



Raman spectroscopy of coal macerals and fluidized bed char morphotypes

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ABSTRACT

Raman spectroscopy analyses were carried out on macerals from a set of coals with increasing rank and their corresponding char morphotypes in order to improve the understanding of the structure of coal char produced in a fluidized bed reactor.

The Raman parameters obtained on collotelinite and fusinite are different from those obtained on the corresponding fused char and fusinoid morphotypes. The highest differences occur between collotelinite and corresponding fused chars, suggesting that major structural changes occur in collotelinite during pyrolysis, while those occurring in fusinite are less pronounced.

Raman parameters of the different fused char and fusinoid portions are similar, suggesting that the heat treatment enhanced the formation of similar structures. However, the fused char portions not only display different optical patterns from fusinoid chars but also have slightly higher reflectance.

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1. Introduction

The structure of coal influences its performance in coal conversion processes, such as pyrolysis and combustion, since the molecular rearrangement of the coal varies with the reaction temperature, heating rate, particle size, oxygen concentration, and the coal rank [1].

The use of Raman spectroscopy in characterizing the structural order of carbonaceous material is well-known, and several features in the Raman spectrum and several Raman parameters have been correlated with changes in their structure and used to characterize their structural ordering. Among these parameters are: the integrated intensity ratio of the D band to G band (ID/IG), the frequency and full width at half maximum of the G and D bands (ω and FWHM, respectively); and the presence of bands in the second-order spectrum [2–9]. Furthermore, the evolution of carbonaceous material during heat treatment is already well-established and the relation between the Raman spectra, Raman parameters, and structures has been discussed [10–23].

A detailed summary concerning the potential of Raman spectroscopy in providing information about coal and char structure is given in Potgieter-Vermaak et al. [24] and char structure in Li [19]. However, most of the Raman studies of coal and char have been conducted on bulk samples and have not been concerned

with the complexity and heterogeneity of coal and char and the impact of each coal and char component to the final result.

Several Raman spectroscopy studies concerning coal and char heterogeneity were conducted by Zerda et al. [25] on maceral concentrates; by Green et al. [26] on cokes prepared at constant temperature over a wide range of optical textures and hence rank of the parent coal, and also on a restricted series of cokes carbonized at different temperatures; by Wilkins et al. [27] measuring liptinite, vitrinite, and inertinite fluorescence intensities; by Marques et al. [28] in vitrinite from high-rank coals; by Guedes et al. [29] on collotelinite, fusinite and macrinite; by Morga [30] on semifusinite and fusinite heated at different temperatures; and by Rodrigues et al. [31] on graphite-like particles developed from anthracites treated at high temperatures.

The present work aims to study the evolution of Raman spectra and Raman parameters on coal macerals and their corresponding pyrolysis char morphotypes, produced in a laboratory-scale fluidized bed reactor at 800 °C, and to investigate the results of artificial thermal effect on the structure of coal. Therefore, petrographic and Raman spectroscopy analysis were performed on selected coal macerals (collotelinite and fusinite) from a set of Penn State Coal Samples Bank coals of increasing rank and char portions (fused char and fusinoids) in order to correlate the Raman-derived parameters of the same coal macerals and corresponding char portions. The use of Raman microspectroscopy enables direct characterization of selected macerals and char portions, thus considering coal and char heterogeneity. This work also follows the approach for the Raman characterization of the main structural features of highly disordered carbon materials proposed by Li et al. [18].

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2. Materials and methods

A suite of nine coals purchased from the “Penn State Coal Samples Bank” were used in this study (Table 1) corresponding to a set of low-ash, vitrinite-rich coals (from 79 to 94 vol.% vitrinite, on a mineral matter free basis) of increasing rank [from Low rank A (subbituminous coal) to High rank A (anthracite A)] [32].

For the char preparation, coal was pyrolyzed in a fluidized bed reactor (1500 mm high and 80.8 mm internal diameter) at 800 °C and heating rate of $>10^4$ °C/s, and in a nitrogen R (99.995%) atmosphere at the LNEG (Laboratorio Nacional de Energia e Geologia, Lisboa, Portugal). The coals were fed at a rate of 1 g/min to the fluidized bed already heated at 800 °C. The evolving gases were continuously analyzed, and the reaction finished when CO was no longer detected. Heat was then switched off, maintaining the nitrogen flow until reaching 50 °C inside the bed. The bed was composed of 369.1 μm mean diameter quartz sand.

Petrographic analyses were performed on coal pellets prepared according to ASTM [33] using a Leitz Orthoplan microscope equipped with a high-resolution digital camera and Diskus-Fossil software at the CGUP (Centro de Geologia da Universidade do Porto). The maceral compositions and mean random reflectance of vitrinite were determined following ISO standard procedures [34,35].

The coal macerals nomenclature follows the International Committee for Coal and Organic Petrography system [36,37]. The petrographic analysis of the chars included the polished block preparation (embedding in epoxy resin and polished surfaces).

The Raman experiments were performed at CGUP on polished sections prepared for organic petrography [38] using a JOBIN-YVON LABRAM spectrometer, and a He-Ne laser was used giving a monochromatic red light of 632.8 nm at a power of 20 mW. Raman spectra were measured with a density filter to avoid thermal decomposition of coal and char by the laser.

