Molecular characterisation of vitrinite in relation to natural hydrogen enrichment and depositional environment

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Abstract

The Py-GC/MS results of the study carried out on two groups of vitrinites (perhydrous and non-perhydrous) of different age and properties and on a trimaceral coal associated with one of the perhydrous group are discussed. Such a study provides information about the effect of natural hydrogen enrichment on vitrinite structure at the molecular level. Moreover, the influence of the different conditions in the sedimentary environment on the chemical structure of the vitrinite is also discussed. This influence is inferred through differences in the distribution and relative amount of phenolic compounds found in the pyrolysates from two samples of two different coal-beds in the same basin but formed under different paleoenvironmental conditions. For vitrinites with a high H/C atomic ratio, despite having a strong perhydrous character, their pyrolysates exhibit the highly phenolic signature typical of lignin-derived material with only minor aliphatic compounds. Thus, the major chemical structural elements in these vitrinites are simple phenols with a high contribution of para alkyl-substituted derivatives. However, there is no parallel relationship between the evolution of the oxygenated functionalities and the reflectance values. From the results obtained a coalification pathway where hydrogenation processes predominate over thermal ones is proposed. The presence of resin-like substances and/or oils (which are two of the causes of natural hydrogen enrichment) in the molecular structure of vitrinites have, therefore, affected the normal evolution of the lignin and contributed to the special properties of this type of materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coal; Vitrinite; Perhydrous vitrinite; Molecular characterisation; Rank; Phenols; Hydrogen-donors

1. Introduction

The main problem in obtaining detailed structural information about coal is the analytical inaccessibility of this material. For this reason, the degradation of coal macromolecules into representative fragments is widely used in a coal characterisation as an alternative to coal analysis in a solid state by spectroscopic methods. It is, thus, possible to obtain data at a molecular level which complement the overall structural information obtained through the spectroscopic analysis of the material in a solid state. The suitability of using a combination of these two methodologies is clearly shown in the studies related to the evolution of lignin, the major vitrinite precursor, and the structural models for lignin-derived vitrinite in the earlier stages of coalification (Hatcher et al., 1988, 1989, 1992, 1994; Hatcher, 1990). Such an approach is also very useful for studies on coal utilisation. Burgess and Schobert (1998) have reported the use of a combination of solid-state 13C-NMR and Py-GC/MS for determining the probable light reaction products of direct liquefaction. In a similar way, knowledge of the molecular structure of coal, facilitates the study of the mechanism or process of natural hydrogen enrichment of vitrinites and it could help to determine how this enrichment affects the physico-chemical and technological properties of coals.

Several methods of degradation have been applied to coal and kerogens (Rullkötter and Michaelis, 1990; Haenel, 1992) but pyrolysis is probably the most widely used. To obtain information on the initial structure of the coal from the different structures identified in the
pyrolysates, the pyrolysis conditions are crucial for minimising secondary reactions. The more widespread use of pyrolysis for obtaining data about coal, macerals and diverse organic matter, in general, at a molecular level has been mainly due to the development of fast micro-scale flash pyrolysis techniques with the subsequent on-line identification of fragments through gas chromatography, mass spectrometry or a combination of these methods (Py-GC/MS) (Meuzelaar et al., 1984a, 1992). It is assumed that such a pyrolysis system mainly yields products of primary degradation.

It has been demonstrated that Py-GC/MS studies provide very useful information on the relationship between coals, coal macerals, and their precursors as well as the chemical modifications of these precursors with the increase in the degree of coalification (Nip et al., 1988, 1992; Hartgers et al., 1994). The pyrolysis patterns of liptinite, vitrinite and inertinite concentrates have also shown that there is a clear distinction between these maceral groups and many similarities within the same maceral group in spite of big differences in depositional environment, geological age, coalification history, sample preparation and sample storage conditions (Meuzelaar et al., 1984b, 1992). Marked correlations between the pyrolysis patterns of coals and rank, depositional environment, maceral composition and reactivity have also been reported (Harper et al., 1984; Meuzelaar et al., 1984a; Durfee and Voorhess, 1985). Furthermore, Py-GC/MS offers special advantages for characterising coals with regard to industrial processes because most coal conversion processes include one or more thermal steps. Thus, numerical models for the direct prediction of technologically significant parameters through Py-GC/MS have been proposed by Harper et al. (1984) and Durfee and Voorhees (1985). Moreover, it has also been reported that a classification system of coals based on pyrolysis data could be more suitable for industrial uses of coal than one obtained through conventional parameters (Carlsen and Christiansen, 1995) or could at least offer useful complementary information. In addition, when analytical pyrolysis is performed on pure vitrinites, more detailed knowledge of the molecular changes associated with the increase in vitrinite reflectance as well as insights into vitrinite reflectance suppression and the process of hydrogen-enrichment in vitrinite can also be obtained (Kruege and Bensley, 1994; Veld et al., 1994; Stankiewicz et al., 1996).

The main objective of this work was to find out how the mechanisms of natural hydrogen enrichment (through different processes such as hydrocarbon impregnation and resinization of higher plant tissues, the precursors of the huminite/vitrinite components of coals) act on the molecular structure of this maceral. Such information could help to explain subsequent anomalous evolution and properties in vitrinite during the coalification process. To achieve this objective the Py-GC/MS results of two perhydrous huminites/vitrinites are discussed and compared with those obtained from normal (non-perhydrous) vitrinites. The composition of the degradation products of the associated (trimaceradic) coal taken from the same coal bed as one of the perhydrous vitrinites is also reported. Furthermore, the information obtained about the influence of the different paleoenvironmental conditions on the molecular structure of vitrinite by examining the pyrolysis results from two non-perhydrous vitrinites from different coal seams, is a secondary objective of this work. For this reason, the vitrinites were selected from the same coal basin but from two different coal seams in which changes in the sedimentary environmental conditions such as, pH, redox, gelification index, were previously determined and reported by Marques (1987) and Jiménez et al. (1999).

