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Modification of coking properties due to oxidation. Effect of relative humidity



M.F. Vega*, E. Díaz-Faes, C. Barriocanal

Instituto Nacional del Carbón (INCAR-CSIC), Oviedo, Spain

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ABSTRACT

This work is a systematic laboratory study of coal oxidation under well-controlled temperature and humidity conditions that attempts to simulate those found in the transport and storage of coking coals. Four bituminous coals of different rank were oxidised at 50 °C under different humidity conditions in order to establish the effect that the moisture of the air medium has on their coking properties. The effect of oxidation was examined by means of the free swelling index (FSI), the Gieseler test, thermogravimetry and coke microstrength measurements. The point of zero charge (pH_{PZC}) was explored as a possible method for detecting coal oxidation.

In general, the results obtained revealed a deterioration of the thermoplastic properties, a decrease in the point of zero charge and a diminution of the maximum rate of volatile matter evolution. It was observed that the highest humidity level (90% rh) retarded the oxidation of the lowest rank coal during the first few days of oxidation, whereas the higher rank coals were affected more by high humidity conditions. It was also found that low volatile coals become more dangerous after oxidation regardless of the humidity conditions. No significant variations were observed in the mechanical strength of the resultant cokes attributable to the humidity conditions.

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1. Introduction

The oxidation of coal continues to be an issue of great concern for the cokemaking industry due to the impairment that this process causes in the properties of the coal and hence in the quality of the resultant cokes [1–4]. The mild oxidation

of coal is a complicated process that is affected by several factors. These can be classified as either intrinsic (particle size, chemical and physical properties of the coal) or extrinsic (temperature, partial pressure of O_2) [5]. Coal is susceptible to oxidation since, as soon as it is extracted from the coal seam, it is exposed to oxygen (air) and changes in temperature and humidity. Therefore, another important variable that needs to be considered is the humidity content of the medium.

It is known that water affects coal oxidation, although its precise role in this process is still unclear. Most of the experiments described in the literature was carried out to study the

* Corresponding author.

E-mail: m.vega@incarcsic.es (M. Vega).<https://doi.org/10.1016/j.jmrt.2018.10.014>2238-7854/© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

influence of inherent water in the oxidation of coal [6–9], with particular focus on the effect of moisture on the spontaneous combustion of coal [10–12]. However, few studies focus on the impact of air humidity on the oxidation process. Moreover, the results from the literature are sometimes contradictory. Some studies collected in the literature suggest that water facilitates the oxidation of coal. Beier noted that at ambient temperature and high humidity levels coal is oxidised to a greater extent [13,14]. Huggings et al. reported that higher temperature and humidity conditions promote the mineral oxidation of bituminous coals. They observed that the presence of water accelerates the oxidation of pyrite, which in turn initiates the oxidation of the maceral [15,16]. However, evidence has also been presented in support of the opposite trend. Ray et al. found that coal stored in high conditions of humidity undergoes a lesser degree of oxidation than under low levels of humidity, concluding that humidity, instead of promoting the oxidation of low-rank coals, acts as a reaction inhibitor [17].

In order to clarify the process by which ambient humidity influences the oxidation of coal, a preliminary study was carried out with four bituminous coals on the basis of their surface chemistry. The pristine coals were subjected to low-temperature oxidation (50 °C) under two conditions of humidity (20 and 90% moisture levels) and in an air atmosphere. The results derived from this study show that the response of the coals to oxidation under different humidity conditions is dependent on their rank, and that the surface of high-rank coals is more affected at high humidity levels [18].

As a complement to that study, the present research work focuses on an analysis of the effect that oxidation under different humidity conditions has on the coking properties of bituminous coals. Towards this end, Gieseler test and the free swelling index were employed while the point of zero charge was tested as a possible method for detecting coal oxidation. A thermogravimetric examination of the pristine coals and their oxidised samples was carried out and the influence of humidity during oxidation on coke contraction was also studied. Finally a microstrength test was employed to assess the extent to which modifications of the coking properties of the oxidised coals affected the quality of the resultant cokes.

2. Materials and methods

2.1. Coals

Four bituminous coals at the extremes of the coking coal range were selected for this study: two low-rank coals with volatile matter contents of 34.2 and 31.0 wt.% db, denominated A and B coals, respectively and two high-rank coals with volatile matter contents of 22.7 and 20.3 wt.% db, denominated C and D coals, respectively. Oxidation was performed in a humidity chamber at 50 °C under conditions of 20 and 90% rh and in a laboratory-forced air convection oven at 50 °C under an air atmosphere. The humidity level inside this oven as measured by means of a hygrometer was 40% rh. The three humidity conditions under study represent completely different environments: very dry (20% rh), low (usually indoor air humidity, ~40% rh) and wet (90% rh). The coals were uniformly distributed in trays in thin layers (particle size < 10 mm), to ensure

that all the particles were subjected to a similar degree of air exposure. Samples 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 letters and numbers representing the oxidation conditions and the number of oxidation days e.g., A20rh-60 stands for coal A oxidised for 60 days below 20% rh.

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

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.

2.2. Ash analysis

The total ash content of the coal samples was obtained by combustion of the organic matter at 815 °C until a constant mass, following the ISO 1171 (2010) standard procedure. The concentrations of oxides (Al, Ca, Fe, K, Mg, Na, Si, P, S and Ti) were determined using X-ray fluorescence spectroscopy (XRF). The XRF apparatus was a sequential wavelength-dispersive Siemens SRS 3000 X-ray spectrometer equipped with a Rh X-ray tube, a 58-position sample turntable, and a flow counter detector. Prior to the XRF analysis the ashes obtained from the coke samples were subjected to a fusion step using lithium tetraborate in order to obtain sample beads for analysis. The device used to prepare the sample was a Philips Perl' X3 automatic fused bead machine.

