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EVALUATION OF THE COMBUSTION BEHAVIOUR OF PERHYDROUS COALS BY THERMAL ANALYSIS

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Perhydrous coals are characterized by a high hydrogen content and exhibit a modified composition and physico-chemical properties in comparison with normal coals. These modifications affect the behaviour of perhydrous coals during pyrolysis and, therefore, may have an influence on the subsequent combustion process. In this work the combustibility behaviour of a series of perhydrous coals was evaluated in order to study the effect of hydrogen enrichment during the thermal treatment of the coals in an oxidant atmosphere. To this end temperature programmed combustion tests for the coals, and air isothermal (500°C) reactivity tests for their chars, were carried out in a thermogravimetric analyser. A clear relationship between the combustion behaviour of the perhydrous coals, and the aromatic to aliphatic hydrogen ratio was found.

Keywords: *combustibility, hydrogen forms, perhydrous coals, TG/DTG*

Introduction

Perhydrous coals are characterized by an abnormally high hydrogen content in relation to their carbon content and coal rank. The factors that contribute to the origin of this type of coal are diverse but in all cases the final result is a material whose physico-chemical properties are substantially modified compared to common coals. Previous studies on perhydrous coals have shown that hydrogen enrichment is responsible for certain anomalous characteristics [1–4]. This type of coal usually displays very low vitrinite reflectance values (a phenomenon known as reflectance suppression) which are not related to other parameters of a chemical nature or to the physical, chemical and technological properties of the coals. The main factors responsible for the low reflectance values are their low aromaticity and condensation indexes. The structural modifications caused by hydrogen enrichment have considerable repercussions on all their properties. The thermostability of perhydrous coals is low and during their thermal treatment they mainly generate oils/tars, even though they are humic coals, which are almost totally or exclusively composed of vitrinite. Perhydrous coals also possess high calorific values and, therefore, they are good candidates for use as a fuel source. However, there is little information about their thermal behaviour during combustion. Thermogravimetric analysis (TG) techniques have been widely used for the assessment of the combustion behaviour of fossil fuels [5–8]. In addition, the combustion rate of coal particles are mostly related to char reactivity [9], which has a significant effect on the degree of carbon burnout [10–12].

The main aim of this work was to study the effect of the special characteristics of a series of perhydrous coals on their combustion behaviour. The study was carried out by subjecting the coals to temperature programmed combustion tests, and the chars to isothermal reactivity tests in air, using a thermogravimetric analyser. The TG results were related to the usual rank parameters and to the forms of hydrogen present in the perhydrous coals.

Experimental

Six perhydrous coals of different geological ages were collected by hand picking from various coal basins located in several countries. The coals were denoted according to their locations and geolocical ages as: UCV (Utah, USA, Cretaceous), TCV (Teruel, Spain, Cretaceous), WJVl and WJVh (Whitby, England, Jurassic), AJV (Asturias, Spain, Jurassic), PGJV (Peniche, Portugal, Jurassic). The main characteristics of the samples are given in Table 1. These coals are composed exclusively of the huminite/vitrinite maceral group, excluding UCV and TCV which contain very low proportions of liptinite. Inertinite was not found in any of the coal samples. They also present low ash contents and a notable calorific value. The unusually high hydrogen content, characteristic of

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Table 1 Main characteristics of the perhydrous coals

Coals	Geological age	Hu/Vi/ vol%	Li/ vol%	Ash/ db%	V.M./ daf%	C/ daf%	H/ daf%	C.V./ MJ kg^{-1}, maf	H_{ar}/H_{al}
UCV	cretaceous	98.6	1.4	1.8	60.2	77.3	5.9	30.8	0.03
TCV	cretaceous	96.6	3.4	3.1	62.4	79.7	6.2	28.4	0.02
WJVh	lower jurassic	100	0.0	2.4	52.1	82.4	5.7	32.3	0.04
WJVI	lower jurassic	100	0.0	2.5	72.1	82.6	7.4	37.0	0.02
AJV	upper jurassic	100	0.0	1.1	54.9	84.8	5.9	34.2	0.07
PGJV	upper jurassic	100	0.0	1.4	57.1	80.5	5.7	32.8	0.06

Hu/Vi – huminite/vitrinite, Li – liptinite, V.M. – volatile matter; H_{ar} – aromatic hydrogen, H_{al} – aliphatic hydrogen, db – dry basis, daf – dry, ash free basis, maf – moist, ash free basis

perhydrous coals, can be seen in Table 1. The values of the aromatic, Har, and aliphatic, Hal, hydrogen ratios obtained from the FTIR spectra of the coals in a previous study [2], indicate that aliphatic structures prevail over aromatic ones.

