FUEL

the science of fuel and energy

Published by IPC Science and Technology Press Ltd

Differential scanning calorimetry studies on coal. 1. Pyrolysis in an inert atmosphere

Om P. Mahajan, Akira Tomita and Philip L. Walker, Jr

Department of Material Sciences, Pennsylvania State University, University Park, Pa. 16802, USA
(Received 19 May 1975)

Results of thermal changes involved during the pyrolysis of twelve US coals of various ranks in a helium atmosphere at 5·6 MPa (gauge) and temperatures up to 580°C are reported. Thermal effects during pyrolysis of coals ranging in rank from anthracite to HVC bituminous are endothermic in nature over the temperature range investigated. Exothermic heats are observed only in the case of sub-bituminous and lignitic coals. The net thermal effects, that is the resultant of endothermic and exothermic heats, go from endothermic to exothermic with increase in carbon content, a transition occurring around 66% carbon and another in the reverse direction at about 75% carbon. A maximum in exothermicity occurs around 71% carbon and in endothermicity at about 81% carbon. Results have been compared with published DTA data on coals. The fallacy in the interpretation of published DTA thermograms of coals, where weight changes accompany thermal effects, is discussed.

In the design of coal conversion processes, information is badly needed on the heats involved in various reactions. We believe that a recent thermal analytical technique, namely Differential Scanning Calorimetry (DSC), when used in conjunction with Thermo Gravimetric Analysis (TGA), makes possible the rapid assessment of heats involved in some important coal processes.

The DSC is a technique in which the ordinate value of an output curve at any given temperature is directly proportional to the differential heat flow between a sample and reference material and in which the area under the measured curve is directly proportional to the total differential caloric input. The term 'scanning' implies that the temperature of both the sample and reference is increased during the experiment at a known heating rate. By this technique, coal samples can be studied under experimental conditions that simulate selected processes.

The present paper describes in detail the experimental set-up and procedure, as well as results of thermal changes involved during the pyrolysis of twelve US coals of different ranks in a helium atmosphere at 5·6 MPa (gauge) and temperatures up to 580°C. Results have been compared with published Differential Thermal Analysis (DTA) data on coals. It is proposed to extend the DSC technique later to the study of heats of hydrogenation of coals in order to understand better the influence of different variables.

EXPERIMENTAL

DSC apparatus

Operating procedure. A DuPont pressure DSC cell, which is capable of operation up to 6·9 MPa and 600°C was used in conjunction with a cell base Module I and a 990 Thermal Analyzer. Coal samples (40 x 70 U.S. Standard mesh) were dried in an oven at 110°C for 2 h before making DSC runs. Except in the case of caking coals, about 20 mg of a dried sample were used in each run. When a 20 mg sample of caking coals was used, swelling upon heating caused the mass to touch the silver lid placed on the constantan thermo-electric disc; to prevent this, about 12 mg of sample was used. An aluminium pan containing the coal sample was placed on the raised platform in the cell and an empty pan was placed on the reference platform. The DSC cell was then evacuated. It was ascertained in a few preliminary experiments that, during weighing and transfer, the coal samples picked up moisture which resulted in spurious thermal changes up to 110°C. In order to circumvent this difficulty, the samples were re-dried in the cell at 110°C in a helium flow. The cell temperature was then lowered to 100°C. The cell was pressurized with helium to 5·6 MPa. The sample was held isothermally at 100°C for 15 min after which the scan was started, using a constant heating rate of 10°C/min. During the run, a slight flow of gas (about 1·0 cm^3/min over the sample) was maintained. As the cell temperature increased, there was a build-up of pressure. However, the pressure was kept constant by bleeding off excess gas through a fine metering valve.

Calculation of heats of reaction. Heats of reaction using the DSC technique are calculated from the following equation

$$\Delta H = \frac{ABE\zeta}{m} \qquad (1)$$

where ΔH = heat of reaction (mJ/mg); A = area of the endotherm or exotherm (mm^2); m = sample mass (mg); B = time-base setting (s/mm); E = cell calibration coefficient at a given temperature (dimensionless); and ζ = y-axis sensitivity (mJ/s mm).

During the pyrolysis of coals, there is a gradual and continuous weight loss over the entire temperature range. Since the displacement of the DSC output curve (relative to the reference base line) which is obtained under identical experimental conditions is proportional to mass, it is evident that as the mass of coal decreases with increase in tempera-