2.3. Thermoplastic properties

The coking properties of the fresh and oxidised coals were assessed by means of the free-swelling index (FSI) and the Gieseler fluidity tests. The FSI was applied following the ISO501:2012 standard procedure. This method consists in heating up a sample of 1 g (<0.212 mm) in a standard crucible for 2.5 min. The profile of the resulting coke is then compared to standard profiles. 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 [19].

2.4. Point of zero charge (pH_{PZC})

The pH at which the coal surface charge has a zero value is referred to as the point of zero charge (pH_{PZC}). At this pH, the charge of the positive surface sites is equal to that of the negative ones. The point of zero charge determines the surface charge at a given pH and this information reveals the possible electrostatic interactions between the coal surface and the chemical species [20]. The pH_{PZC} of the pristine coals and of the oxidised samples was determined according to the

procedure described by Rivera-Utrilla et al. [21]. The estimated uncertainty of the experiments was less than 0.3.

2.5. Thermogravimetric analysis (TG/DTG)

The TG/DTG analysis of the coals was carried out using a TA Instruments STD 2960 thermoanalyser. The samples (10 mg) with a particle size of <0.212 mm were heated to 1000 °C at a rate of 3 °C/min under a nitrogen flow of 100 mL/min. From the data obtained by thermogravimetric analysis the volatile matter evolved up to a specific temperature (VMT) and the derivative weight loss curve (DTG curve) was calculated. The volatile matter evolved over a specific temperature range was calculated as the difference between the volatile matter evolved up to two specific temperatures (VMT₁–VMT₂). In addition, T_{max}, the temperature of maximum volatile matter evolution was derived from the TG/DTG curves [19,22]. The tests were carried out at least twice and the repeatability of the DTG_{max} was ± 0.02% min⁻¹.

2.6. Semicoke contraction

The Koppers–INCAR test was used to assess the variation in charge height during heating. A coal sample of 80 g was heated from the sole in a stainless-steel crucible for 2 h. The change in charge height, compared to the initial state of the coal sample, was recorded on a graph and expressed in mm. Contraction is expressed in negative values. The repeatability for this method is within ± 1 mm.

2.7. Microstrength test

Coke microstrength was assessed with cokes obtained at 1050 °C following the method described by Ragan and Marsh [23]. Two charges of 2 g of coke crushed to sizes ranging between 0.6 and 1.18 mm were rotated in cylinders for 800 revolutions at 25 rpm to obtain three different size fractions: >0.6 mm (R1), 0.6–0.212 mm (R2), and <0.212 mm (R3). The R indices, expressed as the percentage of the initial weight of the charge, were obtained from duplicated tests. The percentage of coke fines (R3 index) was used as an indicator of the microstrength of the resultant cokes. This index is significant within limits of ±0.5% [24].

3. Results and discussion

The petrographic characteristics of the pristine coals are presented in Table 1. A, C and D are American coals whereas B is a Polish coal. It can be seen that the mean vitrinite reflectance, R_o, ranges from 0.95 to 1.44%. The maceral analysis reveals that vitrinite (V) is the predominant maceral group with values between 70.4 and 76.4 vol.%, mineral matter-free (mmf) and that B is the coal with the lowest V content. The liptinite (L) group ranges from 0.4 to 9.1 vol.% mmf. Coals A and B have the highest L content. As for the inert macerals, which did not undergo any changes during the coking tests, coal A has the lowest percentage (15.2 vol.% mmf), whereas coals B–D the highest (ca. 22.5 vol.% mmf).

Table 2 shows the results of the elemental and proximate analyses corresponding to the pristine coals and the samples oxidised for 60 days at 50 °C under an air atmosphere and at 20, 90% rh. These are the most significant data for analysing the effect of the different moisture levels on the oxidation process. The coals are listed in the order of decreasing volatile matter content. They are characterised by an ash content below 9 wt.% and a sulphur content below 1 wt.%, as required for coal destined for use in metallurgical coke production [25]. It can be seen that the volatile matter content decreased after oxidation, especially in the lowest rank coal A, which shows a decrease of ca. 10%. In coals B and C there is a slight diminution in VM content, whereas in the case of coal D the initial value remains almost constant (Table 2). The decrease in volatile matter content due to oxidation is a well-known phenomenon that has been widely reported by other authors and is attributed to devolatilization, which occurs parallel to the oxidation of coal [26]. As expected for oxygen uptake, oxidation produced a decrease in the C/O atomic ratio [2]. However, the behaviour of the coals studied differed depending on the relative humidity during oxidation. After 60 days of oxidation the atomic C/O ratio of coal A varied independently of the humidity conditions. Whereas in the case of coals B, C and D it can be seen that oxidation under conditions of 20 and 90% rh produced the lowest and highest variation in the atomic C/O ratio, respectively. The greatest variations were observed for coals B and D after oxidation below 90% rh (Fig. 1, Table 2).

3.1. Variation of thermoplastic properties

Table 3 shows the parameters derived from the Gieseler test for the pristine coals. Coal fluidity is one of the key factors in the coking process [27,28]. Coals with a VM content between 32 and 34 wt.% db show the maximum degree of fluidity, which falls rapidly outside this rank range [25]. Barriocanal et al. also observed that coals with a similar volatile matter content (ca. 32 wt.% db) exhibited MF values between ca. 500 and 25,000 ddpm [22] like the coals used in the present study (Table 2). The low degree of fluidity in coal B may be due to its high oxygen content, since in low-rank coals the presence of oxygen cross-links prevents fusion. In addition, coal B has the lowest vitrinite content which, like liptinite, is one of the principal macerals responsible for coal plasticity [22,25].

