

THERMAL ANALYSES OF OHIO BITUMINOUS COALS

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ABSTRACT

A suite of twenty-one bituminous coal samples from Ohio were analyzed by differential scanning calorimetry (DSC) and non-isothermal thermogravimetry (TG) techniques. Three regions of endothermic activity may be distinguished in the DSC scans in an inert atmosphere. The first peak (25–150°C) corresponds to loss of moisture from the coal, a second, very broad endotherm peaking in the range 400–500°C corresponds to devolatilization of the organic matter and a partially resolved endotherm at temperatures above 550°C probably corresponds to cracking and coking processes subsequent to the pyrolysis step. Evidence obtained from experiments with sealed pans suggest an autocatalytic effect exerted by the pyrolysis products. The use of the DSC technique to quantify the volatile matter content of coal seems less reliable than the proximate analyses obtained from non-isothermal TG in inert and O₂ atmospheres. Good agreement with ASTM values is observed by the latter method for a range of volatile matter and ash content.

INTRODUCTION

Much attention has been focused in recent years on coal, not unsurprisingly in view of the impending shortage of conventional energy sources and the tremendous reserves which exist in the United States for this fossil fuel. Both direct combustion as well as pyrolytic conversion to liquid and gaseous fuels are being evaluated. Obviously, an understanding of the physical and chemical processes occurring in coal while it is being heated will help in better design and optimization of practical conversion systems. Thermoanalytical methods such as thermogravimetry (TG) and differential scanning calorimetry (DSC) can play an important role in this regard.

The use of thermal methods for characterization of coal is certainly not new [1]. Much of the early work utilizing differential thermal analysis (DTA) has been reviewed by previous authors [2–4]. The controversy centering around the nature of the heat effects (i.e., whether endothermic or exothermic) on pyrolysis of coal also seems to have been partially resolved by a recent DSC study on a variety of coals ranging in rank from anthracite to high-volatile bituminous [5]. One of the aims of

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TABLE I
Proximate analyses and other parameters for Ohio coal^a

| Sample name and number (formation) | Moisture (wt.%) | Volatile Matter (wt.%) | Fixed carbon (wt.%) | Ash (wt.%) | Heating value (kJ g ⁻¹) | Initial deformation (°C) | Softening point (°C) | Fluid temp. (°C) | Free swelling index |
|--------------------------------------|-----------------|--------------------------|--------------------------|------------|-------------------------------------|--------------------------|----------------------|------------------|---------------------|
| Brookville (Allegheny) | | | | | | | | | |
| 1231 | 3.3 | 47.1 (52.6) ^b | 42.4 (47.6) ^b | 7.2 | 30.22 (33.76) | 283 | 293 | 302 | 4.0 |
| 1237 | 3.2 | 41.6 (46.5) | 47.9 (53.5) | 7.3 | 29.67 (33.17) | 215 | 234 | 249 | 2.5 |
| 1239 | 3.4 | 42.8 (48.1) | 46.1 (51.9) | 7.7 | 29.28 (32.92) | 280 | 288 | 296 | 3.0 |
| Lower Kittanning (Allegheny) | | | | | | | | | |
| 1232 ₁ | 4.8 | 23.1 (51.2) | 22.1 (48.8) | 50.0 | 14.09 (31.18) | 288 | 300 | 308 | 0 |
| 1246 | 2.9 | 40.4 (47.9) | 45.6 (53.0) | 11.1 | 29.28 (34.05) | 254 | 266 | 276 | 4.0 |
| 1248 | 2.7 | 41.8 (46.4) | 48.4 (53.6) | 7.1 | 30.53 (33.85) | 214 | 221 | 226 | 4.5 |
| 1251 | 2.9 | 39.7 (45.2) | 48.0 (54.7) | 9.4 | 29.81 (34.02) | 275 | 285 | 299 | 5.0 |
| Middle Kittanning (Allegheny) | | | | | | | | | |
| 1236 | 3.5 | 39.7 (43.5) | 51.5 (56.5) | 5.3 | 30.75 (33.70) | 272 | 282 | 292 | 5.0 |
| 1240 | 3.1 | 37.7 (43.6) | 48.8 (56.4) | 10.4 | 29.35 (33.92) | 284 | 294 | 303 | 4.0 |
| 1245 | 3.6 | 41.2 (46.3) | 47.7 (53.7) | 7.5 | 30.10 (33.83) | 265 | 278 | 286 | 4.0 |

