

ENTHALPIES OF DESORPTION OF WATER FROM COAL SURFACES

J.E. Callanan, B.J. Filla, K.M. McDermott and S.A. Sullivan

Center for Chemical Engineering, National Bureau of Standards*
Boulder, CO 80303

Introduction

During our efforts to develop transferable techniques for the measurement of the heat capacity of coal and to develop a model that would facilitate the prediction of the thermal properties of coal, several series of measurements of the heat capacity of a single coal were made. Changes in thermal properties which appear to be related to weathering of the coal and to its inherent moisture content were observed. This paper deals with two facets of the interaction of moisture with coal surfaces, that are related to our study of these changes.

The first was the observation of significant qualitative and quantitative differences in the initial heat capacity scans as the coal under study became more oxidized (1,2). Particularly significant was the progressive development of an exotherm. As the projected heat balance of any process would be seriously affected by an unanticipated generation of heat, it is important to determine the magnitude of the enthalpy.

Second, our adaptation of a model which permits the prediction of the heat capacity of coal from parameters such as heating rate, ultimate analysis, and moisture content (3) requires a value for the heat of vaporization of water. Since the water interacted with the coal surface, it was not clear that the most suitable value was in fact an enthalpy of vaporization. We wished to determine the energy involved in removing water from the coal experimentally, whatever the nature of the process might be.

This paper describes the measurements and data reduction techniques used to evaluate the energy difference between initial and subsequent runs, a simple technique developed for heat of desorption measurements, and presents results obtained with both procedures.

Experimental

Materials

Two different coals were used for these studies. The first was a high-volatile bituminous coal (PSOC-854), obtained from the Coal Sample Bank at Pennsylvania State University. The second, a premium medium-volatile bituminous coal, was obtained from the Premium Coal Sample Bank at Argonne National Laboratories (4).

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Procedures - heat capacity measurements

Specimen preparation followed our established procedures (5). All preparation was done in a controlled atmosphere, either in a controlled-atmosphere chamber for the specimens sealed in nitrogen (6), or in a glove bag for specimens sealed in argon, helium and carbon monoxide. Representative fractions, obtained by riffing, were heated to 383 K in a stream of dry nitrogen and dried to constant weight. The specimens were pelletized before sealing. Pellet masses, accurate to 0.05 μg , varied from 5.33-21.53 mg. The temperatures are accurate to 0.1 K.

Heat capacity measurements were made with a scanning calorimeter at 5 K/min from 300-520 K. Calorimetry Conference sapphire was used as a standard (7). The running order for the measurements was empty, standard, coal 1, coal 1 repeat, standard, etc. The specimen mass was determined before the initial scan; following each scan of coal, the specimen was cooled and reweighed. The measurements, in air, made early in our development of recommended procedures, involved slightly different running procedures.

Data analysis - heat capacity and enthalpy

A fitting program was applied to the heat capacity data using algorithms developed in these laboratories. For each pair of fitted data, e.g., argon and repeat argon, the area between the curves was determined by numerical integration. This area corresponds to the enthalpy difference between the initial and repeat runs.

Procedures - enthalpy of desorption

The specimens used for the enthalpy of desorption measurements were equilibrated with water in atmospheres of the desired humidity, weighed and transferred quickly to the calorimeter. The calorimeter temperature was set initially a few degrees above the melting point of water. An enthalpic measurement technique was used (8,9). This technique for scanning calorimetric measurements of heat capacities and enthalpies measures the total enthalpy in a step change in temperature. Division by the temperature change gives the heat capacity at the midpoint of the temperature step. The temperature was raised rapidly to the desired final temperature and held constant for an hour; data were taken until the trace returned to the baseline. The repeat scan followed the initial scan immediately, without intermediate weighing. The mass loss, determined by weighing after the repeat run, was used to calculate the enthalpy. We had observed in other studies that mass losses rarely occurred in scans subsequent to the initial scan.

Data analysis - enthalpy of desorption

In the determination of the enthalpy using this procedure, the repeat scan, (for the dry coal) was used as the baseline in the determination of the heat input required by the moist coal (initial scan). The subtraction of the dry coal scan from that for the moist coal yielded a heat input versus time plot, from which the enthalpy of desorption could be determined. The enthalpy was obtained by integrating heat input versus time and dividing by the mass loss of the specimen. Fig. 1 represents a typical plot for the endothermic desorption of water from moist coal at temperatures around 400 K. At higher temperatures (400-500 K), the

coal exhibits the exotherm illustrated in Fig. 2.

