Structural characteristics and geochemical significance of humic acids isolated from three Spanish lignite deposits

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ABSTRACT

Three Spanish lignites of similar low maturity level taken from different deposits and their humic acid (HA) fractions have been characterized by chemical and spectroscopic methods. Some remarkable differences were found in the HA contents, as well as in the distribution of humic and fulvic fractions among the parent lignites. These differences, however, are not reflected by spectral or chemical distinguishing features. The results suggest that lignin-derived materials contributed to the formation of the lignite deposits

Key words: humic acids; lignites; CuO oxidation; ¹³C-NMR spectroscopy

INTRODUCTION

It has been assumed that humic acids (HA) characterize the immature stage in the natural evolution of organic material during the coalification process. In fact they decrease in concentration with coal rank and are virtually absent in high-rank coals [1].

HA in coals have not received much attention in comparison with HA from other origins, which is somewhat surprising since they offer a means of examining coal structure using a starting material that has advantages in relative homogeneity, lower content of inorganic substances and complete solubility in alkali. The characterization of coal HA has been proved to be useful for the elucidation of diagenetic pathways during the coalification process [2] and for obtaining information about the organic source materials and depositional environments [3,4]. These and other related investigations have been carried out mainly with well differentiated lithotypes from the same coal seam or with coals varying in rank, but not, so far as we know, with coals of similar rank and low maturity level.

The characterization study of the parent lignites and their HA has been carried out mainly by solid state NMR spectroscopy, which is a suitable technique for the characterization of geological samples [5], and by cupric oxide (CuO) oxidation. CuO oxidation has been proposed by many authors as a mild degradative method for providing evidence of cellulose and lignin contributions [6,7] and for disclosing the sources of humic material found in sediments [8–10].

The purpose of this work was to study the structural characteristics of HA isolated from closely related lignites and to explore the possible relationships between these parameters and the maturities of the coals from which they derive, and also to evaluate the usefulness of HA as markers of differences in the original biological sources.

MATERIAL AND METHODS

The lignite samples were taken from deposits located at Puentes de Garcia Rodriguez (PGR) in the north of Spain (La Coruña) and from Arenas del Rey (AR) and Padul (P) in the south of Spain (Granada). The three deposits chosen are still in the process of diagenetic evolution as shown in previous works on the distribution of their biomarkers [11–15]. Their main geological features, as well as chemical, geochemical and petrographic data of the parent lignites were published elsewhere [14,16,17].

Before isolation of the HA, the lignite samples were ground to pass a 270 mesh screen and Soxhlet extracted with hexane and toluene until the resulting extracts had only a pale yellow color. HA were extracted from the residue (100 g) with 0.1 N NaOH solutions (three times, 200 ml) and purified by procedures previously described [18]. The elementary composition was determined with a Hewlett-Packard CHN-185 microanalyser.

FT-IR spectra were obtained with KBr pellets (1 mg of sample per 200 mg KBr) on a Nicolet 50X E infrared spectrometer by coadding 100 scans at a resolution of 2 cm⁻¹. High resolution solid state ¹³C-NMR spectra were obtained with the CPMAS technique at 75.4 MHz in a Bruker MSL 300 spectrometer using quantitative acquisition conditions previously described [19].

The alkaline CuO oxidation procedure has been described in detail elsewhere [12,13,20]. In general, 200 mg of sample was degraded with freshly prepared alkaline CuO in a 200-ml Perkin Elmer teflon bomb fitted with a pressure release valve at 170°C (8 h for the lignites and 3 h for the HA in N₂ atmosphere under continuous stirring). The low molecular weight degradation products released were extracted from the acidified digests by repeated extraction with peroxide-free ether, dried, weighed and derivatized with bis(trimethylsilyl)-trifluoroacetamide. The trimethylsilyl (TMS) derivatives were analysed by GC and GC/MS using a Hewlett Packard 5890 A

model gas chromatograph equipped with flame ionization detector (FID) and a Hewlett Packard 5988 A GC-MS-computer system. The separation of compounds was achieved using a 25-m (0.32 mm i.d.) SE-52 fused silica capillary column, with the oven temperature programmed from 100° to 300°C at a rate of 6°C/min with 15 min final hold. Helium at a flow rate of 1.5 ml/min was used as carrier gas.