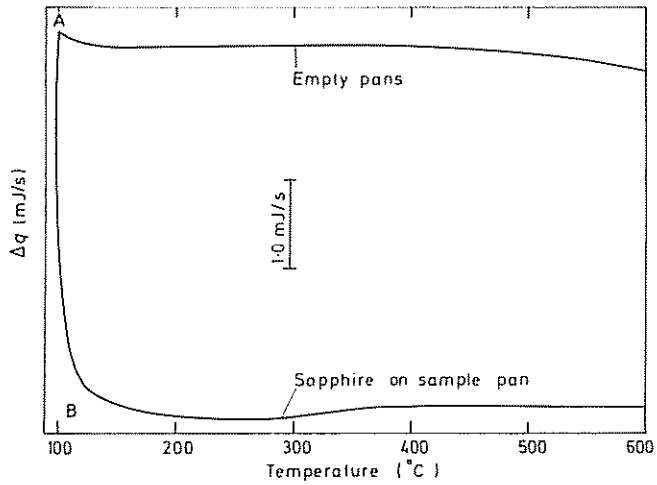

Figure 1 Determination of cell calibration coefficient

ture, the displacement of the output curve relative to the reference base line will vary continuously. Therefore, although the output curves can be integrated to yield accurate values of ΔH, the heats cannot be expressed per unit weight unless the output curve can be corrected for weight changes occurring at different temperatures. Only then can the DSC technique be used as a quantitative tool for measurement of thermal effects involved in the pyrolysis of coals. We have endeavoured to make such corrections in the present study, as described below.

Determination of cell calibration coefficient. Since the cell calibration coefficient changes with temperature, it is essential to determine its value over the entire pyrolysis temperature range. It was determined in the following manner. Empty aluminium pans of about the same weight were placed on the sample and reference platforms. After evacuation, the cell was pressurized with helium to 5·6 MPa. Before starting the scan the system was held isothermally at 100°C for 15 min. A run was then made, using a heating rate of 10°C/min up to 580°C. The procedure was repeated under identical conditions with a weighed sapphire disc in the sample pan. The two scans are shown in *Figure 1*. The calibration coefficient at a given temperature is calculated from the following relation:

$$E = \frac{c_p H_r m}{\zeta \Delta y} \qquad (2)$$

where c_p = heat capacity of sapphire (mJ/mg °C); ζ = y-axis sensitivity (mJ/s mm); H_r = heating rate (°C/s); Δy = difference in y-axis deflection between sample and blank curves at temperature of interest (mm); m = sample mass (mg).

Values of heat capacity of sapphire at 1 atm* and different temperatures are available in the literature[1]. For the calculation of E, it has been assumed that the heat capacity of sapphire does not change significantly with pressure. E increased monotonically from 2·19 at 100°C to 3·50 at 580°C.

TGA apparatus

Determination of weight changes during pyrolysis. Weight changes, under conditions simulating those in the DSC runs, were monitored using a DuPont 951 TGA balance in conjunction with a 990 Thermal Analyzer. A platinum boat (6 x 7 x 5 mm), containing approximately the same weight of oven-dried coal as used in the DSC runs, was suspended from the quartz beam of the balance. The flexible end of the chromel–alumel thermocouple, which is attached to the balance housing, was placed in close proximity to the sample. The reactor was made of a quartz tube (25 mm o.d.) with a reduced end on one side, which acted as an inlet for the reactant gas, and an aluminium retainer ring on the other side which fitted into the balance housing. A small hole in the reactor tube near the metal ring acted as an outlet vent for the outgoing gases. The reactor tube was surrounded by a tube furnace (wound with molybdenum wire) of i.d. only slightly greater than the o.d. of the reactor tube. The balance assembly along with the reactor and furnace were mounted in a carbon steel pressure vessel (built by Autoclave Engineers) which is provided with a quick opening door with Conax pressure-seal outlets. After introducing the sample, the pressure vessel was closed and evacuated, following which it was pressurized with nitrogen to 5·6 MPa. Helium was then introduced into the reactor at a pressure of 5·6 MPa through a pressure flowmeter. After a steady flow of helium was established, the furnace was activated to raise the temperature to 580°C at a heating rate of 10°C/min.

Sample temperature. In the TGA technique, the sample temperature is taken to be that measured by the thermocouple, which is located in close proximity to the sample. It was ascertained in a few preliminary experiments that at atmospheric pressure there was hardly a significant temperature gradient between the sample and thermocouple. However, at elevated pressures and temperatures, significant temperature differences were observed, the magnitude depending upon the distance of separation of the thermocouple and sample. In order to standardize the TGA technique for accurate temperature measurements at high pressures, the decomposition of calcium oxalate, corresponding to the reaction $CaC_2O_4 \rightarrow CaCO_3 + CO$, was studied at a pressure of 5·6 MPa.

The temperature corresponding to the maximum rate of decomposition for a number of experimental runs was found to be 462 ± 5°C. This temperature was also determined under identical experimental conditions by using the DSC technique and was found to be 497°C. For quantitative evaluation of the data during pyrolysis, it has been assumed that when the TGA thermocouple indicates 462°C, the sample temperature is 497°C. It was verified in a few experiments that when the sample boat is removed and an external thermocouple is placed close to the TGA thermocouple, then, irrespective of the distance of separation of the two thermocouples, rectilinear although different heating rates are indicated by the two thermocouples. The rate indicated by the external thermocouple is determined by its distance of separation from the TGA thermocouple. Thus a constant ratio of heating rates is indicated at a given separation, implying that over the entire temperature range the temperatures indicated by the two thermocouples differ in the same ratio. Therefore, from the known difference in temperature between the TGA thermocouple and sample (that is, 462 and 497°C) for the decomposition of CaC_2O_4, it is easy to compute a temperature correction table for the entire temperature range.