2. Experimental

2.1. Selection of samples. General characteristics

The samples selected for this work are huminites and vitrinites of almost pure organic composition. They are of different ages, Cretaceous, Jurassic (huminites/vitrinites) and Carboniferous (vitrinites). These huminites/vitrinites were hand-picked from fresh coal seams, the samples being located inside the vitrain lithotype. The samples are from different Spanish coal basins and they are denoted (see Table 1) as: Pv2 and Pv3 (vitrinites of Stephanian age from commercial coal seams number 2 and 3 respectively from the Puertollano Basin); Av (huminite/vitrinite of Malm age from Asturias) and Tv (huminite of Albian age from the Teruel Basin). Moreover, a trimaceradic coal sample (denoted as Tac coal from the Teruel Basin, see Table 1) which is associated in the same coal bed to the Tv sample was also selected for this work. The samples were petrologically and geochemically characterised and then reported in previous papers (Suárez-Ruiz et al., 1994a,b; Iglesias et al., 1995; Jiménez et al., 1998). A summary of their petrographic composition as well as their reflectance values and chemical properties are given in Tables 2 and 3, respectively. A brief description of the samples studied is also included. For the nomenclature of these materials in low and medium coal rank, the International Committee for Coal Petrology (ICCP) (1963, 1971, 1975, 1998) systems are followed.

2.1.1. Coals from the Puertollano Basin, Spain (Pv2 and Pv3, Table 1)

These samples were taken from coal seams number 2 and 3 from the Puertollano coal basin (Pv2 and Pv3, respectively), in which the coals originated in a lacustrine environment (Wallis, 1983). Differences in physico-
chemical sedimentary conditions for coal seams 2 and 3 were found by Marques (1987) and also described by Jiménez et al. (1999). Marques (1987) suggests the influence of reducing conditions during the formation of coal seam number 2 as result of deeper water and a more oxygen rich environment for coal seam number 3, this being due to the oscillation of the water table covering the peat. These results have been confirmed by data reported by Jiménez et al. (1999). Petrographically, the vitrinites studied in this work are made up of a relatively homogeneous material, collotelinite (Table 2) followed by collodetrinite. Small amounts of telinite,

Table 1
Sample code, location and age of the coals used in this study

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Provenance</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pv2</td>
<td>Puertollano Basin, seam 2, Spain</td>
<td>Stephanian (Carboniferous)</td>
</tr>
<tr>
<td>Pv3</td>
<td>Puertollano Basin, seam 3, Spain</td>
<td>Stephanian (Carboniferous)</td>
</tr>
<tr>
<td>Av</td>
<td>Asturias Basin, Spain</td>
<td>Kimmeridgian (Upper Jurassic)</td>
</tr>
<tr>
<td>Tv</td>
<td>Teruel Basin, Spain (vitrain)</td>
<td>Albian (Lower Cretaceous)</td>
</tr>
<tr>
<td>Tac</td>
<td>Teruel Basin, Spain (clarain)</td>
<td>Albian (Lower Cretaceous)</td>
</tr>
</tbody>
</table>

Table 2
Petrographic composition of the studied coals (values are in vol.% mineral matter free).a

<table>
<thead>
<tr>
<th>Maceral groups</th>
<th>Macerals</th>
<th>Pv2</th>
<th>Pv3</th>
<th>Av</th>
<th>Tv</th>
<th>Tac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huminite</td>
<td>Ulminite</td>
<td>85.5</td>
<td>94.8</td>
<td>14.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gelinite</td>
<td>0.0</td>
<td>0.0</td>
<td>65.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Corpohuminite (Phlobaphinite)</td>
<td>14.5</td>
<td>1.8</td>
<td>0.0b</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attrinite</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitrinite</td>
<td>Telinite</td>
<td>1.9</td>
<td>4.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Collotelinite</td>
<td>94.9</td>
<td>82.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Collodetrinite</td>
<td>3.2</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vitrodetrinite</td>
<td>0.0</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Corpogelinite</td>
<td>0.0b</td>
<td>0.0b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liptinite</td>
<td>Sporinite</td>
<td>0.1c</td>
<td>1.4</td>
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<tr>
<td></td>
<td>Resinite</td>
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<td>0.0</td>
<td>3.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Inertinite</td>
<td>Semifusinite</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fusinite</td>
<td>0.3c</td>
<td>14.0</td>
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<td></td>
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<tr>
<td></td>
<td>Inertodetrinite</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Data are from Suárez-Ruiz et al., 1994 a,b and Jiménez et al., 1998)
b Traces, because of the low amount of these components in the samples they were not counted during the analysis. However, they were identified.
c Impurities.

