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Thermochimica Acta 279 (1996) 93–101

thermochimica acta

A study of the self-heating of fresh and oxidized coals by differential thermal analysis

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Received 11 July 1995; accepted 12 January 1996

Abstract

Differential thermal analysis (DTA) has been used as a method to study the self-heating behaviour of fresh and oxidized coals. Oxidation was performed in air at 200°C for periods of up to 72 h. Six coals ranging from a High A Bituminous coal to a semi-anthracite were used. As the rank of the coal increases, both the self-heating and the end of combustion temperatures also increase. The total heat loss (area under the DTA curve) increases with the rank of the coal. An increase in the self-heating temperature, a decrease in the temperature of the end of combustion and a decrease in total heat flow were observed as a consequence of coal oxidation. A relationship between the total heat loss and the calorific value as determined using the ASTM standard method is pointed out.

Keywords: Coal oxidation; Coal self-heating; DTA

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1. Introduction

When coal is stored under ordinary conditions, progressive changes take place in its chemical and physical properties. These changes are largely caused by the reaction of atmospheric oxygen with coal. This "oxidation" or "weathering" occurs slowly in the case of high-rank coals like anthracites. Nevertheless it is a matter of considerable importance, since even a small amount of oxidation may affect the value of coal for different utilization purposes [1–9].

Self-heating, or spontaneous heating, is a process which results in an increase in the temperature of a mass of coal. This phenomenon is caused by the heat-generating

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Elsevier Science B.V.
PII S0040-6031(96)02859-6

chemical reactions between the oxidant (oxygen) and the fuel (coal). If the generated heat is removed or absorbed by the surrounding environment, then only low-temperature oxidation will occur. However, if the generated heat is not dissipated to the exterior, a self-heating process might occur and spontaneous combustion will eventually happen.

Basically, the factors involved in the self-heating of coal can be divided into two areas: the properties of the coal, which include chemical composition, rank, size of particles, volatile matter content; moisture, etc.; and the environment or storage conditions.

At low temperatures, oxidation reactions are slow and the heat produced by oxidation is small in comparison to the heat of water adsorption [10]. The susceptibility of coal to self-heating and spontaneous ignition has been observed to increase with decreasing rank, with lignite and sub-bituminous coals being more susceptible to self-heating than bituminous coals and anthracites [11].

Much effort has been expended in devising a laboratory test which would reliably predict the behaviour of coal in circumstances known to cause spontaneous combustion. Such techniques [12] include the non-adiabatic heating of coal [13], adiabatic calorimetry [11], the isothermal measurement of heat generation rates [14], the determination of minimum self-ignition temperatures [15], the adiabatic self-heating method [16], etc. Markowa and Rustschev [17] used thermal analysis as a method to assess the antioxidative action of inorganic and organic inhibitors which prevent coals self-igniting.

Differential thermal analysis (DTA) has been used in this work as a method to study the self-heating behaviour of fresh and oxidized coals. This technique was also used to follow the evolution of heat flow in coals as a consequence both of the rank of the coal and of aerial oxidation.

2. Experimental

A Setaram TAG 24 thermal analysis system equipped with a differential thermal analyser was employed. In order to make comparison of samples of different coals possible, factors such as sample weight, heating rate and air flow rate should be well established to have good repeatibility between experimental runs. In all the experiments carried out in this work, samples of coal of 25 mg, an air flow rate of 50 ml min^{-1} and a linear heating rate of 15 K min^{-1} were employed.

Six different coals, ranging from a High A Bituminous coal to a semi-anthracite were used in this work. The most important analytical characteristics of the coals are shown in Table 1. Coal samples were ground and a particle size inferior to 150 μm was used. Representative coal samples were obtained by the use of a small sample divider (riffle).

Air oxidation of coals was performed at 200°C over different periods of time, from 0 to 72 h, in an oven with forced-air circulation. After oxidation, coal samples were stored in argon in order to avoid oxidation before use.

Table 1
Characteristics of the coals used

Coal	Proximate analysis (% wt)			Ultimate analysis (% wt, daf)				
	Moisture	Ash (db)	V.M. (daf)	C	H	N	S	O (diff.)
Va	0.9	18.0	13.0	91.2	3.7	1.9	2.3	0.9
Sa	0.9	26.0	20.8	88.5	4.5	1.9	2.8	2.3
Am	0.5	6.0	25.1	90.3	4.9	1.4	0.8	2.6
Tu	1.0	7.4	26.0	88.1	4.8	1.7	1.5	3.9
Im	0.7	14.4	27.3	84.8	4.4	1.7	0.6	8.6
Pu	1.7	21.8	39.1	80.5	5.3	1.9	1.7	10.6

3. Results and discussion

Fig. 1 shows a typical DTA curve that represents the evolution of heat flow with temperature for a bituminous coal. As characteristic parameters we can use: T_{sh}, the temperature of self-heating; T_{ec}, the temperature of end of combustion; and A, the area under the DTA curve.

