HEAT CAPACITIES OF ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

The thermal effects on coal have been the subject of numerous investigations dating back to the 1890's. (1) Many techniques have been used to study thermal effects, including differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis. DTA and DSC studies of coals by different researchers yield conflicting information (2-5). Numerous heat capacity determination (6-11) have been done on coals over the years. However in these investigations no particular care was taken to check the effects of "weathering" on the measured parameters. A number of the coals investigated were the same as those which are part of the Argonne Premium Coal sample series.

In this communication we report the results of recent DSC investigations on the Argonne Premium Coal Sample series. In these experiments care was taken to correlate the heat capacity with the thermal history of the specimens.

EXPERIMENTAL PROCEDURE

Differential scanning calorimetry was used to determine the response of coal samples to heating. Heating rates of 10K/min. were used. Sample sizes were of the order of 10 to 15 milligrams. Temperatures for the measurements ranged from 100K to 700K. All experiments were done under flowing nitrogen (1 stp l/min.), and the exposure of the samples to the ambient environment was limited to less than two minutes. The heat flow curves were obtained while maintaining constant experimental conditions. The uncertainity in the reproducibility of the data is estimated at one percent. Heat capacities were calculated from the heat flow curves, using sapphire as a standard for comparison. The error in the derived heat capacities is estimated at two percent.

RESULTS AND DISCUSSION

Coal is a complex mixture of organic matter, inorganic matter and water. The usual way of correlating the coal heat capacity data as a function of temperature is to follow Kirov's (6) procedure of expressing the total heat capacity as a weighted sum of the heat capacities of fixed carbon, volatile organic matter, ash and water. Implicit in Kirov's method are the assumptions that these components do not interact, and up to the pyrolysis temperature, the coal does not undergo either a chemical reaction or a structural rearrangement. However, there are a number of experimental findings which bring these assumptions into question.

Mraw (12) has measured the heat capacities of coals as a function of water content and found that one must consider the water associated with a

coal to be composed of two types: freezable water, which forms a liquid layer adsorbed on the coal and nonfreezable water which resides in the form of molecular clusters in the pore structure of the coal. The nonfreezable water contributes an excess low temperature heat capacity to the coal due to the onset of rotational and vibrational motions of the clusters inside the pores.

Measurement of coal char heat capacities (13) and of coal ashes (14) indicate that the heat capacity of the char is not a weight-average sum of the ash free char heat capacity and of the ash heat capacity. Thus, there is additional evidence that Kirov's correlation method must be reconsidered. Furthermore, as noted in the introduction, many coals undergo both endothermic and exothermic reactions at temperatures prior to the onset of pyrolysis breakdown. Therefore, it is even questionable that a meaningful heat capacity can be assigned to a coal at temperatures past the onset of reactions accompanied by thermal effects.

In Figure 1, the heat absorption rate (kJ $kg^{-1}sec^{-1}$), $\dot{Q}$, for the Wyoming Sub-bituminous coal is shown as a function of temperature. These data are derived from the heat flow curves for a given sample by dividing the heat flow (milliwatts) versus temperature curves by the weight of the residual sample at the maximum temperature of a given run. The particular features of the figure to be noted are:

* An endothermic peak at low temperatures due to the "pore" water present;

* Melting and evaporation of the "freezable" water extending over a wide temperature range. This endotherm would mask any other endotherm occurring in the same temperature range;

* Start of an exotherm around 400K;

* An endothermic reaction between 575K and 675K.

In the above context endothermic and exothermic are defined as heat absorption relative to that which would be calculated from the heat capacity versus temperature curve for a non-reactive sample. Such an absorption curve is indicated on the figure.

By repeating the heating curve for the same sample we note the disappearance of the endothermic peaks associated with water desorption and the reduction and eventual disappearance of the high temperature endotherm. The exotherm also decreases in magnitude, at a given temperature with recycling. The sample loses weight on heating. The total weight loss is 55% of the starting weight. The major portion (40-48% of starting weight) of the weight loss is due to the removal of water.

In Figure 2 we show the heat absorption rate versus temperature data for a sample of the Pittsburgh #8 High Volatile-bituminous coal. This coal has much less water. The total weight loss of 3% is almost totally due to water loss. Inspection of Figure 2 shows the existence of a low temperature endotherm starting at 300K. This endotherm persists after the removal of the water and blends smoothly into the exotherm starting about 400K.

Even stronger evidence for the existence of a low temperature, nonwater-related endotherm preceding the exotherm is seen in Figure 3 for the Pocahontas #3 Low Volatile-bituminous coal. For this coal there is no weight loss observed, but a well defined endotherm is seen starting at 300K.