The TMS derivatives of the major lignin-derived CuO oxidation products give characteristic mass spectra at 70 eV electron ionization and were identified by matching with library (Wiley) stored spectra.

RESULTS AND DISCUSSION

The HA content is much lower in the PGR lignite (48–55%) than in the other two samples (83–88%). The high HA concentration may be indicative of anaerobic deposition, since reducing environments are conducive to the preservation of organic matter [21,22].

Although the three lignites are from the Miocene, the lower HA content of the PGR lignite can be explained in terms of its greater maturation level. In this sense, it is noteworthy to point out that the alkali soluble fraction of this lignite does not contain fulvic acids, since the extraction liquid remains colourless after acidification, in contrast with the other samples that contain 5.1% (AR) and 3.1% (P) respectively. The absence of such a fraction could be explained by the general insolubilization process of organic material in sediments with increasing burial depth, which is accompanied by elimination of hydrophilic fractions from the upper layer [22].

Table 1 shows the elemental analysis and atomic ratios of the parent lignites and their respective HA fractions. Because of the high HA concentrations, their composition would be expected to reflect those of the whole

TABLE 1

Elemental analysis and atomic ratios of the lignite samples and their humic acids (on a moisture ash-free basis)

Samples	Ash	C	H	N	S	O ^a	H/C	O/C
PGR	21.8	63.5	4.6	0.9	2.5	28.5	0.86	0.33
HA-PGR	5.4	59.9	4.3	1.2	3.6	34.7	0.86	0.43
AR	25.5	55.9	4.0	2.4	1.7	36.0	0.85	0.48
HA-AR	5.8	58.6	4.5	2.4	—	34.3	0.93	0.45
P	19.2	50.3	5.1	2.3	2.1	40.2	1.21	0.59
HA-P	3.5	53.0	4.9	1.3	—	38.7	1.12	0.55

^aBy difference.

coals. The different values fall within the ranges found by other authors for similar samples [1–3,18,23].

The higher C content and lower O content of the sample PGR might indicate again its greater maturity level. The values of the H/C and O/C ratios indicate that the samples PGR and AR and their respective HA are more aromatic than the samples P and HA-P. Only the latter two present H/C ratios > 1 , which show that the unsaturation in this sample is smaller than in the other samples. In any case, because of the intrinsic chemical complexity of these materials, the elemental composition data can be interpreted only in a very general way in structural or genetic terms, even when plotted on the widely used van Krevelen diagram (H/C vs. O/C atomic ratios).

The FT-IR spectra of the samples (not shown here) were very similar to those reported and largely discussed by other authors [2,3,18]. The large contribution of the HA to their parent lignites is reflected in the similarity between both groups of spectra. The spectra of the parent lignites were only sometimes more diffuse.

Only small differences between the samples were observed. The absorption bands due to aliphatic C–H in the 2900 cm^{-1} region are less prominent in the HA-PGR sample. This HA appears to have a higher acidic character as indicated by the carboxyl vibration at 1720 cm^{-1} . Weak bands at 1510 cm^{-1} were assigned to aromatic C=C. Bands arising from peptidic bonds (1540 and 1665 cm^{-1}) were not observed due probably to the low N content of the samples. A sharp absorption at 1035 cm^{-1} is attributed in part to C–O stretching of polysaccharides and Si–O of silicates.

The ^{13}C -NMR spectra of a typical lignite and its HA are shown in Fig. 1. They can be considered as representative of the whole series discussed in the following. Ranges of relative concentrations of different classes of carbons obtained from the integration of the spectra according to classical subdivisions are also given in Fig. 1.

In general, the solid state NMR spectra are dominated by broad bands assigned to aliphatic (0–100 ppm) and unsaturated carbons (110–160 ppm) and resonances around 175 ppm ascribed to esters and carboxyl carbons. They show striking similarities among them and resemble those of a highly aromatic material [5]. Only resonances for OH substituted aromatic carbons are more prominent in the HA spectra than in the parent lignites. However, no discernable trace of lignin (sharp methoxyl carbon signal at 55 ppm) or carbohydrate structures (distinct signals at 64, 72–76, 84–90, 106 ppm) was apparent. The observed quantitative differences in levels of aromaticity, carboxylic and phenolic aromatic structural groups have been considered [4] as a result of structural variations in the source material of the coal.