Results

Enthalpy differences

The results presented for the enthalpy differences are based on studies on PSOC-854 made over a period of three years and on an initial study of the premium coal. Fig. 3 is a composite of the fitted heat capacity data from each of these studies. The A specimens were prepared and sealed in air; the B, C, and premium specimens were prepared and sealed in nitrogen. The exotherm is apparent in each of the PSOC-854 initial scans; it is not observed in the initial scan of the premium coal. The enthalpy difference between initial and repeat scans for each pair is given in Table 1.

A comparison of heat capacity data from specimens sealed in different atmospheres is given in Fig. 4. The heat capacity of the coal sealed in air is lower than the others. Values obtained in helium are highest. As the heat capacity of the specimens sealed in argon is similar to that for specimens sealed in carbon monoxide and nitrogen, the latter are omitted from Fig. 2. The enthalpy differences for the data obtained in various atmospheres are included in Table 1 also. As we were not aware of the exotherm in the initial studies (in air), the curves used for air were not obtained with the same running sequence as the other data: The scan used as the initial run was made approximately one year after the repeat run depicted. Thus the figure given in Table 1 for the enthalpy difference in air is influenced both by the varying oxidation levels of the specimens and by the effect of the different atmosphere. Because of the difficulty in comparing this with the other enthalpies, this figure is given in parentheses.

Heat of desorption

Representative data obtained using the methods described here for determining heats of desorption are presented in Table 2. The values are slightly higher than the isosteric heats of desorption reported by Allardice and Evans for Yallourn brown coals (10). The heat of vaporization of water as a real gas is 2.26 kJ/g at atmospheric pressure (11). The scatter in the data was less than 10 percent. A further study of repeated desorption and adsorption from the coal surface, not discussed in detail here, showed comparable precision. We have also applied the method described here to water-calcium sulfate and water-molecular sieve systems successfully.

References

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TABLE 1 : $\Delta HI - \Delta HR$ VALUES FOR SEVERAL COALS

YEAR OF STUDY	SPECIMEN FIGURE REF.	ATMOSPHERE	$\Delta HI - \Delta HR$ (J/g K)
1983	A	AIR	(60)
1984	B	N ₂	18
1985	C	N ₂	34
1986	PREM	N ₂	6
1985	ARGON	AR	37
1985	HELIUM	HE	29

TABLE 2 : DSC COAL-MOISTURE DESORPTION DATA

RUN #	TEMP. RANGE (K)	SAMP.MASS (mg.)	% WT. LOSS	ENTHALPY (kJ/g)
CLW04	273-400	11.519	6.41	3.22
CLW05	273-400	10.952	6.15	3.32
CLW06	273-370	11.207	6.82	3.14
CLW07	273-370	14.304	6.01	2.79
CLW08	273-430	14.393	6.91	4.91
CLW09	273-430	11.508	6.21	4.30