| | | | | | | | | | |
|-----------------------------------|-----|-------------|-------------|------|---------------|-----|-----|-----|-----|
| 1249 | 3.4 | 37.3 (43.3) | 48.8 (56.7) | 10.5 | 29.10 (33.82) | 275 | 284 | 294 | 3.5 |
| 1252 | 3.9 | 39.0 (44.1) | 49.5 (55.9) | 7.6 | 29.53 (33.37) | 274 | 282 | 291 | 2.5 |
| Lower Freeport (Allegheny) | | | | | | | | | |
| 1234 | 2.3 | 44.1 (51.1) | 42.2 (48.9) | 11.4 | 29.32 (33.98) | 216 | 229 | 238 | 3.5 |
| Upper Freeport (Allegheny) | | | | | | | | | |
| 1235 | 2.3 | 33.7 (45.2) | 40.9 (57.8) | 23.1 | 24.33 (32.60) | 269 | 279 | 286 | 1.5 |
| 1235 ₁ | 2.5 | 30.7 (43.9) | 39.3 (56.1) | 27.5 | 22.62 (32.35) | 262 | 272 | 281 | 0 |
| 1250 | 2.3 | 37.4 (46.7) | 42.8 (53.3) | 17.5 | 27.03 (33.73) | 243 | 253 | 263 | 4.5 |
| Tionesta (Pottsville) | | | | | | | | | |
| 1238 | 3.5 | 39.3 (46.9) | 44.5 (53.1) | 12.7 | 28.08 (33.52) | 215 | 223 | 230 | 4.0 |
| 1243 | 5.0 | 38.2 (43.2) | 50.2 (46.8) | 6.6 | 29.72 (33.65) | 283 | 301 | 308 | 1.5 |
| Harlem (Conemaugh) | | | | | | | | | |
| 1241 | 3.7 | 33.6 (39.7) | 51.1 (60.3) | 11.6 | 28.85 (34.09) | 290 | 298 | 305 | 4.5 |
| 1244 | 3.3 | 35.7 (41.0) | 51.2 (59.0) | 9.8 | 29.61 (34.06) | 234 | 249 | 262 | 4.0 |
| Ames (Conemaugh) | | | | | | | | | |
| 1242 | 2.8 | 43.1 (53.2) | 37.8 (46.8) | 16.3 | 27.71 (34.26) | 212 | 220 | 229 | 3.5 |

^a ASTM Rank: Bituminous high volatile A.

^b Numbers in parentheses are expressed on "daf" basis.

this study was to probe this aspect further on a suite of coal samples from Ohio and more specifically establish the effect of experimental variables (e.g. gas composition, heating rate, particle size) in influencing the pyrolysis mechanisms.

There appears to be much less frequent use of the TG technique for characterization of coal samples if one were to use the number of papers cited in the literature as a reliable measure [6,7]. This technique appears to lend itself as a rapid and convenient tool for screening and proximate analyses of coal samples [8]. The efficacy of non-isothermal TG analyses for these applications was examined in the present study for Ohio coal samples.

EXPERIMENTAL

A suite of twenty-one bituminous coal samples from Ohio were obtained from the U.S. Department of the Interior (Geological Survey), Reston, Virginia. Tables 1 and 2 summarize the sample location, proximate analyses, ultimate analyses and other relevant parameters for these samples. These analyses were performed by the U.S. Department of Energy Coal Analysis Laboratory in Pittsburgh, Pennsylvania. Prior to TG and DSC analyses to be described below, these samples were stored in sealed, air-tight bags. Small quantities of these samples were crushed to the desired particle size range on a mortar and pestle before transferring them to the DSC or TG assembly. Slight loss of volatile matter and pick-up of moisture were inevitable during this prior treatment. No systematic trends, however, were observed between the various particle size ranges in the TG scans (*vide infra*) which would suggest that such processes had occurred to a significant degree.