Balance calibration. Before the TGA equipment could be used for quantitative estimation of weight changes during pyrolysis, it was essential to calibrate the balance for buoyancy effects at 5·6 MPa and temperatures up to 580°C. Materials chosen for investigating such effects were calcined

* 101·3 kPa

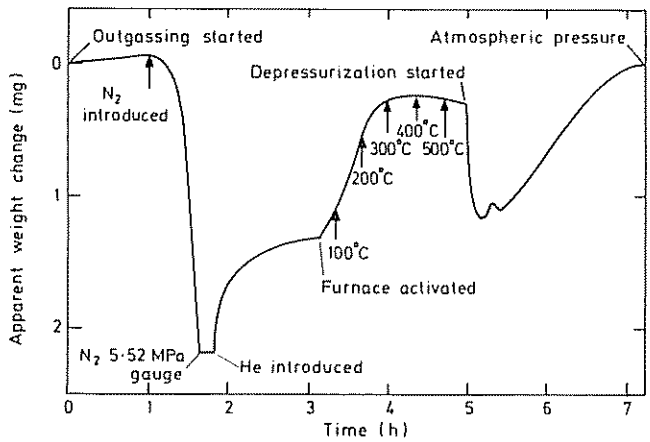

Figure 2 TGA curve for Sterling MT carbon black

alumina and a graphitized carbon black, Sterling MT, which is an ultra-clean carbon devoid of volatile and mineral matter. A typical run using Sterling MT (19·8 mg) in a platinum bucket (85 mg) is shown in *Figure 2*. Alumina behaved identically to the carbon black. It is seen that when nitrogen is introduced into the system, following evacuation, an apparent decrease in weight is observed, the magnitude of the decrease increasing with increase in pressure. As soon as a steady-state condition is attained at 5·6 MPa, nitrogen is replaced by helium at 5·6 MPa. Following the introduction of helium, there is an abrupt increase in weight; the increase continues slowly thereafter and ultimately the weight becomes constant. At this stage, the furnace is activated and the apparent weight changes are recorded as a function of temperature. After completion of the run, when the system is cooled to room temperature and depressurized to atmospheric pressure, the recorder pen that monitors weight changes returns to the initial starting point, thus ruling out the possibility of any spurious weight changes during the experimental run.

With a smaller weight (c. 10 mg) the TGA curve above 100°C is almost identical with and superimposable on that using a 20 mg sample. The TGA curve obtained with alumina or Sterling MT is taken as the reference curve for evaluating weight changes in subsequent runs. The accuracy of the technique was checked by weighing the chars, following pyrolysis, in a Cahn RTL Millibalance, the range of accuracy of which is rated to be ±0·1 mg. There was good agreement between these values and those determined from the TGA runs. As a further check, the coal chars after pyrolysis in DSC runs were cooled and weighed. The reasonable agreement observed (*Figure 3*) for the weight loss at 580°C obtained from TGA and DSC runs in the case of twelve coal samples lends support to the reliability and accuracy of the TGA technique to measure quantitatively weight changes at high pressures and high temperatures.

Computation of corrected DSC output curves

Considering equation (2), it is seen that under given experimental conditions and at a given temperature, E, c_p, H_r and Δq are constant. Therefore, the displacement Δy is directly proportional to mass. This was quantitatively confirmed by taking different weights of four coal samples. In each experimental run following pyrolysis, the char was cooled *in situ* in the DSC cell in a helium atmosphere and the initial displacement, that is the distance AB in *Figure 1*, again measured at 5·6 MPa and 100°C. If it is assumed that the removal of volatile matter during pyrolysis does not significantly change the heat capacity of coals, then the difference between the two initial displacements, that is before and after pyrolysis, may be taken to be proportional to the total weight loss at 580°C. This assumption is reasonably justified, because in many cases there was a very good agreement between the experimental and calculated values of displacement. The theoretical value was obtained by calculating from the initial displacement (AB in *Figure 1*) for the raw coal the value of Δy which a given weight loss at 580°C would correspond to, if a direct proportionality between weight and Δy is assumed.

From the above discussion, it is evident that from a knowledge of weight loss during pyrolysis as a function of temperature, as determined from TGA runs, it is possible to compute the extent to which the DSC output curve has to be displaced at different temperatures to give a corrected output curve.