The coal chars were obtained in a Setaram TGA92 thermogravimetric analyser. A sample mass of approximately 5 mg was heated to 850°C at 15°C min^{-1} in nitrogen at a flow rate of 50 cm^3 min^{-1}. After mass stabilization, the temperature was lowered to 500°C to ensure kinetic control without diffusional constraints, and the atmosphere was switched to air, at the same flow rate, in order to determine the isothermal reactivity of the chars, R, defined as:

$$R = -\frac{1}{m_0}\frac{\mathrm{d}m}{\mathrm{d}t}$$

where m_0 is the initial mass of carbon in the raw char, and m is the mass of unreacted carbon at time t, on a dry ash-free basis. The mass of the sample after completion of the tests was considered to be equal to the mass of the ash.

Similarly, the combustion behaviour of the coal samples was evaluated in the thermogravimetric analyser by means of temperature-programmed combustion tests (TPC). In this case the temperature was increased to 1000°C at a linear heating rate of 15°C min^{-1} and an air flow rate of 50 cm^3 min^{-1}. From these tests some characteristic parameters were obtained in order to evaluate the combustibility of the samples. Thus, the volatile matter initiation temperature, T_v, was evaluated in this work as the temperature where the rate of mass loss reached the value of 0.005% s^{-1}, after the loss of moisture and oxygen chemisorption; the peak temperature, T_p, was defined as the maximum temperature on the DTG curve; the burnout temperature, T_b, was defined as the temperature where the rate of mass loss, after the peak temperature, reached a value of 0.005% s^{-1}. Other common parameters extracted from the DTG curves are T_{50}, the temperature at 50% burnoff of organic matter, and R_p or reactivity value at the peak temperature.

Results and discussion

Char isothermal reactivity

Significant differences were found between the isothermal reactivities of the chars produced from the perhydrous coals as can be seen in Fig. 1, where the evolution of the reactivity to air at 500°C with the reaction time is shown. The reactivity of the chars obtained from the pyrolysis of coals UCV, TCV, WJVh and WJVl increased rapidly, passed through a maximum and then decreased sharply. The maximum was more prominent in the chars obtained from the pyrolysis of WJVl and WJVh. The existence of maxima on the reactivity curves is ascribed to pore growth followed by the collapse of the pore structure [13]. In the case of chars AJV and PGJV the shape of the curves was very similar, showing very low and nearly constant reactivity values in comparison with the rest of the samples.

In order to ascertain whether the perhydrous coals show a relation between char reactivity and the usual rank indicators [14–16], the maximum reactivity value was taken as a reactivity parameter and represented *vs*. the volatile matter or the H/C atomic ratio, as shown in Figs 2 and 3. As can be observed in these figures, there is a good linear correlation between char reactivity and the volatile matter or H/C atomic ratio. The usual behaviour of decreasing reactivity with an increase in the usual coal rank indica-

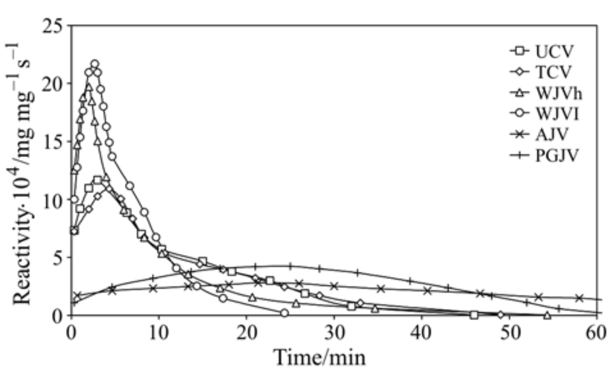

Fig. 1 Variation in the char isothermal reactivity with time

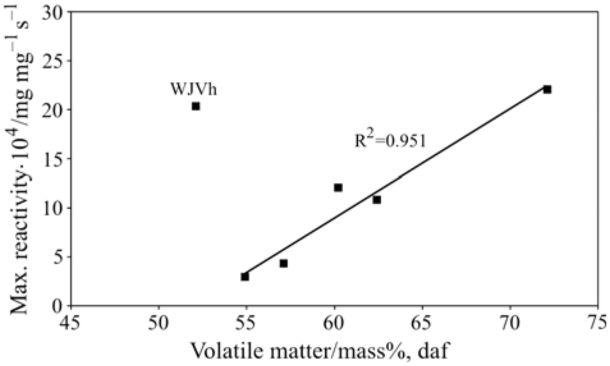

Fig. 2 Char maximum reactivity *vs*. the volatile matter content of the parent coals