A DuPont 990 Thermal Analysis system* fitted with the accessory TG and DSC modules were used for the thermal analyses. A nominal sample size of 10–25 mg and a heating rate of $10^{\circ}\text{C min}^{-1}$ (unless otherwise stated) were employed for the measurements. In a typical TG or DSC experiment, the cell was initially purged with a high rate ($\sim 2000 \text{ cm}^3 \text{ min}^{-1}$) of ultra high purity N_2 to remove traces of O_2 . The samples were then loaded and the sweep gas flow rate was reduced to the nominal value of $\sim 500 \text{ cm}^3 \text{ min}^{-1}$. The heating program was then initiated at the desired rate, the upper temperature limit being $\sim 575^{\circ}\text{C}$ for DSC scans and $\sim 1100^{\circ}\text{C}$ for TG experiments. Aluminum sample pans were employed for DSC measurements and platinum boats for the TG scans. A thin layer of the sample was uniformly spread in either case to facilitate efficient contact with the sweep gas.

For proximate analyses by TG, the samples were initially heated in N_2 atmosphere to $\sim 1000^{\circ}\text{C}$. They were then cooled to ambient temperature and the cell was back-filled with O_2 . A subsequent scan to $\sim 700^{\circ}\text{C}$ resulted in combustion of the residual carbon, the cessation of this process being indicated by a plateau in the TG scan (*vide infra*).

* The use of a trade name or product does not imply endorsement by the authors or by the funding organization.

TABLE 2

Ultimate analyses on present coal samples

| Sample number | Element (wt.%) ^a | | | | |
|-------------------|-----------------------------|------|-----|-----|-------------------|
| | H | C | N | S | O (by difference) |
| 1231 | 6.2 | 78.6 | 1.9 | 3.3 | 10.1 |
| 1232 ₁ | 6.4 | 73.5 | 2.2 | 5.7 | 12.4 |
| 1234 | 6.1 | 78.9 | 2.2 | 4.5 | 8.3 |
| 1235 | 5.8 | 78.0 | 2.2 | 4.1 | 10.0 |
| 1235 ₁ | 5.8 | 78.2 | 2.0 | 3.2 | 10.8 |
| 1236 | 5.6 | 80.7 | 2.1 | 2.5 | 9.1 |
| 1237 | 5.7 | 78.6 | 1.9 | 3.2 | 10.6 |
| 1238 | 5.7 | 78.3 | 2.1 | 5.7 | 8.2 |
| 1239 | 5.9 | 78.6 | 1.8 | 2.7 | 11.1 |
| 1240 | 5.6 | 80.8 | 1.9 | 2.3 | 9.3 |
| 1241 | 5.6 | 82.2 | 2.1 | 0.6 | 9.3 |
| 1242 | 6.1 | 78.5 | 2.1 | 7.7 | 5.7 |
| 1243 | 5.6 | 80.2 | 2.1 | 1.3 | 10.7 |
| 1244 | 5.6 | 81.4 | 2.2 | 1.8 | 9.0 |
| 1245 | 5.7 | 80.1 | 2.0 | 3.1 | 9.1 |
| 1246 | 6.0 | 80.0 | 2.0 | 4.1 | 7.9 |
| 1248 | 5.6 | 79.1 | 1.9 | 5.7 | 7.7 |
| 1249 | 5.7 | 80.8 | 1.9 | 2.5 | 9.2 |
| 1250 | 5.7 | 79.5 | 1.8 | 4.1 | 8.8 |
| 1251 | 5.7 | 80.1 | 2.0 | 2.6 | 9.6 |
| 1252 | 5.6 | 79.7 | 2.0 | 2.4 | 10.3 |

^a daf basis.

RESULTS AND DISCUSSION

DSC

Figure 1 illustrates representative DSC scans on Ohio coal samples. Essentially similar behavior was noted for all the other samples examined in the present study, the only difference being the intensity of the 400–500°C peak (marked "B" in Fig. 1) and minor variations in the extent to which other peaks (denoted by "A" and "C" respectively in the figure) were accentuated in the thermograms. An important conclusion that one can immediately draw from these data, however, is that the thermal behavior is completely *endothermic*, confirming the conclusions reached by previous authors on bituminous coals [5]. We note here that these authors report *exothermic* effects for sub-bituminous and lignitic coals [5]. This result suggests that the DSC technique may be an effective indicator of coal rank (by way of contrast, the earlier DTA studies have yielded rather conflicting results, cf., refs. 2 and 3).

