Effect of mild oxidation on the surface chemistry of bituminous coals under different humidity conditions

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ABSTRACT

The influence of humidity conditions on the oxidation of four coals has been studied on the basis of their surface chemistry. A systematic study was carried out in which four coals of different rank were oxidised at 50 °C in two conditions of humidity (20 and 90% moisture levels) and in an air atmosphere. The changes in the surface functional groups were measured by means of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS).

The lowest rank coals were the most affected by oxidation in all the humidity conditions applied. In the case of the higher rank coals, higher moisture levels promoted the oxidation process. The number of oxygen-containing structures increased after oxidation, the most abundant being the carbonyl and carboxyl groups.

1. Introduction

The oxidation of coal causes changes in the coal mass and its elemental composition, which impairs the coking properties and has a direct impact on the quality of the resultant cokes (Casal et al., 2003; Cimadevilla et al., 2005; Crelling et al., 1979; Nelson, 1989; Seki et al., 1990; Smędowski and Piechaczek, 2016; Valia, 1990). The oxidation of coal at low temperature is a complicated process that begins with the transport of oxygen to the surface of the coal particles and the formation of unstable carbon-oxygen complexes. The initial chemisorbed unstable intermediates mainly consist of peroxygen and hydroperoxides (Liotta et al., 1983; MacPhee et al., 2004). The decomposition of the unstable intermediates leads to the formation of gaseous products and stable oxygen-bearing functional groups including hydroxyl (phenolic-OH), carbonyl (−CO), and carboxyl (−COOH) (Gethner, 1985; Rhoads et al., 1983; Wu et al., 1988). Other stages may lead to the degradation of these stable complexes and the generation of new active oxidation sites (Wang et al., 1999).

There are many factors affecting this process, such as the composition, particle size, temperature or oxygen concentration (Davidson, 1990; Wang et al., 2003). The influence of moisture also plays an important role in the oxidation process considering that a minimum amount of water is necessary for the oxidation to occur (Nelson, 1989). Nevertheless the role of humidity in this process has still to be fully clarified. It is known that the presence of moisture in the air can cause an increase in the temperature, thereby further promoting the oxidation

of coal (Itay et al., 1989). Moisture is necessary for pyrite oxidation to take place but it may also cause the formation of hydroperoxides (Davidson, 1990).

The results collected from the literature on the effect of humidity on the oxidation process of bituminous coals are contradictory. Beier et al. noted that coals weathered for a long time were more affected by high humidity conditions (Beier, 1985, 1983). However, Ray et al. (1990) observed that coal samples stored at 80 °C under 40% relative humidity (rh) underwent a greater degree of oxidation than under 80% rh. The functional groups present on the coal surface act as sorption sites for oxygen and moisture.

The objectives of the present work were to examine the role of humidity in the oxidation of coals of different rank and to analyse the main structural changes caused on the coal surface. DRIFTS and XPS were used to monitor changes in the surface chemistry of the oxidised samples.

2. Materials and methods

2.1. Coals

Four bituminous coals were selected for this study two of them with a volatile matter of around 32 wt% and the other two with a low volatile matter of around 21 wt%. These coals which are at the extremes of the coking coal range were chosen because it was thought they would show different responses to oxidation. Fresh samples of each coal were

stored prior to use under vacuum at − 18 °C. For the oxidation test, about 1 kg of each fresh coal was uniformly spread on trays in order that all the particles would be exposed to similar conditions. The particle size was less than 10 mm.

Oxidation was performed in a humidity chamber at 50 °C at relative humidity levels of 20 and 90%. In addition oxidation in a forced air convection laboratory oven at 50 °C was carried out. The humidity level inside this oven as measured by a hygrometer was 40% rh. Representative samples of the oxidised coals were collected after 10, 20, 40 and 60 days and crushed to the size required for each test. The oxidised samples were labelled with the letter of the corresponding coal followed by the humidity conditions and the number of oxidation days e.g., A20Hd-60 stands for coal A oxidised for 60 days under 20% rh.

Proximate analyses were performed following the ISO 562 and ISO 1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was determined by means of a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144DR (ASTM D-5016) for sulphur and a LECO VTF-900 for the direct determination of oxygen.

A petrographic examination of the fresh coals was carried out on a MPV II Leitz microscope by means of reflected white light using immersion objectives (32 ×) in accordance with the ISO 7404-5 procedure for vitrinite reflectance and the ISO 7404-3 procedure for maceral group determination.

The Gieseler test was carried out in a R.B. Automazione Gieseler plastometer PL 2000 following the ASTM D2639-08 standard procedure, described in detail in a previous paper (Díaz-Faes et al., 2007).

2.2. Surface chemistry

Coal samples with a particle size of less than 0.063 mm were examined by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The samples were left to dry at 35 °C overnight before analysis. The spectra of the pristine coals and the oxidised samples were measured using a collector diffuse reflectance accessory inserted into a Nicolet Magna-IR560 spectrometer. A mercury cadmium telluride detector (MCT-A) that operates at a sub ambient temperature was used. Data were collected in the range of 650–4000 cm^{-1} by applying 128 scans for each sample. Semiquantitative analyses were carried out using the integrated area (A) of the absorption bands to calculate selected indices.

