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PROBLEMS IN THE DSC AND DTA STUDY OF THE BURNING PROPERTIES OF FUELS AND OTHER ORGANIC MATERIALS

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ABSTRACT

It is shown that DSC curves reveal considerably less energy release than the true reaction heats of the oxidation of organic materials. This fact may be due to the low oxidation rate of some primary volatile products, especially carbon monoxide, inevitably forming during the oxidation of organic and carbonaceous materials at the temperatures of DSC experiments. The measured heat is strongly affected by the experimental conditions and can be brought closer to the net heat of combustion by catalytic oxidation of the carbon monoxide formed inside the measuring cell. The goals of DSC and DTA studies of fuels should be the correct characterization of burning properties and a rough estimation of calorific values belonging to the volatiles and the char formed during burning. In this direction, further research is needed.

INTRODUCTION

The thermal effects of the oxidation of solid fuels and other organic materials have been studied by DTA for about 40 years [1–3]. The aim of these examinations were "to enable the burning characteristics to be determined" [1], to study the "combustion characteristics" of coals [2], and to find a "relationship between the calorific value and the peak area" in the DTA study of peats and other materials of biological origin [3]. Following the development of instrumentation in thermal analysis, the goals of investigations have become more and more quantitative. Thus, Fyans and Earnest [4–6] have studied the oxidation of coals by DSC and reported a surprisingly good agreement between the area of the DSC peaks and the ASTM calorific values. On this basis, they recommended differential scanning calorimetry as an alternative method to the time-consuming bomb calorimeter measurements [4,6]. Rogers and Bibby [7] examined the oxidation of oil shales and found good linear correlation between the DTA peak areas and the bomb-calorimetry values of the heat of combustion. González-González and Campos-López [8] calculated reaction kinetic parameters from DSC curves of the oxidation of a special wax. Jha [9] used DSC to obtain kinetic

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parameters for modelling the in situ (underground) combustion of oil shales.

Unfortunately, very little attention has been paid in the literature to an important problem which makes the quantitative results of DSC and DTA studies of oxidation processes questionable. The problem lies in the fact that in DSC and DTA experiments oxidation starts around 200°C and the majority of the sample burns below 600°C. Below 600°C, however, complete oxidation of the organic materials cannot be ensured without special catalysts [10–13]. (Note that this is also the central problem of elemental analysis [10,11].) Incomplete burning may be mainly due to carbon monoxide evolved during heating of the various organic materials. The oxidation of cokes, chars and other carbonous materials also produces a considerable amount of carbon monoxide as a primary product [12,13]. The ignition temperature of carbon monoxide is well above 600°C and its oxidation is a slow process below this temperature. At 540°C, for example, carbon monoxide has a half-life of about 10–20 min in oxygen [14].

We have found only one paper dealing with the thermoanalytical implications of this problem: it was the work of Dollimore and Mason on the thermal decomposition of various oxalate salts in air [15]. They have found that carbon monoxide, evolved from oxalates at about 500°C, is more or less oxidized depending on the catalytic activity of the solid residue of decomposition. In the case of magnesium oxalate, however, the amount of carbon monoxide oxidized into carbon dioxide was so low that the heat of oxidation could not counterbalance the heat of decomposition and only an endothermic peak was observed. When the porcelain crucible of their apparatus was replaced by a platinum crucible, an exothermic peak was observed, since the platinum catalyzed the oxidation of carbon monoxide. This experiment clearly shows that the heat of oxidation measured in the thermoanalytical instruments strongly depends on the catalytic activities of the sample and sample holder and thus the usual forms of DSC and DTA measurements cannot strictly characterize the burning properties of samples examined.

EXPERIMENTAL

Apparatus

TG–MS measurements were carried out in a system built from a Perkin-Elmer TGS-2 thermobalance, a Balzers QMG-511 quadrupole mass spectrometer and a PDP-11/34 minicomputer [16,17]. The DSC measurements were made with a Perkin-Elmer DSC-2 in a flow of high-purity oxygen. Following Fyans' recommendation, the sample block cover has been modified to avoid condensation of evolved water vapour in the sample block [4].

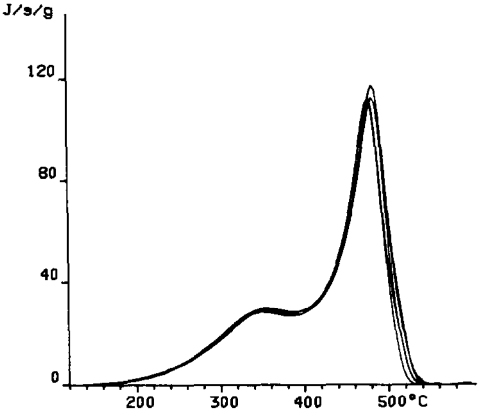

Fig. 1. Reproducibility of the DSC measurements of the oxidation of natural coals. Five DSC curves of coal I at 40°C $\min^{-1}$.