The depletion of the thermoplastic properties of coal as a consequence of the oxidation process is well documented [1,4,29]. In the present work, a decrease in the Gieseler maximum fluidity (MF), expressed as a percentage of the initial values, was observed for all coals with the increase in oxidation time. Nevertheless, the responses of the coals differed depending on the parent coal and the conditions of humidity (Fig. 2). In the case of the lowest rank coals (A and B) it can be seen that the MF decreased to the same extent independently of the humidity level, coal B being the most affected. In the case of coal A the decrease in fluidity, as measured by the Gieseler test, accelerated after 20 oxidation days to the point where it lost ca. 80% after 60 oxidation days. Whereas the MF of coal B decreased more rapidly (ca. 80% after 20 days) to the point where by the end of the study it had lost almost all of its fluidity (99%). The reason for this may be that coal B has the highest oxygen content. It is well known that low-rank coals

Table 1 – Petrographic characteristics of the pristine coals.

Coals	A	B	C	D
Mean vitrinite reflectance, R_o (%)	1.00	0.95	1.29	1.44
Vitrinite (vol.% mmf ^a)	75.8	70.4	76.4	76.1
Liptinite (vol.% mmf ^a)	9.1	8.3	1.0	0.4
Fusinite (vol.% mmf ^a)	1.9	5.4	18.3	18.1
Semifusinite (vol.% mmf ^a)	8.7	13.7	1.4	3.3
Other inertinites (vol.% mmf ^a)	4.6	2.3	2.9	2.1

^a Mineral matter free.

Table 2 – Proximate and ultimate analyses of the pristine coals and their samples oxidised for 60 days at 50 °C under conditions of 20% rh, an air atmosphere and 90% rh.

	Ash (wt.% db ^a)	VM ^b (wt.% db ^a)	C (wt.% db ^a)	H (wt.% db ^a)	N (wt.% db ^a)	S (wt.% db ^a)	O (wt.% db ^a)
A	7.0	34.2	80.8	5.1	1.8	0.98	4.3
A20Hd-60	7.5	31.3	80.5	4.9	1.7	0.93	4.8
Aair-60	7.6	31.0	81.2	5.0	1.7	1.00	4.8
A90Hd-60	6.5	30.9	82.0	5.0	1.7	0.91	4.7
B	7.1	31.0	81.2	4.8	1.6	0.59	5.1
B20Hd-60	6.9	29.9	80.8	4.7	1.5	0.57	5.8
Bair-60	7.0	30.1	81.0	4.8	1.5	0.57	6.4
B90Hd-60	7.7	29.9	78.8	4.8	1.4	0.59	6.5
C	8.2	22.7	81.3	4.5	1.9	0.54	3.2
C20Hd-60	9.0	21.7	81.0	4.4	1.7	0.53	3.4
Cair-60	10.1	20.7	80.5	4.3	1.7	0.53	3.5
C90Hd-60	9.0	21.5	81.1	4.4	1.7	0.53	3.6
D	8.5	20.3	81.7	4.3	1.8	0.71	2.8
D20Hd-60	8.5	20.3	81.8	4.4	1.8	0.73	3.0
Dair-60	8.1	20.8	81.8	4.4	1.7	0.68	2.9
D90Hd-60	8.7	20.5	82.0	4.4	1.7	0.76	3.8

^a Dry basis.
^b Volatile matter.

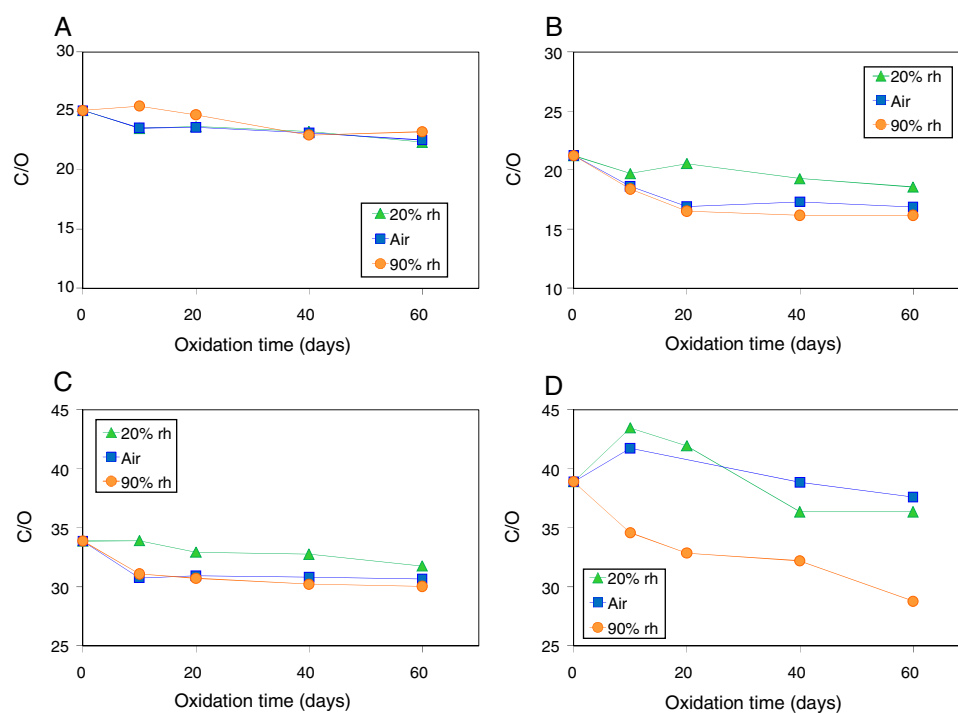
**Fig. 1 – Variation in the atomic C/O ratio of coals oxidised at 50 °C under conditions of 20% rh, an air atmosphere and 90% rh.**

Table 3 – Gieseler parameters of the pristine coals.