Reference base lines for corrected DSC output curves

Since during pyrolysis coals decompose over a wide range of temperature, it is obvious that in order to calculate the value of ΔH it is essential to have a sensible reference base line. Since the heat capacity of any solid varies with temperature, it will result in a shift of the base line with temperature. Thus, it is desirable to have a reference material with a heat capacity closely matching that of coals. In the present work, we have determined base lines individually for all the coal samples following pyrolysis. In each case, the char following pyrolysis at 580°C was cooled to 100°C in a helium atmosphere before starting the scan. During each run, the reference material was an empty aluminium pan. The output curves, that is the base lines, were essentially the same for all the devolatilized coals at temperatures above 200°C.

Coals studied

Table 1 presents ultimate and proximate analyses for the coals studied. Volume percentages of vitrinites in the coals,

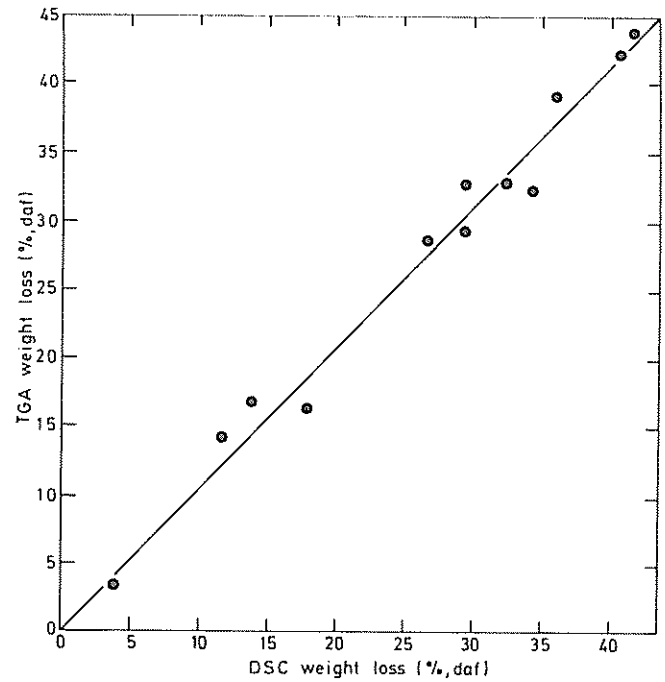

Figure 3 Relation between weight loss in DSC and TGA runs

Table 1 Analyses of coals

PSOC Sample No.	ASTM rank	State	Proximate analyses (%) Ash (dry)	Fixed C (daf)	VM (daf)	Ultimate analyses (% daf) C	H	N	S*	O (by diff.)	Vitrinite content (vol %, mmf)
85	Anthracite	Pa.	8·3	92·3	7·7	91·2	3·9	0·60	0·83	3·4	97·5
130	MV	W. Va.	6·4	76·9	23·0	90·6	4·3	1·1	0·51	3·5	72·7
127	LV	Pa.	5·7	79·4	20·6	89·6	5·0	1·0	0·52	3·9	77·7
135	MV	Ala.	5·0	75·2	24·9	88·4	4·9	0·25	0·59	5·8	83·1
95	HVA	Wash.	21·1	57·9	42·1	81·6	6·1	1·1	0·95	10·3	79·3
24	HVB	Ill.	11·8	58·1	41·9	80·1	5·5	1·1	2·3	11·1	88·1
22	HVC	Ill.	10·1	57·2	42·8	78·8	5·8	1·5	1·8	12·1	88·4
190	Sbb.B	Ill.	8·5	58·5	41·5	75·6	5·3	1·1	2·1	15·9	84·1
97	Sbb.A	Wyo.	9·8	45·6	54·4	75·0	5·5	0·58	0·93	18·0	80·3
100	Sbb.C	Wyo.	5·0	39·3	60·7	72·1	5·3	0·81	0·34	21·5	64·7
87	Lignite	N.D.	8·2	45·8	54·2	71·2	5·3	0·56	0·46	22·5	84·2
89	Lignite	N.D.	11·6	42·7	57·3	63·3	4·7	0·47	0·98	30·6	58·7

* Organic sulphur

as estimated by reflectance measurements, are also listed in the Table.

RESULTS AND DISCUSSION

DSC output curves, before and after correction for weight changes, for nine coal samples are plotted in *Figure 4*. Curves for the other three samples are not included, for reasons of space. When the curve runs below the base line, an endothermic process is indicated; when the curve runs above, an exothermic process.

Values of ΔH can be expressed either per unit weight of starting coal or per unit weight of coal left unreacted at a given temperature, as determined from the TGA runs. On the basis of theoretical considerations discussed in the preceding pages, it is more appropriate to express ΔH per unit weight of coal left unreacted. However, in designing coal conversion plants, one is primarily interested in the values of ΔH for a given starting weight of coal. For the sake of comparison therefore we have calculated the values of ΔH on both bases. For calculating ΔH, the corrected output curves were divided into several segments, consecutive segments being separated by 50°C. For each segment, ΔH was calculated by taking an average value of E and an average weight of coal left unreacted or starting weight of coal, as the case may be. Values of ΔH for the various coal samples are given in *Table 2*. It is seen that as would be expected the values of ΔH calculated by the two methods differ for each coal sample, the magnitude of the difference depending upon the weight loss for a given segment in the output curve. In the discussion of results which follows, we have considered values of ΔH expressed per gram weight of starting coal.

