# XRD study of coal microstructure evolution during air oxidation

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## RESUMEN

Se ha estudiado la oxidación del carbón en aire a 270°C en tres carbones bituminosos durante 2-6 días. La microestructura de las muestras oxidadas se estudió mediante XRD y la evolución de la porosidad por adsorción de $CO_2$ a 298 K. Se encontró que bajo estas condiciones, los carbones pierden peso debido a reacciones químicas. El análisis de XRD de estos materiales reveló que en las primeras etapas de oxidación, los grupos alifáticos del carbón desaparecen dejando una estructura más aromática. También en los pasos iniciales, los apilamientos de pocas capas de grafeno reaccionan aumentando el número promedio de capas en la estructura apilada y disminuyendo la fracción de estructura ordenada. La disminución de la distancia interplanar entre capas, $d_{002}$, y el aumento en el número medio de capas por apilamiento, sugiere una reorganización en el carbón, dejando una estructura más ordenada en los carbones oxidados. El análisis del área superficial disponible para la adsorción de $CO_2$ reveló que la porosidad no era accesible en las muestras oxidadas.

**Palabras clave:** oxidación de carbón, difracción de rayos X, estructura de apilamiento, porosidad del carbón.

## SUMMARY

Coal oxidation in air at 270°C of three bituminous coals during 2-6 days, was studied. The microstructure of the oxidized samples was studied by XRD and also the evolution of porosity by $CO_2$ adsorption at 298 K. It was found that under these conditions, coals lose weight due to chemical reactions. Analysis of XRD of these materials revealed that in first stages of oxidation, aliphatic groups in coal disappear leaving a more aromatic microstructure. Also in the initial steps, stacks of low number of graphene layers react, increasing the mean number of layers per stack in the structure and decreasing the fraction of or-dered structure. The decrease in the interplanar distance between layers, $d_{002}$, and the increase in the mean number of layers per stack suggests coal reorganization, leaving a more ordered structure in oxidized coals. Analysis of the surface area available for $CO_2$ adsorption revealed that porosity was not accessible in the oxidized samples.

**Keywords:** Coal oxidation, X-ray diffraction, stacking structure, coal porosity

## RESUM

S'ha estudiat l'oxidació del carboni en aire a 270°C en tres carbons bituminosos durant 2-6 dies. La microestructura de les mostres oxidades es va estudiar mitjançant XRD i l'evolució de la porositat per adsorció de CO2 a 298 K. Es va trobar que sota aquestes condicions, els carbons per-den pes a causa de reaccions químiques. L'anàlisi de XRD d'aquests materials va revelar que en les primeres etapes d'oxidació, els grups alifàtics del carbó desapareixen dei-xant una estructura més aromàtica. També, en els passos inicials els apilaments de poques capes de grafè reaccio-nen augmentant el nombre mitjà de capes en l'estructura apilada i disminuint la fracció d'estructura ordenada. La disminució de la distància interplanar entre capes, d002, i l'augment del nombre mitjà de capes per apilament, sug-gereix una reorganització del carbó, deixant una estructura més ordenada en els carbons oxidats. L'anàlisi de l'àrea superficial disponible per a l'adsorció de CO2 va revelar que la porositat no era accessible en les mostres oxida-des.

**Paraules clau:** oxidació de carbó, difracció de raigs X, es-tructura d'apilament, porositat del carbó

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## INTRODUCTION

Coal preoxidation has been reported as a fundamental step in the preparation of activated carbons with high micropore volume. Previous studies [1-5] have reported increments of the 500% in the surface area of activated carbons when there was a preoxidation treatment of 7 days at 270 °C. FTIR analysis of this oxidation treatment [6,7] found that oxidation in air at 270°C causes an oxidation and decarboxylation of the oxygenated superficial groups, oxidizes the aliphatic compounds and generates a coal structure more aromatic, less substituted and more condensed.

Previous results [1-4] found that the activated carbons obtained with preoxidised coals with different times of preoxidation, developed preferentially the narrow microporosity, and generated activated carbons with higher surface areas and higher relative densities.