It is our belief that the low-temperature endotherm followed by exothermic behavior is associated with a free-radical polymerization reaction in the coal. Petrakis and Grandy (15) have reported that a substantial number of free radicals are present in coal heated between 375 and 700K. We feel that the 300K to 400K endotherm is associated with free-radical formation. The recombination of the free radicals is sufficiently exothermic that the overall behavior is exothermic above 400K. The overall reaction is rather slow and does not approach completion in the time span of the experiment.

The high temperature endotherm could be due to either the softening of the partially reacted coal and/or to bond-breaking reactions in the unreacted coal. Previous studies (16) have shown that the reaction is reversible as long as the material is kept below 630K. Hydrogen bond-breakage has been postulated (4) as a source of this endotherm. However, additional free-radical formation can not be ruled out. If the coal is pretreated in flowing steam at around 610K it yields more volatile products during steam pyrolysis at high temperatures (17). But if the pretreated coal is exposed to air (O_2) even for a few minutes the steam pyrolysis yield of the coal reduces to levels below that of untreated coal.

The heat absorption curves of the other coals are qualitatively similar to those shown. The major differences between the coals, are due to the difference in water content, the progressive reduction in the magnitude of the exotherm at a given temperature as the rank (carbon content) of the coal increases.

Heat capacity data can be extracted from the heat absorption rate curves using the relation:

$$C_p(T) = \dot{Q}(T)/\dot{T}(T) \qquad 1)$$

where $C_p(T)$ is the heat capacity in $kJkg^{-1}K^{-1}$ at a given temperature and $\dot{T}(T)$ is the actual (determined) heating rate at the same temperature.
In our experiments $\dot{T}(T)$ is nominally 0.1667 K/sec. However, for each experiment the actual heating rate was determined by running the heat absorption rate curve for a sapphire standard under the same exact experimental conditions as those for the sample runs.

The heat capacities were calculated based on the assumption that up to 270K there is no weight loss on heating. The heat capacities above 300K were calculated by extrapolating the heat absorption rate curves which would have been obtained in the absence of heat absorbing or heat releasing reactions. The calculated heat capacities are shown in Figure 4 and are also tabulated in Table 1.

There was no general trend with coal rank observable in the heat capacities. This was not, surprising since the heat capacity was not

separated into contributions due to the organic, inorganic and water components.

At the present time (May 1987) work is still in progress to complete the data for the rest of the Argonne Premium Coal Sample series, to prepare and measure ash heat capacities, and to investigate the effect of accelerated weathering on the heat absorption rates and on the heat capacities.

Table 1. Heat Capacity ($kJkg^{-1}K^{-1}$) of Argonne Premium Coals

Temp(K)	Wyoming Sub-bit	Illinois #6 HV-bit	Blind Canyon HV-bit	Pittsburgh #8 HV-bit	PA-Up.Freeport MV-bit	Pocah. #3 LV-bit
100	0.179	0.325	0.485	0.410	0.396	0.256
125	0.307	0.466	0.660	0.574	0.605	0.762
150	0.503	0.584	.815	0.683	0.667	0.969
175	0.727	0.760	0.902	0.800	0.698	1.137
200	0.973	0.958	1.001	0.956	0.799	1.241
225	1.312	1.251	1.121	1.103	0.882	1.270
250	1.841	1.515	1.159	1.169	0.970	1.333
275	1.771	1.481	1.206	1.228	1.075	1.348
300	1.415	1.277	1.252	1.281	1.156	1.355
325	1.244	1.167	1.219	1.364	1.070	1.390
350	1.307	1.237	1.267	1.409	1.205	1.411
375	1.355	1.270	1.332	1.459	1.265	1.432
400	1.389	1.317	1.351	1.500	1.315	1.453
450	1.463	1.363	1.423	1.573	1.385	1.480
500	1.507	1.422	1.494	1.646	1.450	1.508
550	1.559	1.443	1.538	1.701	1.486	1.522
600	1.576	1.467	1.577	1.756	1.534	1.536
650	1.608	1.511	1.618	1.792	1.548	1.543
700	1.609	1.514	1.650	1.828	1.586	1.550

ACKNOWLEDGEMENT

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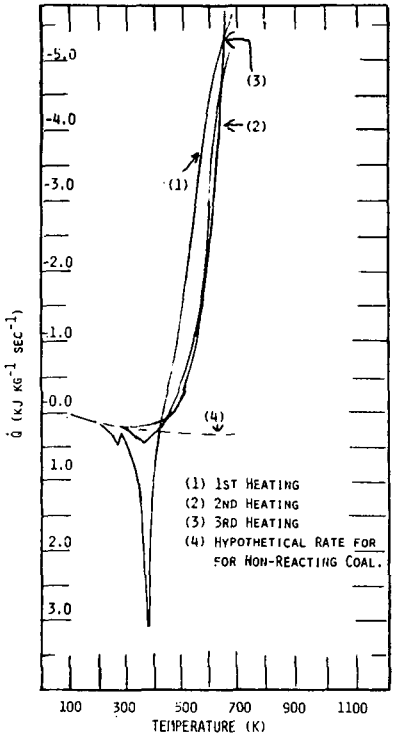

FIGURE 1. WYOMING SUB-BITUMINOUS COAL; HEAT ABSORPTION RATE.