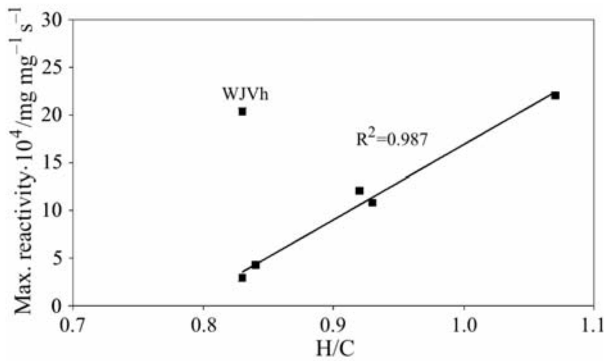

Fig. 3 Char maximum reactivity *vs*. the H/C atomic ratio of the parent coals

tors is also evident in these figures. There is however, an outlier (WJVh) that deviates from the trend displayed by the other samples.

The structure and optical texture of the chars was observed using a Zeiss Axioplan microscope in reflected light and also using crossed polars and a 1 λ retarding plate. It can be observed in Fig. 4 that all the char structures are isotropic, but there is a clear difference between the structure exhibited by PGJV and AJV and the other chars. While UCV, TCV, WJVh and WJVl present massive type morphotypes and a poorly developed pore structure, the chars from AJV and PGJV show a highly primary porous structure. Moreover in AJV significant secondary porosity has developed on the char walls with large vacuoles. With the exception of WJVh, the char reactivity results are in

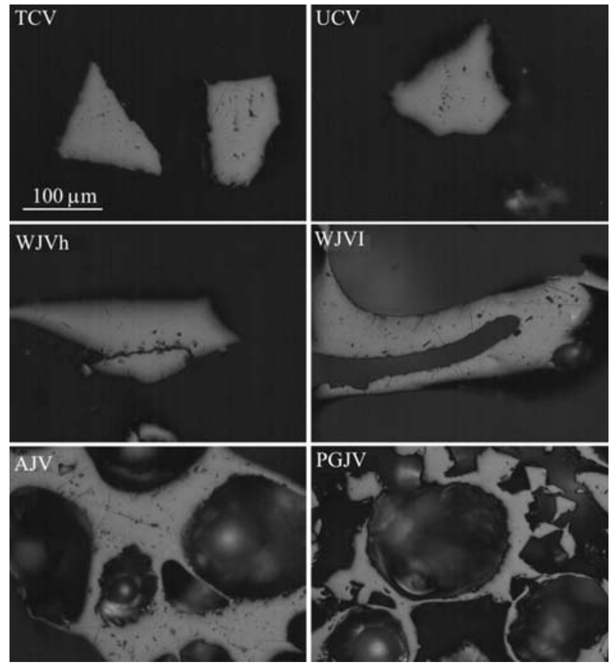

Fig. 4 Microphotographs of the chars obtained from the perhydrous coals

accordance with what might be expected a priori from an observation of the optical texture of the chars and the variation of volatile matter or hydrogen content of the parent coals. The anomalous behaviour of WJVh in comparison with that of the other perhydrous samples has already been pointed out [2]. In that study WJVh had a less pronounced perhydrous character than the other perhydrous series, which is reflected by its lower volatile matter content, and the different source of its aliphatic hydrogen, among other factors.

