



The influence of nitric acid oxidation of low rank coal and its impact on coal structure[☆]

R. Alvarez, C. Clemente*, D. Gómez-Limón

E.T.S de Ingenieros de Minas, Universidad Politécnica de Madrid, Rios Rosas, 21, Madrid 28003, España, Spain

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Abstract

FT-i.r. was used to examine the behaviour of a Spanish lignite during its oxidative treatment with nitric acid with a view to assessing the different forms of sulphur reduction and the changes produced in the coal structure, as a result of the action of the reagent. Inorganic sulphur decreases rapidly and practically disappears, even under mild attack conditions (50 °C, 20% acid concentration). At first, organic sulphur undergoes a rapid decrease but more energetic conditions are required to maintain the reduction. Reduction may even reach 53% under such conditions.

Unfortunately, energetic attacks (90 °C) lead to a high-level of coal organic matter solubilization and an increase in oxygen content. Basically, the oxygen appears as carbonyl group within the desulphurized coal.

The nitric acid causes effective nitration of the coal, the nitrogen being incorporated especially as aromatic nitrogen. The substitution is easily produced (50 °C) when there are two adjacent aromatic hydrogens per ring. The isolated hydrogens in aryl- or polycyclic aromatic structures, are more resistant to attack under mild conditions but not so at 90 °C. As nitration progresses, more electrophilic molecules appear and aliphatic hydrogen tends to increase after initially decreasing under mild attack and increases more so under more energetic condition. This aliphatic hydrogen compensates for the decrease in aromatic hydrogen.

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1. Introduction

Several authors have studied coal desulphurization using oxidative treatments. Among such studies, the desulphurization due to reaction with nitric acid [1] revealed that pyritic sulphur and sulphate reduction is relatively rapid and complete, while organic sulphur reduction is not practically produced in high rank coals [2]. However, such reduction may be partially achieved in low rank coals [1,3], though there is a considerable attack to the organic matter which results in the dissolution of part of the sample, and hence causes a diminution in the amount of organic carbon recovered.

How these reactions affect the diverse functionalities of organic sulphur [4,5] has also been studied, using atmosphere pressure–temperature programed reduction

techniques, but there are few researches into how nitric acid treatment affects desulphurized coal structure. Some studies have been carried out using other preparations, such as chlorination [6,7], pyrolysis [8] or the obtaining of active carbon materials via oxidative nitric treatment [9].

Concern over how nitric acid, used as a desulphurant, affects the coal structure produced by the coal oxidation method is relatively recent and still has not been exhaustively studied. Hayatsu [10] had already used a 70% nitric acid concentration, as a coal oxidation method, but this was to examine structure from the point of view of solubilized products and not from that of nitric acid effect. Alvarez et al. [11], using FT-i.r. studied how the structure of those coals treated with nitric acid varies according to the variation in coal rank. They showed that effective nitration was produced and, also how nitrocompound-formed bands migrate. Rubiera et al. [12] also studied the action of nitric acid, combined with demineralization. They further showed

* Corresponding author. Tel./fax: +34-9133-66948.

E-mail address: cclemente@qyc.upm.es (C. Clemente).

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that nitration occurs. Pietrzak and Wachowska [13] too have revealed that changes in coal structure take place when it reacts with nitric acid, and other oxidants.

Pilawa et al. [14] used the electron paramagnetic resonance spectroscopy technique to detect changes in paramagnetic centre systems: changes were here caused by alterations in chemical coal structures, during the oxidation of demineralized coal and pyrite-free coal. This showed that the amount of paramagnetic centres decreased in simple aromatic units with sharply Gauss lines.

In the present investigation, very low rank coal (lignite B) from Galicia (Spain) was chosen, since low rank coals show more alteration and suffers greater dissolution during nitric acid treatment [1,3,15] than high rank coals [2].

Composition variation was determined by chemical analysis using ASTM standards, and structural variations were investigated by means of infrared spectrometry.

2. Experimental

2.1. Sample

Coal was taken from the region of Galicia (Spain) and, as a base sample, it was prepared to -0.25 mm. The main characteristics of the sample are shown in Table 1, and the ultimate analysis appears in Table 2.