The information given by the spectroscopic methods indicates that despite the lipid removal treatment to which the parent lignite was subjected the HA

Fig. 1. Solid-state ^{13}C -NMR spectra of the lignite from Padul (P) and its humic acid fraction (HA-P)

contains paraffinic structures linked to them. These structures were found to be hydrophobic compounds joined in different association levels [13,15]. In general the spectral features are rather similar and failed to distinguish between the samples. No significant differences attributable to diagenetic differences between the parent lignites were evident.

Total ion chromatograms (TIC) of the CuO degradation products of the samples PGR and HA-PGR are presented in Fig. 2. They can be considered representative for all the samples. The yields of oxidation products amounted to 41–45% of the initial weights for the lignite samples and 55–60% for the HA as calculated from the ether extracts.

In contrast with more drastic oxidation procedures, such as permanganate degradation, which yielded mainly straight-chain alkanes and benzenepolycarboxylic acids with the HA-PGR sample [24], the CuO oxidation products consisted of some low molecular weight alkanolic acids, α,ω -dicarboxylic acids, methyl substituted benzoic acids, benzenepolycarboxylic acids and a suite of simple substituted carboxyl phenols, which have been considered as retaining distinguishing characteristics of the parent lignin com-

Fig. 2. Total ion chromatograms (TIC) of the lignite from Puentes de García Rodríguez (PCR) and its humic acid fraction (HA-PGR). Peak identities (as unsilylated precursors) are 1 = *p*-hydroxybenzaldehyde; 2 = *p*-hydroxyacetophenone; 3 = *m*-hydroxybenzoic acid; 4 = vanillin; 5 = acetovanillon; 6 = *p*-hydroxybenzoic acid; 7 = syringaldehyde; 8 = aceto-syringone; 9 = vanillic acid; 10 = syringic acid; 11 = *p*-coumaric acid; 12 = ferulic acid. Other compounds: a = alkanolic acids (C3–C5); b = methyl substituted benzoic acids; c = α,ω -dicarboxylic acids (C4–C9); d = benzenepolycarboxylic acids

pounds. Although some authors [25] suggest that phenolic compounds may arise from glucose, Almendros and Leal [26] failed to detect significant amounts of phenolic compounds in the CuO degradative oxidation of artificial, carbohydrate-derived humic-like polymers.

The relative yields of lignin-derived phenols (estimated as TMS esters by GC/MS analysis) were highest for the HA fractions, although only small dif-

ferences between the samples were found. However, as discussed by Ertel and Hedges [10], these values are not directly related to the amount of lignins in the samples. In addition, as occurs in general with chemical degradative methods, absolute accuracy of quantitative data from CuO oxidation cannot be ensured [27]. However, as it is apparent from Fig. 2, the high acid/aldehyde ratio within the syringyl family in the samples PGR and HA-PGR (peaks 10/7) suggests that the remnant lignin components have undergone some microbial alteration [10]. Nevertheless, the distribution of aldehydic and acidic phenols within the vanillyl family is similar in all the samples to that obtained by CuO oxidation of vascular plant tissues [10]. This can be considered as evidence of lack of alteration of lignin during the diagenesis, which confirm the low maturation level of the lignite studied.

In any case, the occurrence of aldehydic, ketonic and acidic forms of vanillyl and syringyl phenols suggests that lignin polymers have been incorporated in the macromolecule of the lignites and are still identifiable. Considering these lignin derived phenols exclusively, the different samples exhibit similar alkaline CuO oxidation behaviour, which indicates that no differences in depositional input for these deposits were detected.

In conclusion, the results obtained support the view [7] that during the humification process lignin is incorporated into the lignites. This work provides no evidence for the incorporation of cellulose. On the other hand, structural characteristics of HA as revealed by the methods used here failed to distinguish between lignite samples of similar maturity level.

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