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A COMPARATIVE THERMOANALYTICAL STUDY OF LOW-TEMPERATURE REACTIVITY OF BROWN COAL WITH DIOXYGEN AND RADIOFREQUENCY-ACTIVATED OXYGEN

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ABSTRACT

The kinetic features of oxidation of a Spanish brown coal by dioxygen (studied by means of TG and DTA) and by oxygen plasma (carried out in a low-temperature ashing apparatus) are compared. It is concluded that slowness in brown coal oxidation by radiofrequency-activated oxygen is associated with formation of sulphate and nitrate artifacts which prevent the access of the oxidizing agent to the surface of organic coal matter.

INTRODUCTION

The nature and concentration of inorganic constituents, together with the concentration of active sites and the active surface area, are the essential intrinsic factors which determine the reactivity of coal towards gaseous reagents. Thus, changes in reactivity may be attributed to changes in one or more of these factors. In the case of coal oxidation, some doubt still exists about whether semiconducting mineral species, or free radicals present in the organic matter of coal are responsible for the initiation of this reaction (1). Cole et al. have recently (2) suggested that these two phenomena may be associated with each other. Nevertheless, the positive roles of minerals such as pyrite (3), calcite (4,5) or kaolinite (6) favouring carbonaceous matter oxidation are well-known facts.

In the course of a systematic study on the optimal use of low-temperature ashing (LTA) treatment of coal with radiofrequency-activated oxygen, we have found low oxidation rates for brown coals whose reactivities towards molecular oxygen are, however, expected to be high. In order to explain the reason of this apparent anomaly, we compare in this work the reaction rates of a Spanish brown

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coal with both, dioxygen and radiofrequency-activated oxygen. Further information concerning the role of inorganic components is provided by FT-IR spectra of LTA residues of the raw coal.

EXPERIMENTAL

Materials. A run-of-mine brown coal from As Pontes (NW of Spain) was studied. Its analysis is reported in Table I. Results of a more detailed characterization of the inorganic constituents of this coal can be found elsewhere (7,8).

Methods. Simultaneous TG/DTA runs were performed in a Stanton-Redcroft STA-781 apparatus provided with a CETA computer system for data treatment. A 13-mg coal sample, ground to < 0.212 mm, was used in each run. Oxidation experiments were carried out under 99.995 % pure O_2, at atmospheric pressure, using a flow rate of 50 STP ml min^{-1}. Temperature-programmed oxidation (TPO) experiments were done at various heating rates (see below). A pyrolysis run was carried out using 99.998 % pure argon instead of oxygen, at a heating rate of 10 K min^{-1}, keeping the rest of experimental conditions identical.

Low-temperature ashing treatments were carried out in an LTA-504 (LFE Co.) apparatus. Standard experimental conditions were: radiofrequency power, 150 W; pressure, 200 Pa; oxygen flow, 15 STP ml min^{-1}; sample particle size, <0.232 mm; sample mass, 0.5 or 1 g (four samples being oxidized in parallel).

FT-IR spectra were recorded in a Perkin-Elmer mod. 1750 spectrometer. Pellets containing 1 wt. % coal dispersed in KBr (total mass, 120 mg) were used.

TABLE 1

Analysis of As Pontes coal*.

Moisture	16.0	C	37.9
Volatile matter	39.1	H	3.0
		N	0.6
Ash	43.9	S (total)	4.3
		O (diff.)	10.3
Mineral matter (only discrete mineral phases)	47.7	S pyritic	2.2
		S sulphate	0.2
Higher calorific value (kJ g^{-1})	14.95	S organic (diff.)	1.9

* All results, unless otherwise indicated, are given as wt. %, and refer to db coal (except for moisture content).

RESULTS AND DISCUSSION

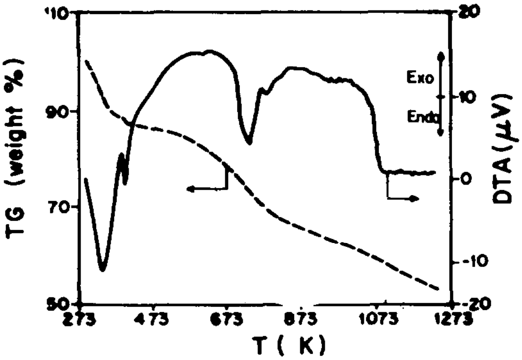


Figure 1. TG and DTA curves for As Pontes coal pyrolysis under argon at 10 K min^{-1}.

Prior to oxidation studies, the pyrolysis behaviour of As Pontes coal was examined (Fig. 1) in order to ease the understanding of its combustion behaviour. Besides two weight losses, coincident with DTA endothermal peaks at 335 and 399 K (ascribable to loss of water), a multi-step loss of volatile matter took place over a broad temperature interval. The rate of weight loss was maximal at 722 K, this being close to an endothermal peak in DTA (733 K) which is superimposed on a broad, exothermal band (Fig. 1).

