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**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.

Keywords *bituminous coal, oxidation, surface chemistry, XPS*

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. (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 ISO562 and ISO1171 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 28599 and 420 ddpm. Despite having a similar rank, coals A and B have very different MF values (28599 and 500 ddpm, respectively). This may be related with the higher oxygen content of coal B, since it is 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 Figure 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 10 %. 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, Figure 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 (Figure 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 A (15.2 vol.% mmf). As these macerals are porous, this might favour the diffusion of oxygen into the coal mass (Misra and Singh, 1994) leading to a greater increase in oxygen.

3.1 Surface chemistry characterization

Infrared spectroscopy has been widely used in the study of coal oxidation because it is a very sensitive technique for following the changes in oxygen functionalities (Casal et al., 2003; Ibarra and Miranda, 1996; Rhoads et al., 1983). The DRIFT spectra of the pristine coals and their oxidised samples for 60 days under 20 %, 90 % rh and under air atmosphere are shown in Figure SM1. A series of absorption bands can be appreciated in the spectra: the broad absorption band with the maximum centred near to 3300 cm^{-1} is mainly due to the OH bonds of the hydroxyl groups. The bands between 3100 and 2990 cm^{-1} are assigned to the stretching of aromatic C-H. The 2990 – 2795 cm^{-1} range is associated to the stretching of the aliphatic C-H bond. The range between 1750 and 1540 cm^{-1} corresponds to the C=C and C=O stretching modes.

The band at 1600 cm^{-1} corresponds to the C=C stretching vibrations of the aromatic rings (Painter et al., 1983). A shoulder is observed on the left-hand side of the C=C band. This is assigned to C=O, indicating that various types of C=O groups (esters, ketones, aldehydes, carboxylic acids or a combination of these groups) may be present (Ibarra and Miranda, 1996; Painter et al., 1983). The range between 900 and 700 cm^{-1} corresponds to the out-of-plane aromatic C-H vibration modes that reveal differences in the substitution patterns of the aromatic structures. The shape of the DRIFT spectra of the fresh coals is quite similar although it should be noted that in the spectra of coal A the relative intensity of the band assigned to OH groups (at ca. 3300 cm^{-1}) is higher than that of coal D, whereas the relative intensity of the band assigned to the ether groups (at ca. 1100 cm^{-1}) is lower (Figure SM1). This indicates larger amount of hydrophilic groups which is in accordance with the lower rank of coal A (Kelemen and Kwiatek, 1995). The DRIFT spectra of the coal samples oxidised for 60 days in different humidity conditions show all the typical absorption bands found in the initial coals. From a qualitative point of view, no clear evidence of mild oxidation-formed carbonyl and carboxylic groups was detected by DRIFT spectroscopy under any of the oxidation conditions (Figure SM1). Although no qualitative changes were observed in the bands corresponding to oxygen functional groups or in the relative intensity of the aromatic and aliphatic hydrogen absorption bands, a semi-quantitative analysis was carried out in order to gain a better knowledge of the modifications caused by oxidation on the coal surface. The amount of oxygenated functional groups and the evolution of the aliphatic structures with oxidation were measured using the indices in Table 2. The CO/Hal ratio is one of the most commonly used to estimate the evolution of C=O structures (Ibarra and Miranda, 1996; Nelson, 1989). The CO/Har+Hal ratio represents the carbonyl region intensity (CO) compared to the aromatic plus aliphatic C-H stretch

region intensity (Har+Hal). The CO/Car index is based on the ratio of the oxygen-containing structures to the aromatic carbon content and the A_{1445}/A_{1375} index is considered to be an estimation of the length of the aliphatic chains (Casal et al., 2003). **Table 3** shows the values of the DRIFTS indices for the pristine coals and their samples oxidised for 60 days under 20 and 90 % humidity levels and an air atmosphere. For all the studied coals, an increase in the value of the first three indices compared to those of the pristine coals is observed. This suggests an increase in oxygen content structures and, as expected, this tendency is more noticeable in the lowest rank coals (A and B). In the case of coal A, the indices vary independently of the humidity conditions. With respect to coal B, the greatest variation in these indices was observed under 20 % rh. This seems a priori to be in disagreement with what was observed in the oxygen analysis, where after oxidation under 20 % rh the increase in oxygen content was lower than in the other moisture conditions. Here it should be noted that the information obtained from the elemental analysis refers to the bulk matrix of the coal while the **DRIFTS analysis** provides information about the coal surface. Hence, the differences in oxygen content can be attributed to the technique used. The decrease in the A_{1445}/A_{1375} ratio indicating a reduction in the length of the aliphatic chains of the coals after oxidation.

The CO/Hal, CO/Har+Hal and CO/Car indices were selected to study the evolution of oxidation with time in the lowest humidity conditions (20 % rh). In the case of the lowest rank coals is where the most significant differences were observed (**Figure 3**). It can be seen that for coals A and D, the three indices remain almost constant up to 40 oxidation days, and then they increase sharply and to a greater extent in the case of coal A. In the case of coal B the indices increase progressively, whereas for coal C they

maintain their initial value during the first 20 oxidation days and then increase but only slightly.

Because of the difficulties associated with the study of the surface chemistry of coal, XPS was also used to confirm the results obtained by DRIFTS. The wide scan spectra in the binding energy range of 0–1000 eV for the fresh coals and their samples after 60 days of oxidation at 20 % rh, in air and 90 % rh are presented in Figure SM2 (coals A, B) and Figure SM3 (coals C, D). Unfortunately, there was no C90rh-60 coal sample available to carry out the test on this sample. Coals A and D are of different rank and showed more differences in their surface chemistry, so their spectra will be commented on more detail. For all the studied coals, the elements identified were carbon (C1s), oxygen (O1s), nitrogen (N1s), aluminum (Al2p) and silicon (Si2p). A check was made for the presence of sulphur (S2p) on the surface of the coals but this element was not detected. C and O were the most abundant elements on the sample surfaces. The surface composition expressed in terms of atomic percentage (calculated on an ash free basis) and the bulk composition (calculated on a hydrogen and ash free basis) for the fresh coals and their oxidised samples are listed in Table 4. Both the bulk and surface compositions have higher carbon contents than any other element, though the C content is higher in the bulk composition than on the surface whereas oxygen is much more abundant in the surface composition than in the bulk. As expected, the pristine coals with high volatile matter content have higher oxygen content both in the surface and in the bulk. Oxidation was carried out under different humidity conditions and affected the surface and the bulk of the lowest and the highest rank coals in different ways. The surface oxygen content of coal A oxidised at 20 % rh was higher than that of the fresh coal and the samples oxidised in air and at 90 % rh. On the other hand, the surface oxygen content of the oxidised coals B, C and D increased to a similar