Broadly, three regions of endothermic activity may be distinguished in the DSC scans: a first dehydration peak in the range from ambient to ~150°C; a second, very broad endotherm (sometimes exhibiting fine structure) which spans the range

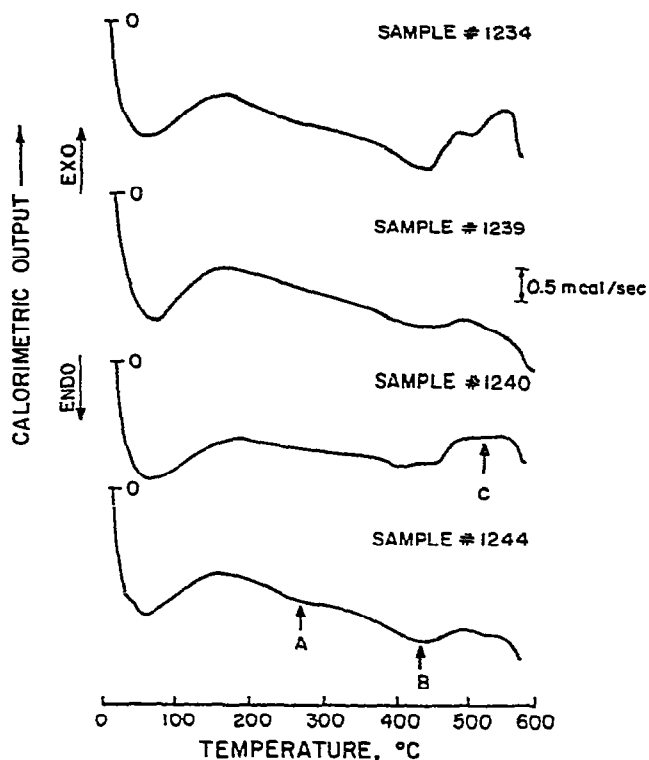


Fig. 1. Representative DSC scans on selected Ohio bituminous coals. Heating rate: $10^{\circ}\text{C min}^{-1}$; atmosphere: dry, ultrapure N_2 . Sample in open pan.

1500°C and culminates in a noticeable peak between 400 and 500°C ; and a final, sharper endotherm at temperatures $\geq \sim 550^{\circ}\text{C}$, a major portion of which is lost (cf. Fig. 1) because of the temperature capabilities of the present DSC cell. This process, however, is nicely resolved in the TG scans, particularly at low heating rates (vide infra).

That the first endotherm corresponds to loss of moisture from the coal is clearly shown by the fact that the peak is greatly attenuated in a subsequent scan after preliminary heating of the sample at $\sim 110^{\circ}\text{C}$ for 30 min in the DSC cell. The broad activity in the range 150 – 500°C undoubtedly corresponds to pyrolytic fragmentation of the carbon skeletal structure in coal with the final endotherm at temperatures above 550°C (and probably also the peak marked "C" in Fig. 1) to be attributed to cracking reactions of the products evolved in the pyrolysis process (vide infra).

The net area of the endotherm in the region 150 – 500°C should be directly related to the volatile matter content of the coal. The data illustrated in Fig. 2, however, show that this correlation is not straight forward. Figure 2a shows the relationship for the volatile matter content expressed on daf basis. The data scatter is significant although there is much better correlation when the normalized peak areas are plotted