Coal	Ts (°C) ^a	Tf (°C) ^b	Tr (°C) ^c	Tr – Ts (°C) ^d	MF (ddpm) ^e	FSI
A	382	441	487	105	28599	7
B	408	440	473	65	500	4
C	407	467	503	96	971	7 _{1/2}
D	418	472	505	87	420	8

^a Softening temperature, defined as the temperature at which the stirrer starts to rotate.

^b Maximum fluidity temperature.

^c Resolidification temperature, defined as the temperature at which the stirrer stops rotating.

^d Plastic range.

^e Maximum fluidity expressed in dial divisions per minute (ddpm).

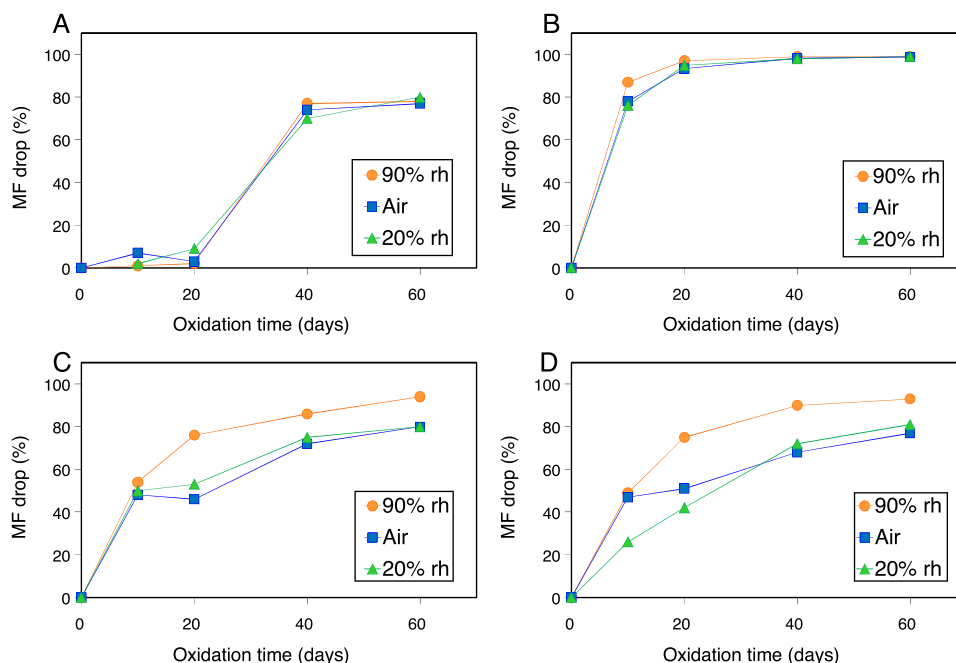


Fig. 2 – Gieseler fluidity decrease in the oxidised samples at 50 °C under conditions of 20/90% rh and an air atmosphere with oxidation time.

have more oxygenated groups, which are more reactive and therefore more labile than groups in high rank coals. These latter are considered to have a more aromatic and condensed structure [30,31]. A different behaviour was observed in the higher rank coals (C and D) in which, different humidities led to very different results in the fluidity test, with oxidation below 90% rh producing the greatest drop in fluidity. In both coals MF decreases gradually with oxidation time (Fig. 2). With regard to the plastic range, which is defined as the difference between the resolidification and softening temperatures, a decrease with oxidation time was observed in all the coals studied. As observed for the variation in the MF the diminution in plasticity was independent of the humidity conditions in the case of lowest rank coals (A, B) becoming more noticeable after oxidation below 90% rh in the higher rank coals (C, D), especially in coal D (see Fig. SM1).

In a previous research work [18], the pristine coals and their oxidised samples at 50 °C over 20, 40 and 60 days under different humidity levels, were analysed by means of DRIFT spectroscopy. The bands found in the spectra of the fresh

coals were typical of bituminous coals and no qualitative differences were apparent in the spectra of the oxidised samples. Therefore, semi quantitative indices were calculated to establish the evolution of the oxygen functional groups: CO/Aal, CO/Aal + Aar and CO/Car, defined as the ratios of the oxygen-containing structures of the C=O bond, to the aliphatic hydrogen content (Aal), aliphatic plus aromatic hydrogen content (Aal + Aar) and aromatic carbon content (Car), respectively [18]. In the present research work these indices have been used to establish their relationship with the variation in the thermoplastic properties (Fig. 3). It can be seen that the highest values of these indices correspond to the lowest Gieseler MF (expressed as log base 10). Although the trends coincide in all four cases, the relationship is not as clear in coals C and D because their indices do not vary much. This confirms that impairment of thermoplastic properties is due, at least partly, to the formation of groups with oxygen functionalities. As a consequence of oxidation, the introduction of oxygen-bearing groups into the macromolecular structure of the coal at the expense of aromatic and aliphatic hydrogens, which are a key