value in all humidity conditions. It was expected that the bulk and the surfaces of coals would show the same pattern of behaviour, in which case the amount of oxygen on the surface of the samples Aair-60 and A90rh-60 would be around 23.6 % as in the case of the sample oxidised at 20 % rh (A20rh-60). The fact that this is not the case was due to the oxygenated groups on the surface of the fresh coals and the effect of interactions between the humidity and these groups. As explained above, 20 % rh is a very dry environment and in these conditions there is only a small number of water molecules available in the medium to form hydrogen bonds with the hydrophilic groups on the surface of coal A. On the other hand, when the humidity is higher, instead of promoting oxidation, as in the case of coals C and D, the water molecules may block the reactive sites on the hydrophilic surface of coal A and cause a decrease in the oxidation reaction. These results are in agreement with those derived from the DRIFTS analysis which suggested that coal A has the highest hydrophilic surface.

In order to complete the study of the oxygenated surface groups, the high resolution XPS spectra of C (1s) and O (1s) were deconvoluted using Gaussian-Lorentzian peaks. Figures 4 to 7 show the corresponding spectra for coals A, B, C and D and the oxidised samples for 60 days in different conditions of humidity, respectively. C_{graphitic} (BE = 284.7±0.1 eV) appears in all of the samples and the areas under the curve are the highest in all cases.

C_{graphitic} values change significantly in coal A due to oxidation. Initially, 74 % of the surface carbon of the fresh coal A is C_{graphitic}, but this percentage decreases to 45±1 % with oxidation time under the three conditions of humidity. For coal B, the values of C_{graphitic} also change after oxidation, although to a lesser extent than in the case of coal A. The percentage of surface C_{graphitic}, of 66 % in the case of the fresh coal, decreases to 59 ± 4 % in the oxidised samples (Figure 5). In the fresh coal A, the

oxygen on the surface is bonded to carbon, forming hydroxyl groups ($BE = 286.0 \pm 0.1$ eV) and carboxyl groups ($BE = 289.3 \pm 0.1$ eV), with the contribution of 24 % and 3 % of the area under C (1s) curve, respectively. However, in the oxidised samples under the three conditions of humidity (i.e. A20rh-60, Aair-60 and A90rh-60) in addition to the hydroxyl and carboxyl groups already present in the fresh coal, carbonyl groups ($BE = 287.2 \pm 0.1$ eV) are also apparent (3, 3 and 6 %, respectively for the 3 samples oxidised). These results for coal A were to be expected, since hydroxyl and carboxyl oxygen are abundant in low rank coals, and the number of hydroxyl groups is not only substantial but persists with increasing coal rank (Kelemen and Kwiatek, 1995).

In contrast, for coal D the values of $C_{\text{graphitic}}$ only change slightly with the oxidation reactions, since the values corresponding to the fresh coals and the three oxidised samples i.e. D20rh-60, Dair-60 and D90rh-60 are around 61 ± 3 %. Only C associated to hydroxyl and carboxyl groups appear on the surface of the both the fresh and oxidised samples of coal D in percentages of 36 ± 2 % and 4 ± 1 % respectively, averaging the values of the fresh and oxidised samples. In the case of coal C, the variation of $C_{\text{graphitic}}$ is similar to that of coal D, the average value for the fresh and oxidized samples is 54 ± 4 . C associated to hydroxyl and carboxyl groups appear in the surface of the oxidized samples of coal C in percentages of 45 ± 1 % and 3 ± 1 % respectively averaging the values for the oxidized samples.

With respect to the humidity of the environment, only slight differences were observed in the distribution of the chemical groups as determined by XPS which was not sensitive enough to detect variations in the oxygen functionalities as function of the humidity conditions, possibly because of the mild conditions employed in the oxidation tests.

In the deconvolution of O(1s), the peaks corresponding to the C=O bond (BE = 530.7–531.7 eV) (de la Puente et al., 1997; Desimoni et al., 1990; Solís-Fernández et al., 2011), the C-O bond in alcohols, ethers and peroxides (BE = 532.3–532.7 eV) (Desimoni et al., 1990; Solís-Fernández et al., 2011) and the C-O bond in acids, esters and hydroperoxides (BE = 533.1–533.8 eV) (Desimoni et al., 1990; Solís-Fernández et al., 2011) appear in all the samples. In the case of coal A, the amount of oxygen in the carboxylic groups increases from 57 % to 88±6 % for the oxidised samples, whereas the amount of oxygen in the alcohol and ether groups decreases (Figure 4). A possible explanation for this is that these groups are acting as intermediates in the oxidation process (Gethner, 1985; Wu et al., 1988). The deconvolution of the high resolution O(1s) spectra of coal B (Figure 5), also shows a decrease in the amount of oxygen in the alcohol and ether groups and an increase in the amount of C=O oxygen bonds. In the case of coals C and D the results observed are similar, although less noticeable (Figures 6 and 7 respectively). The groups detected in the deconvolution of the high resolution O(1s) spectra of the samples supported the results of the deconvolution of C(1s).