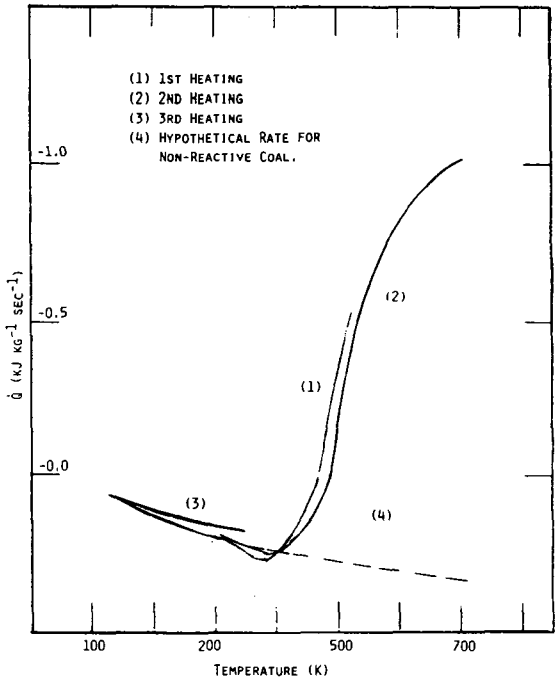

FIGURE 2. PITTSBURGH #8 COAL; HEAT ABSORPTION RATE.

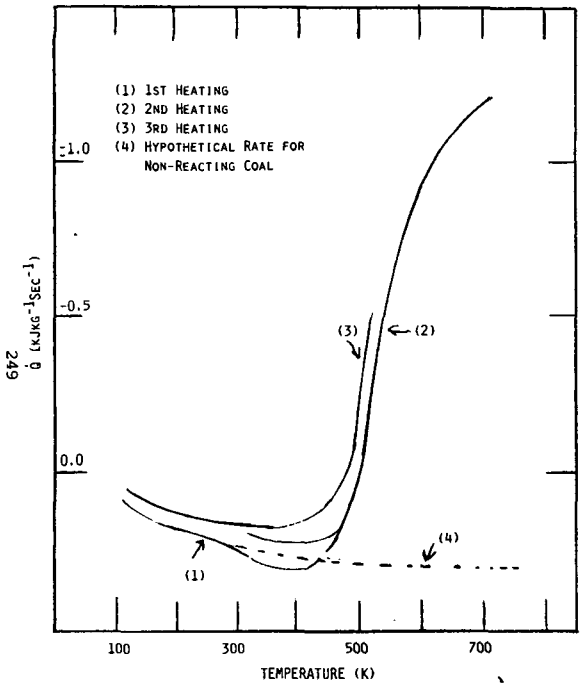

FIGURE 3. POCAHONTAS #3 COAL; HEAT ABSORPTION RATE.

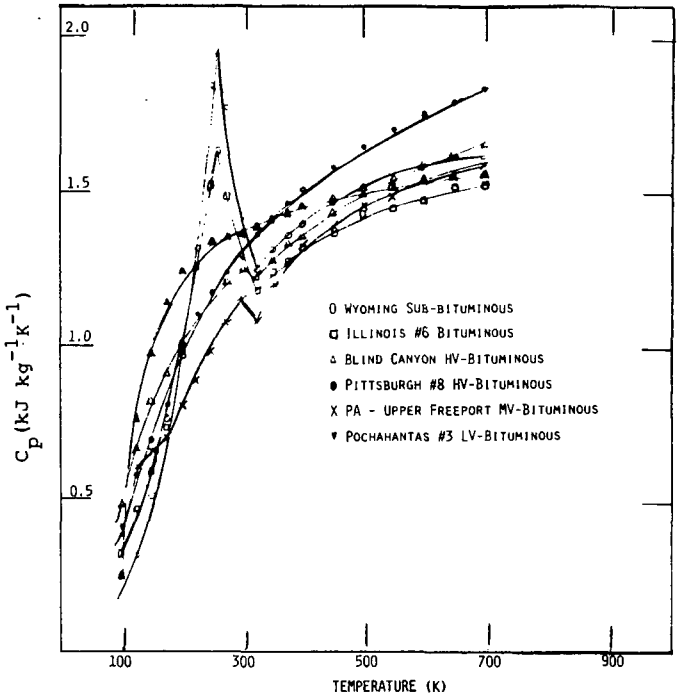

FIGURE 4. HEAT CAPACITY OF ARGONNE PREMIUM COALS.