The first part of the curve corresponds to a global endothermic process which is the result of oxidation reactions (exothermic) and water adsorption (endothermic). This period finishes when oxidation reactions predominate and the global energetic balance begins to be exothermic, at the temperature of self-heating, T_{sh}. After a period of increasing rate of heat loss, a maximum is reached. The temperature of the end of combustion, T_{ec}, is obtained when the rate of heat flow is zero. The area under the DTA curve represents heat evolution during the combustion of the sample, so it could be related to the heating value of the coal sample.

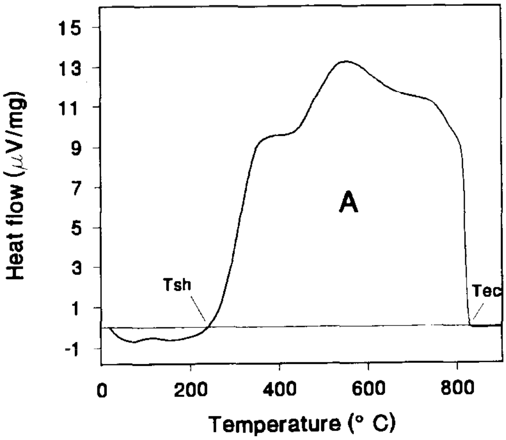

Fig. 1. Typical DTA curve with characteristic parameters corresponding to a bituminous coal.

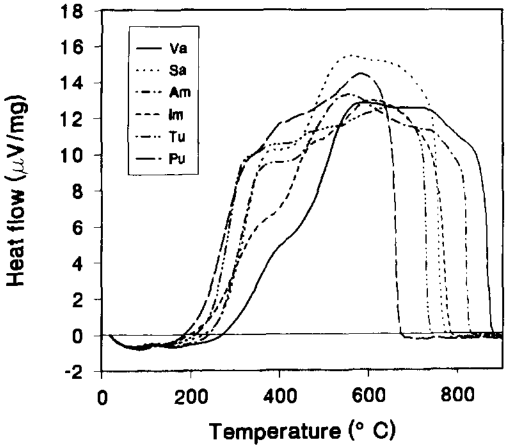

Fig. 2. DTA curves for the coals studied.

Fig. 2 shows the evolution of the heat flow for the six coals studied. As can be seen there is a clear difference between the temperatures of self-heating of the different coals. This temperature is lower in coals of low rank. Thus in the case of Pu coal, a temperature of 180°C has been attained (see Table 2). This means that there is a high risk of

Table 2
Characteristic parameters from the DTA curves for the fresh and oxidized coals

Coal	Oxidation time/days	T_{sh}/°C	T_{ec}/°C
Va	0	270	880
	1	285	845
	5	290	830
Sa	0	230	775
	1	265	735
	5	302	725
Am	0	238	830
	1	278	813
	5	280	794
Im	0	205	785
	1	275	750
	5	290	750
Tu	0	210	740
	1	260	740
	5	280	740
Pu	0	180	675
	1	255	665
	5	265	645

autogenous heating in a stockpile of such a coal and in extreme cases, spontaneous combustion can even result.

The temperature of the end of combustion, T_{ec}, increases strongly with the rank of the coal (see Fig. 2 and Table 2). As a consequence, the area under the DTA curve also increases with coal rank, in accordance with the corresponding increase of the calorific value of coals with rank.

Concerning the effect that air oxidation produces on the heat flow of the coals studied, the following observations can be made from Fig. 3 and Table 2. A significant increase in the self-heating temperature was observed. A general tendency of a slight decrease in T_{ec} temperatures can be observed in coals as a consequence of air oxidation, except in Tu coal, in which it remains constant. Sa coal exhibits the biggest modification in T_{ec}. A decrease in the area under the DTA curve was obtained, which agrees with the loss of heating value observed in coals as a consequence of oxidation [2–5].

Air oxidation of coal produces an increase in the volatile matter content [9,18,19]. For example, Sa coal passes from 20.8% of fresh coal to 34.6% in coal oxidized for 5 days at 200°C. Nevertheless, combustion of volatile matter in the latter case produces less energy. This confirms that fresh coals liberate light hydrocarbons with a high H/ C ratio [20] and a corresponding higher heating value than those produced from oxidized coals, with a higher content in CO_2 and H_2O, and thus a corresponding lower H/C ratio. All these observations agree with the shape of the DTA curves: in general, a strong decrease in the area corresponding to heat evolution at temperatures up to about 425°C, pertaining to the combustion of lighter volatiles.