Temperature programmed combustion tests of the coals

The behaviour displayed by the perhydrous coals during combustion is shown in Fig. 5 and the characteristic parameters extracted from these curves are given in Table 2. The DTG profiles present different zones with an initial peak at about 100°C due to the loss of moisture. Thereafter, between 150 and 350°C three different behaviours are observed. Coal WJVh pres-

Table 2 Characteristic parameters extracted from the combustion profiles of the perhydrous coals

Sample	T_v/°C	T_{p1}/°C	T_{p2}/°C	T_{50}/°C	T_b/°C	$R_{T_{p2}}$/s^{-1}
UCV	271	424	510	536	766	0.73
TCV	279	426	486	518	756	0.73
WJVh	295	–	507	531	752	0.76
WJVI	270	440	506	526	737	0.78
AJV	336	439	575	582	822	0.68
PGJV	323	443	545	570	795	0.71

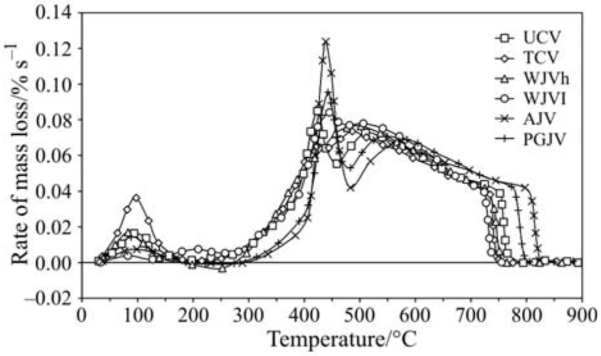

Fig. 5 DTG profiles of the perhydrous coals during temperature programmed combustion tests

ents a distinct net mass gain due to oxygen chemisorption, which is typically observed in normal non-perhydrous coals, within the high volatile bituminous rank range. In the case of UCV, TCV, AJV and PGJV there is a trade-off between the mass gain due to oxygen chemisorption, and the mass loss due to the evolution of thermally labile compounds and the existence of aliphatic structures with low dissociation bonds in the carbonaceous matrix. The mass loss of WJVl can be attributed to the presence of free hydrocarbons in the coal matrix, and the same behaviour was attained in this temperature range for these coals during thermal treatment in an inert atmosphere [3].

The most significant variation in the DTG curves of the coals studied is observed in the zone above 300ºC. These curves show two peaks for all samples with the exception of WJVh. Although there is some overlapping between the volatiles and char combustion steps, it is quite clear that the first peak is due to the release and combustion of the volatiles, while the second peak corresponds to the combustion of the char. In the case of coals AJV, PGJV and UCV there is an intense volatile peak, which is much lower in the case of TCV and WJVl. This preliminary peak is due to the combustion of volatiles, which occurs at the surface of the material. However the reaction is not sufficient to sustain the combustion of the char and, as a result, two peaks appear in the combustion profiles. The temperatures at which these peaks appear are designated as T_{p1} and T_{p2} in Table 2. In line with the results attained during the pyrolysis of the perhydrous coals [3], the temperature T_{p1} is clearly lower in the case of coals UCV and TCV. On the other hand, coals AJV and PGJV exhibit the highest values for peak temperature T_{p2}, and burnout temperature, T_b. This is in agreement with the low reactivity of their chars, as revealed in the study of the char isothermal reactivity.

The characteristic temperatures obtained in the temperature programmed combustion tests (T_v, T_b, T_{p2} and T_{50}) do not clearly correlate with the usual rank indicators such as volatile matter, or H/C atomic ratio unlike the case of normal (non-perhydrous) coals with a similar carbon content. An example of this is given in Figs 6 and 7 which show the variation of temperatures T_v and T_b, with volatile matter content and H/C atomic ratio. Although there is a trend towards increasing combustibility (i.e., a decrease in the temperature values) with the

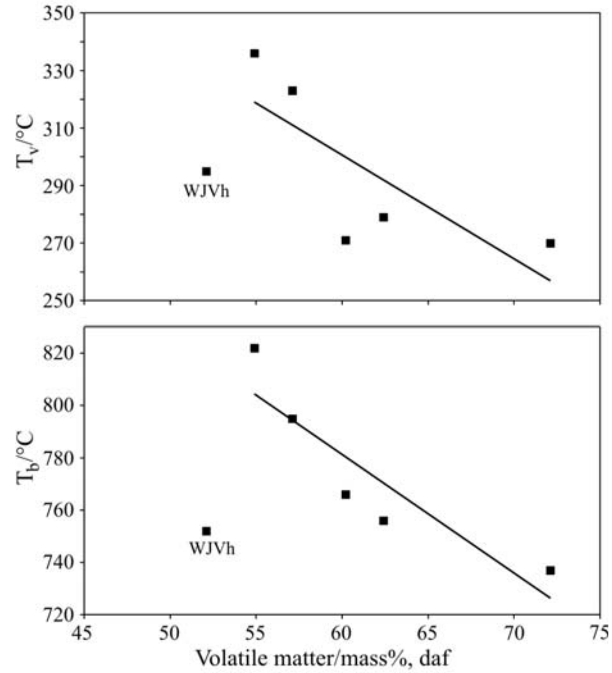

Fig. 6 Variation in temperatures T_v and T_b with the volatile matter content of the coals