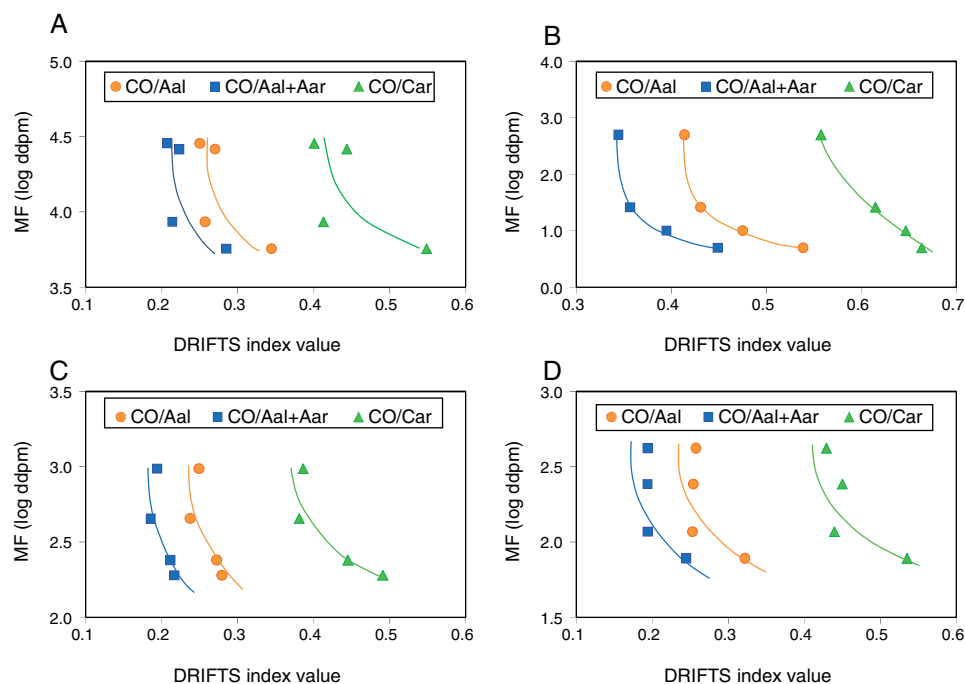


Fig. 3 – Relationship between the Gieseler MF of coals A, B, C and D and the ratios calculated from DRIFT spectra (CO/Aal; CO/Aal + Aar; CO/Car).

factor in the development of fluidity, leads to an increase in cross-link density that inhibits plasticity during the carbonization process [32–34].

The raw coals and their oxidised samples were also subjected to the FSI test (see Table 3, where only the values of the fresh coals are presented to avoid repetition). However this technique is not as sensitive as the Gieseler test and only in the case of coal B was any significant variations observed. The FSI of the pristine coals ranges between 4 and 8. It was observed that coals with similar thermoplastic properties (B: 500 ddpmm and D: 420 ddpmm) showed different FSI values (4 and 8 for B and D coals, respectively). Despite the fact that coals with sufficient plasticity also have a good swelling index, there is not always a good correlation between these two properties [25]. The FSI values of B coal decreased from 4 to 2_{1/2}, 3 and 2_{1/2} after 60 days of oxidation under 20% rh, air and 90% rh, respectively. No change in the FSI was observed for the rest of the coals.

3.2. Point of zero charge (pH_{PZC})

The pH of the point of zero charge (pH_{PZC}) is an easy and readily accessible method for detecting any modification in the oxygen groups on the surface of the samples and can be used to check whether the surface of the coals has been modified by oxidation. The pH_{PZC} value indicates which fresh coal contains more acidic surface groups. In the present research work this was coal C whose pH_{PZC} was 4.5, followed by coal A (5.3), coal D (5.9) and coal B (6.9). The results derived from the study of the surface chemistry of coals A, B, C and D [18] do not provide a satisfactory explanation of these pH_{PZC} values in view of the organic functional groups present on the surface of the coals. Therefore the role of mineral matter also needs to be

taken into account. The percentages of major-element oxides obtained by XRF analysis of the pristine coals, in relation to the coal mass, are listed in Table 4. It can be seen that coal B has a higher percentage of basic oxides i.e., Na₂O (0.13%), MgO (0.23%) and CaO (0.72%) than coals A, C and D i.e., ca. 0.03%, 0.06% and 0.18%, respectively. In addition, coal B has the lowest percentage of acidic oxide SiO₂ (2.27%) (Table 4). In order to establish a relationship between the chemical composition of the coal ashes and the type of mineral matter present in coal, the detrital/authigenic index (I) was calculated:

$$I = (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{TiO}_2) / (\text{Fe}_2\text{O}_3 + \text{MgO} + \text{CaO} + \text{SO}_3) \quad (1)$$

By means of this index it is possible to assess the dominant detrital or authigenic attachment of the ash-forming elements in coal [35]. In the case of bituminous coals the mineral matter is formed mainly by silicates (e.g. kaolinite, Al₂Si₂O₅(OH)₄; quartz, SiO₂), carbonates (e.g. calcite, CaCO₃; siderite, FeCO₃; dolomite, CaMg(CO₃)₂), sulphides (e.g. pyrite, FeS₂) and sulphates (e.g. gypsum CaSO₄·2H₂O) [36]. Silicates commonly have a predominantly detrital genesis, while carbonates, sulphides and sulphates have mostly an authigenic origin in coal [37]. Coal B has the lowest I index value (2.4), which suggests that it may be enriched in elements associated with authigenic minerals, i.e. carbonates, sulphides and sulphates. These minerals have a higher basic character and therefore could impose their own surface charge on the coal, which would explain the higher pH_{PZC} value (6.9) for this coal. On the contrary, coal C, has the highest I index value (13.5). In

Table 4 – Ash chemical composition (wt.%) of the pristine coals as determined by XRF and detrital/authigenic index (I).