As can be observed in Fig. 4, coal oxidation originates an important decrease in the "combustion interval", defined as the difference between the temperatures of the self-heating (T_{sh}) and the end of combustion (T_{ec}). The decrease in the combustion interval is especially noticeable in Im and Sa coals. In the case of the latter, air oxidation reduces it by more than 120°C.

Fig. 5 presents the evolution of the total heat flow rate (area under the DTA curve) for coals oxidized to different degrees. Coals Va and Tu undergo little variation in total heat flow rate with coal oxidation. Coals Sa, Am and Im exhibit the largest variation, mainly in the first stages of oxidation. The behaviour of the lowest rank coal in the series, Pu coal, is qualitatively different to the other coals studied, as it presents a slight continuous decrease in total heat flow rate on oxidation.

Fig. 6 shows the variation of the total heat flow rate against the O/C ratio of the coals, the latter being an indicator of the degree of oxidation. As can be observed, the values corresponding to the evolution of the total heat flow rate follow a linear variation with respect to the O/C ratio of the coals, regardless of the characteristics of the parent coals.

A relationship between the area under the DTA curve, expressed as the total heat flow rate, and heating value obtained from the adiabatic bomb calorimeter following ASTM standards [21] can be observed in Fig. 7. This confirms the existence of a quantitative relation between the two different procedures. However, when exact values must be used for combustion calculations or economic transactions, the values obtained following the ASTM standard test must be given priority.

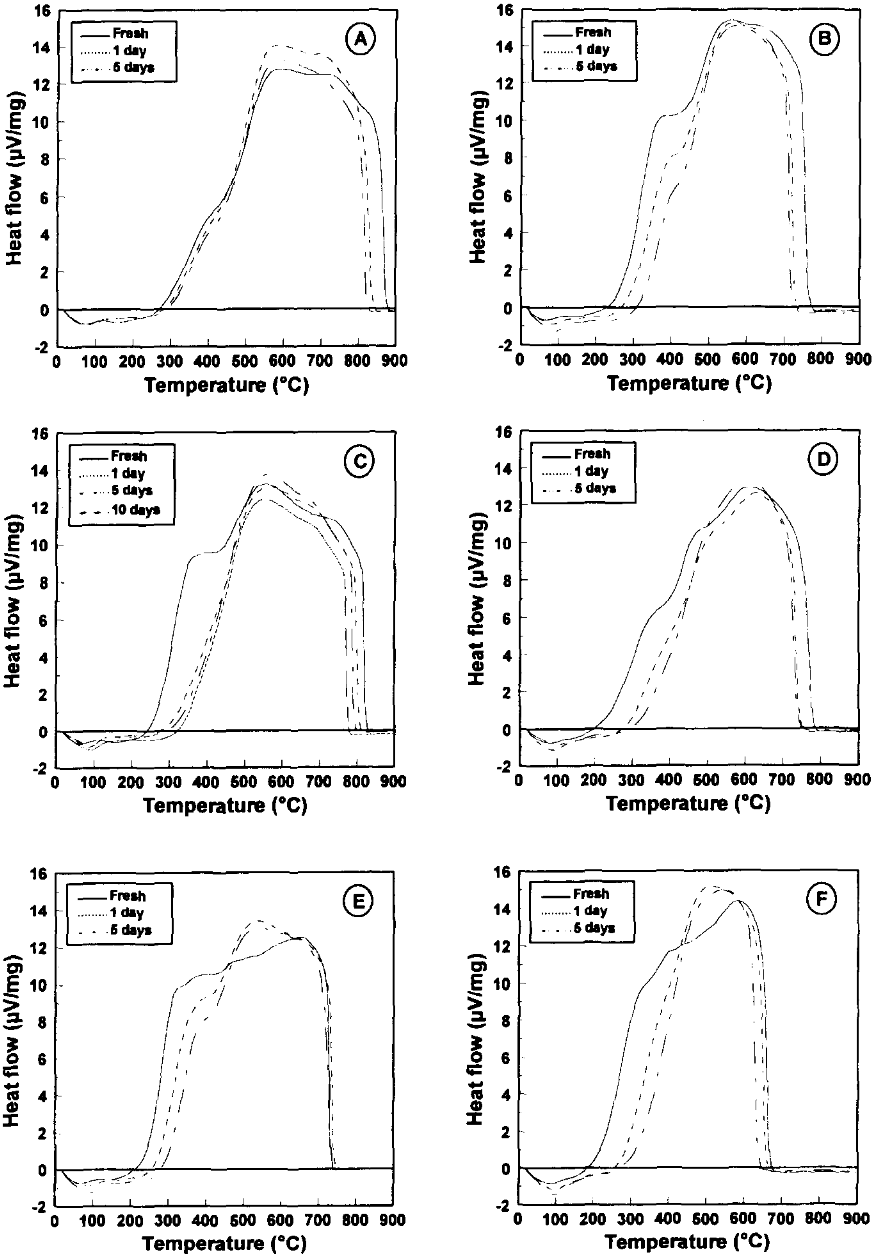

Fig. 3. Evolution of DTA curves as a consequence of coal oxidation: A, Va coal; B, Sa coal; C, Am coal; D, Im coal; E, Tu coal; and F, Pu coal.