Coal is composed of a series of graphene layers stacked in units of different numbers of layers (2-6) depending on the coal rank [8-10], and this structures and stacks varies with heat treatments [10-12]. This stacks generates the 002 diffraction line which can be observed in powder XRD of coals and has been used as a tool for the characterization of coal and carbon microstructure. [8-14]

First model and methodology based in a Fourier transform analysis of the $I_{002}$ intensity band for the analysis of the structure of coal, was reported by Hirsh [8]. This model considers stacked layers organized in units which are linked by aliphatic and amorphous carbon. The analysis of the 002 peak of XRD allows to calculate parameters such as the interlayer spacing, the crystallite size (Scherer approximation) [9,11], and the aromaticity [9]. A Fourier analysis of this diffraction line also permits to calculate the distribution of the layers stacked in the crystallites, the mean number of layers per stack and the fraction of stacked structure [10-13]. The use of the Fourier transform approximations is useful because the little size of the stacks causes a broad band in the coal 002 reflection, giving an ambiguity in the calculation of $d_{002}$ and $L_c$.

Recently Sharma et al. have studied coal microstructure and its evolution with heat treatment by HRTEM. The results evidence the presence of the stacks of layers in the coals and they have compared the Hirsch methodology of XRD analysis for coals, with a methodology to obtain structural parameters from HRTEM data, and they found a good correlation between these methodologies.

In the present study, the coal microstructure evolution during air oxidation treatments of three bituminous coals was analyzed by means of the Hirsh approximation using XRD of these materials.

## EXPERIMENTAL
### Samples

The oxidations were studied with bituminous coals from the northern region of Colombia (Department of El Cesar). Proximate analysis of the samples is presented in table 1.

**Table 1.** *Proximate analysis of coals*

| Coal | Moisture (%) | Volatile matter (%) | Fixed carbon (%) | Ash (%) |
|------|--------------|---------------------|------------------|---------|
| M15 | 4.8 | 31.0 | 58.1 | 6.1 |
| M240 | 7.0 | 27.7 | 60.9 | 4.4 |
| M210 | 8.2 | 33.6 | 52.0 | 6.2 |

### Oxidation treatment

The starting material was ground and sieved, and a particle size <2 μm was selected for the analysis. Then, samples of approximately 10 g were oxidized in air at 270 °C in an oven, during 2 – 6 days.

### Surface area

Adsorption isotherms of the oxidized materials were measured with $N_2$ at 77K and $CO_2$ isotherms at 273 K in a Quantachrome Autosorb 3B gas sorption system. Before analysis, samples were out gassed at 250 °C and $1 \times 10^{-3}$ mbar during 2 hours. Surface area was measured applying BET equation to $N_2$ adsorption isotherms and, micropore volume obtained from Dubinin-Raduschevich equation with data of $CO_2$ isotherm. $CO_2$ was employed as the analysis gas, because the materials exhibit low areas and narrow pore sizes, which make it difficult to perform the analysis with other gases, e.g. $N_2$ at 77 K.

### X-Ray analysis

Samples were washed with HF (0.3M), HCl (0.3 M), and then with distilled water for ash removal. X-Ray measurements were performed with Rigaku Miniflex equipment. Samples were packed in an aluminium holder and scanned with a step scan mode (0,1 °/step) and a step time of 8 s. Measurements were made over the 10-50 ° 2θ.

X ray diffraction spectra were first corrected for Lorentz and Polarization factors, before analysis. The distribution of probabilities of finding a stack with N layers, the mean value of layers per stack ($\bar{N}$) and the fraction of stacked aromatic carbon ($P_s$) were calculated as Yoshisawa et al. reported previously [10,13].

The fraction of aromatic carbon in the materials was calculated with the areas below the $I_{002}$ and the $\gamma$ peak of the deconvoluted diffraction patterns. For this analysis, the spectra were fitted to the theoretical-calculated independent scattering of carbon atom, and then, the integrated area of the two peaks devonvoluted was calculated. Deconvolution of the peaks was performed with Peak fit software. We approximate a value of aromaticity for the samples. assuming that the integral areas under the $I_{002}$ and the $\gamma$ peak be equal to the number of aromatic carbons ($C_{ar}$) and aliphatic carbons ($C_{al}$) respectively. The ratio of carbon aromatic atoms to carbon saturated or aliphatic carbon is defined as: [9]

$$f_a = \frac{C_{ar}}{C_{ar}+C_{al}} \quad (1)$$

The interplanar distance of the $I_{002}$ band, corresponding to the spacing between layers in a stack, was determined with the first derivative of the deconvolution $I_{002}$ peak.