Coal	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	SO ₃	I ^a
A	0.04	0.08	1.96	3.72	0.01	0.20	0.18	0.10	0.56	0.13	6.3
B	0.13	0.23	1.97	2.27	0.53	0.12	0.72	0.08	0.43	0.51	2.4
C	0.04	0.05	2.77	4.40	0.05	0.19	0.13	0.15	0.29	0.08	13.5
D	0.02	0.04	2.73	4.27	0.12	0.18	0.22	0.14	0.54	0.11	7.8

^a $I = (SiO_2 + Al_2O_3 + K_2O + Na_2O + TiO_2) / (Fe_2O_3 + MgO + CaO + SO_3)$.

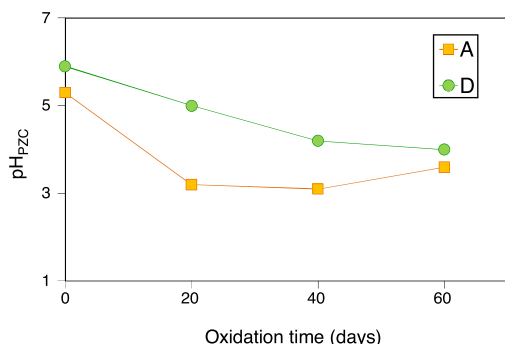


Fig. 4 – Evolution of the pH_{PZC} of coals A and D with oxidation time at 50 °C under conditions of 90% humidity.

this case the higher content in detrital minerals might explain its lower pH_{PZC} value (4.5).

The pH_{PZC} of the oxidised samples was compared with that of the fresh samples. Fig. 4 shows the variation in the pH_{PZC} of coals A and D with oxidation time and 90% rh. This humidity condition was selected due to the fact that coal D underwent greater variations at high humidity levels. It can be seen that the pH_{PZC} of coal A (lowest-rank coal) and coal D (highest-rank coal) decreased after several days of exposure at 50 °C and 90% rh. Hence the number of oxygenated groups increased due to oxidation reactions. In the case of coal D, which experienced a clear increase in oxygen content with time under these humidity conditions (Table 2), the pH_{PZC} decreased with time. Fig. 5 shows the pH_{PZC} of the fresh A, B, C and D coals and the 60-day oxidised samples at 50 °C under conditions of 20% rh, air and 90% rh. The fresh samples contained more acidic surface groups than the basic surface groups since their

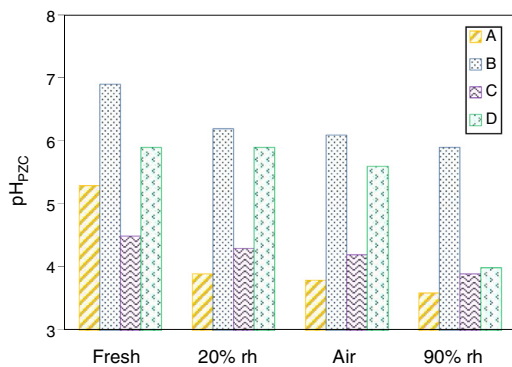


Fig. 5 – The pH_{PZC} of the fresh coals A, B, C, D and the samples oxidised for 60 days at 50 °C under conditions of 20/90% humidity and air.

pH_{PZC} was below 7. Furthermore the difference between these two groups was greater in the oxidised samples considering that their pH_{PZC} values were smaller than those of the fresh samples. The pH of the oxidised samples decreased after oxidation under the different humidity level conditions. It is well known that oxidation produces an increase in acidic functional groups, which is higher in lower rank coals [3]. In fact, the greatest variation in pH_{PZC}, was observed in coals A and B, whereas the value corresponding to coal C did not change significantly and coal D only underwent a noticeable decrease in pH_{PZC} after 60 oxidation days under 90% rh, in accordance with the greater effect on Gieseler fluidity and C/O atomic ratio due to oxidation under high humidity for the highest rank coal.

3.3. Thermogravimetric analysis

The main parameters derived from the thermogravimetric analysis of the pristine coals vary with rank (Table 5). These variations are due to the differences in the macromolecular network of coals, since high-rank coals have more condensed structures with a smaller proportion of thermally-labile groups than low-rank coals. Consequently, as the coal rank increases, the reactions that occur during pyrolysis take place at higher temperatures, the maximum rate of volatile matter evolution (DTG_{max}) proceeds at a slower rate and the coke yield increases [19]. The amount of volatile matter released up to the pre-plastic stage (VM400) and during the plastic stage (VM400–500) is higher in the coals with a higher VM content (A,B). Whereas volatile matter evolved during the post-plastic stage (VM500–750) is higher in lower VM coals (C, D).

Fig. 6 displays the variation in DTG_{max} with oxidation time for the oxidised samples at 50 °C in the different humidity conditions (20 and 90% rh and air). In general the DTG_{max} value decreases with the oxidation time although, the results differ depending on the coal and the humidity conditions. It can be seen that the DTG_{max} value of coal A remains almost constant during the first 20 oxidation days although oxidation under conditions of 90% rh produces the lowest variations. Coal B undergoes the greatest decrease in DTG_{max}, whose value diminishes sharply during the first 10 oxidation days, remaining almost constant thereafter as observed in the variation of Gieseler MF. After 60 oxidation days the DTG_{max} value decreases to the same extent independently of the humidity conditions. The DTG_{max} of coals C and D decreases gradually and the DTG_{max} of coal D is the least affected by oxidation. In the case of coals C and D, contrary to what was observed for coals A and B, oxidation under 90% rh produces the greatest drop in this parameter.

Table 5 – Parameters derived from the thermogravimetric analysis of the pristine coals performed at 3 °C/min.