Table 3
Vitrinite reflectance values (Ro,%) and chemical parametersa of the coals used in this studyb,c

<table>
<thead>
<tr>
<th>Sample</th>
<th>RO (%)</th>
<th>V.M. (%daf)c</th>
<th>C (%daf)</th>
<th>H (%daf)</th>
<th>O (%)</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pv2</td>
<td>0.63</td>
<td>34.2</td>
<td>82.6</td>
<td>4.8</td>
<td>10.0</td>
<td>0.70</td>
</tr>
<tr>
<td>Pv3</td>
<td>0.70</td>
<td>31.5</td>
<td>83.1</td>
<td>4.7</td>
<td>9.7</td>
<td>0.68</td>
</tr>
<tr>
<td>Av</td>
<td>0.39/0.72e</td>
<td>54.9</td>
<td>84.8</td>
<td>5.9</td>
<td>7.4</td>
<td>0.83</td>
</tr>
<tr>
<td>Tv</td>
<td>0.23</td>
<td>64.2</td>
<td>81.7</td>
<td>6.2</td>
<td>9.5</td>
<td>0.92</td>
</tr>
<tr>
<td>Tac</td>
<td>0.38</td>
<td>44.9</td>
<td>79.9</td>
<td>5.3</td>
<td>11.8</td>
<td>0.80</td>
</tr>
</tbody>
</table>

b Data are from Suárez-Ruiz et al., 1994 a,b and Jiménez et al., 1998).
c daf: Dry ash free.
d d: diff: Difference.
e 0.72: Data obtained on phlobaphinite.
2.1.2. Coal from the Asturias Basin, Spain (Av, Table 1)

This sample is a jet, originated from drifted wood and deposited in transitional facies of a marine-continental sedimentary environment (Valenzuela et al., 1986). Av coal is found as a vitrain lithotype of 8 cm maximum width in the Kimmeridgian sediments on the top of the Pliensbachian series, which are considered as source-rocks in this part of the Jurassic basin in the North of Spain (Suárez-Ruiz and Prado, 1995). Impregnation by oils/hydrocarbons, which were generated from the Pliensbachian sediments from which they migrated, during the initial diagenetic stages of the evolution of this vitrain was the process responsible for the hydrogen-enrichment of this coal. Consequently it exhibits special chemical composition properties and vitrinite reflectance suppression (Suárez-Ruiz et al., 1994a). The maceral group of huminite/vitrinite is the only organic component of this sample, ulminite being the most important petrographic component, followed by phlobaphinite (Table 2). Only ulminite, because of its specific nature and physical features (high porosity), was found to have absorbed the oils/hydrocarbons from the lower sediments (Pliensbachian source-rocks). This explains the differences in vitrinite reflectance between the huminite/vitrinite macerals (Table 3). The Av sample shows a high H/C atomic ratio and gives very high oil and gas yields in spite of its huminitic/vitrinitic composition. Considering all of the geological data known at present, in addition to those corresponding to this coal, phlobaphinite reflectance (0.72%) is regarded as being the closest value for determining the real rank reached by this sample which is of high-volatile bituminous coal rank.

2.1.3. Coals from the Teruel Basin, Spain (Tv and Tac, Table 1)

These samples were taken from the number 4 coal seam of the Escucha Formation located in the underground Concepción Coal Mine. According to the published data (Querol et al., 1991), coal seams from the Escucha Formation originated in a delta-estuary depositional environment. The Tv sample is a vitrain lithotype located at the top of the coal seam and derived from drift wood carried away by streams and incorporated into a swamp. It is mainly made up of humotelinite (huminite maceral group) with 3.4% resinite (Table 2) that appears as filling in cell cavities. The huminite is also characterised by its relatively high H/C ratio (Table 3) and perhydrous character when compared with other coals from this formation. It also shows suppressed reflectance (Suárez-Ruiz et al., 1994b). All of these features are due to the special nature of the precursor plant tissues of this coal: a humotelinitic structure saturated with resinite and resinite-like substances resulting from a resinization process undergone by the original plant tissues which occurred before the incorporation of this material into the depositional environment (Suárez-Ruiz et al., 1994b). This process (defined in Stach et al., 1982 and Taylor et al., 1998), has been reported as typical for some Cretaceous and Tertiary coals especially those derived from conifer woods in which the saturation of the plant tissues by resinous substances took place. Moreover, the Teruel Coal Basin was located inside the tropical belt during the Albian time and these authors mentioned above, have also indicated that in the tropics there are many resin-bearing angiosperms. Resins, therefore, were very abundant in the flora at that time.

The Tac sample (Table 1) is a trimaceralic coal which corresponds to the whole coal (clarain lithotype) of seam number 4, adjacent to the Tv sample. In consequence, the three maceral groups appear in different concentrations, with that of huminite being the major component of this coal (Table 2). The nature of the huminite is different to that found in the Tv coal, and so, humocollinite is the main component. The random reflectance of the Tac coal is higher than that described for the Tv sample because of the suppressed reflectance shown by this coal (Table 3). Nevertheless, both coals from seam number 4 of the Escucha Formation, have reached the same rank corresponding to the beginning of the bituminisation interval (Suárez-Ruiz et al., 1994b).

2.2. Analytical procedures

For this work, all the samples were analysed by Py-GC/MS. Analytical pyrolysis was carried out at 600°C for 20 s in a CDS (chemical data system) Pyroprobe 2000 unit consisting of a Pt coil heated at a rate of up to 20°C min⁻¹ in a He atmosphere. The sample (2 mg) was placed in a quartz tube, using quartz wool for end plugs. The volatile pyrolysis products were transferred on-line to the inlet of a Hewlett Packard 5988A GC–MS through a home-built interface heated at 280°C.
Chromatographic separation was achieved in a fused silica capillary column (HP-5; 30 m length, 0.25 mm i.d., 0.25 μm film thickness). Oven temperature was programmed from 40 to 300°C at a rate of 6°C min⁻¹ and held isothermally for 10 min. Helium (1 ml min⁻¹ flow rate) was used as carrier gas. The quadrupole mass spectrometer detector was set at 70 eV. Identification of the compounds was achieved by a mass fragmentograph, library search and comparison with literature data. When possible, identification was accomplished by comparison with authentic standards. This was done in an indirect way by means of the injection of commercial phenolic compounds and aromatic hydrocarbons in a gas chromatograph equipped with mass detection. The mass spectra and the relative retention times of such compounds were thus, obtained and compared to the Py-GC/MS data of the studied samples.