Conclusions

Surface chemistry was found to be very useful for explaining the different responses of the bituminous coals to oxidation depending on their rank. Low volatile coals were more affected at high moisture levels, whereas in the case of the lowest rank coal (A) the effect observed was different depending on whether the bulk or the surface of the coal was under study. After 60 days, the bulk properties were affected in a similar way under all conditions of humidity whereas the oxygen content on the surface of coal A appeared to be higher under conditions of low humidity. This difference may be related

to their different surface chemistries. Coal A had more hydrophilic surface than that of the highest rank coals and after oxidation under conditions of high humidity the surface oxygen content decreased, possibly due to water molecules blocking the reactive sites on the surface of the coal. The DRIFTS analysis revealed a reduction in the relative amount of methylene groups and an increase in groups with oxygen functionalities. XPS analysis of the functional groups showed a decrease in C_{graphitic} and an increase in carboxyl O-C=O groups. In coal A the formation of carbonyl groups was also detected.

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References

- Beier, E., 1985. Exchange of gases during the longterm storage of coal and other materials in air. *Erdoel Erdgas Kohle* 38, 127–129.
- Beier, E., 1983. Gas exchange of black coal and other substances when stored for decades in contact with air. Presented at the Proceedings - 1983 International Conference on Coal Science., Proceedings - 1983 International Conference on Coal Science., pp. 735–738.
- Casal, M.D., González, A.I., Canga, C.S., Barriocanal, C., Pis, J.J., Alvarez, R., Díez, M.A., 2003. Modifications of coking coal and metallurgical coke properties induced by

coal weathering. *Fuel Process. Technol.* 84, 47–62. doi:10.1016/S0378-3820(03)00045-6.

Cimadevilla, J.L.G., Álvarez, R., Pis, J.J., 2005. Effect of coal weathering on technological properties of cokes produced at different scales. *Fuel Process. Technol.* 86, 809–830. doi:10.1016/j.fuproc.2004.08.002.

Crelling, J.C., Schrader, R.H., Benedict, L.G., 1979. Effects of weathered coal on coking properties and coke quality. *Fuel* 58, 542–546. doi:10.1016/0016-2361(79)90175-3.

Davidson, R.M., 1990. Natural oxidation of coal. IEA Coal Research, London.

de la Puente, G., Pis, J.J., Menéndez, J.A., Grange, P., 1997. Thermal stability of oxygenated functions in activated carbons. *J. Anal. Appl. Pyrolysis* 43, 125–138. doi:10.1016/S0165-2370(97)00060-0.

Desimoni, E., Casella, G.I., Morone, A., Salvi, A.M., 1990. XPS determination of oxygen-containing functional groups on carbon-fibre surfaces and the cleaning of these surfaces. *Surf. Interface Anal.* 15, 627–634. doi:10.1002/sia.740151011.

Gethner, J.S., 1985. Thermal and oxidation chemistry of coal at low temperatures. *Fuel* 64, 1443–1446. doi:10.1016/0016-2361(85)90348-5.

Ibarra, J.V., Miranda, J.L., 1996. Detection of weathering in stockpiled coals by Fourier transform infrared spectroscopy. *Vib. Spectrosc.* 10, 311–318. doi:10.1016/0924-2031(95)00060-7.

Itay, M., Hill, C.R., Glasser, D., 1989. A study of the low temperature oxidation of coal. *Fuel Process. Technol.* 21, 81–97. doi:10.1016/0378-3820(89)90063-5.

Kelemen, S.R., Kwiatek, P.J., 1995. Quantification of organic oxygen species on the surface of fresh and reacted argonne premium coal. *Energy Fuels* 9, 841–848.

- Liotta, R., Brons, G., Isaacs, J., 1983. Oxidative weathering of Illinois No.6 coal. *Fuel* 62, 781–791. doi:10.1016/0016-2361(83)90028-5.
- Loison, R., Foch, P., Boyer, A., 1989. *Coke: Quality and Production*. Elsevier, London.
- MacPhee, J.A., Giroux, L., Charland, J.-P., Gransden, J.F., Price, J.T., 2004. Detection of natural oxidation of coking coal by TG-FTIR - Mechanistic implications. *Fuel* 83, 1855–1860. doi:10.1016/j.fuel.2004.02.017.
- Misra, B.K., Singh, B.D., 1994. Susceptibility to spontaneous combustion of Indian coals and lignites: an organic petrographic autopsy. *Int. J. Coal Geol.* 25, 265–286. doi:10.1016/0166-5162(94)90019-1.
- Nelson, C.R., 1989. *Chemistry of coal weathering*, Coal science and technology. Elsevier, Amsterdam.
- Painter, P.C., Starsinic, M., Squires, E., Davis, A.A., 1983. Concerning the 1600 cm⁻¹ region in the i.r. spectrum of coal. *Fuel* 62, 742–744. doi:10.1016/0016-2361(83)90317-4.
- Ray, U.A., Seewald, H., Van Heek, K.H., 1990. Determination of the extent of oxidation of weathered coal by reactivity measurements. *Erdoel Erdgas KohleEKEP* 106, 123–128.
- Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A., Painter, P.C., 1983. Further studies of coal oxidation. *Fuel* 62, 1387–1392. doi:10.1016/0016-2361(83)90104-7.
- Seki, H., Ito, O., Iino, M., 1990. Effect of mild oxidation of bituminous coals on caking properties. *Fuel* 69, 317–321. doi:10.1016/0016-2361(90)90093-6.
- Smędowski, Ł., Piechaczek, M., 2016. Impact of weathering on coal properties and evolution of coke quality described by optical and mechanical parameters. *Int. J. Coal Geol.* doi:10.1016/j.coal.2016.08.005.

- Solís-Fernández, P., Paredes, J.I., Villar-Rodil, S., Guardia, L., Fernández-Merino, M.J., Dobrik, G., Biró, L.P., Martínez-Alonso, A., Tascón, J.M.D., 2011. Global and local oxidation behavior of reduced graphene oxide. *J. Phys. Chem. C* 115, 7956–7966. doi:10.1021/jp2003744.
- Valia, H.S., 1990. Effects of coal oxidation on coke making, in: ISS-Ironmaking Conference Proc. Iron And Steel Society, Detroit, pp. 199–209.
- Wang, H., Dlugogorski, B.Z., Kennedy, E.M., 2003. Coal oxidation at low temperatures: Oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. *Prog. Energy Combust. Sci.* 29, 487–513. doi:10.1016/S0360-1285(03)00042-X.
- Wang, H., Dlugogorski, B.Z., Kennedy, E.M., 1999. Experimental study on low-temperature oxidation of an Australian coal. *Energy Fuels* 13, 1173–1179. doi:10.1021/ef990040s.
- Wu, M.M., Robbins, G.A., Winschel, R.A., Burke, F.P., 1988. Low-temperature coal weathering: its chemical nature and effects on coal properties. *Energy Fuels* 2, 150–157.