The influence of heating rate on thermal behaviour of this coal under a oxygen atmosphere is shown in TPO plots A-D of figure 2. DTA, TG and DTG curves were plotted against time due to the strongly exothermal character of coal combustion, which distorts these curves when plotted against temperature (observe, e.g., the big exothermal effect in T vs. t curves of plots C and D). The most remarkable feature in figure 2 is the strong influence of heating rate on TPO profiles. At low heating rates (plots A-B), two weight losses along with corresponding DTA exothermal peaks (at 542 and 612 K for a heating rate of 5 K min^{-1}) appear. According to the literature (4,9,10), the first peak should correspond to initial release and subsequent ignition of volatiles, and the second one to combustion of the remaining char; SO_2 formed from the different sulphur forms should contribute to both peaks, according to recent results of Boudou et al. (11). A moderate increase of heating rate (plots C-D) modifies dramatically the TPO profiles, leading to a single step in DTA, TG and DTG curves which begins suddenly at temperatures close to 573 K (plot D). This shows that As Pontes coal is very prone to oxidation, as should be expected from its low-rank characteristics: for this coal, $\bar{R}_0$ = 0.26, while the volatile matter content of its organic matter equals 54.8 wt. % (12).

The rate curves for oxidation in LTA, shown in figure 3, are qualitatively similar to some previously reported curves (13-15). Times necessary for complete oxidation are shorter than those mentioned by Gluskoter (13), Frazer and Belcher (14) and Nankervis and Furlong (16), but longer than those needed by Adolphi and Störr (15) and Korobetskii et al. (17). Therefore, it is not valid to establish