	Ti (°C) ^a	Tf (°C) ^b	Tf – Ti	VM400 (%) ^c	VM400–500 (%) ^c	VM500–750 (%) ^c	DTGmax (%/min) ^d	Tmax (°C) ^e	CY (%) ^f
A	336	797	461	14.6	56.0	22.6	0.83	451	67.8
B	361	802	441	11.3	57.4	24.4	0.89	438	68.4
C	359	836	477	9.7	51.4	30.1	0.56	469	76.8
D	378	831	453	7.5	50.8	32.9	0.50	472	78.6

^a Temperature at 5% conversion.

^b Temperature at 95% conversion.

^c Volatile matter evolved up to a specific temperature (T) or in a specific temperature range and normalised to 100%.

^d Maximum rate of volatile matter evolution.

^e Temperature of maximum volatile matter released.

^f Coke yield at 1000 °C.

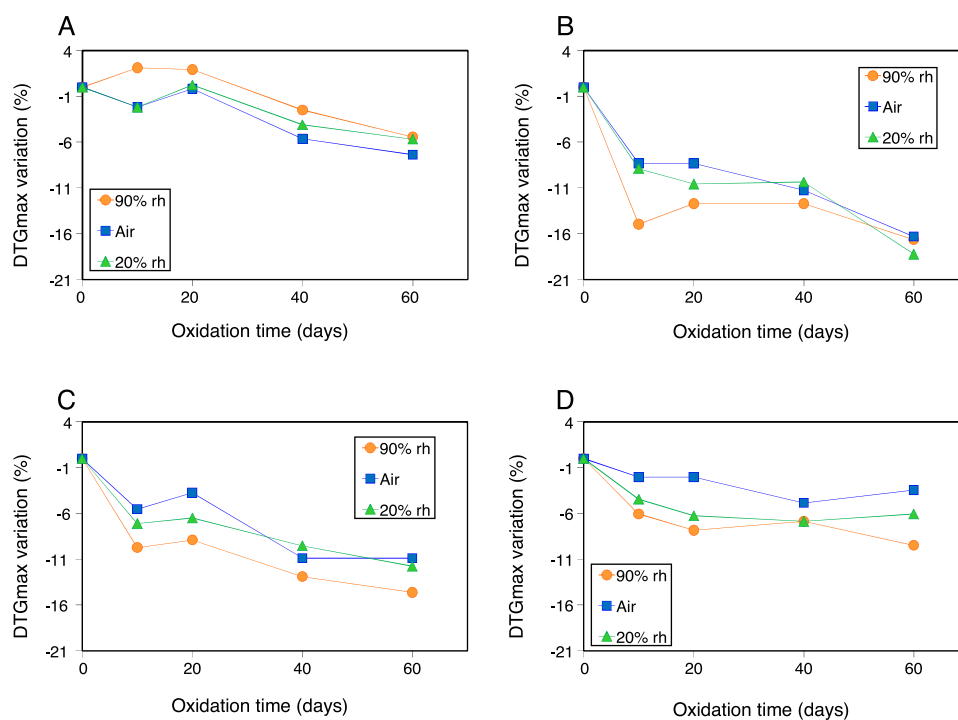


Fig. 6 – Variation of the DTGmax of oxidised samples at 50 °C under conditions of 20/90% rh and air atmosphere with oxidation time.

Fig. 7 shows the relationship between the Gieseler MF and the DTGmax of the pristine coals and the samples oxidised under the different humidity conditions. In all the coals the same general trend is observed: as DTGmax decreases, the Gieseler MF decreases. As a consequence of oxidation, more labile groups are formed, which are evolved in the pre-plastic stage. The lack of aliphatic hydrogens, which are decisive for the development of fluidity [34,38], explains the decrease in the release of VM as well as the impairment of the thermo-plastic properties [39].

3.4. Semicoke contraction

The semicoke contraction of the pristine coals was tested by means of the Koppers-INCAR test. According to the criterion

applied in this test, that coals with a contraction >10 mm are not dangerous [40], the pristine coals, with K-I contraction values of –20, –24.5, –15 and –11 mm for coals A, B, C and D, respectively, can be considered safe coals. Previous studies have established that dangerous coals become even more dangerous as a result of air oxidation, whereas safe coals do not undergo any significant changes in their K-I contraction value [40,41]. The impairment of the thermoplastic properties of oxidised coals due to an increase in their oxygen content generates a thinner and more viscous plastic stage that obstructs the release of volatile matter, resulting in an increase in coking pressure and a decrease in contraction [42].

Although C and D can be considered as safe coals, their K-I contraction values are close to the limit beyond which the coal must be considered as dangerous. For this reason,