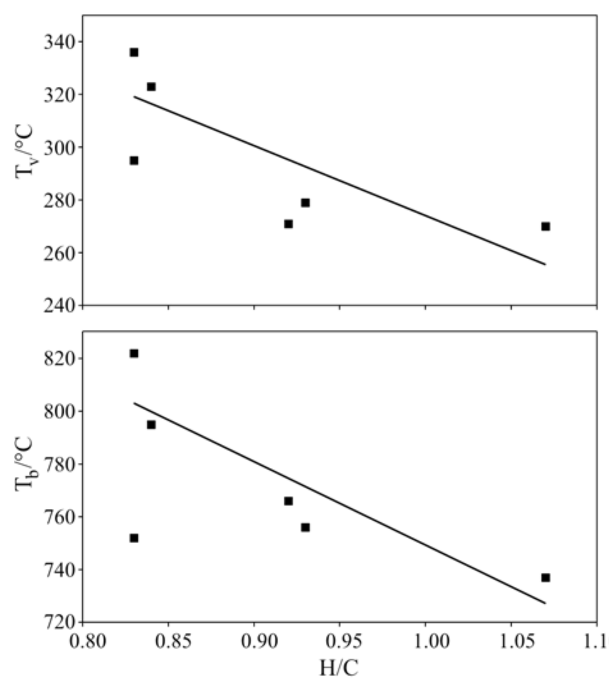

Fig. 7 Variation in temperatures T_v and T_b with the H/C atomic ratio of the perhydrous coals

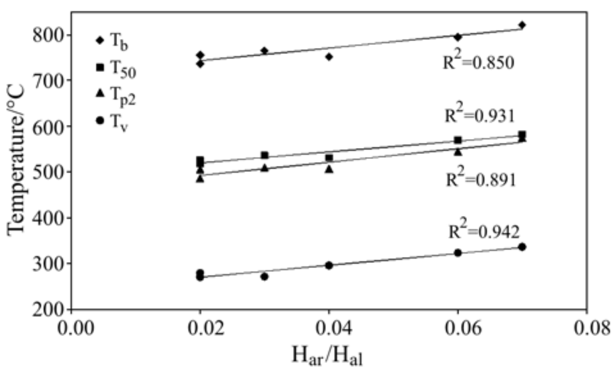

Fig. 8 Variation in the characteristic temperatures evaluated from the combustion profiles with the H_{ar}/H_{al} ratio of the perhydrous coals

increase in volatile matter content and H/C atomic ratio, there are clear deviations that are more evident in the case of WJVh. In addition, the values found for the different temperatures reflect the influence of the hydrogenated nature of the coals on their behaviour during the combustion process. The hydrogen enrichment process therefore must have produced modifications in the macromolecular network structure of the perhydrous coals. These modifications differ depending on the hydrogen source and the organic evolution pathway followed by these perhydrous coals. In general, the aromatic structures found in the coals are made up of 1–2 rings, with a prevalence of aliphatic over aromatic structures [2]. The variation of the characteristic temperatures with the H_{ar}/H_{al} ratio, obtained from FTIR analysis, is displayed in Fig. 8. It can be observed in this figure that there is a remarkable correlation between the characteristic temperatures and the H_{ar}/H_{al} ratio and that the coals with a higher proportion of aliphatic hydrogen present a better combustibility behaviour.

Conclusions

A direct relation was found between the reactivity of the chars and the volatile matter content or H/C ratio of the parent perhydrous coals. Char WJVh was an exception to this trend, due to the less perhydrous character exhibited by this coal in comparison with the other perhydrous coals. The organic substances responsible for the hydrogen enrichment of the perhydrous coals have a clear effect on their combustion behaviour. Although the perhydrous coals normally have a complex composition, it was found in this work that their combustion behaviour is closely related to the aromatic to aliphatic hydrogen ratio, i.e., the greater the aromatic character, the higher the characteristic temperatures.

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