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	28599	500	971	420
<i>Petrographic characteristics</i>				
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.

Table 2. Semiquantitative indices derived from the DRIFT spectra.

Index	Band region (cm ⁻¹)
CO/Hal	(1750-1640) / (2990-2750)
CO/Har+Hal	(1750-1640) / (3120-2290) + (2990-2750)
CO/Car	(1750-1640) / (1600)
A ₁₄₄₅ /A ₁₃₇₅	(1445) / (1375)

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Table 3. DRIFTS indices of fresh and oxidised coals at 50 °C under 20 %, 90 % rh and air atmosphere for 60 days.

	CO/Hal	CO/Har+Hal	CO/Car	A ₁₄₄₅ /A ₁₃₇₅
A	0.25	0.21	0.40	4.45
A20Hd-60	0.34	0.29	0.55	4.02
Aair-60	0.33	0.28	0.53	4.35
A90Hd-60	0.34	0.29	0.53	4.23
B	0.41	0.34	0.56	3.86
B20Hd-60	0.54	0.45	0.66	3.62
Bair-60	0.48	0.40	0.59	3.66
B90Hd-60	0.50	0.42	0.65	3.34
C	0.25	0.19	0.39	3.80
C20Hd-60	0.28	0.22	0.49	3.56
Cair-60	0.32	0.24	0.61	3.49
C90Hd-60	0.29	0.23	0.56	3.45
D	0.26	0.19	0.43	3.99
D20Hd-60	0.32	0.24	0.54	3.84
Dair-60	0.30	0.23	0.54	3.85
D90Hd-60	0.31	0.24	0.50	3.69

Table 4. Bulk and surface composition of fresh coals and their samples oxidised for 60 days at 50 °C under conditions of 20 %, 90 % humidity and under an air atmosphere.

		C (at.%)	N (at.%)	S (at.%)	O (at.%)
A	Bulk	94.1	1.8	0.4	3.7
	Surface	81.5	0.7	-	17.8
A20rh-60	Bulk	93.8	1.6	0.4	4.2
	Surface	75.2	1.2	-	23.6
Aair-60	Bulk	93.8	1.6	0.4	4.1
	Surface	87.7	1.1	-	11.3
A90rh-60	Bulk	93.9	1.7	0.4	4.1
	Surface	83.9	1.5	-	14.7
B	Bulk	93.8	1.6	0.3	4.4
	Surface	82.5	0.8	-	16.8
B20rh-60	Bulk	93.3	1.5	0.2	5.0
	Surface	76.1	0.8	-	23.2
Bair-60	Bulk	92.8	1.4	0.2	5.5
	Surface	70.3	1.0	-	28.7
B90rh-60	Bulk	92.6	1.4	0.3	5.7
	Surface	75.6	0.6	-	23.8
C	Bulk	95.1	1.9	0.2	2.8
	Surface	84.7	1.3	-	14.0
C20rh-60	Bulk	94.9	1.8	0.2	3.0
	Surface	71.7	0.6	-	27.7
Cair-60	Bulk	95.0	1.6	0.2	3.1
	Surface	70.4	1.2	-	28.4
D	Bulk	95.5	1.8	0.3	2.4
	Surface	88.9	0.9	-	10.2
D20rh-60	Bulk	95.2	1.8	0.3	2.6
	Surface	81.3	0.9	-	17.8
Dair-60	Bulk	95.4	1.7	0.3	2.6
	Surface	81.8	0.9	-	17.3
D90rh-60	Bulk	94.7	1.7	0.3	3.3
	Surface	81.8	0.7	-	17.5