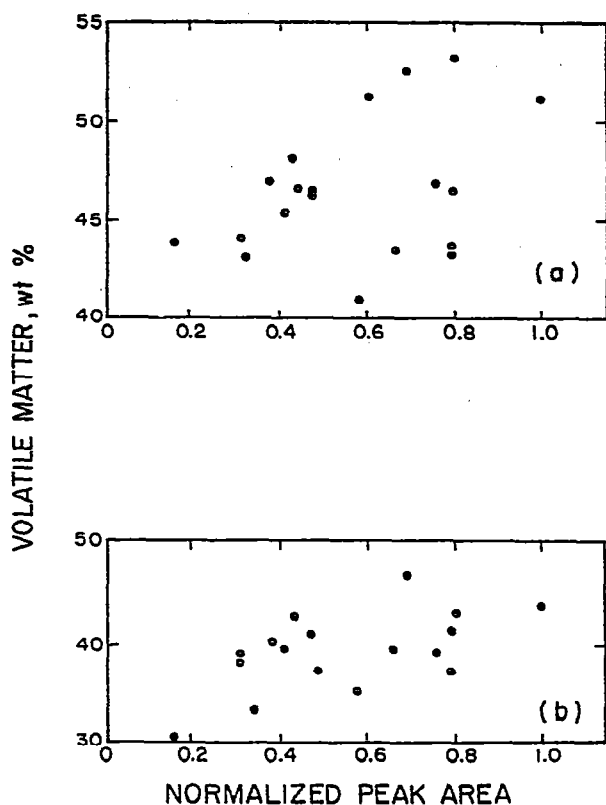


Fig. 2. Correlation of normalized DSC endotherm areas (150–550°C, cf., Fig. 1) with volatile matter for the coal samples listed in Tables 1 and 2. The data in (a) and (b) refer to volatile matter "as received" and expressed on daf basis, respectively. The peak areas were measured for samples in open pan and at a heating rate of $10^{\circ}\text{C min}^{-1}$.

versus the weight percent of the volatiles without correction for the ash and moisture content (Fig. 2b). Obviously, DSC data must be used with caution for quantification of volatile matter content. On the other hand, TG yields more reliable data for this purpose on the same set of samples (*vide infra*). The variation in the DSC baseline induced by loss of volatile matter (cf., ref. 5) cannot account for the data scatter in Fig. 2 since the use of the correction procedure outlined by previous authors [5] did not improve the correlation to a significant extent.

The sensitivity of the DSC response to ambient atmosphere and sample containment is illustrated by the data shown in Fig. 3. Figure 3a shows a typical scan for the sample in an open pan and Fig. 3b, the corresponding data for an identical sample in a sealed pan. The upward shift ($\sim 20^{\circ}\text{C}$) in the first endotherm for the sealed pan case (compare Figs. 3a and b) is consistent with the behavior observed for dehydration processes [9] and furthermore confirms the above assignment for the origin of this peak. The pyrolysis seems to, however, occur at a faster rate in the presence of a self-generating atmosphere as evidenced by a downward shift in the 150–500°C endotherm in the sealed-pan case. This points towards a catalytic effect induced by

contact of the evolved gases with the pyrolyzing sample. Autocatalytic effects have been invoked for the pyrolysis of oil shale [10]. There is therefore precedence for the behavior observed in the present case (Fig. 3) although further work is clearly needed to verify the mechanistic aspects.

The extreme sensitivity of the thermal behavior of coal to ambient atmosphere is illustrated by the data shown in Fig. 3c. In this case, a small amount of O₂ (~1%) was bled into the purge gas stream in the DSC cell. The endothermic behavior observed in the previous case (Fig. 3a) reverts to a broad exothermic peak arising from combustion of the organic matter. Similar behavior, although to a less marked degree, is also observed when N₂ sweep gas of industrial grade purity was used. These data underscore the influence of experimental variables on the nature of thermal effects observed in coal.

Two other variables that were investigated, namely heating rate (5–50°C min⁻¹) and particle size (range from -10 to +16 U.S. standard mesh to -250 + 300 U.S. standard mesh) had relatively minor effects on the DSC thermograms for the present coal samples.