Considering the data in *Table 2* and corrected curves in *Figure 4*, it is seen that the thermal effects during pyrolysis of coals, varying in rank from anthracite to HVC, are endothermic in nature over the temperature range studied. Exothermic heats are observed only in the case of subbituminous and lignitic coals. However, there is a distinct difference in the thermal behaviour in the two cases. The lignites give endothermic effects at lower temperatures and exothermic heats at high temperatures. This order is reversed in the case of subbituminous (Sbb)-A coal, PSOC-97. The Sbb-C coal, PSOC-100, gives exothermic heats over the entire temperature range (*Figure 4*). The behaviour of Sbb-B coal, PSOC-190, is rather peculiar; it gives two well defined endotherms and exotherms.

Endothermic and exothermic heats are plotted in *Figure 5* as a function of carbon content. It is seen that endothermic heats go through a minimum around 72% carbon content and a maximum around 81% carbon. The maximum in exothermicity occurs around 71% carbon content. The

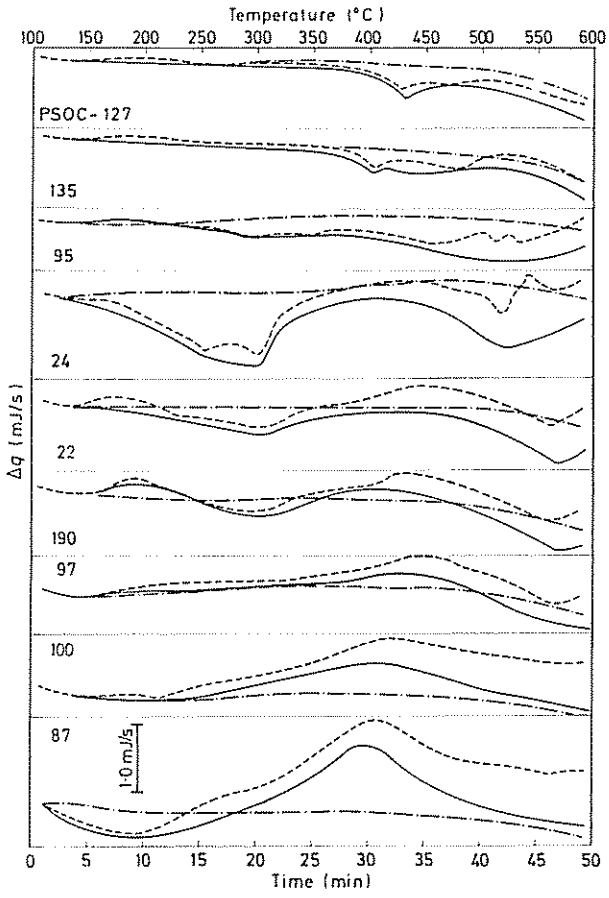

Figure 4 DSC curves for various coals. Base line (— · —), uncorrected output curve (— — —), and corrected output curve (——)

Table 2 Endothermic and exothermic heats resulting from pyrolysis

PSOC Sample No.	ΔH (endothermic)		ΔH (exothermic)		Net ΔH		Wt loss at 580°C (% daf)
	A*	B†	A	B	A	B	
85	10·9	10·5	Nil	Nil	+10·9	+10·5	3·8
130	106	97·5	Nil	Nil	+106	+97·5	13·5
127	112	105	Nil	Nil	+112	+105	12·1
135	84·5	75·6	Nil	Nil	+84·5	+75·6	17·6
95	282	242	Nil	Nil	+282	+242	29·3
24	268	224	Nil	Nil	+268	+224	34·1
22	106	95·8	Nil	Nil	+106	+95·8	26·6
190	53·6	44·0	23·9	22·2	+29·7	+21·8	29·3
97	26·8	19·3	27·6	26·4	−0·8	−7·1	32·3
100	Nil	Nil	93·8	74·9	−93·8	−74·9	35·7
87	31·8	30·6	154·1	118·1	−122·3	−87·5	40·6
89	88·8	84·1	68·3	51·9	+20·5	+32·2	41·5

A*, ΔH calculated as J/g coal left unreacted (daf basis)
B†, ΔH calculated as J/g starting weight (daf)

net thermal effects, that is the resultant of the endothermic and exothermic heats, are plotted in *Figure 6* as a function of carbon content. It is seen that as the carbon content increases, heat effects go from endothermic to exothermic, a transition occurring around 66% carbon and another in the reverse direction at about 75% carbon. The maxima in exothermicity and endothermicity occur around 71% and 81% carbon content, respectively.

