International Journal of Thermophysics, Vol. 8, No. 1, 1987

Experimental Determination and Modeling of the Heat Capacity of Coal in Various Atmospheres

J. E. Callanan,[1] S. A. Sullivan,[1] and R. A. MacDonald[2]

Received February 3, 1986

During the development of transferable measurement techniques for the heat capacity of raw coal, it was observed that the atmosphere in sealed sample cells affected the thermal behavior, particularly during the initial measurements. The model which had been used to represent the specific heat of coal did reproduce the results in air but failed to reproduce the deep exotherm of the thermograms obtained in nitrogen. The specific heat of coal has been determined in helium, argon, and carbon monoxide to provide insight into possible modifications to the model. The results of initial and repeat runs in the five different atmospheres and the impact of these results on the modeling are presented and discussed. The agreement between the experimental heat capacity and that predicted by the model, up to 500 K, is excellent and supports Merrick's predictions for the heat capacity of coal.

KEY WORDS: atmospheric effects; coal; heat capacity; modeling; water desorption.

1. INTRODUCTION

A recent survey of the status of thermophysical property measurements for coal indicated that often these properties were known only approximately, for few or poorly characterized coals, with little agreement among investigators as to appropriate measurement procedures [1]. Our laboratory has developed procedures, using commercially available apparatus, that give consistent results for the heat capacity of coal.

---

[1] Chemical Engineering Science Division, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

[2] Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A.

A differential scanning calorimeter (DSC) was chosen for the heat capacity measurements because it was considered to have requisite accuracy (±2–3% from ambient temperatures to 900 K) for materials as heterogeneous as coal. The DSC is easy to use, rapid, and commercially available; therefore it is likely that industry might adopt measuring techniques that use it. More sophisticated and inherently more accurate apparatus would be too expensive, from both equipment and personnel considerations, for widespread use by industry or academia.

Procedures used in grinding and drying coal can affect its properties. Differences in sample preparation and in measurement procedures contribute significantly to the poor reproducibility of heat capacity measurements of coal. With the procedures that we recommend [2], the precision within a group of replicate measurements is generally ±7.5%. However, the average, or fitted, values for groups of replicate measurements agree to 2–3%.

The model for carbonization of coal proposed by Merrick has been used for heat capacity [3, 4]. One of the advantages of this model is that it requires no assumptions about intermediate products released during coal processes; it deals with end products which can be measured. The model is general and can be adapted to different processes which coal may undergo. Furthermore, the same model can be used for several properties which are of interest in our experimental program, e.g., thermal conductivity and diffusivity, thermal expansion, and heat capacity. Merrick's model has been adapted and modified to allow for release of water below 525 K, as observed in experiments [14]. When used to represent data up to 500 K, agreement with experiment is within the established error of the calorimeter. The interplay of experiment and modeling has been important to the development of both satisfactory procedures for the measurements and an appropriate model.

During the experimental heat capacity work, it was noted that the atmosphere present in individual specimen cells affected the results. The model being applied could reproduce the results obtained in air but was less satisfactory for those in nitrogen. This paper describes the experimental studies used to gain insight into reasons for this discrepancy.

2. EXPERIMENT

2.1. Material

The coal used in this work was a high-volatile bituminous Colorado coal with a low sulfur and mineral content. It was provided by the Coal

Table I. Analytical Information for PSOC 854 Coal

Proximate analysis (wt % daf[a])				Maceral content (wt % dmmf[b])	
Volatiles, 42.65				Vitrinite, 93.0	
Fixed carbon, 57.35				Inertinite, 5.8	
				Liptinite, 1.2	
Ultimate analysis (wt % daf)					
C	H	O	N	S	Cl
81.04	5.85	11.12	1.54	0.43	0.03

[a] Dry, ash free.
[b] Dry, mineral matter free.

Sample Bank at Pennsylvania State University and identified as PSOC-854. Table I lists characterization information. It was ground to 150 μm (100 mesh) and dried to a constant weight at 378 K before use.

2.2. Procedures

For our initial studies, the ground coal was dried in an oven at 383 K, riffled and pelletized in air, and sealed in air in anodized aluminum specimen pans. At least five replicate specimens were prepared and studied in each series of measurements. These procedures were used for all measurements made in air reported in this paper. For all work reported here for controlled atmospheres, the coal was dried and riffled, and specimens were pelletized and sealed, entirely in a controlled atmosphere [5].