TG

Figure 4 shows a representative TG scan illustrating its utility for proximate analyses of coal. The data extracted from such scans are assembled in Table 3 for selected coal samples. These data agree within limits of experimental error with those determined by the ASTM method (cf., Table 1). Again particle size changes did not result in systematic changes in the weight loss plateau corresponding to the

TABLE 3

Thermal analysis data ^a on selected coal samples

| Parameters | Sample number | | | | | |
|--|----------------|----------------|-----------------------|-------------------|------|----------|
| | 1231 | | | 1232 ₁ | | |
| | A ^b | B ^c | Reported ^d | A | B | Reported |
| Volatiles + moisture (wt.%) ^e | 45.5 | 45.5 | 50.4 | 30.0 | 28.5 | 27.9 |
| Fixed carbon (wt.%) ^e | 47.0 | 48.5 | 42.4 | 23.0 | 29.5 | 22.1 |
| Ash (wt.%) ^e | 7.5 | 6.0 | 7.2 | 47.0 | 42.0 | 50.0 |
| DSC peak temp ^f | 449 | 449 | 449 | ill-defined | | |
| DTG peak temp ^f (°C) | 445 | 445 | 445 | 460 | 460 | 460 |

^a Heating Rate: 10°C min⁻¹.

^b Particle Size: -250 + 300 mesh.

^c Particle Size: -10 + 16 mesh.

moisture/volatile matter and fixed carbon/ash regimes (cf., Table 3).

Figure 5 shows the fractional weight loss, α for the pyrolysis reaction plotted as a function of temperature with heating rate as the variable parameter. The initial weight loss corresponding to moisture evolution was subtracted out and the α values were computed at each temperature from the expression

$$\alpha = (w_0 - w_t) / (w_0 - w_f) \quad (1)$$

where w_0 = initial mass of dry sample, w_t = mass of sample at temperature T and w_f = final mass remaining after loss of volatile matter. At heating rates $\leq 5^\circ\text{C min}^{-1}$, a second, gradual weight-loss region spanning the temperature range from $\sim 500^\circ\text{C}$ to 1000°C becomes more pronounced. This process corresponds to the endothermic activity noted in the DSC scans at temperatures above $\sim 550^\circ\text{C}$ (*vide* Fig. 1 and the accompanying discussion above). The much longer residence times for the exiting gases at the lower heating rates would result in the preponderance of cracking and coking processes which are expected to occur at temperatures up to $\sim 1000^\circ\text{C}$.

The rates of the pyrolytic reaction at the various heating rates are plotted in Fig. 6. These derivative TG plots were constructed from data such as those shown in Fig. 5. The systematic shift in the $d\alpha/dT$ peaks to higher temperatures with increasing heating rate (see inset in Fig. 5) reflects the thermal lag induced by limitations in the rate of supply of heat to the pyrolyzing samples. The extrapolated temperature corresponding to the "true" isothermal pyrolysis point is 406°C for this particular sample.

In conclusion, thermal effects in Ohio bituminous coals are endothermic in nature as long as O_2 is rigorously excluded from the vicinity of the pyrolyzing samples. The endothermic peak areas show a reasonable correlation with the "as-received" volatile

| 1235 ₁ | | | 1242 | | | 1244 | | |
|-------------------|------|----------|------|------|----------|------|-----|----------|
| A | B | Reported | A | B | Reported | A | B | Reported |
| 32.5 | 36.3 | 33.2 | 44.5 | 41.0 | 45.9 | 33.0 | — | 39.0 |
| 40.0 | 41.5 | 39.3 | 41.5 | 44.0 | 37.8 | 54.5 | — | 51.2 |
| 27.5 | 22.3 | 27.5 | 14.0 | 14.0 | 16.3 | 12.0 | — | 9.8 |
| 479 | 479 | 479 | 432 | 432 | 432 | 449 | 449 | 449 |
| 450 | 450 | 450 | 448 | 448 | 448 | 442 | 442 | 442 |

^d See Table 1.

^e As received.

^f Nominal error: $\pm 2^\circ\text{C}$.