Low sample masses have been applied, from 0.15 to 0.6 mg, to avoid self-heating and mass-transport problems. The gas flow rate was 20 ml $\min^{-1}$. The sample pan and its lid were gold. Experiments have shown that the highest reaction heats were measured when the sample pan was covered with a lid and the lid was perforated around its middle point by a vent of about 0.5 mm diameter. This requirement can be explained in the following way: without a lid, the primary products to be oxidized spend too little time in the hot zone of the instrument. Without a vent on the lid, the oxygen supply is uncertain. The sufficiency of the oxygen supply was also checked by theoretical calculations. The magnitude of the highest oxygen consumption was estimated to be about 10^{-7} mol s^{-1} at the applied heating rates and sample masses while diffusion through the vent is about 10^{-6} mol s^{-1} and there is also a flow of oxygen through the join between the sample pan and the lid. The instrument was coupled with a digital voltmeter and the data output onto a punch tape. The punch tapes were processed by a PDP-11/34 minicomputer and the results drawn by a plotter. The programs were written in Fortran. The aim of the digital data processing was correct baseline processing and reliable integration of the data. The baselines were measured by repeating the measurement after burning out the sample without opening the sample block. In many cases, subtraction of an additional linear baseline was also necessary to bring both ends of the oxidation curves to zero. The reproducibility of the whole measurement process is illustrated by Fig. 1. The standard deviation of the obtained reaction heats was about 500 J g^{-1} for the coal samples examined and 200 J g^{-1} for the pure charcoal.

Samples

The natural coal samples were low-grade Hungarian sub-bituminous coals from the mines of the Nograd basin, from Szorospatak (I) and Menkes (II).

TABLE 1

Composition of the dried coal samples

Sample	Ash [wt%]	Volatiles [wt%]	Total sulphur [wt%]	Organic phase [wt% daf]			
				C	H	O	S
I	31.7	27.5	0.3	74.6	5.1	18.4	0.3
II	44.6	22.1	2.6	75.4	5.2	16.8	1.2

TABLE 2

Comparison of the oxidation heats measured by DSC and the net heats of combustion (J g^{-1})

	Without catalyst	With CuO	With CuO + $PbCrO_4$	Net heat of combustion
Pure charcoal	27800	31800	–	32800 (estimated)
α-Lactose	8200	12700	–	14300 (from ref. 18)
Coal I	16400	16100	17700	19200 (bomb calorimetry)
Coal II	13100	13100	13800	15700 (bomb calorimetry)

The coals were ground in a ball mill and dried at 105°C in a nitrogen atmosphere before measurements. Characterization of the coal samples was made by the Hungarian Central Development Institute for Mining. The proximate and ultimate analysis data are summarized in Table 1. The net heat of combustion is shown in the last column of Table 2.

Pure charcoal was made from Merck's "Active Charcoal for Analysis" (Merck Catalogue No. 2186) by an additional carbonization at 1000°C in a nitrogen atmosphere for 30 min. The other compounds used in the experiments were analytically pure reagents purchased from Reanal Co., Hungary.

RESULTS AND DISCUSSION

The evolution of carbon monoxide and carbon dioxide during the oxidation of pure charcoal has been measured by thermogravimetry-mass spectrometry. In the case of Fig. 2, the sample pan has been covered in the same way as in the DSC measurements. Figure 2 shows that the relative amount of carbon monoxide is considerable below 570°C. At 450°C, for example, the CO/CO_2 ratio is close to unity. The next figure (Fig. 3) belongs to an isothermal experiment measured with an open crucible at 520°C. Figure 3 shows that the CO/CO_2 ratio does not change significantly at constant temperature. Its value is between 0.7 and 0.8 while the corresponding value

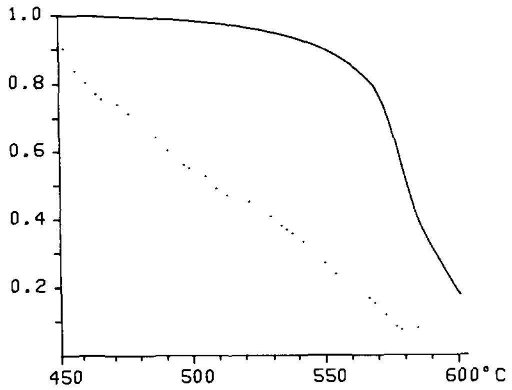

Fig. 2. Non-isothermal TG–MS measurement of the oxidation of pure charcoal in a covered sample holder at 10°C min^{-1}: (———) mass; (······) CO/CO$_2$ ratio.

on Fig. 2, at 520°C, is only between 0.4 and 0.5. This may be due to the lid applied in the case of Fig. 2, as outlined in the Experimental Section.