3. Results and discussion

Fig. 1 and Table 4 show the Py-GC/MS results for the huminites/vitrinites (Tv, Av, Pv2 and Pv3) and the trimaceralic coal (Tac). Pyrolysis experiments were performed on non-extracted samples so that some of the compounds present in the pyrolysates may arise from those physically trapped inside the coal network. The relatively low values of the S1 peak from the Rock-Eval pyrolysis (<2.0 mg HC/g rock) (Suárez-Ruiz et al., 1994b; Jiménez et al., 1998) indicate a very low amount of free hydrocarbons. For this reason, evaporative products can only be minor contributors to the total components identified in the chromatograms.

Fig. 1 shows big differences in peak intensities. The intensity of the peaks in the chromatograms from the Av and Tv samples is much stronger than that of the other samples (Pv2, Pv3 and Tac). Here, the intensity decreases in the following order Tac > Pv3 > Pv2. The chromatograms clearly show that perhydrous huminites/vitrinites are more susceptible to degradation than the non-perhydrous samples, giving rise to a higher amount of pyrolysate. This result agrees with the oil and gas production obtained by means of the Gray–King pyrolysis at 550°C of the samples as reported by Iglesias et al. (1995) through the FTIR study of the samples. The small size of the entities contributes, through the cleavage of weak non-aromatic bonds, to the high conversion ratio of the materials. At the same time, the high hydrogen content of the samples (due to natural hydrogen-enrichment) provides a large amount of hydrogen for stabilising the free radicals formed during the thermal treatment. The aromatic structures in the perhydrous vitrinites are less condensed than those present in the non-perhydrous samples as demonstrated by Iglesias et al. (1995) through the FTIR study of the samples. The small size of the entities contributes, through the cleavage of weak non-aromatic bonds, to the high conversion ratio of the materials. At the same time, the high hydrogen content of the samples (due to natural hydrogen-enrichment) provides a large amount of hydrogen for stabilising the free radicals originated during heating, increasing the production of light components. It should also be taken into account that the presence of resinous material with a cyclopolaric nature in the vegetal structure of the Tv huminite and impregnation by a heavy fraction of oils/hydrocarbons in the Av sample may enhance the process of hydrogen transfer. On the other hand, the non-perhydrous vitrinites (Pv2 and Pv3) are made up of more condensed aromatic structures which may not be detected by Py-GC/MS nor released in the experimental conditions used. Moreover,
in these samples the amount of hydrogen is small (lower H/C ratio, see Table 3) so that, polymerisation of the radical intermediates is probably favoured. As a result a small yield of pyrolysate is obtained (Figs. 1 and 2).

The vitrinite maceral group mainly derives from the lignin, cellulose and tannins present in higher plants. In accordance with this origin, it is assumed that the pyrolysis of the vitrinites gives rise to predominantly gaseous products, aromatic hydrocarbon and phenolic compounds. However, the n-alkane/n-alkene series are also commonly found in vitrinite pyrolysates (Nip, 1988, 1992; Hatcher et al., 1992; Hartgers et al., 1994; Veld et al., 1994; Stankiewicz et al., 1996). The presence of normal hydrocarbons in vitrinite pyrolysates is attributed to the incorporation of aliphatic components from materials other than the precursors of vitrinite. Thus the incorporation of aliphatic substances from microorganisms and lipid products through migration during deposition and/or early diagenesis is possible (Stach et al., 1982; Zhang et al., 1993; Gentzis and Goodarzi, 1994; Hartgers et al., 1994; Stout and Boon, 1994; Stankiewicz et al., 1996). Lipoidal or bituminous material may also have been assimilated within the vitrinite during coalification (Hutton and Cook, 1980; Nip et al., 1992; Mastalerz et al., 1993; Gentzis and Goodarzi, 1994). It is known that during the coalification process, liptinitic components undergo primary cracking. They are thermally degraded and become more or less fluid giving rise to a set of secondary products. It is precisely the mobility of the low-molecular-weight products generated in this stage which promotes migration and subsequent accumulation into other materials such as the microporous structure of huminite and vitrinite in coals or other organic particles in rocks. Jet in oil shales and source rocks is an example of impregnated coal. It is known that this type of coal, in most cases, originated from drift wood which has been secondarily impregnated with bitumen from the surrounding environment (Stach et al., 1982; Taylor et al., 1998). The immediate consequence of the incorporation of aliphatic material into the vitrinite is an abnormally high hydrogen content with important implications for the physico-chemical properties of vitrinite. Suppression of vitrinite reflectance is one of the consequences of the natural hydrogen-enrichment of vitrinites.

Table 4 shows predominantly aromatic compounds for the pyrolysates with only minor aliphatic compounds. No series of n-alkanes and n-alkenes were detected. The very light 1,3-pentadiene, 1,3-cyclohexadiene and 1,3,5-hexatriene compounds (peaks 1, 2 and 5) were the only important aliphatic components in the pyrograms with a very low contribution with respect to the benzene and phenol derivatives (Fig. 1). Regarding the presence of aliphatic material in the vitrinites, the most important implications concern the perhydrous...
samples Av and Tv. It is clear that their perhydrous character, which is the cause of their peculiar properties and vitrinite reflectance suppression is not due to the incorporation of lipoidal substances into the biopolymers from lignin, cellulose or tannin as was reported for other perhydrous vitrinites (Mudkhopadhyay, 1994). The characteristics, composition and behaviour found for the Tv sample (Suárez-Ruiz et al., 1994b) also differ from the behaviour caused by the presence of resinite-derived material dispersed within the vitrinite proposed by Fowler et al., (1991) for Tertiary lignites. On the other hand, in the case of the Av sample (this huminite/vitrinite is considered as Spanish jet), comparison between its pyrolysate and that reported for another well-known coal with very similar properties, Whitby jet (Watts et al., 1997) shows clear differences. The pyrolysate from Whitby jet contains significant quantities of aliphatic hydrocarbons which are not found in that of the Av coal. Thus, although the impregnation/adsorption of bituminous substances can be considered as the factor mainly responsible for the special properties of jets and other coals affected by this type of process (Teichmüller, 1992), it is clear that the nature of the substances incorporated into the structure of these coal samples is different. Whereas Whitby jet has been impregnated by substances like hydrocarbons from the parent rock (Watts et al., 1997), hydrocarbons generated and migrated from other very different rocks (Pliensbachian source-rocks) have affected the nature and consequently the composition of the Av huminite/vitrinite (Suárez-Ruiz et al., 1994a).

