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Organic Petrology applied to materials and coal by-products characterization

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Abstract

Optical microscopy is a very unique tool to find out about the structural order of carbonaceous materials and coal by-products. It has two main utilization ways as an instrument to distinguish and quantify different phases in a polished surface and as a record of the reflectance of a given material. Using one or both capabilities there are significant contributions to different aspects of coal utilization and materials science, which are the main objective of this review.

The most traditional applications deal with the characterization of fuels for any utilization process (maceral and vitrinite reflectance analysis), in which coal petrographic techniques are the only ones able to identify and characterize the individual components of a blend. The next step is the contribution to the study of transformed coal products. In this way coke petrology has developed a complete optical texture classification system in which coke texture can be related to coke properties such as reactivity or mechanical strength. The contribution to coal combustion through the characterization of chars and identification of the parent material in fly ashes is also relevant and no less important is the following of hydrogenation processes. Half way between material and coal science are the subjects related to coal tar and petroleum pitches based cokes for different applications. In this case organic petrology can be used not only to quantify the amount of different phases but also to follow through the reflectance the structural transformation. In any process in which pitches act as binder, optical microscopy is a useful tool to quantify the components and to study the interfaces.

Due to the versatility of C–C bonds, the structure of carbon materials can vary from the disordered isotropic optical texture to the well-ordered graphitic-like texture. These transformations can be followed by the measurement of anisotropy. While it is true that optical microscopy has much less resolution than other microscopy techniques such as HRTEM it has the possibility to account for sample heterogeneity which is very difficult to attain with other high resolution instruments. Some other contributions of organic petrology to materials science in relation to mechanical properties are also reviewed

Keywords: Organic petrology, reflectance, anisotropy, materials science

1. Introduction

Optical microscopy is a very unique and versatile tool to find out about the structural order of carbonaceous materials and coal by-products as reviewed by Crelling and Gray (1998). Although it has lower resolution than other microscopy techniques such as scanning electron microscopy (SEM) or high resolution transmission electron microscopy (HRTEM), it has the advantage of describing very easily the heterogeneity of the sample. This is of particular significance in the scenario of carbon materials science, in which frequently heterogeneous precursors are used and also different components are blended in order to achieve the desired properties of the product. In this paper the most common configuration of the optical microscope for the study of carbon materials and coal by-products will be described first. Afterwards the main application of quantification of phases and reflectance in relation to carbon materials properties will be reviewed.

2. Configuration of the optical microscope for the study of carbon materials.

The large variety of carbon materials is due to the especial characteristics of carbon atom, which can be bonded with different configurations to yield allotropic forms as different as diamond, graphite or fullerenes, in addition to many intermediate forms that approach more or less to graphite lattice. Carbon materials are generally prepared using as precursor a carbon-rich product such as coal, biomass, petroleum residues submitted to thermal treatments of variable severity or from vapor phase deposition. These components are essentially opaque to the visible light and are generally studied using incident light optical microscopy. This technique requires polished samples either blocks of pellets depending on the aim of the study and a horizontal surface which maximizes the amount of light returning to the oculars. If quantitative reflectance measurements are to be made a photomultiplier and some standards of known reflectance are required. Recent advances in image analysis systems allow the replacement of the photomultiplier by a camera which permit the record of large amounts of images, which can be treated in further steps.

Optical microscopy can be also operated in a number of modes that allow the maximization of the contrast between the components under study. Accordingly for coal examination typically immersion oil is used but dry or water immersion objectives may be used in the case of materials likely to react with the immersion oil such as source rocks or mild thermally treated carbon materials. The use of blue-violet or ultra-violet excitation for the study of carbons has been only scarcely applied except for the study of low maturity precursors such as peat or lignite. Nevertheless the study of composites made up of complex mixtures of opaque and translucent components as it is the case of automotive brakes (Weiss et al., 2006) may take advance of the contrast provided by fluorescence microscopy. The use of polarized light allows the determination of optical anisotropy, one of the properties used to discriminate and find out about the degree of structural order in carbon materials. Typically crossed polars and a turning stage are used for the study of optical texture. Quite often a retarder plate is added, which gives an homogeneous common color to the isotropic materials allowing the simultaneous observation of isotropic and anisotropic components in the surface with crossed polars. The most commonly used retarder plate is that of 1 λ giving a magenta color for isotropic materials. Alternatively a rotating polarizer can be used to assess anisotropy, which has the advantage of being more easily implemented in automatically operated microscopes (Crelling et al., 2005).