## RESULTS AND DISCUSSION

### Weight loss of the samples

The weight loses (corrected for moisture) of the samples are presented with the corresponding times of oxidation in table 2. From the $CO_2$ adsorption isotherms, not shown, the Dubinin-Radushkevich narrow micropore volume ($V_{oDRCO2}$) is assessed. From the $N_2$ adsorption isotherms, the apparent BET surface area, the Dubinin-Radushkevich ere obtained. This is an evidence of a slow gasification that occurs in the oxidation treatment of coals at 270°C. The weight changes during an oxidation treatment for

coals has been reported previously [2,17] and it was found that the weight changes depend of the temperature of the oxidation, the nature of the coal and the particle size. The weight could increase due to the addition of oxygen or it can decrease due the elimination of water, $CO_2$ and CO. At 270°C and small size particles, it is expected the second phenomena to be predominant, as the results shows.

**Table 2.** *Gas adsorption analysis of the oxidized coals. Specific surface area and micropore volume data calculated from $CO_2$ adsorption isotherms at 273 K.*

| Coal | Oxidation time (h) | $S_{BET-N_2}$ (m²/g) | $V_{o\,DR-CO_2}$ (cc/g) |
|------|------|------|------|
| M15 | 48 | 127 | 0.067 |
| | 96 | 150 | 0.072 |
| | 144 | 183 | 0.092 |
| M240 | 48 | 190 | 0.096 |
| | 144 | 187 | 0.092 |
| M210 | 48 | 172 | 0.085 |
| | 144 | 158 | 0.074 |

The surface area of the initial and final oxidized coals is presented in table 2. It is observed that for coals M240 and M270 there is a slight decrease in the surface area and micropore volume of the oxidized coals, while M15, and presents an increase.

The surface area of the initial and final oxidized coals is presented in table 2. It is observed that for coals M240 and M270 there is a slight decrease in the surface area and micropore volume of the oxidized coals, while M15, and presents an increase in the area surface and in volume of micropore.

We believe that the loss of amorphous structure during oxidation process, this could result in an increase of the surface area of oxidized materials. However, results show that this porosity generated, does not is accessible to gas adsorption. Therefore are required further treatments of gasification (activation) for the opening of this porosity and that is accessible to the gases.

**X-ray characterization**

Experimental diffraction profiles, before correction, are presented in figure 1. The corrected and deconvoluted peaks for different oxidized coals of the M15 and M240 samples are presented in figure 2. It is evidenced the decrease in the $\gamma\gamma$-band with the oxidation treatment for the two samples. This is an evidence of the loss of aliphatic chains and the increase of the aromaticity ($f_a$) of the coals with the oxidation treatment. The evolution of the aromaticity ($f_a$) with time, for the different materials (table 3, figure 4), shows that the oxidized coals have lost almost all the aliphatic chains at 10-15% of burn-off.
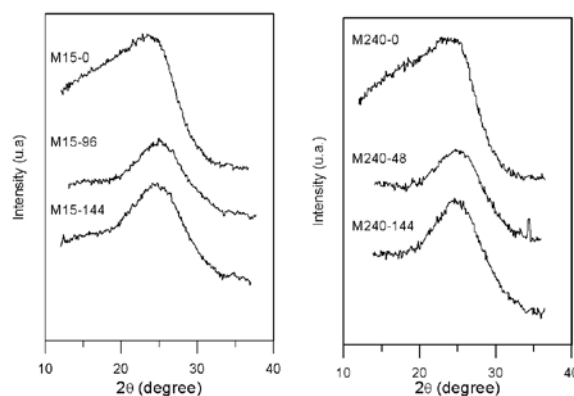


**Fig. 1.** *Experimental XRD spectra for coals M15 and M240 with different times of oxidation (0, 96 and 144 hours for M15 and 0, 48 and 144 for M240)*