Although the highly aromatic nature of the pyrolysates derived from Tv and Av seem to contradict the FTIR results, which indicate a high proportion of aliphatic compared to aromatic structures in these samples (Iglesias et al., 1995), this contradiction is only apparent. It should be borne in mind that such a preponderance is inferred through the A factor. To calculate this factor the amount of aromatic structures is estimated through the aromatic \(C=\tilde{C}\) stretching mode at 1600 cm\(^{-1}\) (Ganz and Kalkreuth, 1987). In the stretching region of aromatic \(C=\tilde{C}\) bonds the FTIR spectra of the Tv and Av vitrinites not only show this band but also a significant absorption band at 1500 cm\(^{-1}\). The relative intensity of the bands at 1600 and 1500 cm\(^{-1}\) depends, to a considerable extent, on the substitution/condensation of the aromatic ring (Bellamy, 1975; Schenk et al., 1990). In the light of these considerations and given the nature of the pyrolysates, it can be concluded that the perhydrous character (high H/C atomic ratio) of the Av and Tv samples must be associated with the presence of poorly condensed aromatic structures and a high proportion of aliphatic over condensed aromatic structures rather than with a preponderance of aliphatic over aromatic structures.

Even though Tv huminite has a very low value of reflectance (Table 3), lignin-derived markers such as guaiacol or dihydroxybenzenes were not detected (Fig. 1 and Table 4). Thus, among the aromatic compounds found in the pyrolysates of the samples, simple phenols, benznes and in a smaller proportion naphthalenes predominate. Dibenzofurans, thiophenes and naphthols are also present in all samples but in smaller quantities. Phenol, cresol C2- and C3-alkyl phenols were identified in all coals (Fig. 1 and Table 4) whereas C4-alkyl phenols were only clearly identified in the pyrolysates from the Av and Tv coals. Although pyrolysis yields a similar number of products in the samples studied here, the relative proportion of the major classes of compounds and the internal distribution of the isomers differ from one sample to another.

Fig. 3a shows the relative abundance (using toluene, peak 6 in Fig. 1, as a reference, 100%) of phenols and naphthalenes in the pyrolysates. Phenolic compounds are more abundant in the degradation products from Tv and Av than in the other samples including Tac, the coal
associated with the Tv sample in the same coal-bed. Phenolic structures are therefore more preponderant in the Av and Tv samples than in the other coals. The results also agree with the presence of more poorly condensed aromatic structures in these vitrinites. The presence of simple phenols is usually associated with highly-degraded lignin. In the subbituminous coal rank, the coal structures are phenolic and pyrolysis leads mainly to phenols and alkyl phenols. In the bituminous coal rank, the amount of alkylbenzenes increases strongly with respect to the phenols (Hatcher et al., 1992). However, variation in pyrolysis patterns depends not only on rank but also on composition as well as on the depositional environment and geological history of the coal samples (Meuzelaar et al., 1984a). The dependence of the phenolic yields on factors other than rank is clear in the case of the samples studied here for which a straightforward relationship between the amount of phenols found in the pyrolysates and rank is not observed. In the Av coal, the high yield of phenols can be considered consistent with the reflectance value of ulminite (0.39%, see Table 3) but it disagrees with the real degree of evolution (high-volatile bituminous rank) reported for this coal (Suárez-Ruiz et al., 1994a). In fact, in the Av sample the reflectance measured on the phlobaphinite (0.72%, Table 3) is regarded as being the closest value to the real rank reached by this sample. On the other hand, for the Tv huminite, the phenolic yield seems to be consistent with the real rank reached by the raw vitrain (assigned to the beginning of the bituminization interval) although the absence of lignin-derived markers typical of low-rank coals disagrees with the data from vitrinite reflectance (0.23%, Table 3). With respect to the associated coal (Tac), the higher amount of phenols in the pyrolysis products of Tv (Fig. 3a) can be explained by the presence of inertinite macerals and the different nature of the huminite in Tac (mainly humocollinite and non-perhydrous humotelmite, see Table 2). According to Nip et al., (1992) alkylbenzenes and naphthalenes are the major degradation products of inertinite macerals.

For the non-perhydrous vitrinites, Pv2 and Pv3, in agreement with their rank, the amount of phenols might be expected to be close or slightly higher in the Pv2 pyrolysate than in Pv3. The results given in Fig. 3a, however, show the inverse trend with a slightly higher value for phenols in Pv3 than in Pv2 and this cannot be rationalized in terms of rank differences. In the raw samples (Pv2 and Pv3) formed in a lacustrine environment the incorporation of sedimentary lipids is probable. Sedimentary lipids contain fatty acids and/or alcohols so that they could have liberated free fatty acid and/or alcohol after hydrolysis during the initial organic accumulation and coalification steps. These compounds (fatty acid and alcohol) are assumed to have reacted with the phenolic OH group of lignin leading to long chain alkyl aromatics (Dong and Ouchi, 1989). The incorporation of sedimentary lipids is easier in a reducing environment. In relatively oxic environments, however, these materials are preferentially degraded whereas the more resistant woody materials are comparatively well preserved. In the light of these considerations, the differences found in the amount of phenols between Pv2 and Pv3 pyrolysates could be interpreted to be the result of the different conditions existing in the depositional environment of these two seams (Marques, 1987; Jiménez et al., 1999). In fact in accordance with data from these authors, coal-bed number 3 (coal sample Pv3) from the Puertollano coal basin seems to have been formed under neutral or alkaline and relatively oxidizing conditions during the peat stages unlike the conditions under which seam number 2 (coal sample Pv2) originated.