X-Ray photoelectron spectroscopy (XPS) measurements were taken on a SPECS spectrometer equipped with a Phoibos 100 hemispherical analyser. The X-ray radiation source was a monochromatic Al Ka (1486.74 eV) set to operate at 100 W of X-ray power and an anode voltage of 14.00 kV. The photo-excited electrons were analysed in constant pass energy mode, using a pass energy of 50 eV for the survey spectra and 10 eV for the high resolution core level spectra. CasaXPS software was employed to process the data. The compositions in terms of atomic percentage (at.%) were determined from the wide scan spectra on the basis of the integrated peak areas of the main XPS peaks and their respective sensitivity factors. The amount of each group present on the coal surface was calculated from the area beneath the curves obtained from the deconvolution of the curves C (1s) and O (1s).

3. Results and discussion

Table 1 shows the main characteristics and petrographic analysis results for the fresh coals, listed in order of decreasing volatile matter. It can be seen that their ash content is below 9 wt%, within the required value for coal destined for metallurgical coke production (Díez et al., 2002). In accordance with their rank, high volatile coals have a larger oxygen content. The coal plasticity of the pristine coals varies between 28,599 and 420 ddpm. Despite having a similar rank, coals A and B have very different MF values (28,599 and 500 ddpm, respectively). This may be related with the higher oxygen content of coal B, since it is

Table 1
Main characteristics and petrographic composition of the fresh coals.

Coals	A	B	C	D
Ash (wt% db[a])	7.0	7.1	8.2	8.5
Volatile matter (wt% db[a])	34.2	31.0	22.7	20.3
O (wt% db[a])	4.3	5.1	3.2	2.8
MF (ddpm)[b]	28,599	500	971	420
Petrographic characteristics				
Mean vitrinite reflectance, Ro (%)	1.00	0.95	1.29	1.44
Vitrinite (vol% mmf[c])	75.8	70.4	76.4	76.1
Liptinite (vol% mmf[c])	9.1	8.3	1.0	0.4
Fusinite (vol% mmf[c])	1.9	5.4	18.3	18.1
Semifusinite (vol% mmf[c])	8.7	13.7	1.4	3.3
Other inertinites (vol% mmf[c])	4.6	2.3	2.9	2.1

[a] Dry basis.
[b] Maximum Gieseler fluidity expressed in dial divisions per minute (ddpm).
[c] Mineral matter free.

well established that in low-rank coals the presence of oxygen cross-links prevents fusion (Loison et al., 1989; Barriocanal et al., 2003). Besides, coal B has a lower content in vitrinite (70.4 vol% mmf), which is one of the principal macerals responsible for coal plasticity (Loison et al., 1989; Díez et al., 2002) and higher inertinite content (21.4 vol% mmf). The mean vitrinite reflectance ranges between 0.95 and 1.44%. Low-rank coals (A and B) have the highest liptinite (L) content, 9.1 and 8.3 vol% mmf, respectively. The fusinite (F) content is higher in the low volatile coals.

The evolution of the volatile matter (VM) of the four coals with the increase in oxidation time is shown in Fig. 1. At zero days of oxidation time, the VM of fresh coals A, B, C and D is 34.2, 31.0, 22.7 and 20.3 wt %, respectively. Coal A underwent the highest volatile matter decrease and, taking into consideration the three different humidity conditions, the values fell by as much as 3%. In contrast, coal D experienced the lowest VM variation i.e., about 1%. This was to be expected as it is generally accepted that low-rank coals are more affected by oxidation (Nelson, 1989). The three humidity conditions under study represent completely different environments: very dry (20% rh), low, usually indoor humidity (air, ~40% rh) and wet (90% rh). Moreover, it should be noted that during the first days of oxidation the VM values showed a greater decrease (except in the case of coal D), but later this effect was mitigated, the VM becoming almost stable.

Similarly, Fig. 2 shows that the oxygen content variation was greater during the first few days of oxidation, while the values obtained after 40 and 60 days were similar to each other. Oxygen content at 90% rh was slightly higher for all the samples (except in the case of coal A), the results from oxidation in the convection oven showing greater fluctuation probably because the humidity in an air-forced oven cannot be controlled as tightly as in a humidity chamber. However, it should be noted that a small variation in the oxygen content fixed during oxidation has a significant influence on coking capacity (fluidity, swelling). Consequently the fixation of 0.1–0.3 wt% oxygen is enough to modify fluidity significantly, without causing any deterioration of other coking properties whereas, if oxygen is incorporated in larger amounts (1–2 wt %) the coking properties are greatly reduced and in some coals totally destroyed (Loison et al., 1989).

In the evolution of the oxygen content of the four coals with oxidation time (Fig. 2), two different behaviours can be observed. Coals B, C and D are more greatly affected by humidity conditions and the higher the humidity is, the greater the effect. Coal B experienced the greater variations in oxygen content which were 0.7, 1.3 and 1.4 wt% for 20% rh, air and 90% rh, respectively at 60 days. On the other hand, coal A increased its oxygen content with oxidation time but to a lower extent and almost no difference was observed between the different humidity conditions. The reason for this behaviour might be related to petrographic composition, since coals B, C and D have a higher content in inertinite type macerals (from 21 to 24 vol% mmf) compared to coal