**Table 3.** *Structural parameters calculated from XRD spectra for coals and the oxidized coals.*

| Coal | Oxidation time (h) | Burn-off, % | $\tilde{N}$ | $P_s$ | $f_a$ | $d_{002}$ (nm) |
|------|------|------|------|------|------|------|
| M15 | 0 | 0 | 2.54 | 0.1677 | 0.796 | 0.370 |
| | 48 | 6 | 2.66 | 0.1553 | 0.791 | 0.357 |
| | 72 | 13 | 2.84 | 0.1043 | 0.951 | 0.355 |
| | 96 | 15 | 3.00 | 0.1094 | 0.967 | 0.351 |
| | 144 | 25 | 2.75 | 0.1460 | 0.962 | 0.353 |
| M210 | 0 | 0 | 2.56 | 0.1302 | 0.775 | 0.371 |
| | 48 | 9 | 3.00 | 0.1009 | 0.927 | 0.355 |
| | 96 | 20 | 2.83 | 0.1033 | 0.958 | 0.355 |
| | 144 | 27 | 2.86 | 0.1114 | 0.947 | 0.351 |
| M240-0 | 0 | 0 | 2.57 | 0.1501 | 0.764 | 0.366 |
| | 48 | 8 | 3.05 | 0.0899 | 0.845 | 0.347 |
| | 96 | 18 | 2.94 | 0.1051 | 0.972 | 0.354 |
| | 144 | 29 | 2.82 | 0.1139 | 1.000 | 0.353 |

The distribution of probabilities of finding a stack with N layers (fig. 2) shows that oxidation treatment of the samples causes an initial increase in the probability of finding a stack with a major number of layers. This could be explained by two different phenomena: There are rearranges of the microstructure of coal in the heat treatment at low temperature and long times, or there is a gasification of the aliphatic chains and some of the ordered structures (those of the lowest number of layers, e.g. N=2) which causes the increase of the number of stacks of high number of layers. This also can be reflected in the evolution of the mean number of layers per stack ( $\tilde{N}$ ) (table 3 and fig. 3). This parameters increases in the initial part of the oxidation treatment, with a maximum at 10-15% burn-off, then with major burn-offs this parameter begins to decrease. The decrease in the mean number of layers per stack coincides with the disappearance of the $\gamma$ band. At this point, the ratio of aromatic to aliphatic carbon ( $f_a$ ) becomes close to 1. (Table 3)
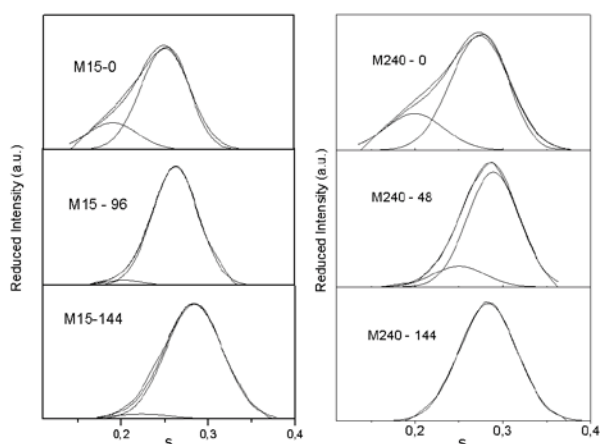


**Fig.2.** *Corrected and deconvoluted XRD spectra for coals M15 and M240 oxidized 0, 96 and 144 hours and 0, 48 and 144 hours*
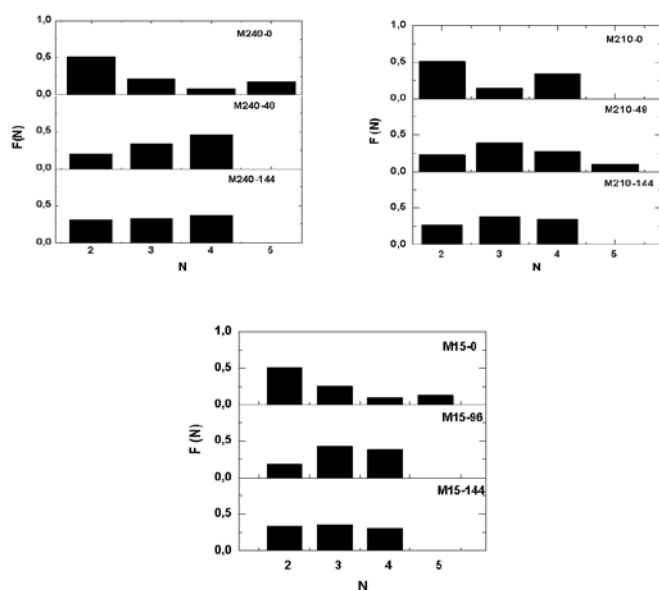


**Fig. 3.** *Distribution of the probability to find a stack with N layers, for original coals (M15-0, M240-0, M210-0) and oxidized coals during 48, 96 and 144 hours.*