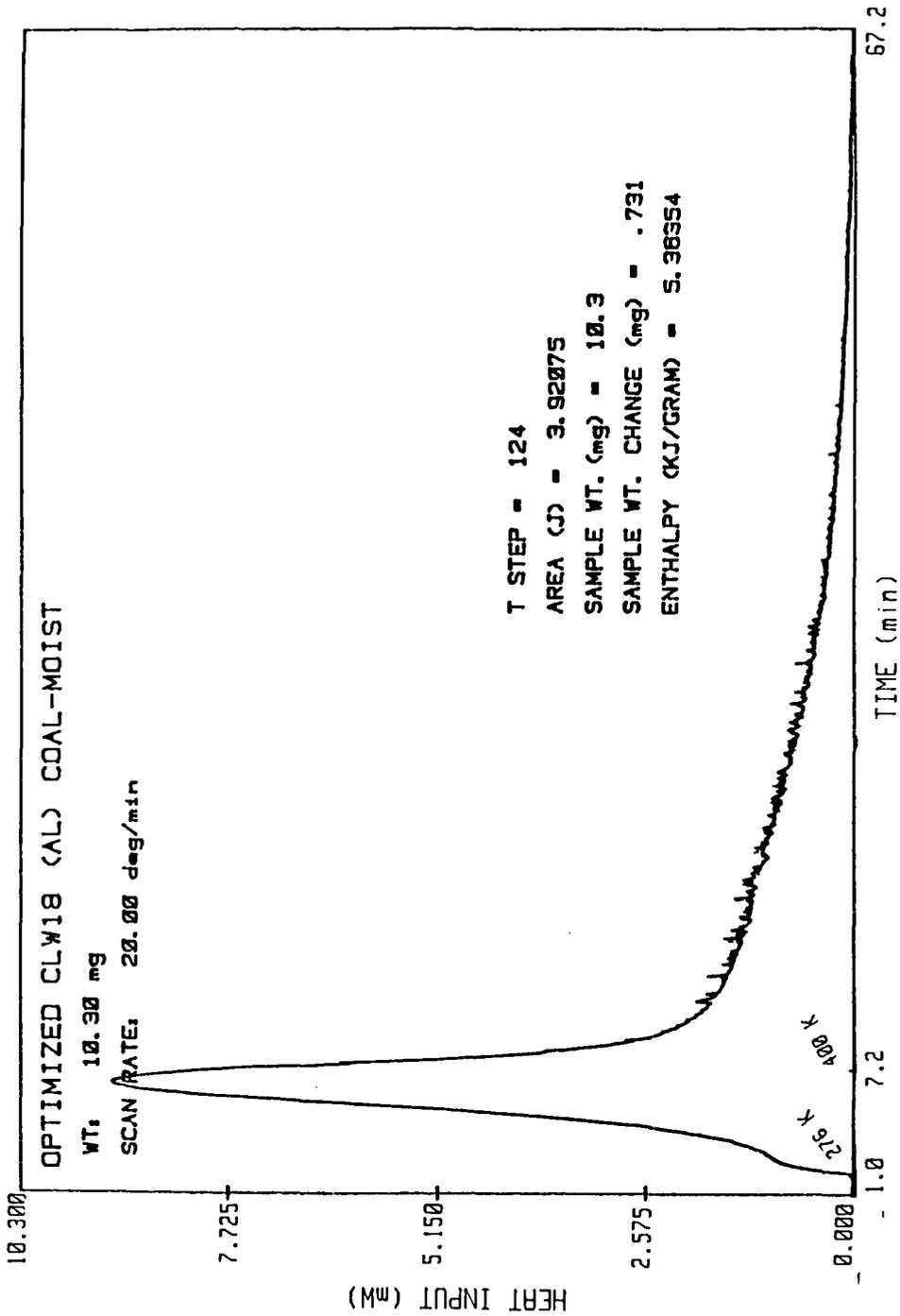


Fig. 1. Moisture desorption plot of PSOC-854 coal equilibrated in 70% relative humidity air at 295 K.