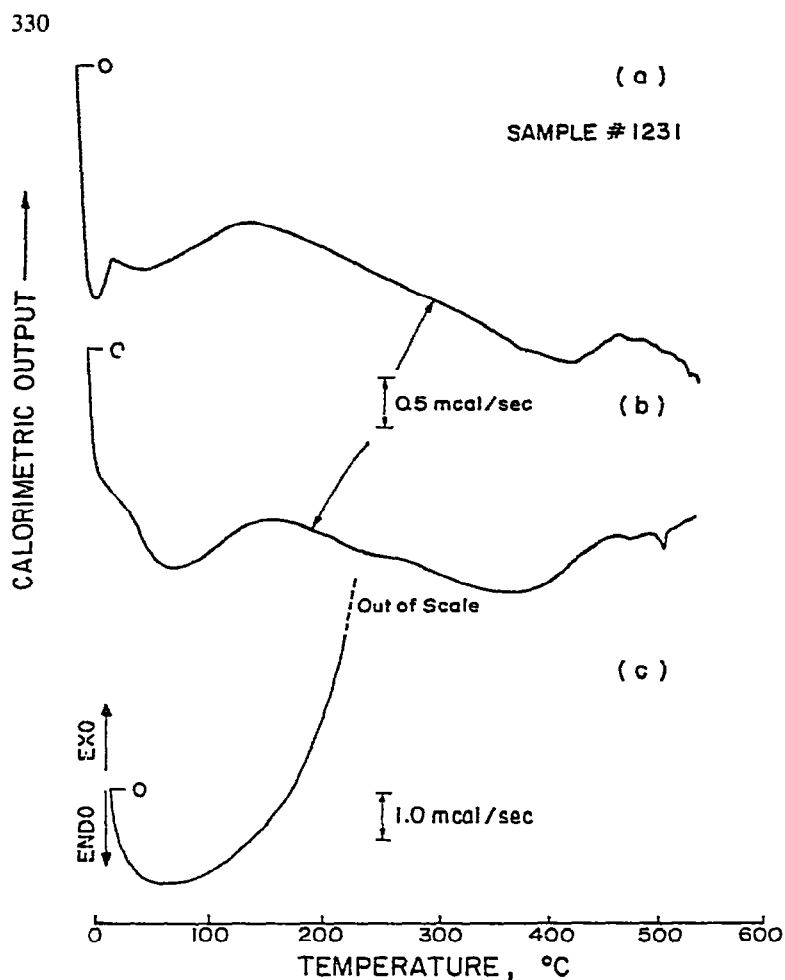


Fig. 3. Influence of ambient atmosphere and sample containment on DSC thermograms for representative coal sample no. 1231. The data in (a) and (b) were obtained with open and sealed pans respectively in N_2 atmosphere. The scan in Fig. 3(c) was obtained with open pans exposed to 1% O_2/N_2 gas mixture. Heating rate: $10^\circ C \text{ min}^{-1}$.

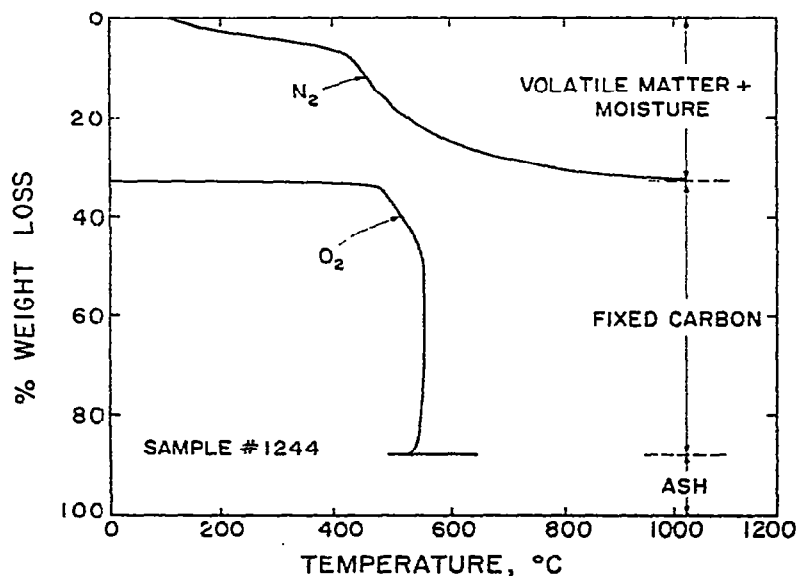


Fig. 4. A typical non-isothermal TG (heating rate: $10^\circ C \text{ min}^{-1}$) scan on Ohio coal (sample no. 1244). The initial sample mass was 22.14 mg in this experiment.