Glass[2] has reported that ash, that is mineral matter, has a negligible effect on DTA thermograms of coals. On this basis, it can be surmised that the thermal effects observed in the present study are affected to a negligible extent by differences in total mineral-matter content and mineral-matter composition in the different coals.

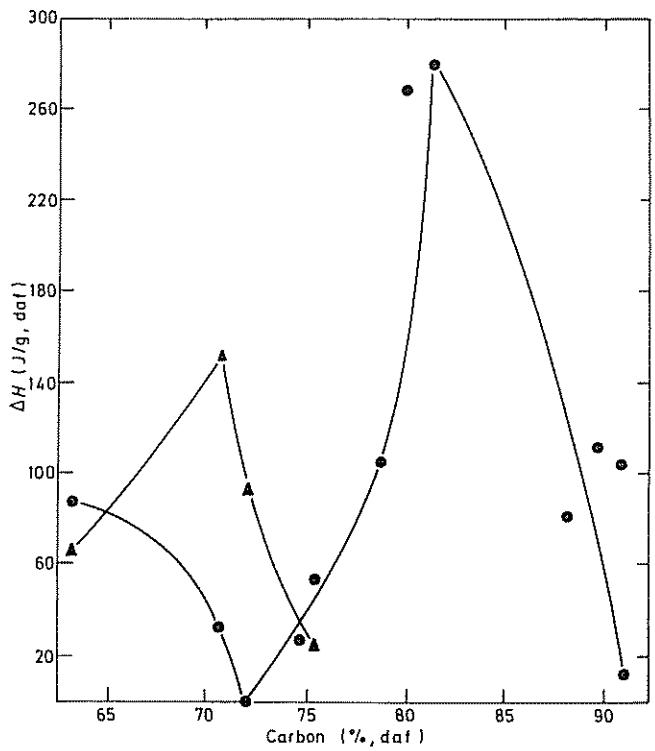

Figure 5 Endothermic (●) and exothermic (▲) heats during pyrolysis as a function of carbon content

When the DSC and TGA curves are considered (*Figures 4* and *7*), it is seen that in most cases there is essentially no correlation between either the magnitude or the temperature

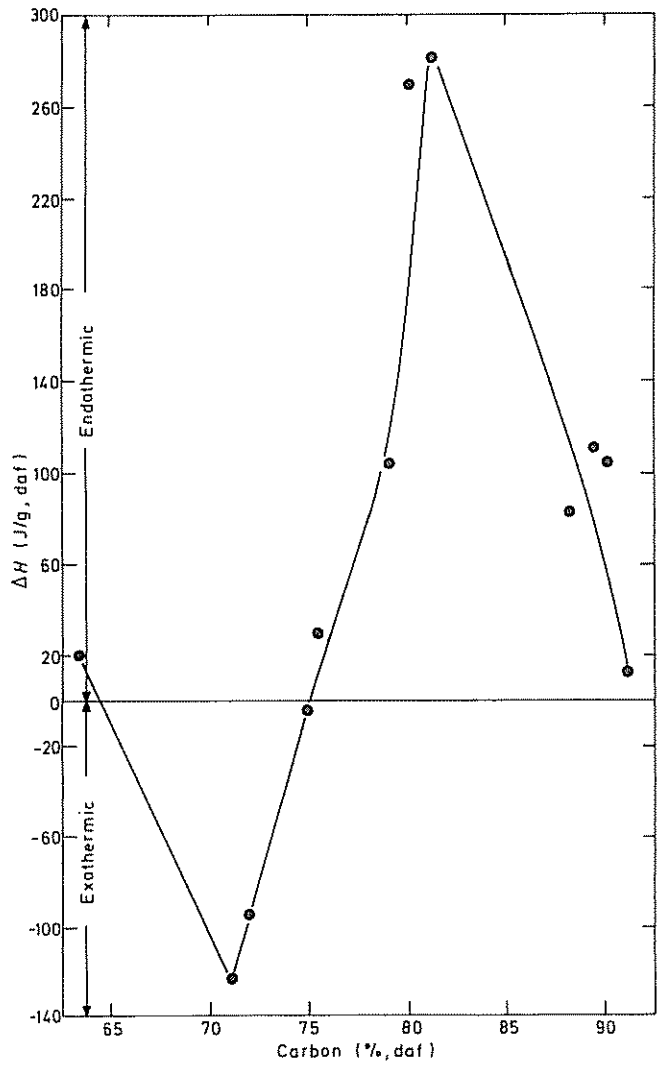

Figure 6 Net thermal effects during pyrolysis of coals as a function of their carbon content