3. The use of optical microscopy for observation and quantification of components in a polished surface

The simple observation of a polished surface of a carbon material can yield a lot of useful information without further attempts for quantification, such as identification of the various components in the case multicomponents materials, presence and location of cracks and fissures, existence of preferential orientation, etc.

Different branches of coal and carbon science have taken advantage of the fact that the proportion of components recorded in a surface randomly selected from a granulated pellets is proportional to their amount in volume in the sample. This is the basis of well-established maceral analysis in coal (ISO 7404-3, 1994) which is extensively used for the characterization of feed fuels in both combustion and coking processes. In the characterization of feed fuels optical microscopy is the only technique able to discriminate the presence of various coals in a blend and record individually their composition. This is done by the protocol described by Davis (2000).

Optical texture analysis in metallurgical coke (ASTM D5061-92) and petroleum coke are other typical applications of optical microscopy to coal and petroleum coke processing. In the case of metallurgical coke the optical texture keeps relation with coke reactivity and mechanical strength both relevant parameters for its behavior in the blast furnace (Gray and De Vanney, 1986; Gransden et al., 1991). In the case of petroleum coke the size of the optical texture keeps relation with feedstock composition and severity of thermal treatment (Ruiz et al., 1990). Among other applications with less standardized analytical procedures the formation and evolution of mesophase from any precursor (Grint and Marsh, 1979) and studies of optimization carbon-carbon or metal-carbon composites preparation can be mentioned. The applications are indeed as numerous as the combination possibilities of any carbon material with any other product. Just as examples Blanco et al. (2000) used optical microscopy to quantify the development of mesophase in thermally treated coal tar pitches and to monitor efficiency of a separation process. Optical microscopy has also been the key for understanding the influence of the type of granular reinforcement in the microstructure of pitch-based carbon composites (Méndez et al., 2003). The mechanical properties of carbon-carbon composites have shown to be strongly influenced by the matrix structure, which in turn depends on the deposition conditions employed. Thus lower fracture stress and elastic modulus has been found for isotropic matrix due to the low matrix density and columnar structure is attributed to the presence of matrix cracks (Oh and Lee, 1988). Optical microscopy has been used for monitoring the processing of unidirectional carbon-carbon composites (Casal et al., 2001) and as control for the preparation of pitch-based carbon-copper composites for electrical applications (Queipo et al., 2004).

In the field of coal combustion optical microscopy has been of use for the morphological description of the chars both using systems based on visual inspection (Bailey et al., 1990) or on routines applied on automatically acquired images (Alvarez et al., 1997; Wu et al., 2006). In both cases the objective was to improve the combustion models by adding morphological criteria. A different approach was that followed by Milenkova et al. (2003) in which optical microscopy was applied to unburned carbon in fly-ashes in order to trace the coal/coals mainly responsible for the loss in efficiency. This approach is also interesting if the unburned carbon is to be used as adsorbent or precursor because the optical texture of the residual carbon is related to the surface area of the chars (Alonso et al., 2001a)

In the field of active carbons prepared from coal precursors, optical microscopy has also shown to very useful to study the influence of oxidation severity or steps of pyrolysis on the adsorptive properties of the carbons (Ruiz B. et al. 2006).

The use of image analysis has facilitated the measurement of some parameters such as size of a given object, orientation or any other attributes related to morphology (i.e. roundness, sphericity, etc). It must be kept in mind that whereas automatic systems are much worse than human eye in the identification and discrimination, they are much more efficient in measurement provided that the image has phases contrasted enough for the computer to operate.

4. The use of optical microscopy for the measurement of carbon materials reflectance.

The reflectance of any material depends on its refraction index and absorption coefficient which are specific for each substance and relate to each other through Fresnel-Beer equation. The measurement of the refraction index of a substance is not easy and requires the determination of reflectance in various immersion media. It is therefore common to work for comparative purposes with parameters easier to measure as it is the case of reflectance itself. The measurement procedure is rather simple and consist of recording the reflectance of the substance under a set of established operation conditions and compare it with the reflectance of a standard measured in the same conditions.

In the case of coal, measurement of reflectance is a well-established procedure and the reflectance of a coal maceral (collotelinite) is used as rank parameter. The corresponding ISO standard (ISO 7404-5 1994) establishes the use of monochromatic light (546 nm) and immersion oil with a refractive index of 1.518 at 23 ºC. Typically a similar procedure is followed for the determination of reflectance of other carbon materials.