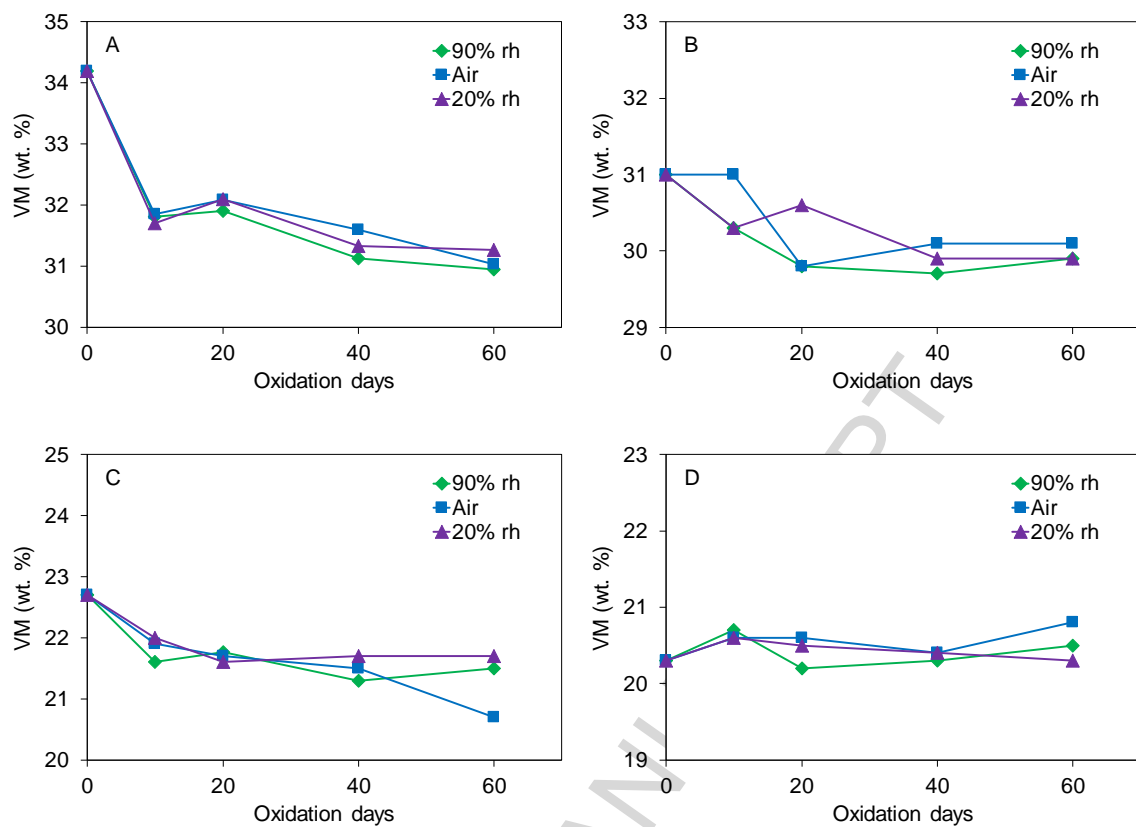


Figure 1. Variation in the volatile matter of coals A, B, C and D oxidised at 50 °C under 20/90 % rh and air.

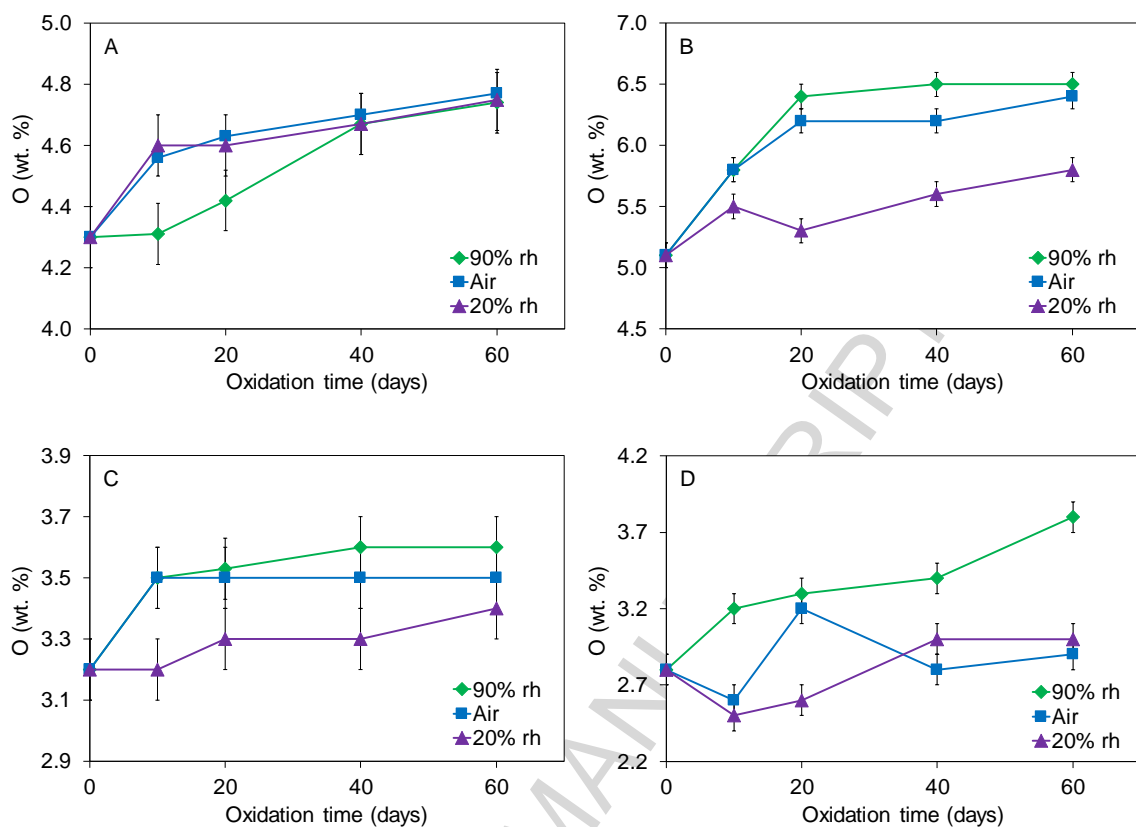


Figure 2. Variation in the oxygen content of coals A, B, C and D oxidised at 50 °C under 20/90 % rh and air.