A $\times 100$ air objective (0.95 numerical aperture) lens of an Olympus optical microscope was used to focus the laser beam on the sample and also to collect the scattered radiation. A highly sensitive CCD camera was used to collect the Raman spectra. Initially, extended scans from 1000 cm^{-1} to 3600 cm^{-1} were performed on each sample. However, since no well-resolved second-order features were obtained on the macerals and their corresponding chars from the coal set studied, only the first-order Raman spectrum from 1000 to 1800 cm^{-1} was used for comparison between coal macerals and char morphotypes.

3. Results and discussion

Collotelinite and fusinite are among the most common vitrinite and inertinite macerals of coal, respectively; and thus, any transformation occurring in these macerals most probably has important technological impacts.

In this study we performed Raman analyses on these two macerals with air objectives, and the contrast is lower than using oil-immersion objectives. Therefore, undoubted identifications can only be made between coal macerals and char portions presenting distinct visual patterns and reflectance.

On what concerns the chars, fused char is formed by a mesophase composing the walls of carbonaceous cenospheres and networks (Fig. 1), and of other char morphotypes. Visually, these are rounded edge materials tending to spherical shape, with newly formed porosity characterized by distorted vacuoles due to volatile matter evolution. Depending on the coal rank, this charred matter is isotropic or anisotropic, mosaic coke ranges from being absent to having well-developed domains.

In this study, these fused char portions are assumed to be mostly derived from collotelinite and other vitrinite macerals, since all the coal samples are vitrinite-rich. However, some reactive semifusinite may also fuse and form a mesophase.

Fusinoïd portions, retain the original morphology of fusinite coal maceral, or its fragments, i.e. highly reflecting well preserved cellular structure [39], and are isotropic morphotypes (Fig. 1).

Since Raman spectrum is quite sensitive to lattice order breakdown, Raman spectroscopy should provide information about graphite and the disordered carbon present. Since the work of Tuinstra and Koenig [2] on graphite, in the investigation of both coal and char structures the Raman features G band (graphite band) and D band (defected band) have generally been used. However, Li et al. [17,18] note that for highly disordered carbonaceous materials, differing considerably from polycrystalline graphite, other bands representing important structural defects or intermediates should also be considered in understanding structural changes during pyrolysis and gasification. Raman spectroscopy is an important tool for the characterization of carbon structure of coal and char. Based on the trials with chars from coals of different rank, biomass and model compounds, Li [19] proposed deconvolution of the Raman spectrum over the range of 800–1800 cm^{-1} into 10 bands:

- (i) The G band centered at 1590 cm^{-1} mainly represents the aromatic ring quadrant breathing with little contribution from graphitic structures.
- (ii) The D (1300 cm^{-1}) band represents mainly aromatics with not less than six rings.
- (iii) Two bands, an R band at 960 cm^{-1} and a S_R band at 1060 cm^{-1} , were assigned to the contributions from ether and benzene related/accompanied structures respectively.
- (iv) The S (1185 cm^{-1}) band, showing together with S_1 (1230 cm^{-1}) band as the shoulder of the D band, mainly represents $C_{\text{aromatic}}-C_{\text{alkyl}}$, aromatic (aliphatic) ethers, C–C on hydroaromatic rings, hexagonal diamond carbon sp^3 , and C–H on aromatic rings.
- (v) Three bands, the V_r (1380 cm^{-1}), G_r (1540 cm^{-1}), and V_l (1465 cm^{-1}) bands, making up the “overlap” between the

Table 1

Proximate, ultimate and petrographic analysis of coals from the Penn State Coal Samples Bank. Coal samples were stored in Argon.

Sample	R_r (%)	Rank (ISO 11760, 2005)	Moist. wt.%	Ash wt.% (db)	Volatile matter	C wt.% (daf)	H wt.% (daf)	N wt.% (daf)	St wt.% (db)	O diff. wt.% (daf)	V % Vol. (mmf)	I % Vol. (mmf)	L % Vol. (mmf)
DECS-24	0.42	Low A	13.2	13.39	47.14	76.26	5.30	1.32	6.38	14.07	90	7	3
DECS-18	0.50	Medium D	6.81	12.25	46.93	79.08	5.80	1.44	4.80	11.59	86	6	8
DECS-23	0.69	Medium C	2.00	9.44	43.53	81.95	5.63	1.49	4.27	9.13	79	14	7
DECS-12	0.81	Medium C	2.40	10.25	40.13	83.32	5.69	1.37	1.25	8.81	83	9	8
DECS-14	0.95	Medium C	1.46	10.52	36.42	85.20	5.46	1.45	2.01	6.94	89	8	3
DECS-3	1.19	Medium B	1.10	5.37	28.73	87.37	5.88	1.74	0.69	4.44	94	6	0
DECS-19	1.60	Medium A	1.01	4.60	19.19	89.87	4.90	1.14	0.78	3.54	90	10	0
PSOC-1515	2.30	High C	2.44	29.17	11.92	88.07	3.91	1.13	0.82	6.21	91	9	0
DECS-21	4.22	High A	3.99	11.15	5.08	90.33	4.01	0.80	0.57	4.38	87	13	0

R_r : Vitrinite mean random reflectance.
V, I, L: Vitrinite, inertinite, liptinite.

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