Two types of reflectance can be measured: random reflectance in which unpolarized light is used and the measured value represents an average of the light reflected in any spatial direction and maximum reflectance or bireflectance in which polarized light is used and either the maximum value or both maximum and minimum values (bireflectance) are recorded during 90 º stage rotation (Taylor et al., 1998). As graphite has an optical structure corresponding to a negative uniaxial crystal, the structure of coal was at the beginning considered to be similar. Nevertheless exceptions have shown to be so common that this rule does not necessarily apply and coal depending on its thermal and burial history can be either uniaxial or biaxially negative or even positive if tectonic stress has been strong enough (Kilby 1988). Figure 1 shows schematically the various indicating surfaces frequently observed in coals and the reflectance values recorded at variable sections.

The structure of carbon materials based on graphite-like structure vary between isotropic for a disordered material and that of graphite. Structures of variable length and number of units are formed in between with a preferential orientation due to the stacking of growing aromatic planar units. Overall the higher the carbon content, the higher the reflectance and the more perfect the ordering, the higher the anisotropy. As in a polished surface only a section of the particle is found, the use of polarized light in combination with a rotating stage will yield a similar reflectance for isotropic materials regardless the position of the stage, a maximum reading corresponding to maximum reflectance and a minimum value corresponding to an apparent minimum if the structure approaches to uniaxial negative and an apparent minimum and apparent maximum reflectance if the structure is biaxial negative. Kilby (1988 and 1991) developed a graphic procedure to extract from these readings the real maximum and minimum reflectances.

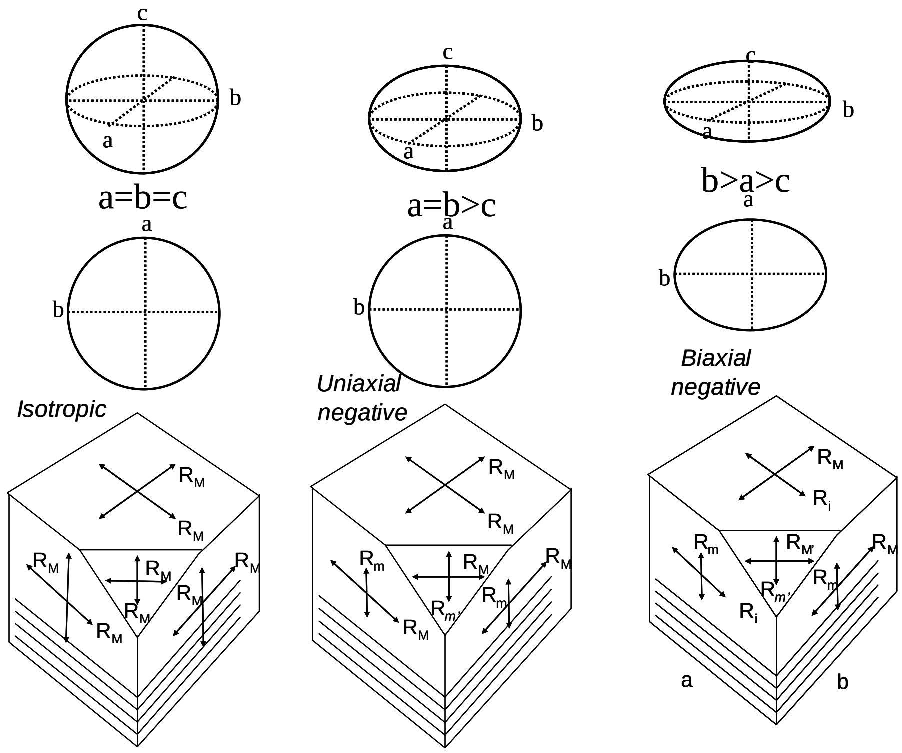

Figure 1. Reflectance indicating surface shapes and corresponding reflectance readings expected from sections of various orientations. R_M=Real maximum Reflectance, R_m=real minimum reflectance and $R_{M'}$ and Rm'=apparent maximum and minimum, respectively (simplified from Kilby 1988)

The advances in optical microscopy and image analysis have allowed the development of procedures to do bireflectance mapping of microscopy fields by recording various images from a given field using a rotating polarizer at various positions (Crelling et al., 2005). This procedure has been successfully applied to the characterization of various carbon materials and coal-derived products.