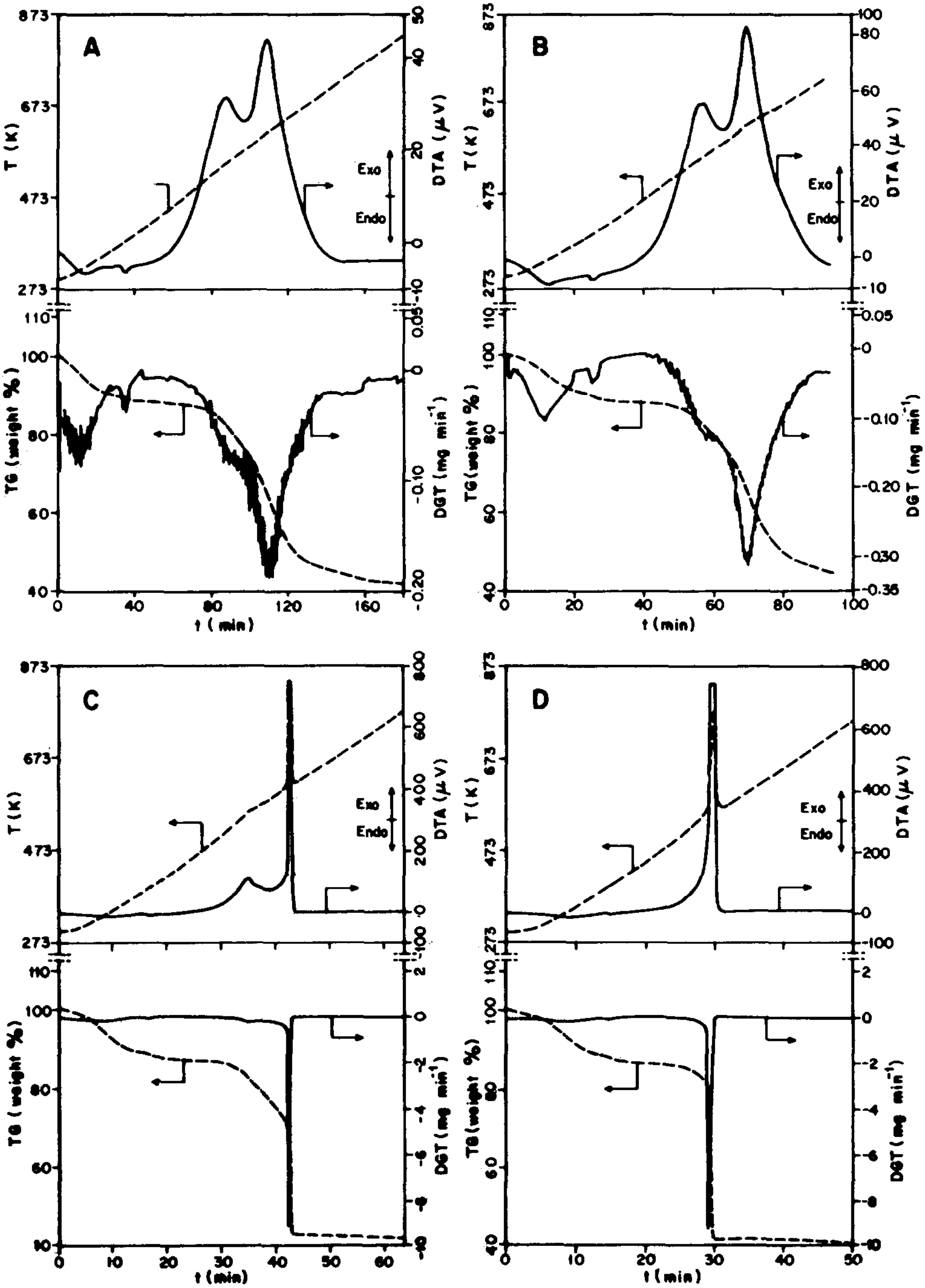


Figure 2. Thermoanalytical curves for As Pontes coal under O_2 atmosphere at heating rates of 3 (A), 5 (B), 8.5 (C) and 10 K min^{-1} (D).

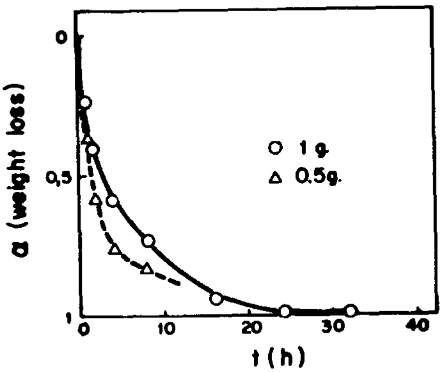
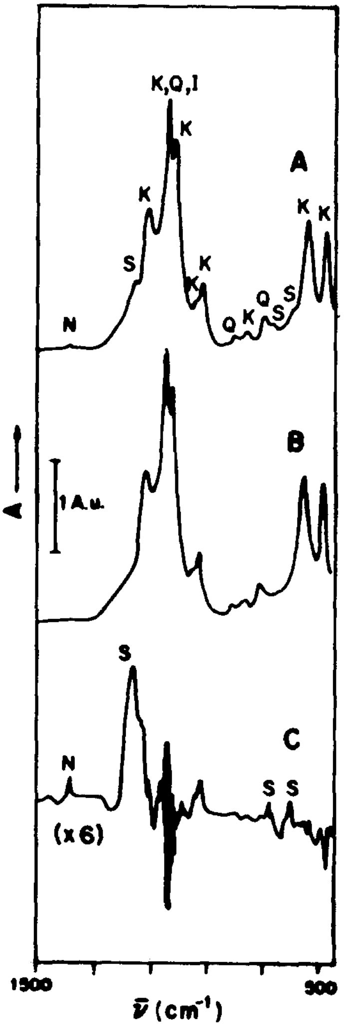


Figure 3. Oxidation rate curves in LTA.



quantitative comparisons, bue to big differences in coal characteristics and/or operation parameters. On the other hand, oxidation rates during LTA for As Pontes coal were lower than those obtained by us in identical conditions for higher-rank coals (18).

In previous works (14, 19), low oxidation rates for lignites in LTA have been associated to formation of artifact compounds from ion-exchanged elements in carboxyl groups. Thus, we have examined the FT-IR spectra of LTA residues of As Pontes coal. As figure 4 shows, the LTA of the raw coal contains sulphate and nitrate species which are absent from the LTA of coal previously submitted to extraction of ion-exchangeable cations by ammonium acetate. X-ray diffractograms confirmed (7) the presence of finely-divided bassanite ($CaSO_4 \, . \, \frac{1}{2} \, H_2O$). Thus, sulphate species formed in LTA conditions seem to have a morphology more adequate for hindering oxygen access to organic coal matter than that of sulphate species which form in more conventional combustion conditions in the presence of molecular oxygen.

Figure 4. FT-IR spectra of the LTA residues of raw As Pontes coal (A), and of this one previously extracted by ammonium acetate (B). Spectrum C is the (A-B) difference. Inorganic species are identified as follows: I, illite; K, kaolinite; Q, quartz; N, nitrates; S, sulphates.

CONCLUSIONS

TG and DTA results show that As Pontes brown coal is very reactive towards molecular oxygen. During the LTA treatment with oxygen plasma, FT-IR spectra evidence the formation of sulphate and nitrate species from organic sulphur and nitrogen, and organically-bound alkaline and alkaline-earth elements. These species seem to hinder subsequent access of activated oxygen to the surface of organic coal matter, thus explaining the low rate of reaction of this coal with radiofrequency-excited oxygen.

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