using pyrolytic techniques, it is evident (Fig. 3) that among the guaiacyl BC moieties the relative abundance of 3-MeOH, 4-OH BC over 3,4-diOH BC decreases dramatically from the peat to the lignite (from 5 to 0.6), indicating that the demethylation of the MeOH groups at C-3 and the formation of catechols is more accentuated in the PGR lignite than in the Padul peat. A similar trend was observed for the syringyl BC acid structures. In the HA from Padul, the relative abundances of the 3,5-diMeOH-4-OH BC acid over the respective 3-MeOH-4,5-diOH BC and 3,4,5-triOH BC acids is higher than in the HA from PGR lignite (from 5 to 1.3). This is also consistent with the demethylation of the methoxyl groups at C-3 and C-5 and the formation of the corresponding catechols in the PGR lignite.

5. Conclusions

Product distribution, obtained under normal pyrolysis conditions versus thermochemolysis conditions, is vastly different in the case of aliphatic polymers. However, this discrepancy was not observed for an aromatic synthetic lignin, which gave pyrograms without and with alkylating reagents well related with the structural make-up of the polymer. In any case, pyrolysis in the presence of TMAH seems to be an appropriate technique for the detection of the building-blocks of polymeric structures having carboxyl groups either free or in ester form.

Like the pyrolysis-methylation procedure, pyrolysis-butylation consists mainly of a saponification/esterification reaction at high temperature. In contrast to the former, pyrolysis-butylation seems to be a suitable technique to examine some of the proposed trends in coalification process, such as demethylation and demethoxylation of the lignin macromolecule with increasing rank.

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References

- [1] F. Martin, F.J. Gonzalez-Vila, J.C. del Rio and T. Verdejo, *J. Anal. Appl. Pyrol.*, 28 (1994) 71.
- [2] J. De Leeuw and M. Baas, *J. Anal. Appl. Pyrol.*, 26 (1993) 175.
- [3] F. Martin, J.C. del Rio, F.J. Gonzalez-Vila and T. Verdejo, *J. Anal. Appl. Pyrol.*, 31 (1995) 75.
- [4] P.G. Hatcher and D.J. Clifford, *Org. Geochem.*, 21 (1994) 1081.
- [5] P.G. Kralert, R. Alexander and R.I. Kagi, *Org. Geochem.*, 23 (1995) 627.
- [6] F. Martin, J.C. del Rio, F.J. Gonzalez-Vila and T. Verdejo, *J. Anal. Appl. Pyrol.*, 35 (1995) 1.
- [7] P.G. Hatcher, H.E. Lerch III, R.K. Kotra and T.V. Verheyen, *Fuel*, 67 (1988) 1069.
- [8] S.H. Stout, J.J. Boon and W. Spackman, *Geochim. Cosmochim. Acta*, 52 (1988) 405.
- [9] J.M. Challinor, *J. Anal. Appl. Pyrol.*, 29 (1994) 223.
- [10] P.G. Hatcher and R.D. Minard, *Org. Geochem.*, 23 (1995) 991.
- [11] H.A. Anderson and J.D. Russell, *Nature*, 260 (1976) 567.
- [12] P.E. Kolattukudy, *Science*, 208 (1980) 990.
- [13] P.J. Holloway, *Phytochemistry*, 22 (1983) 495.
- [14] K. Freudenberg and A.C. Neish, *Constitution and Biosynthesis of Lignin*, Springer-Verlag, Berlin, 1968, p. 129.
- [15] D. Brawn and J. Pomakis, *Makromol. Chem.*, 175 (1974) 1411.
- [16] P.E. Kolattukudy and B.B. Dean, *Plant Physiol.*, 54 (1974) 116.
- [17] O. Faix, M.D. Mozuch and I.K. Kirk, *Holzforschung*, 39 (1985) 203.
- [18] F. Martin, *Fuel*, 54 (1975) 236.
- [19] J.C. del Rio, F.J. Gonzalez and F. Martin, *Org. Geochem.*, 18 (1992) 67.
- [20] F.J. Gonzalez-Vila, J.C. del Rio, G. Almendros and F. Martin, *Fuel*, 73 (1994) 215.
- [21] F. Martin and F.J. Gonzalez-Vila, in B. Allard, H. Borén and A. Grimvall (Editors), *Humic Substances in the Aquatic and Terrestrial Environment*, Springer-Verlag, Berlin, 1991, p. 105.
- [22] J.C. Del Rio, F.J. Gonzalez-Vila, F. Martin and T. Verdejo, *Org. Geochem.*, 22 (1994) 885.
- [23] D.E. McKinney, J.M. Bortiatynsky, D.M. Carson, D.J. Clifford and P.G. Hatcher, *Org. Geochem.*, (1995) in press.