Some examples of application of anisotropy measurements are those of carbonization of anthracites to prepare graphitic materials (Pusz et al., 2002; González et al., 2004). Due to the poor graphitizing ability of anthracites, which do not pass upon heating through a truly plastic stage, their capacity for structural re-organization is rather limited and therefore only limited contraction and improved order is achieved. These transformations are easily followed by bireflectance measurements which also indicate that the graphitizing ability of anthracite improves as they approach in rank to the low volatile coals with the best plastic properties. Bireflectance measurements are also of use to determine the peak temperature of the boiler in the combustion of anthracites because this temperature has shown to be responsible for the final bireflectance achieved by the particles regardless the anisotropy of the parent anthracite (Mendez et al., 1999). Maximum reflectance and bireflectance has been used to quantify fiber anisotropy and has been related to the tensile modulus (Bensley et al., 1994).

Reflectance has also shown the utility to follow the transformations occuring in coal during mild thermal treatment (Goodarzi, 1984) or liquefaction process (Davis et al., 1991) and image analysis techniques has been used to describe the heterogeneity of the particle (Crelling and Bensley, 1995).

In combustion chars reflectance has shown be related to the severity of the thermal treatment (Alonso et al., 1999; Hurt et al., 1995) if a similar parent coal is used. On the contrary for similar thermal histories the higher the rank of the parent coal, the higher the char reflectance up to the medium volatile bituminous coal rank. For medium volatile bituminous coal to semianthracite rank interval coal plastic properties improve and strong reorganization of carbonaceous material occur under the conditions of combustion chamber resulting in large reflectance increase (Figure 2) with significant scatter in the values and a marked drop in surface area (Alonso et al., 2001b).

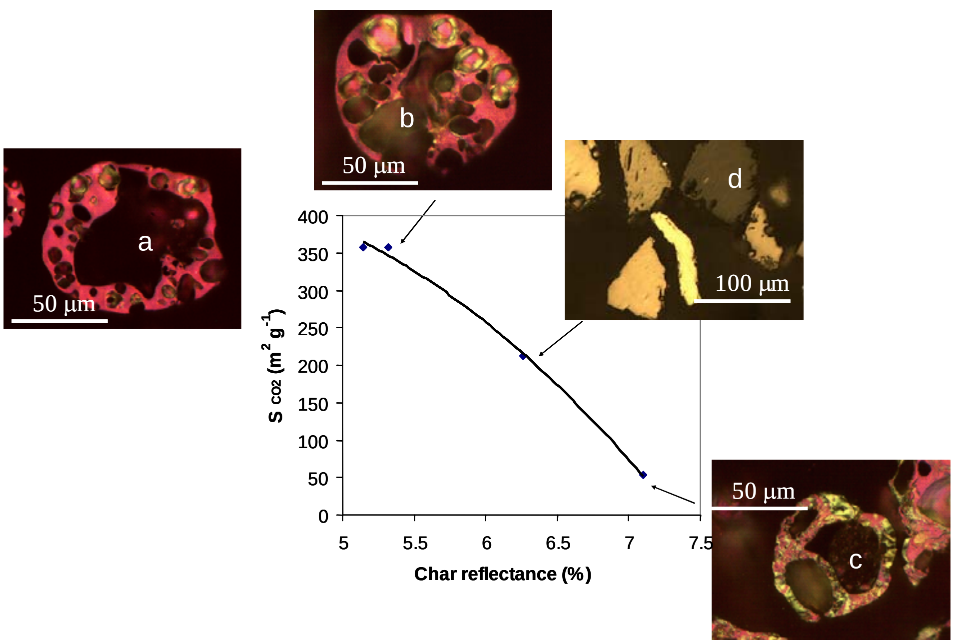

Figure 2. Some examples of variation of combustion char reflectance and surface area. Chars were prepared from high volatile bituminous (a and b) medium volatile bituminous (c) and anthracite (d) coals at 1300 ºC (based on Alonso et al., 2001b)

For a similar degree of order in the carbons the reflectance has shown to be related to the surface area (Duber and Rouzoud, 1999). The relationship between surface area and reflectance of the material has also been observed in activated carbons from sascharose precursor (Duber et al., 2002).

5. Conclusions

The application of optical microscopy to the study of carbons have multiple applications which make use of two main capabilities: i) the possibility of quantifying phases readily distinguished in a surface and ii) the measurement of reflectance intensity and bireflectance which reflect the structural order of the carbonaceous material. The combination of both capabilities, this is the record of quantitative reflectance readings on different sort of materials is a very unique posibility of optical microscopy which has no concurrence for describing the asociation of multicomponents samples.

The possibilities are innumerous and are only limited by the ability of the observer to find those illumination conditions which provide the desired contrast between the phases that want to be radily distinguished. The permanent contribution of optical microscopy to understand the transformation of carbons during processing is shown by the amount of work produced since the review by Crelling and Gray (1998).

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