An increase in the total C0–C2 phenol yield (Fig. 3b) with the increase in vitrinite reflectance of the parent sample to 0.65% has been reported for vitrinite rich coals and vitrinite concentrates (Venkatesan et al., 1993). Such a behaviour has been attributed to the formation of simple alkyl phenols at the expense of methoxylphenol precursors via the loss of the methoxy group. For the coal samples studied here the plot of the relative amount (toluene as reference) of C0–C2 phenols in the pyrolysate versus the vitrinite reflectance of the parent coal (Fig. 3b) does not show the same trend. Indeed, it should be emphasized that the high values of the C0–C2 phenols were found for the perhydrous vitrinites with the lowest values of reflectance.

The most intense peak of those corresponding to the phenolic compounds is peak 19 (Fig. 1) due to the contribution of the m- and p-cresol isomers which are not separated in the chromatographic conditions used in this work. The NMR analysis of the oils obtained by means of Gray–King pyrolysis (Iglesias et al., 1997) has shown that the main sites of phenolic compound substitution in the degradation products from Av and Tv coals are positions 2 and 4 whereas phenol derivatives substituted in the meta position with respect to the OH group are almost absent. According to these results, peak 19 in the pyrolysates from Av and Tv (Fig. 1) can be considered as being mainly due to p-cresol. Fig. 4 shows the contribution of the intensity of this peak to the total intensity of the peaks identified as phenol derivatives in the chromatograms. As can be seen, Av and Tv pyrolysates show the highest contribution. The results obtained concerning the contribution of phenols and p-cresol in the Av and Tv pyrolysates indicate that the major chemical structural elements of the huminites/vitrinites that form the Tv and Av samples are phenols with a preponderance of para-alkyl substitution. This structural feature clearly explains the presence of the aromatic mode at 1500 cm⁻¹ as well as the high intensity of the 815 cm⁻¹ mode in the out-of-plane bending
region of the aromatic C–H bonds in the FTIR spectra (Iglesias et al., 1995).

Fig. 4 also shows clear differences between results obtained for Pv2 and Pv3. Moreover, significant differences between the composition of the pyrolysates from Pv2 and Pv3 are also evident when the contribution of phenol and alkyl phenols from C1 to C3 to the total amount of phenols is considered (Fig. 5). The Pv2 pyrolysate shows a higher phenol and contribution of cresols than Pv3 pyrolysate. Pv3, however, is rich in C2- and C3-alkyl phenols. Thus, phenol derivatives in the pyrolysate from Pv3 show a higher degree of alkyl substitution than those present in the Pv2 pyrolysate. These differences are not due to rank because of the very close degree of evolution of the two materials. It is also unlikely that they arise from a change in the composition of the vegetal precursors because, according to the data reported by Wagner (1985), the plant megafossils which originated from the different coal seams in Puertollano are similar throughout the entire stratigraphic interval which is representative of this basin. Taking into account the fact that phenol and cresols can also be formed by the pyrolysis of more highly substituted phenolic structures, the different degree of substitution between the Pv2 and Pv3 pyrolysates suggests that differences in the aliphatic structures were present in the initial materials. This could have arisen from the presence in the Pv3 sample of a higher amount of less-structured material (Table 2). This again underlines the influence of the physico-chemical conditions of the depositional environment on the distribution of phenol derivatives in the degradation products of coals. Similarly, the structural differences in the aliphatic moieties of Tv and its associated coal, Tac, reported through a FTIR study (Iglesias et al., 1995) explain the different contribution of phenol, cresols, C2- and C3-alkyl phenols found in their pyrolysates as can be seen in Fig. 5.

The internal distribution of phenol derivatives is depicted in Fig. 6 in which the peak intensities were normalised to the highest peak in the distribution pattern. Peak 16 = phenol; peak 18 = o-cresol; peak 19 = m-, p-cresol; peak 21 = 2,4-+2,5-dimethylphenol; peak 23 = 3-+4-ethylphenol+3,5-dimethylphenol.