Measurements were made with a DSC, scanning at 5 K/min, from 315 to 500 K. Calorimetry Conference sapphire was used as a standard [6]. Studies in air and the early work in nitrogen followed the pattern: empty pan, standard, unknowns. In addition, the standard was rerun following the unknowns to provide an estimate of error. This estimate was obtained by treating the second sapphire as a sample, applying the required corrections [7], and comparing the results with literature values for sapphire [6]. Corrections for pan weight and instrument error were applied. Measurements in the other gases as well as the final studies in nitrogen were made by a more elaborate procedure which extensive studies of the accuracy and precision of a DSC had shown to be appropriate [7]. The precision of the measurements was ±7.5 %. Average, or fitted, values for three sets of coal agreed within ±2–3 %.

The atmospheres selected for study in addition to nitrogen and air were helium, argon, and carbon monoxide. Oxygen in air unquestionably reacts with coal, oxidizing it rapidly even at low temperatures. Helium and argon can be expected to be unreactive. At temperatures above those in this study carbon monoxide has been shown to activate the coal surface [8], particularly when calcium is present in the mineral component of the coal, as it is in PSOC-854.

3. EXPERIMENTAL RESULTS

3.1. Air

An examination of the heat capacity versus temperature curve for about 20 specimens measured in air showed consistent but unusual trends, illustrated in Fig. 1. The initial portion of the heat capacity curve was essentially linear; this portion was followed by a mild exotherm, then immediately by an endotherm. This is in contrast to a "normal" heat capacity curve. In the absence of a transition, the heat capacity increases smoothly and approaches an asymptote as all possible vibrations are excited. The introduction of a new form of molecular motion as the temperature increases may result in various geographic features: peaks,

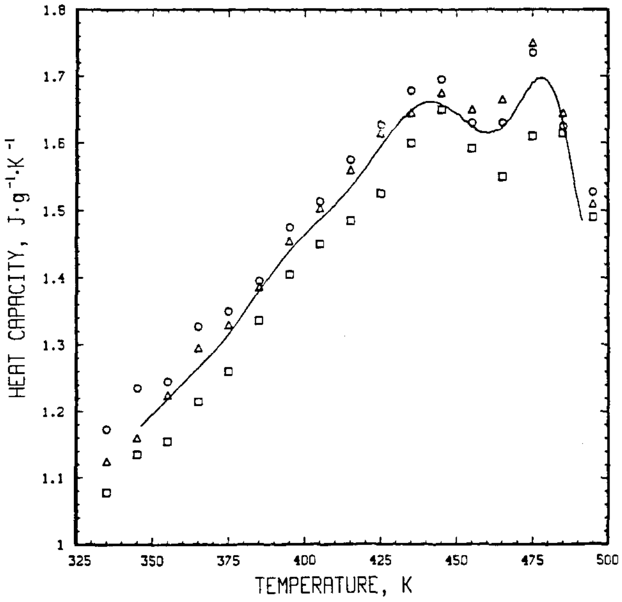

Fig. 1. Heat capacity of coal (PSOC 854) in air. Solid line, fitted value; symbols, individual data points for replicates. Specimens 1, 2, and 3: ○, △, and □.

plateaus, rolling hills. But valleys, as seen in the exotherm here, are not observed.

However, the overall trend of the deviations from linearity was exothermic, even though endothermic trends were observed within the exothermic region. These effects were reproducible and apparently slowly reversible. A second measurement of the heat capacity, an hour after the first, was linear. The same specimen, run a few days later, showed effects almost identical to those noted in the initial run. Thermogravimetric analyses of the specimens, after the heat capacity runs, indicated that the specimens, as sealed, had different water contents though they had been dried before encapsulation. The area of the endothermic region could be related quantitatively to the amount of water released.

The suspicion that the unusual heat capacity curve was related to water was confirmed by several means. First, the thermogravimetric traces showed no general breakdown of coal structure at the temperatures concerned; at higher temperatures, above 540 K, the same sample showed the well-characterized breakdown of the organic structure. Second, Ratcliffe has shown through gc-ms measurements that water is the principal species evolved in this temperature region [9]. Third, Carling determined the most probable mineral reactions, given the inorganic species present in the coal [10]. He found that at 400 K, kaolinite and pyrophyllite were present in nearly equal proportions. At 450 K, no kaolinite was predicted to be present; the pyrophyllite was predicted to have doubled. Conversion of kaolinite to pyrophyllite occurs with release of water. Also, the water content at 300, 350, and 400 K was constant; at 450 K it was predicted to increase. This study was part of a collaborative effort between the National Bureau of Standards and Sandia National Laboratory, Livermore.