Incomplete burning of the samples can be demonstrated directly by DSC measurements, if such catalysts are added to the sample which increase the rate of oxidation of carbon monoxide. The increased measured reaction heat in these experiments may be due to the catalytic oxidation of carbon monoxide (formed in the primary reactions) inside the sample holder. We have chosen catalysts commonly used in elemental analysis: CuO and a mixture of CuO and PbCrO$_4$ [10,11]. These are thermally stable compounds having no transitions in the temperature range of the DSC measurements. Their heat capacity was counterbalanced by putting the same amount of catalyst into the reference holder as well. The catalyst was not mixed with the sample since we wanted only a small contact surface between the catalyst and the sample. In other words: the aim of these measurements was

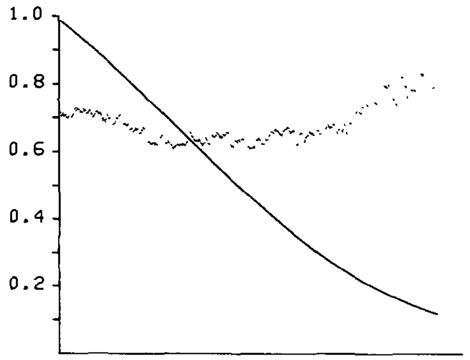

Fig. 3. Isothermal TG–MS measurement of the oxidation of pure charcoal at 520°C in an open sample holder: (———) mass; (······) CO/CO$_2$ ratio.

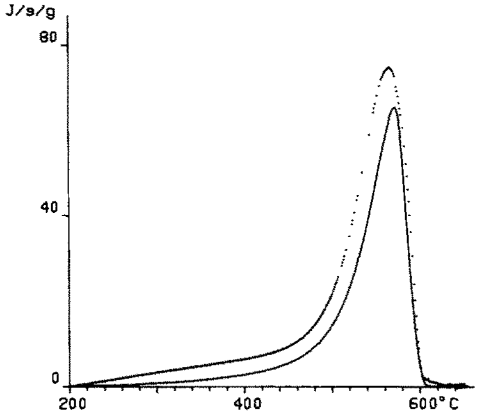

Fig. 4. DSC curves of pure charcoal at 10°C min^{-1}: (———) without catalyst; (······) covered with CuO.

to oxidize the evolved carbon monoxide to carbon dioxide without interfering significantly in the primary processes. Thus the catalysts were placed in a layer above the samples so that the gaseous products had to go through the layer of catalyst before leaving the sample pan. The mass of the catalyst layer was about 1 mg in all experiments.

Figure 4 shows how a layer of CuO catalyst has increased the evolved heat of oxidation of a pure charcoal. The overall reaction heat has been increased from 27800 to 31800 J g^{-1}. The latter value is close to the theoretical heat of combustion of pure carbons, 32800 J g^{-1} [18].

Naturally, the area of a DSC peak cannot completely achieve the net heat of combustion since the energy used for heating the sample diminishes the observed exothermic reaction heat. In the case of pure carbons, this energy can be estimated to be about 600 J g^{-1}. Similar values can also be obtained for the other samples used in our experiments. In this way, the agreement between DSC results with CuO catalyst and the theoretical reaction heat can be regarded as good.

Figure 5 shows the effect of CuO catalyst on the DSC curve of the oxidation of α-lactose monohydrate, $C_{12}H_{22}O_{11} \cdot H_2O$. The large changes in the characteristics of the DSC curve may be due to the liquid state of the sample at the temperature of oxidation: the liquid has probably entered into the pores of the catalyst and the resulting high contact surface also allowed a catalytic thermal decomposition. The corresponding reaction heats are shown in Table 2. The catalyst led to an increase of about 50% but this increased value is still considerably less than the net heat of combustion of α-lactose monohydrate on perfect combustion [18]. The difference between the peak area and the net heat of combustion may be attributed to the fact that the majority of the oxidation took place below 400°C where the catalytic

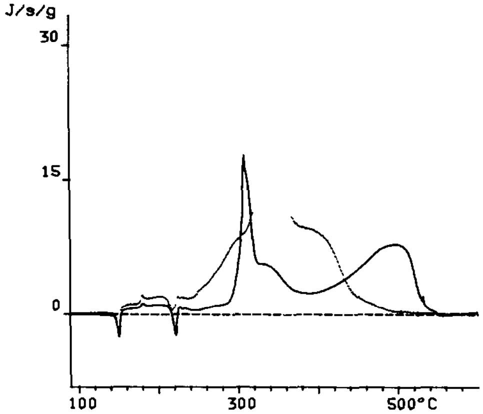

Fig. 5. DSC curves of α-lactose ($C_{12}H_{22}O_{11}\cdot H_2O$) at 10°C min^{-1}: (———) without catalyst; (······) with CuO.