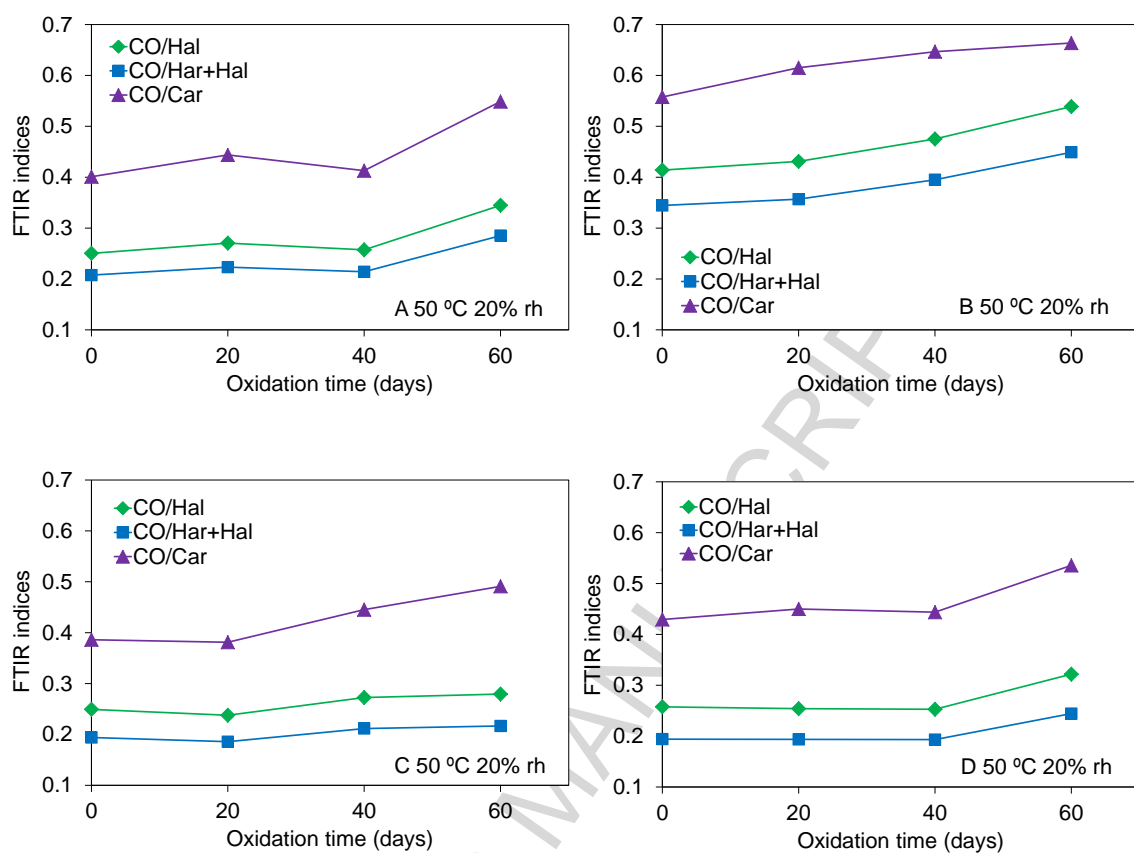


Figure 3. Evolution of the DRIFTS indices of coals A, B, C and D with oxidation time at 50 °C under 20/90 % rh and air.

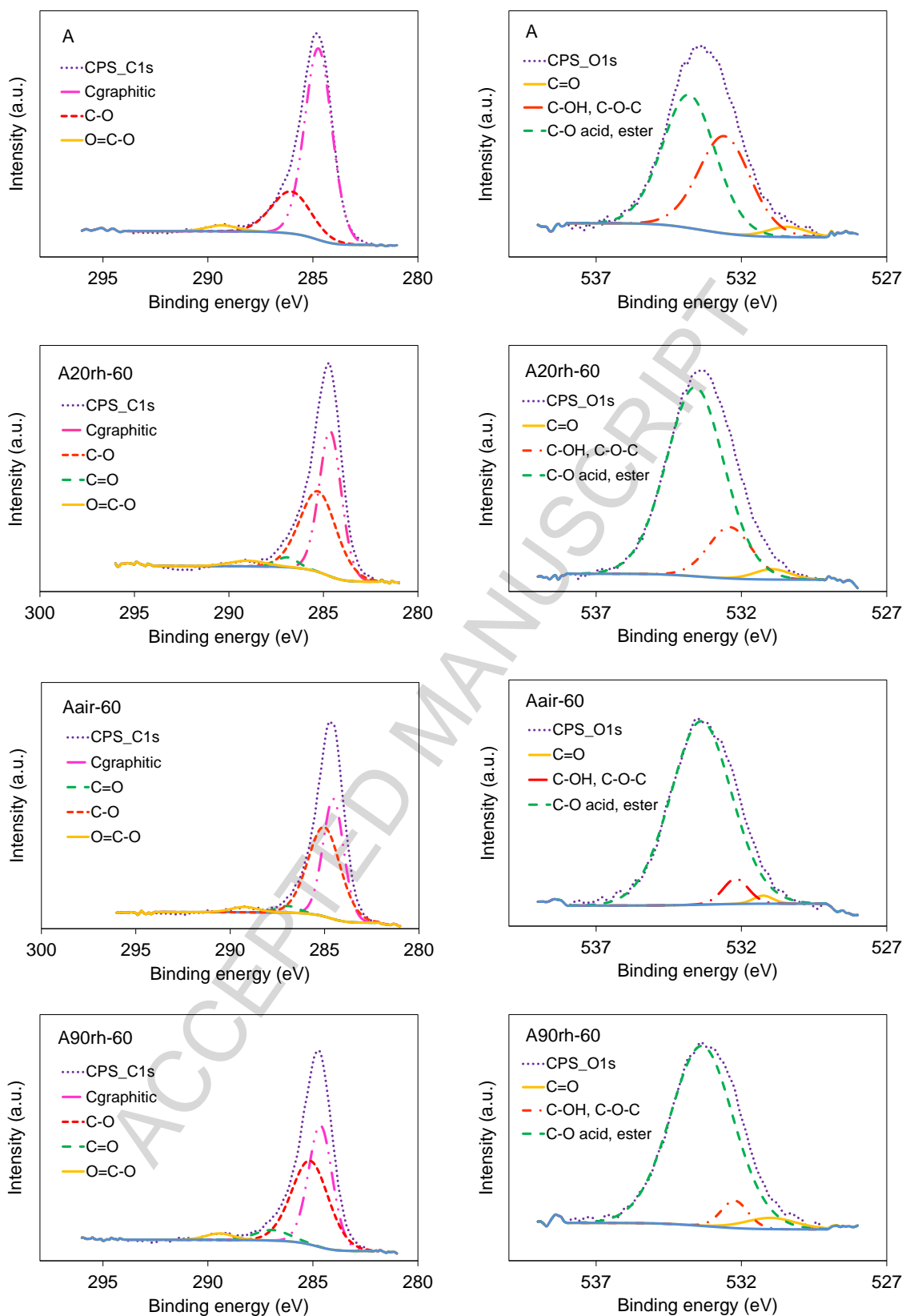


Figure 4. XPS spectra corresponding to the C(1s) and O(1s) of fresh coal A and its samples oxidised for 60 days at 50 °C under 20 % rh, air and 90 % rh.