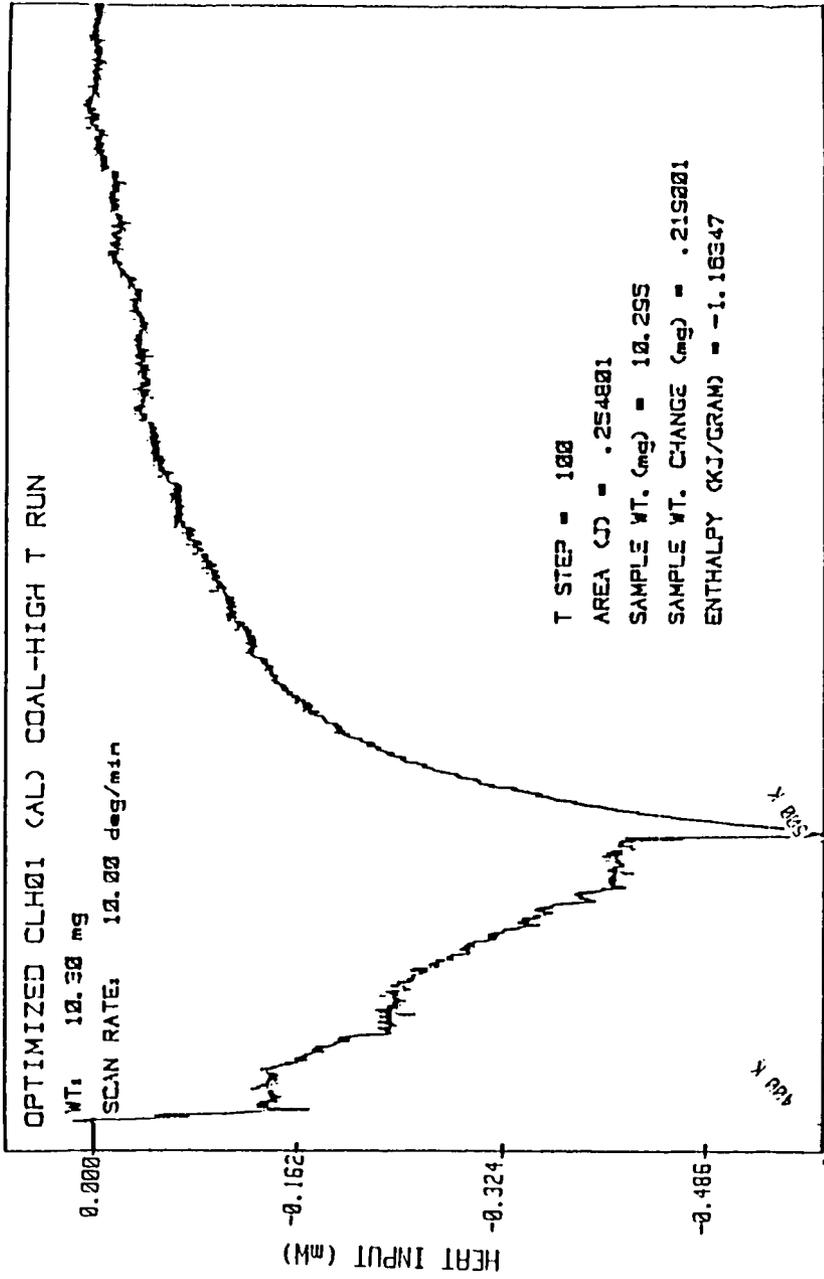


Fig. 2. Moisture desorption exotherm of PSOC-854 coal after drying to constant weight at 400 K.

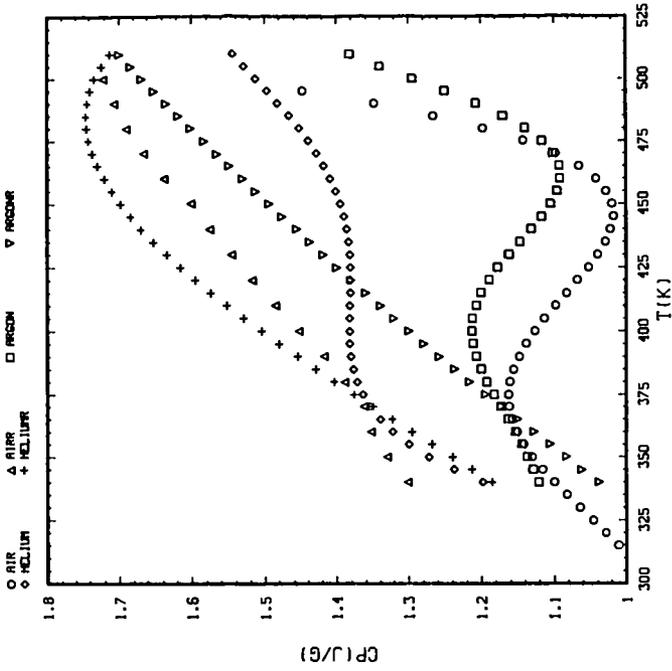


Fig. 4. Heat capacities of PSOC-854 in various atmospheres. The R after the designation of the gas denotes a repeat run.

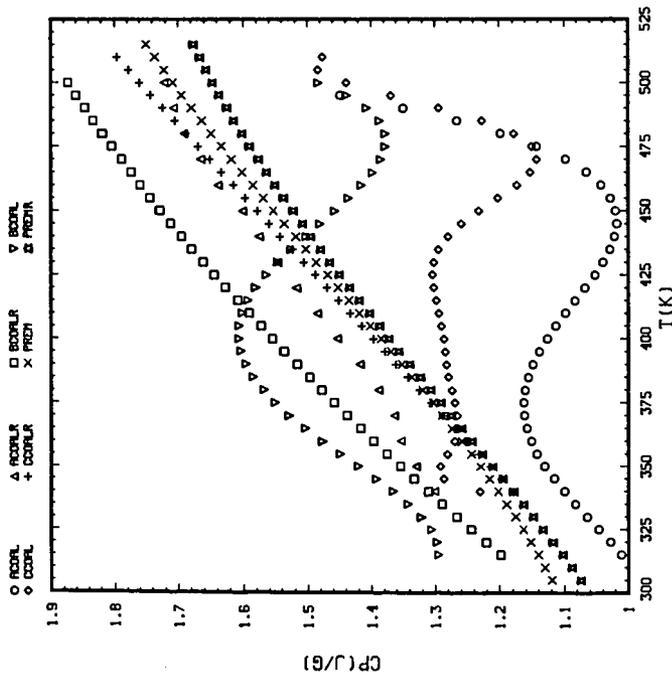


Fig. 3. Heat capacities of coals as a function of increased oxidation. PSOC-854: ACOAL, 1983; BCOAL, 1984; CCOAL, 1985. Prem, premium coal. The R after the designation of the gas in the legend denotes a repeat run.