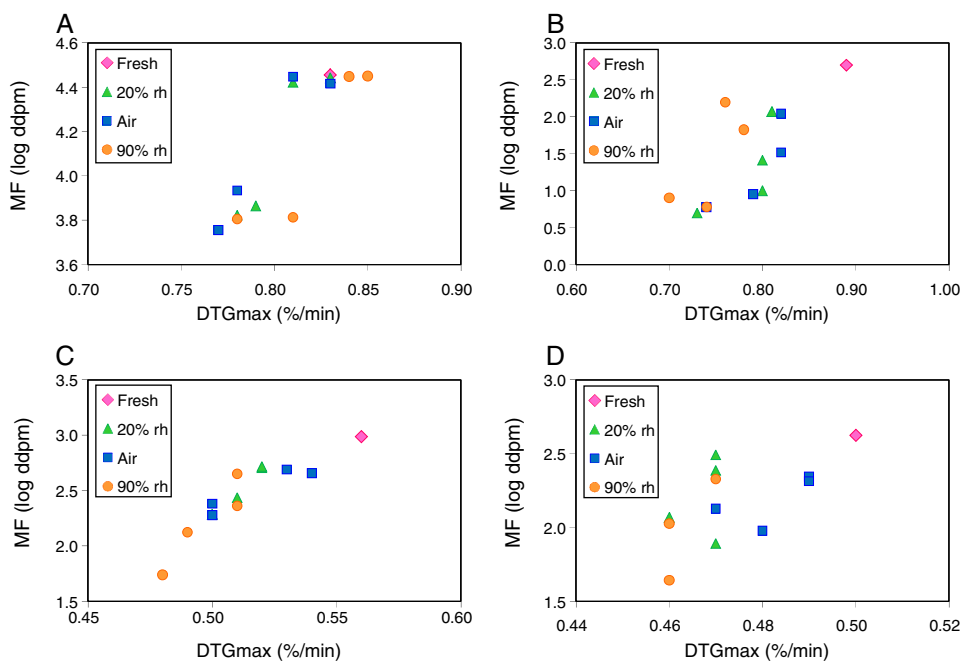


Fig. 7 – Relationship between the DTGmax of the fresh and oxidised samples at 50 °C under different humidity conditions (20/90% rh and air) and the Gieseler MF.

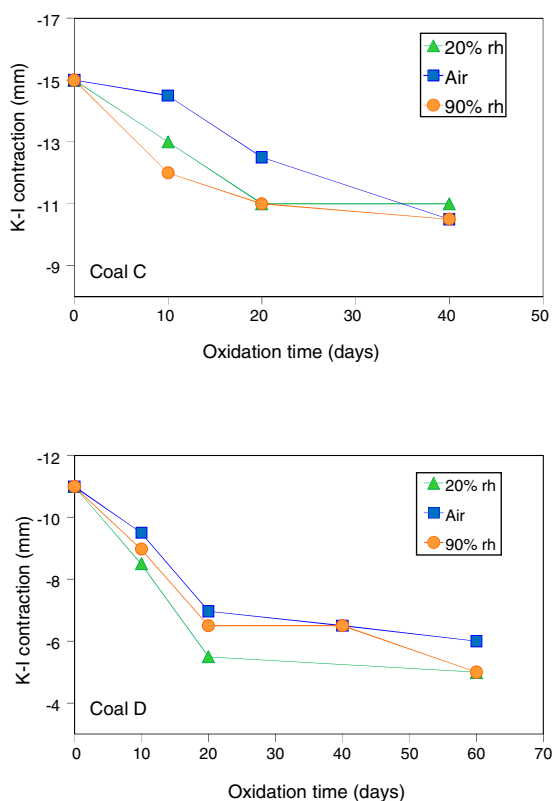


Fig. 8 – Contraction of the plastic layer as a function of oxidation time for fresh coals C, D and their oxidised samples at 50 °C under conditions of 20/90% rh and air.

C and D were the coals used to assess the influence of humidity conditions during oxidation on K–I contraction. The results obtained are shown in Fig. 8. In both coals a gradual decrease in the K–I contraction value is observed during the first 20

oxidation days. From then on, these values remain almost constant. The influence of humidity is not clear since no significant differences could be ascribed to the different levels of humidity. The main difference between the two coals is that, after 40 oxidation days, coal D becomes less safe (K–I contraction values ca. –10.5 mm and ca. –6.5 mm, for coals C and D, respectively).

3.5. Coke microstrength

The quality of the cokes obtained from the fresh coals and their samples oxidised under conditions of 20/90% rh, was assessed by means of the microstrength test. The R3 index corresponds to the fraction <0.212 mm, which means that cokes with a higher R3 index have a lower mechanical strength. In the case of the fresh coals, cokes produced from low-rank coals have a higher R3 index (41 and 53%, respectively for coals A and B) than cokes produced from high-rank coals (36 and 33%, respectively for coals C and D). The results derived from this study suggest that the effect of the humidity conditions on the oxidation of coal, observed in the coking properties of the coals, did not have a direct impact on the quality of the resultant cokes. The values of the R3 index of the highest rank coal D remained unaltered regardless of the humidity conditions used during the oxidation process. In the case of the cokes obtained from coals A, B and C a slight impairment of the mechanical strength was observed after oxidation, although the humidity conditions were not determinant, either. The relationship between the Gieseler maximum fluidity of the fresh coals and their samples oxidised below 20 and 90% rh levels and the microstrength R3 index of the resultant cokes seems to indicate that, as the maximum fluidity of the coal decreases, the quality of the resultant cokes deteriorates.

However, the differences observed were not significant enough to establish a clear and definitive relationship (Fig. SM2).

4. Conclusions

The responses of four bituminous coals to oxidation under different levels of humidity (20, 90% rh and an air atmosphere) differed depending on the nature of the raw coal. The lowest rank coal (A) was affected to the same extent independently of the humidity conditions, although the highest humidity level (90% rh) seemed to retard the oxidation process at least during the first 20 days of the oxidation treatment. In the case of coal B the humidity conditions were not particularly decisive. In contrast, oxidation below 90% rh clearly caused a greater impairment of the coking properties in higher rank coals; e.g. the reduction in fluidity after 60 oxidation days below 90% rh was higher than 10% compared to that observed at lower humidity levels. The point of zero charge appears to be a promising method for detecting an increase in acidic surface groups after oxidation. Coal contraction in the low volatile coals decreased during the first 20 days of oxidation (ca. 23% and 43% for coals C and D, respectively) after which it remained almost constant. The highest rank coal D became dangerous after only 10 days of oxidation (K–I contraction values ca. 9 mm) regardless of the humidity conditions. Not all the changes observed in the coking properties of the coals oxidised at different humidity levels were accompanied by any serious impairment of the quality of the resultant cokes.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jmrt.2018.10.014](https://doi.org/10.1016/j.jmrt.2018.10.014).

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