Fig. 7. Ratio between m-, p-cresol (peak 19) and o-cresol (peak 18).
Five C2-alkyl phenols are represented by only two GC peaks (peaks 21 and 23 in Fig. 1). They were tentatively identified as 2,4-dimethyl phenol and 2,5-dimethyl phenol (peak 21) and 3-ethyl phenol, 4-ethyl phenol and 3,5-dimethyl phenol (peak 23). Again, the absence of alkyl-substituted phenols in the meta position in the pyrolysates from the Av and Tv samples means that these isomers cannot occur in unresolved mixtures. 2,6-Dimethyl phenol and 2-ethyl phenol were also identified in all the samples but in very small amounts. For Pv2, Pv3 and Tac minor quantities of 2,3-dimethyl phenol and 3,4-dimethyl phenol were detected. In Fig. 6 only the main isomers are considered (peaks 21 and 23). For Av, Tv and Tac coals the intensity of peak 21 is higher than that of peak 23 whereas in Pv2 and Pv3 these peaks appear in similar proportions. This implies a higher contribution from 2,4-dimethyl phenol in Tv, Av and Tac than in the Pv2 and Pv3 coals. The distribution pattern of alkyl phenols in the Mesozoic samples (Av, Tv and Tac) is very close to the results reported by Hatcher et al., (1988, 1989 and 1992) for the composition of the degradation products from coalified gymnospermous wood. Hatcher et al. (1988) interpreted the preponderance of 2,4-dimethyl phenol as an indication that the carbon linkage at the C-4 position associated with the three-carbon side-chain of lignin is retained. The C2-phenol distribution in the degradation products from the Carboniferous vitrinites (Pv2 and Pv3) is, however, more difficult to relate with the structure of the lignin. This may be attributed to the rank reached by the Pv2 and Pv3 samples (Hartgers et al., 1994) but a tannin-related origin may also help to explain the C2-phenol distribution (van Bergen et al., 1995). Unfortunately, there is no straightforward interpretation for the origin and distribution of phenols in pyrolysates of coals and no specific markers were detected in the samples because of their medium rank. However, taking into account the different ages of the samples it is more likely that the results are attributable to the source of the phenolic compounds present in the pyrolysates due to differences in the vegetal precursor. In particular, it is possible to attribute the distribution to the different proportions of periderm (bark) and xylem (wood) tissues that contributed to the formation of the vitrinite in the samples. Megafloral studies in the Puertollano stratigraphic series (Wagner, 1985) have shown that lycophytes trees were predominant in forest swamps in late Stephanian (Carboniferous). Lycophytes gave rise to large amounts of bark but little secondary xylem or true wood.
The distribution patterns of benzene and naphthalene derivatives were also investigated and they are depicted in Figs. 8 and 9, respectively. For these figures the peak intensities were normalised to the highest peak in each case. It is assumed that differences in rank have little influence on the distribution patterns of benzene derivatives and a similar distribution of this class of compounds has been reported for vitrinites and inertinites (Nip et al., 1988; Krüge and Bensley, 1994). In agreement with this, the distribution of benzene derivatives given in Fig. 8 is very close for P0, P1 and TAC samples. The TV and TV coals also show a similar distribution while differing considerably from that of the other samples. Thus, the proportion of benzene \( m-, p- \) xylene and C3-alkylbenzenes is higher in TV and TV than in the other pyrolysates. The distribution of naphthalene derivatives (Fig. 9) is also similar for TV and TV but again it differs from that found in the other samples. Naphthalene was only detected in trace amounts in TV and TV whereas the other pyrolysates show significant proportions of this compound. Furthermore, the amount of C2-alkynaphthalenes is higher in TV and TV than in the others. The distribution of naphthalenes not only shows differences between the perhydrous and non-perhydrous vitrinites but also between the non-perhydrous samples. Thus, the enrichment in naphthalene of

![Graphs showing differences in distribution patterns between Av and Tv coals.](image-url)
Pv2 with respect to Pv3 vitrinite deserves special emphasis. The differences found in the distribution of benzenes and naphthalenes in Av and Tv with respect to the other samples suggests that in pyrolysates these compounds had a different origin. It is very likely that such compounds in the Av and Tv huminites/vitrinites arise from those which have been trapped in the vitrinite network. Either that or they constitute fragments of such compounds rather than originate from the coal matrix. This view is supported by the abundance of this type of compounds in the extracts derived from these huminites/vitrinites (Fig. 10). It is very likely, therefore, that such compounds proceed from the resinite in the Tv sample and the hydrocarbons or petroleum-like substances adsorbed by the ulminite in the Av sample. However, their contribution is of minor importance with respect to phenols as shown in Fig. 3a.

The results also show that, in agreement with the ligneous nature of the raw materials (drift-wood), the pyrolysates derived from the perhydrous huminites/vitrinites Av and Tv exhibit the highly phenolic character typical of lignin-derived material, there being no evidence of any very significant incorporation of materials other than lignin. It is clear, however, that the evolution of these samples took place in a different way to that described for lignin during normal evolution/coalification processes. It is known that during the coalification process irreversible chemical reactions are produced within the huminite/vitrinite network. Such macromolecular changes, which include decarboxylation, dehydroxylation, demethylation, aromatisation and finally polycondensation of the aromatic lamellae, control the increase in huminite/vitrinite reflectance throughout the rank series. For the perhydrous huminites/vitrinites studied here, the Py-GC/MS results show that there is no parallel relation between the evolution of the oxygenated functionalities and the reflectance values (Fig. 3b). This could be due to the effect of the presence of hydrogen-donor compounds during the evolution of the samples. In other words, a model based on hydrogenation is probably a more suitable evolution pathway than the thermal model commonly used for explaining coalification. This implies a preponderance of hydrogenation over condensation reactions which could explain the unexpectedly low values of reflectance in the raw materials. As has been reported during the artificial hydrogenation of vitrinite (Shibaoka and Russell, 1981; Davis et al., 1991) the presence of hydrogen restricts the growth of polycyclical aromatic units, the factor mainly responsible for the increase in reflectance.