In Fig. 1 the X-ray diffractogram (Cu α line) of the initial coal sample is shown, together with that of coal treated with nitric acid 20 wt% at 90 °C during 60 min. The main insoluble minerals observed, for this type of coal included: quartz (Q); mica group minerals (M); and clay minerals. Among the clay minerals, outstanding are those of the kaolin group (K). As minerals sensitive to nitric acid attack, a high gypsum content (G) and some characteristic pyrite peaks (P) are indicated.

2.2. Experimental procedure

Nitric acid treatment was carried out using 25 g of coal and 500 cm³ of 20 or 30 wt% nitric acid. The equipment used is that described in previous work [1–3,15],

Table 1
Characteristics of Galicia raw coal

Characteristics	db	daf
Ash	32.9 wt%	—
Volatile matter	40.1 wt%	59.76 wt%
Fixed carbon	27.0 wt%	40.24 wt%
Calorific value	13.36 MJ/kg	19.91 MJ/kg
Organic S	3.43 wt%	5.11 wt%
Sulphate S	0.94 wt%	1.40 wt%
Pyritic S	0.80 wt%	1.19 wt%
Nitrogen	0.90 wt%	1.34 wt%
CO ₂	0.27 wt%	0.40 wt%

Table 2
Ultimate analysis

Element	wt% (db)	wt% (daf)
C	41.3	61.6
H	3.4	5.1
S	5.2	7.7
N	0.9	1.3
O (by difference)	16.2	24.3

though special precautions were taken at 90 °C, when the reaction becomes violent, leading to the risk of overflow because of the large quantity of froth produced. Given this reaction, the procedure was eventually changed; first putting the coal into the flask and only then adding the acid, through a new side tube, at reaction temperature. This considerably decreased froth production. However, using 30 wt% nitric acid results in greater control difficulty, making only precise tests with long reaction times feasible, until the coal climbing the flask walls finally descended to again form part of the attack liquid.

FT-i.r. measurements were carried out using KBr pellets with 1 wt% of coal. In the figures presented, all spectra were

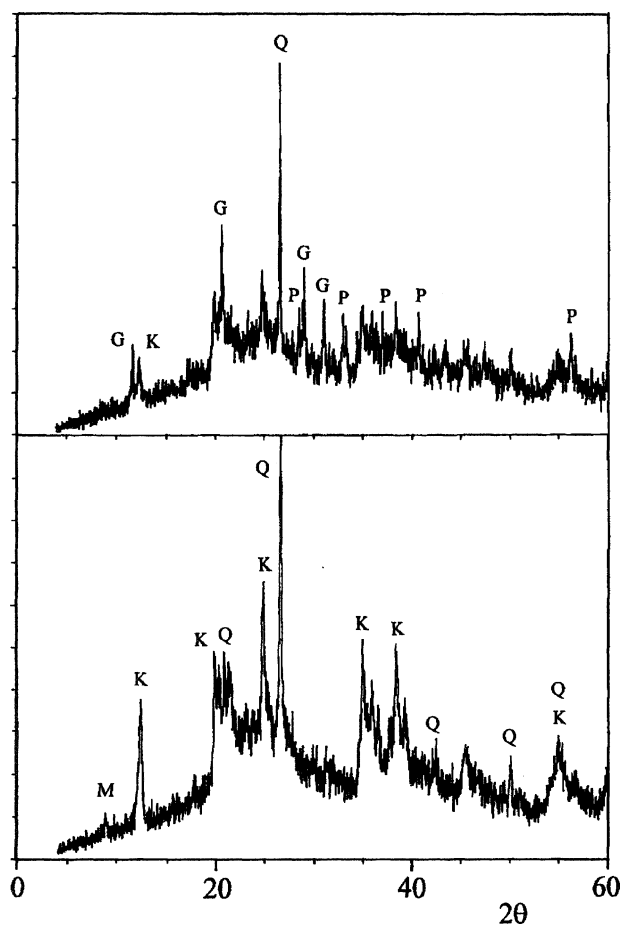


Fig. 1. X-ray diffractogram. Upper part relates to initial coal and lower part to treated coal with 20 wt% nitric acid, 90 °C, and 60 min.

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