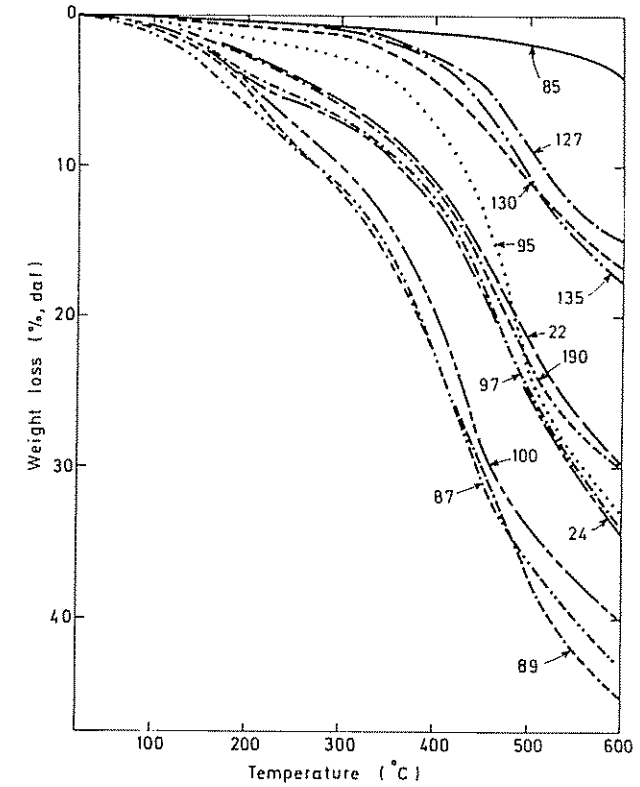

Figure 7 TGA pyrolysis curves for various coals

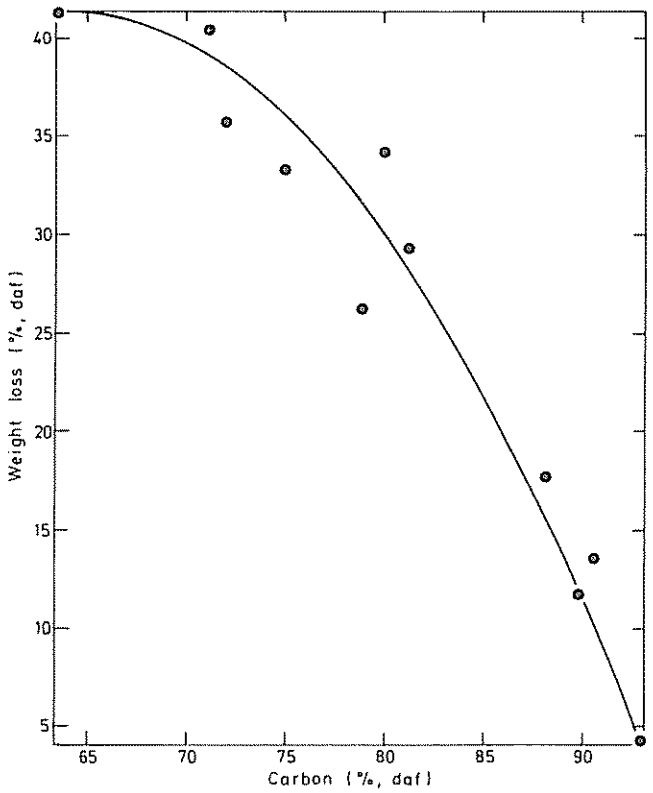

Figure 9 Weight loss during pyrolysis in relation to carbon content of coals

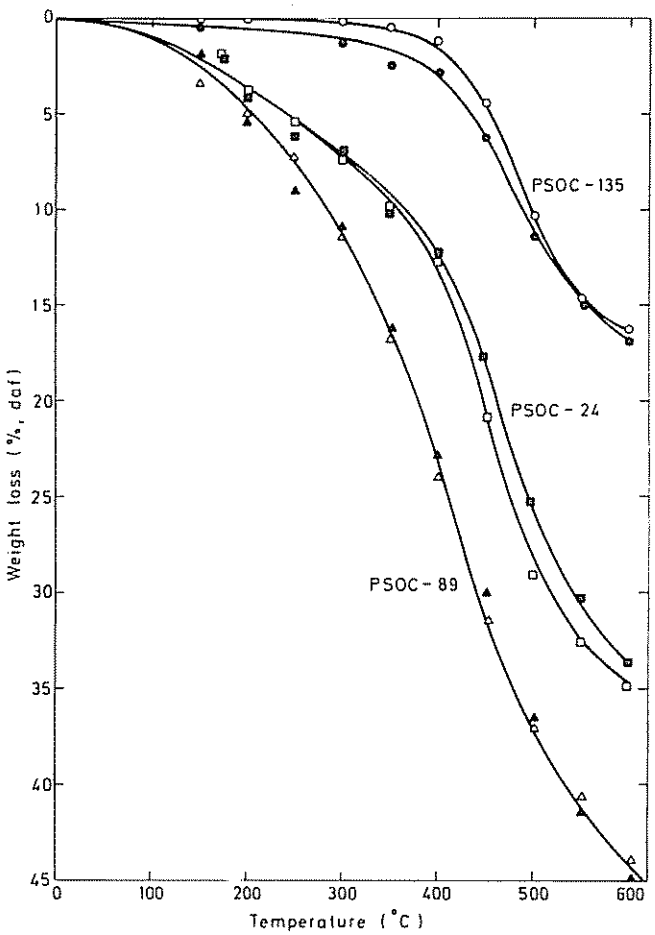

Figure 8 TGA pyrolysis curves at 100 kPa and 5·6 MPa. Solid points denote data at 5·6 MPa