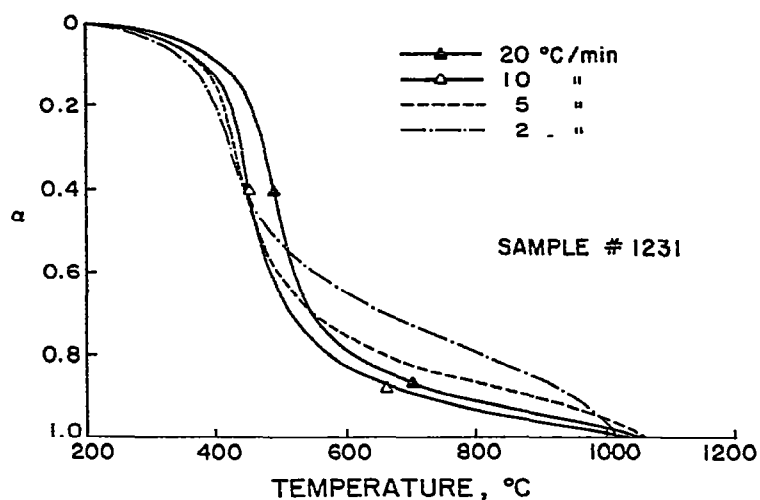


Fig. 5. Normalized fractional weight-loss vs. temperature curves (see text) for a representative Ohio coal sample. Heating rate is shown as the parameter.

matter content of the coal. More reliable estimates of this parameter (which is a direct measure of the "energy richness" of the coal sample) are provided by TG measurements. Proximate analyses as determined by TG show good agreement with

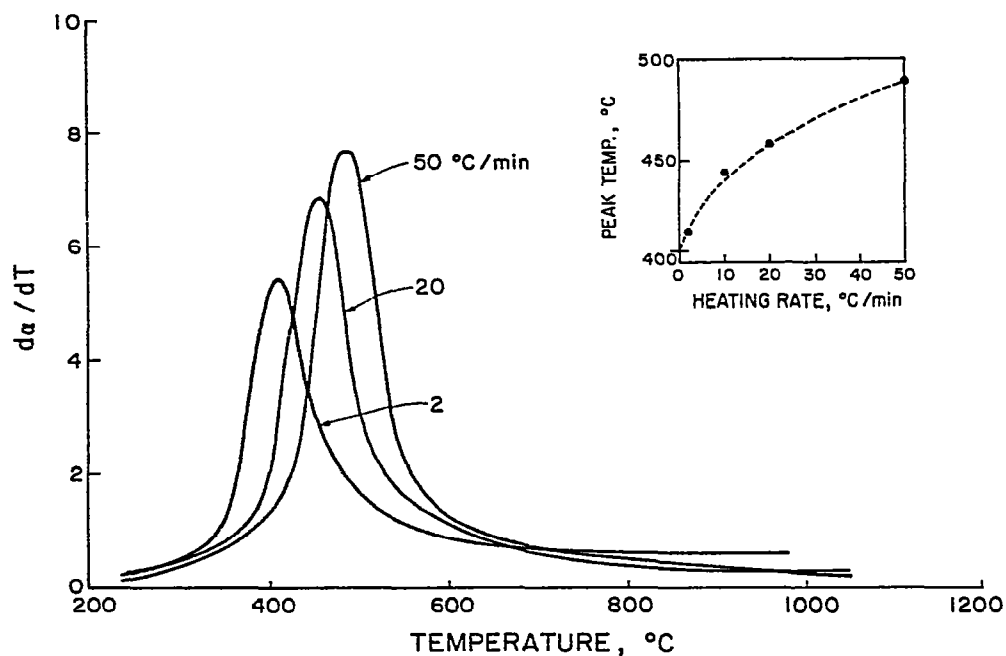


Fig. 6. Derivative TG vs. temperature plots for the data in Fig. 5. Only three heating rates are shown for clarity. Inset: Variation of DTG peak temperature with heating rate for sample 1231.

ASTM values. TG scans at low heating rates ($\leq 5^{\circ}\text{C min}^{-1}$) are able to resolve multiple processes in the overall pyrolysis reaction.

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