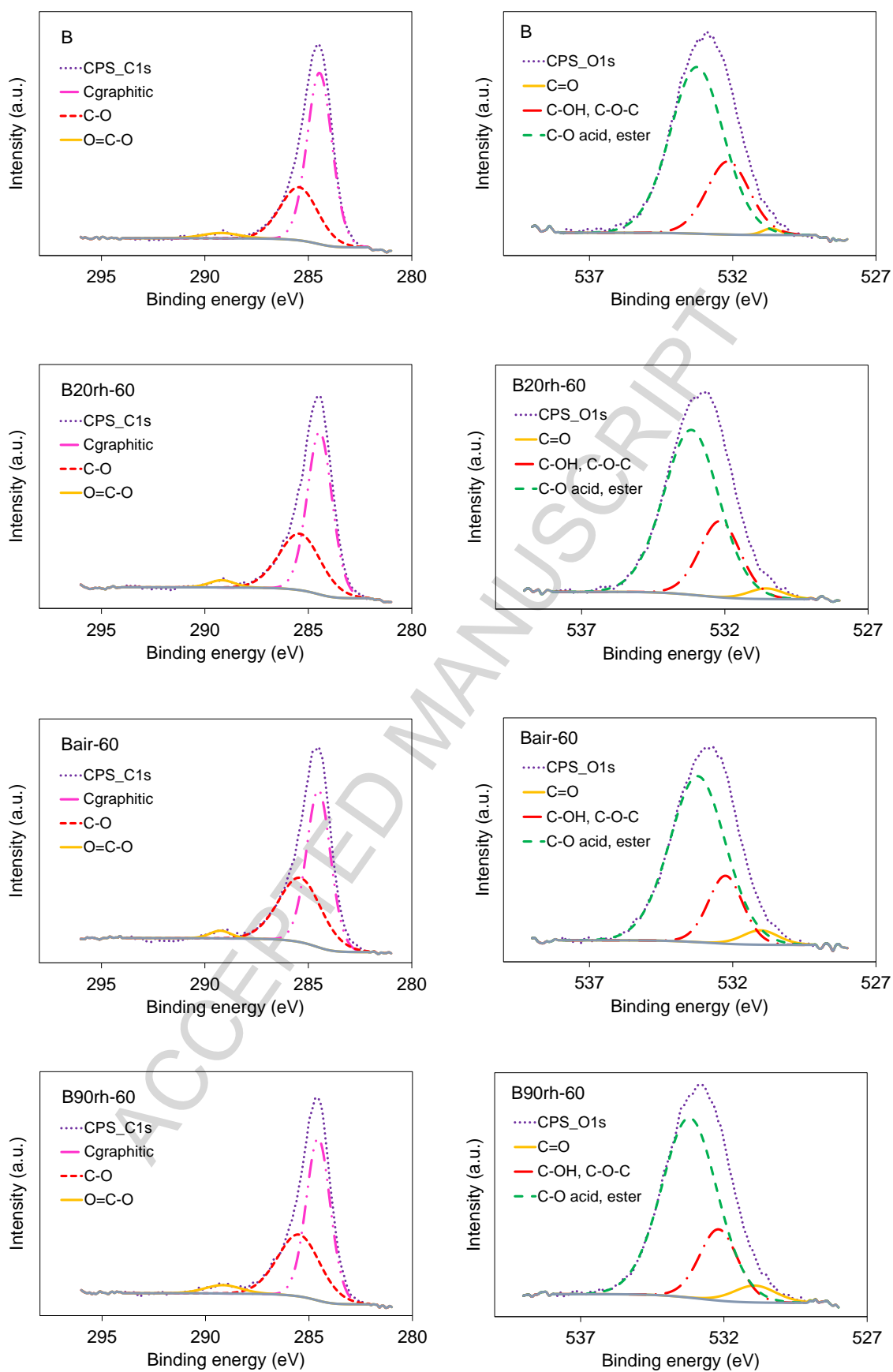


Figure 5. XPS spectra corresponding to the C(1s) and O(1s) of the fresh coal B and its samples oxidised for 60 days at 50 °C under 20% rh, air and 90% rh.