The fraction of crystalline (or stacked) structure ($P_s$), decreases at the initial stage of the oxidation when the number of stacks in the layers grow. Then, for major oxidation times it shows an increase in the M15 sample and an almost constant value for M240 and M210. This evolution could be an evidence of the initial gasification of the stacked carbon of low number of layers which contribute to the increase in the mean number of layers stacked. When the stacks of low numbers of layers have reacted, the layers of higher number of layers would react and then it explains the decrease in $\tilde{N}$ for higher degrees of burn off. Another important parameter in the structural characterization of coals is the interlayer spacing of the stacks ($d_{002}$), which reflects the distance between the graphene layers in the stacks of the coal. According to Takagi et al. [11], the value of $d_{002}$ is related to the perfection in the stacking structure periodicity, a decrease in this value indicating a more ordered structure ($d_{002}$ for the graphite structure is 0.335 nm). It is difficult to measure exactly the value of the interlayer spacing for coal XRD because of the broad band of the $I_{002}$ diffraction band. To overcome this difficulty, $d_{002}$ was measured with the first derivative of the deconvolution $I_{002}$ peak. The results (Table 3, Figure 4) show that the interlayer spacing decreases with the oxidation treatment, this is an evidence of some organization of the layers and a more organized structure due to the thermal treatment. Previous studies [10-12] revealed that coal reorganizations were present with heat treatments at high temperatures, usually above 600°C, due possibly to the mobility of the layers in the fluidity stage of the coals.

## CONCLUSIONS

The XRD study of the air oxidation at 270°C of three bituminous coals from El Cesar basin (Colombia), revealed that this treatment causes a gasification of coal, which eliminates the aliphatic structure and increases the aromatic structure. There is also evidence about the loss of stacks with low number of layers and an increment in the layers per stack. The diminution in the interlayer spacing suggests also that coal reorganization occurs which favors the stacking of layers, forming a more organized structure in the oxidized coals, and which is degradated at higher times of oxidation. The surface characterization of oxidized coals shows that no open porosity is developed in oxidized coals

## ACKNOWLEDGEMENTS

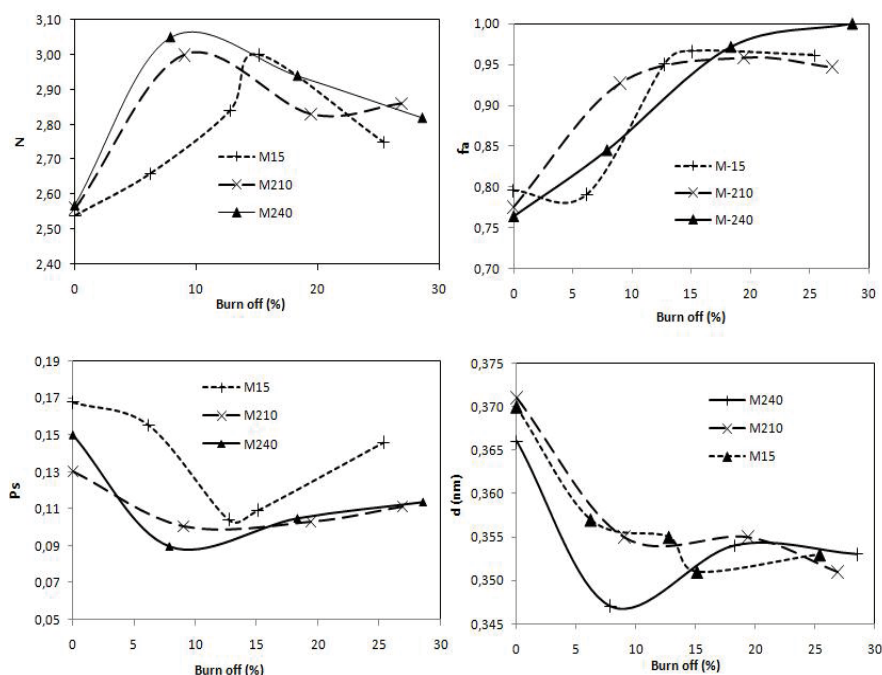**Fig. 4.** *Evolution of microstructural parameters for coals at different oxidation times. Mean number of aromatic layers per stack ( $\bar{N}$ ), aromaticity ($f_a$), fraction of stacking structure ($P_s$) and interlayer spacing ($d_{002}$) variations with burn off of the materials.*

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