corresponding to a maximum (or a minimum) in the thermal effects and the extent as well as rate of weight loss as determined from the TGA runs. This is not surprising when it is realized that the mechanism of pyrolysis of coals is highly complex. It is probable that the observed thermal effects are the resultant of several competing reactions, which may thermally oppose or cancel each other, even though each reaction individually may be contributing to weight loss.

It is instructive to compare the DSC results presented in this paper with DTA results published in the literature. Since the DSC results have been obtained at high pressures while in the DTA technique pyrolysis was carried out either in vacuum or an inert medium at ambient pressure, a truly meaningful comparison obtained with the two techniques under different experimental conditions may not be completely justified. However, we have ascertained in a few TGA runs (*Figure 8*) that variation in pressure from ambient to 5·6 MPa had slight or no effect on weight changes during pyrolysis in helium. Therefore, by assuming that pressure has no significant effect on thermal changes during pyrolysis, a comparison, at least qualitative in nature, can be made between DSC and DTA pyrolysis results. Whitehead *et al*[3] [5] showed that thermograms of various coal types, ranging from lignite to semi-anthracite, give exothermic peaks that shift towards higher temperatures with increasing rank. Berkowitz[6] confirmed the predominant exothermic character of pyrolysis of coals up to about 550°C but the thermograms were substantially rank-independent over the 73–90% (daf) carbon range. However, Glass[2] has observed that the thermal effects are mainly endothermic in nature. At this stage, it is emphasized that at least a part of the difference in the pattern of thermograms obtained by various workers is undoubtedly due to different experimental conditions employed. However, it is noteworthy that while the

published DTA results do not indicate any rank dependence[2–8], thermal effects observed with the DSC technique (used probably for the first time in coal studies) show a well-defined dependence on coal rank.

The DSC can also be used as a DTA technique so that the output curves may be regarded as thermograms. Owing to its quantitative nature and ease of sample handling, DSC is rapidly replacing conventional DTA techniques. We have suggested in this paper how the output curves can be corrected for weight changes so that the corrected curves are indicative of thermal changes alone. It is unfortunate that in interpreting the DTA thermograms of coals, different workers have ignored the displacement of the thermograms due to weight changes. The inherent drawback in the conventional DTA technique and consequential fallacy in the interpretation of thermograms of coals becomes evident when one considers the output curves before and after correcting for weight changes (*Figure 4*). It is interesting to note that after correction there is a significant change in the shape of the output curves and in some cases the correction leads to a total or partial reversal of the thermal effects. For instance, in the case of coals PSOC-127, 135, 95 and 22, the uncorrected curves, if considered as DTA thermograms, indicate slight apparent exothermic effects at lower temperatures (that is, 150–200°C), which after correction either disappear or give endothermic effects. Furthermore, the exothermic effects observed at higher temperatures in the uncorrected curves of samples PSOC-135, 95, 24, 22, 190 and 97 become either entirely or partly endothermic in character after correction. The behaviour of PSOC-95 is rather peculiar. The uncorrected curve is quite wavy; and if it is considered as a DTA thermogram, it indicates small endotherms and exotherms. However, following correction the wavy character disappears altogether and the whole curve is indicative of a smooth endotherm.

Weight losses of coals during pyrolysis runs are plotted against carbon content on a daf basis in *Figure 9*. It is seen that as the carbon content decreases, the weight loss increases, as expected.

ACKNOWLEDGEMENTS

The authors wish to thank Dr Ian Harrison for very useful discussions and interest in this study. Professor W. Spackman supplied the coals used in this study. The research was supported by the NSF on Contract No.GI-38974.

REFERENCES

1 Ginnings, D. C. and Furukawa, G. T. *J. Am. chem. Soc.* 1953, **75**, 522
2 Glass, H. D. *Fuel, Lond.* 1955, **34**, 253
3 Whitehead, W. L. and Breger, I. A. *Science*, 1950, **111**, 279
4 Breger, I. A. and Whitehead, W. L. *Fuel, Lond.* 1951, **30**, 247
5 King, L. H. and Whitehead, W. L. *Econ. Geol.* 1955, **50**, 22
6 Berkowitz, N. *Fuel, Lond.* 1957, **36**, 355
7 Pampuch, R. and Roga, B. *Prace Glownego Inst. Gorn., Ser. B.*, Komun No.183, 1956, 15
8 Kessler, M. F. and Romovackova, H. *Fuel, Lond.* 1961, **40**, 161