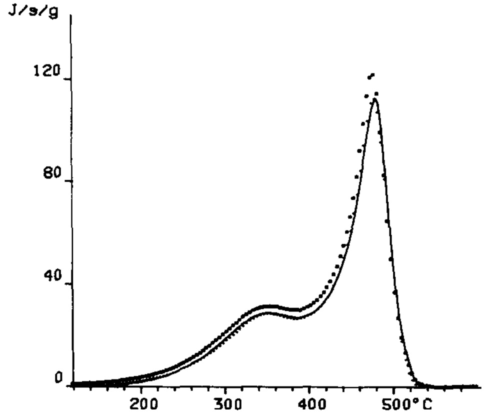

Fig. 6. DSC curves of coal I at 40°C min^{-1}: (———) without catalyst; (······) covered with CuO; (■■■) covered with CuO–$PbCrO_4$ catalyst.

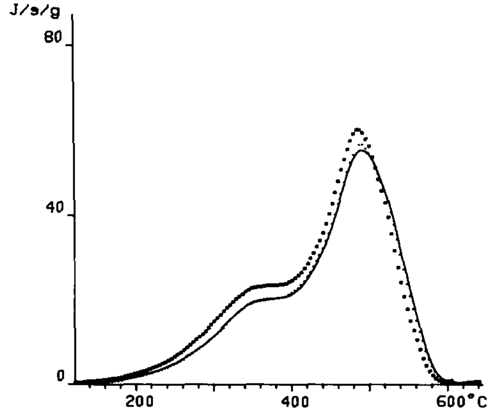

Fig. 7. DSC curves of coal II at 40°C min^{-1}: (———) without catalyst; (······) covered with CuO; (■■■) covered with CuO–$PbCrO_4$ catalyst.

activity of CuO is less than at the higher temperatures of charcoal oxidation [11].

The oxidation of the coal samples is shown in Figs. 6 and 7. The most characteristic feature of these figures is the lack of the effect of CuO catalyst. This observation can be attributed to the sulphur content of the coals (see Table 1), since sulphur compounds evolving during thermal decomposition of the coals are catalyst poisons. The CuO–$PbCrO_4$ catalyst is less sensitive to sulphur [11], hence it could slightly increase the heat evolved. Nevertheless, the peak areas given in Table 2 are less than the corresponding bomb calorimetry values of the net heat of combustion.

CONCLUSIONS

The above examples, as well as the observations of Dollimore and Manson on the oxidation of various oxalic salts [15], clearly illustrate that DSC and DTA curves of the oxidation of organic materials are the results of very complex processes and depend on the catalytic activities of the materials present in the experiment as much as on the real burning properties of the sample. We do not doubt that one can find good correlation between the peak area and the net heat of combustion within a given series of samples and under rigorously fixed experimental conditions, but a correlation of this type can hardly have general validity. The height of the measured DSC and DTA signals may depend on such accidental factors as the temperature at which the volatiles develop from the given sample, the time the volatiles spend in the hot zone of the measuring cell and the catalytic or catalyst-poisoning effects of the mineral content and the various impurities of the samples. The outlined problems naturally lead to the question: why should DSC and DTA be used in combustion and oxidation studies? The main advantage of various thermoanalytical techniques in this field is their ability to characterize some important partial processes of combustion: the formation of voltatiles and oxidation of the resulting char. These processes usually appear in two or more peaks on the thermoanalytical curves. If the problems described in this paper were solved, DSC and DTA could correctly characterize the calorific values belonging to the volatiles produced in the various steps of thermal decomposition as well as the heat of oxidation of the resulting char. In our opinion, the outlined problems could be solved by developing special measuring cells in which some catalyst would promote the oxidation of the volatile products of thermal decomposition and of the carbon monoxide produced during oxidation of the resulting char. The requirements of the catalytic oxidation would be considerably slighter here than in the elemental analysis: a conversion of about 97% would be quite acceptable. In this direction more research would be necessary. The main problem seems to be the choice of a proper catalyst among the numerous catalysts proposed in the literature for the oxidation of carbon monoxide and other compounds. The catalysts tested in the present paper are far from optimal.

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