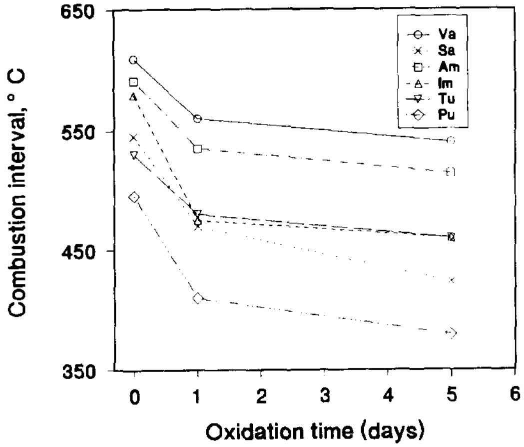

Fig. 4. Modification of the "combustion interval" as a consequence of coal preoxidation.

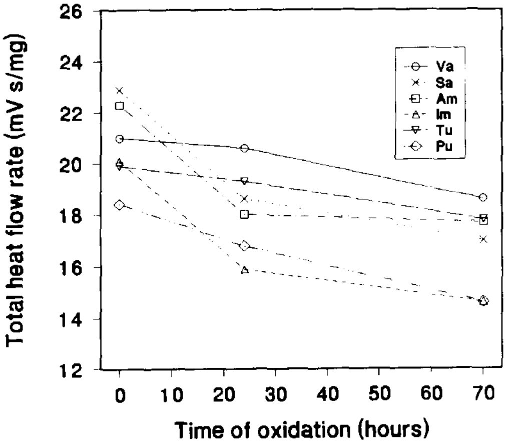

Fig. 5. Modification of the total heat flow (area under DTA curve) with the time of coal oxidation.

4. Conclusions

Differential thermal analysis enables the self-heating tendency of coals to be differentiated. Self-heating temperatures between 180 and 270°C were observed for the coals studied. The lowest temperatures correspond to the lower rank coals. Coal oxidation gives rise to an important modification both in the characteristic temperatures (self-heating and end of combustion temperatures) and in the heat flow rate. The characteristics of the volatiles released up to about 425°C seem to be mainly respon-

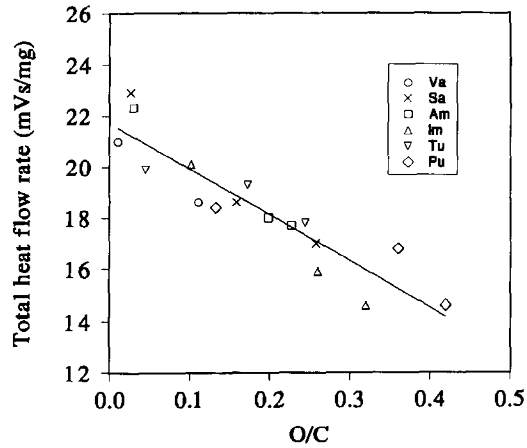

Fig. 6. Evolution of the total heat flow rate with O/C ratio of coals.

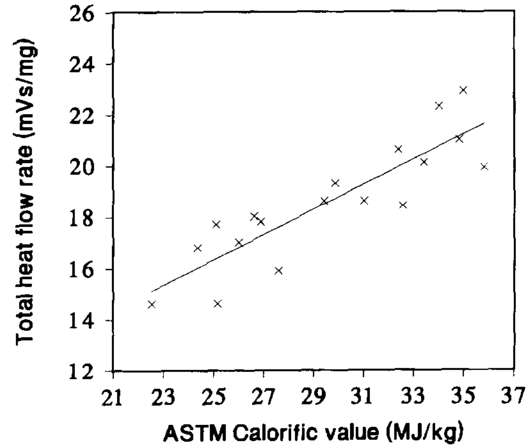

Fig. 7. Relationship between total heat flow rate (DTA experiments) and calorific value (ASTM test).

sible for the loss in calorific value of the coals as a consequence of oxidation. A relationship between the total heat flow (area under the DTA curve) and the ASTM heating value has been pointed out.

Acknowledgements

The authors wish to thank the Spanish DGICYT (Project PB93-0157) for financial support of this work. Fellowship support to G. de la Puente by FICYT is gratefully acknowledged.

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