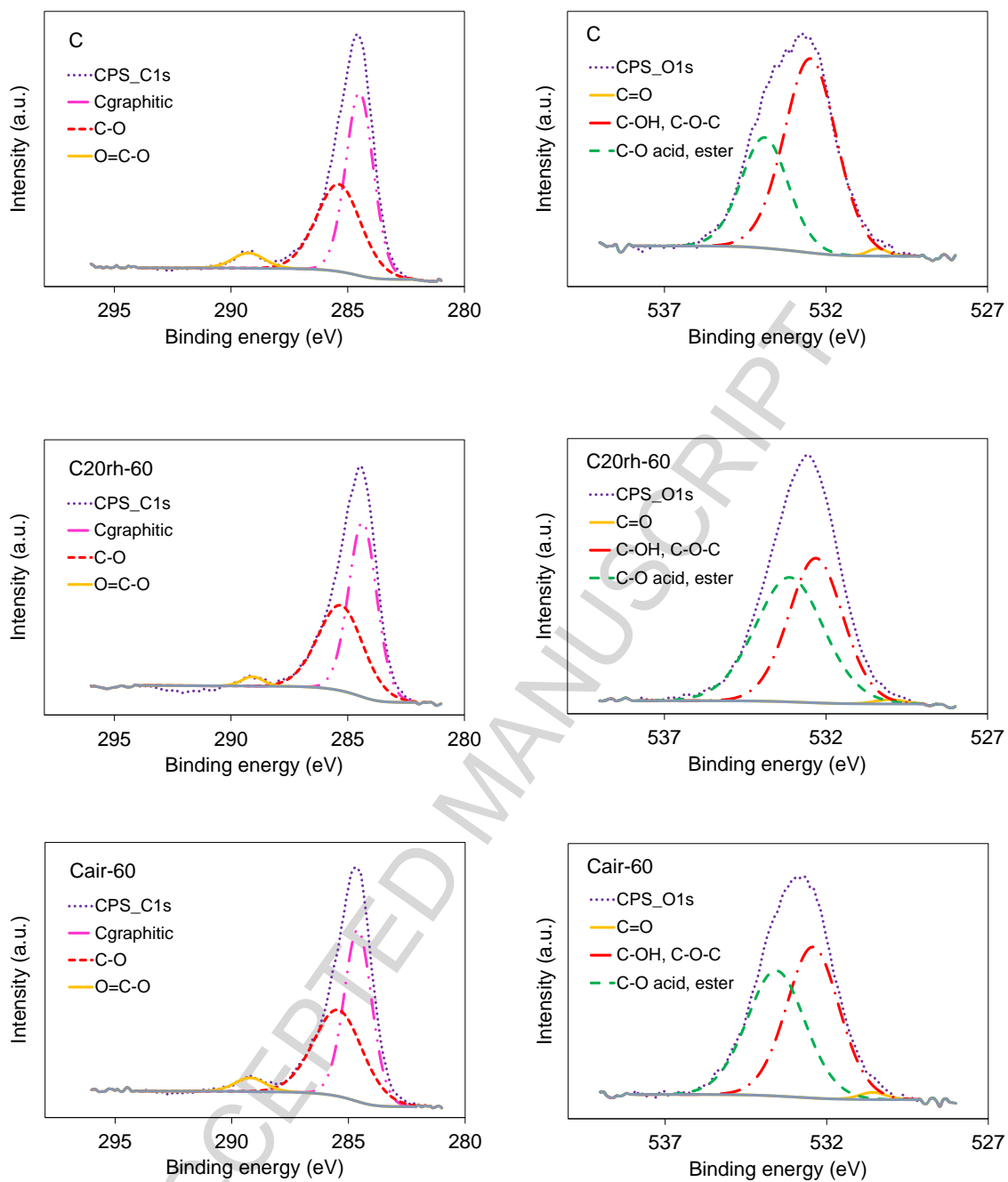


Figure 6. XPS spectra corresponding to the C(1s) and O(1s) of the fresh coal C and its samples oxidised for 60 days at 50 °C under 20% rh and air.

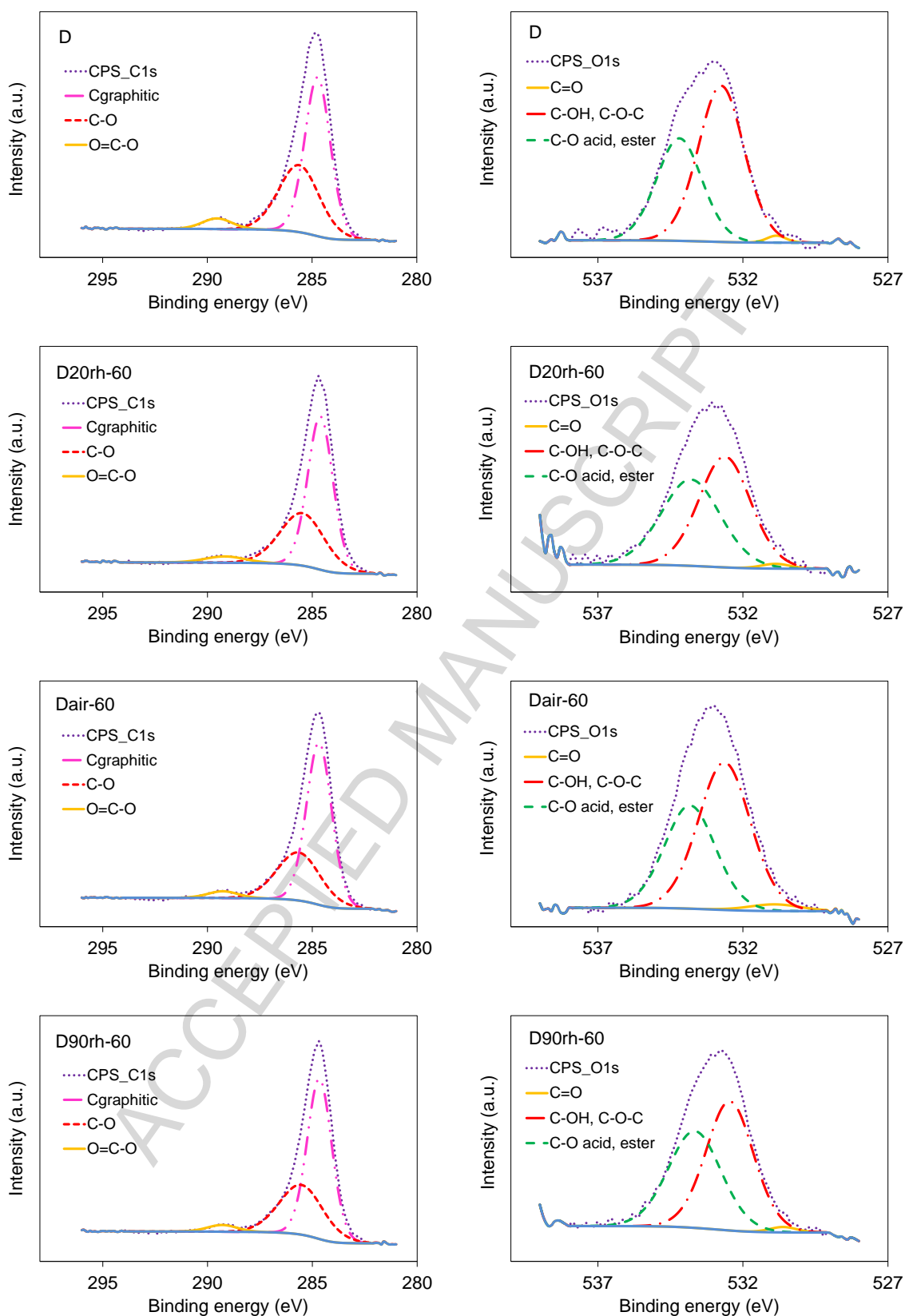


Figure 7. XPS spectra corresponding to the C(1s) and O(1s) of the fresh coal D and its samples oxidised for 60 days at 50 °C under 20 % rh, air and 90 % rh.

Highlights:

1. High humidity prevented oxidation on the surface of the lowest rank coal.
2. High rank coals were more affected by oxidation in conditions of high humidity.
3. The pH_{PZC} was an easy and accessible method for detecting coal oxidation.
4. Carbonyl and carboxyl were the main functional groups detected after oxidation.

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