Although the presence of resin-like substances and oils in the molecular structures of the vitrinite also seems to enhance the process of hydrogenation and, therefore, hinder the normal growth of reflectance, such compounds act at different stages of evolution. This explains why in Tv the composition of the pyrolysate agrees more with the real degree of evolution reached by this sample than with reflectance whereas for the Av sample, the highly phenolic composition of its pyrolysate is unexpected given the real rank reached by the raw vitrinite. At the same time this partly explains the structural differences in the raw huminites/vitrinites. In Tv huminite, the factor responsible for the hydrogenation process is the presence of the compounds in the resin which has a cycloparaffin-like nature. Such compounds arise from the resinization of the vegetal tissues and, therefore, they were present before the incorporation into the depositional environment. According to studies on the hydrogenation of oxygenated compounds (Ceylan and Bredenberg, 1982; Bredenberg and Ceylan, 1983) the absence of lignin-markers in the pyrolysate of Tv huminites could be attributed to the enhancement of \( O \)-demethylation reactions that form phenols in the presence of hydrogen-donor compounds. For the Av huminite/vitrinite the factor responsible for the enhancement of the hydrogenation reactions might be the retention of the heavy fraction (polar compounds) of hydrocarbons in the microporosity of the ulminite. The important and significant role of the polar fraction of hydrocarbons in the process of hydrogen transfer has been demonstrated in studies on artificial coalification (Mansuy and Landais, 1995; Mansuy et al., 1995). Hydrocarbon retention took place during earlier diagenesis when the oxygenated functionalities were probably mainly phenolic. Phenolic compounds are not very reactive during liquefaction (Cronauer et al., 1979). Furthermore, studies on the artificial evolution of carbonaceous materials such as coalified wood by means of hydropyrolysis (Hatcher et al., 1994) have shown that the preservation of the phenolic structure is due to the presence of hydrogen which stabilises the oxy radicals. It is clear, therefore, that the condensation of phenols to aryl ethers or dibenzofuran-like structures described during coalification to the rank of high-volatile bituminous coal is a hindering factor in Av coal.

Finally, comparison of the composition of the pyrolysate from Tv huminite with that reported for other ulminites (vitrinite of low-rank coals) (Syskes et al., 1994) shows clear differences in the chemical composition of this maceral for similar values of vitrinite reflectance. In both cases the composition of the pyrolysate can be related to the lignin structure. Moreover, in both cases the precursor of the ulminite is a woody tissue which is in agreement with the definition and composition of this maceral but although initially it has a high hydrogen content. However, whereas methoxy phenols are abundant components of the pyrolysate in ulminite A studied by Syskes et al. (1994) these kind of compounds are absent in the pyrolysate derived from the ulminite in the Tv sample. This is probably due to the different source of high hydrogen content initially pre-
sent in the vegetal tissue precursor and the effect that this has during the subsequent evolution process.

4. Conclusions

The molecular characterisation of perhydrous huminites/vitrinites by means of Py-GC/MS and the comparison of the results obtained with those found for normal (non-perhydrous) samples shows the effect of the presence (in the molecular structure of vitrinite) of resin-like substances and oils on both the thermal behaviour and the coalification pathway of these coal samples and the evolution of their properties. The effect is that it provides sufficient hydrogen to enhance the processes of hydrogenation to the detriment of those of aromatisation/condensation typical of thermal processes and coalification.

In agreement with the higher conversion rate during the pyrolysis of perhydrous vitrinites (in comparison with non-perhydrous samples), the intensity of the peaks in the pyrograms of the Av and Tv huminites/vitrinites (perhydrous coals) is higher than in the others. This easy degradation is a result both of the reduced condensation of the aromatic units present in the perhydrous vitrinites and the higher amount of hydrogen available for stabilising the radical intermediates formed during thermal treatment.

The hydrogen-enrichment undergone by two of the coals studied here is not reflected in a preponderance of aliphatic components in the pyrolysates. On the contrary, all the pyrolysates show a similar qualitative composition which is mainly aromatic with only minor aliphatic compounds. No n-alkane/n-alkene series were detected, the main components being benzene, phenol and naphthalene derivatives. The differences between samples arise from the relative abundance and distribution patterns of the predominant classes of compounds.

 Phenolic compounds are much more abundant in the pyrolysates from perhydrous huminites/vitrinites than those from the non-perhydrous samples. Furthermore, the pyrolysates derived from perhydrous coals also show a higher contribution of para alkyl-substituted phenols. This indicates that the main chemical structural elements in the raw vitrinites are simple phenols with a preponderance of para alkylsubstituted phenols. This means that the main chemical structural elements in the raw vitrinites are simple phenols with a preponderance of para alkyl-substituted phenols. Such structural units explain the unusual features of the aromatic structures found in the FTIR of these vitrinites (aromatic band at 1500 cm⁻¹ and relative intensity of the bands due to the aromatic CH out-of-plane bending modes between 900 and 700 cm⁻¹). Furthermore, the composition of the pyrolysates suggests that the perhydrous character of these samples seems to be related to the presence of poorly substituted/condensed aromatic units and a high proportion of aliphatic over aromatic structures rather than a preponderance of aliphatic over aromatic structures.

The presence of simple phenols, which are associated with highly-degraded lignin typical of samples of sub-bituminous coal rank in the vitrinites that are hydrogen-enriched indicates that processes which have caused this enrichment irreversibly modify the normal evolution of lignin. In the case of the Tv sample, the resinization of the precursor vegetal tissues before their incorporation into the depositional environment causes a modification of the lignin units into phenolic structures without any parallel increase in vitrinite reflectance. In the case of the huminite/vitrinite that is affected by hydrocarbon impregnation (Av sample) the presence of such substances seems to prevent the condensation of phenols into dibenzofuran-like structures and aromatic hydrocarbons described during coalification to the bituminous coal rank, which is the real degree of evolution reached by this sample. An evolution pathway in which hydrogenation preponderates over condensation is proposed for explaining the results obtained and confirming the suppression of reflectance in these huminites/vitrinites. The hydrogenation mechanism may be favoured during the evolution of these vitrinites by the presence of cyclopafaraffin-like compounds derived from the resin in Tv and the retention of the polar fraction of oils inside the microporosity of the ulminite in the Av sample.

Finally, the differences between the relative amounts of phenols and their internal distribution in the two non-perhydrous Carboniferous vitrinites cannot be explained in terms of differences in rank. However, they can be closely related to the different environmental conditions in which the coals originated.

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