3.2. Nitrogen

Some of the variability observed in earlier heat capacity measurements in this laboratory was believed to be caused by water introduced from the atmosphere in processing. In an effort to reduce this variability, a controlled-atmosphere chamber, designed for use with premium, or unoxidized, coals, was used [5]. All processing of the ground coal was carried out in an atmosphere of dried nitrogen; the atmosphere in the sealed specimen cells was nitrogen. For specimens sealed in nitrogen the temperature of the exothermic trend was somewhat higher than those sealed in air. More startling, however, was the depth of the exotherm. As Fig. 2 shows, the heat capacity often decreased to the same values as it had at the start of the measurements, at a temperature 100 K lower.

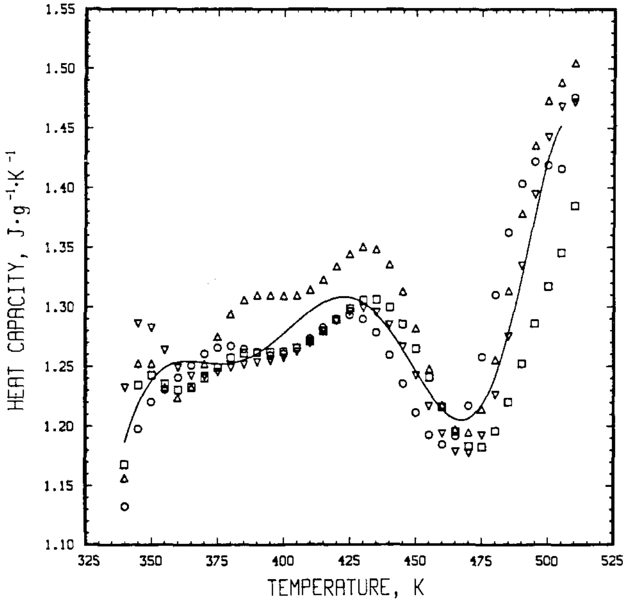

Fig. 2. Heat capacity of coal (PSOC 854) in nitrogen. Solid line, fitted value; symbols, individual data points for replicates. Specimens 1, 2, 3, and 4: ○, △, □, and ▽.

Above 475 K, the differences between the initial and subsequent runs diminish. The exothermic behavior, whatever its cause, appears to be over by 525 K, as evidenced by measurement to 600 K. At higher temperatures the initial and subsequent curves come together.

3.3. Helium, Argon, and Carbon Monoxide

Three series of five specimens, sealed in helium, argon, and carbon monoxide, respectively, were run in the following sequence: standard, first run on specimen, second run on specimen, standard, etc. Again, the first run showed distinctive thermal effects; the repeat runs were uneventful heat capacity measurements.

For helium, the heat capacity of the initial and repeat runs was very similar for the first 40 K; this is in sharp contrast to the behavior of the specimens in the other gases. After the first 40 K, some event, of necessity exothermic, resulted in a plateau in the initial curve. The magnitude of this exotherm was very different from what was observed with the other gases studied.

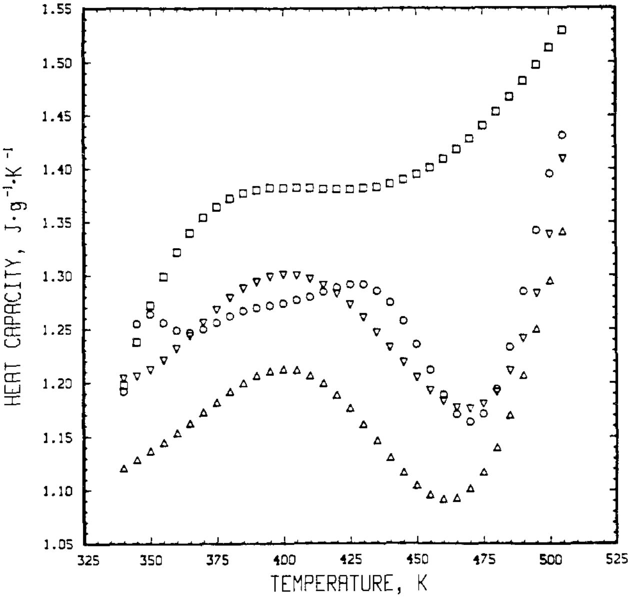

Fig. 3. Heat capacity of initial runs of coal (PSOC 854) in various atmospheres. Nitrogen, ○; argon, △; helium, □; carbon monoxide, ▽.

Qualitatively the results for argon, carbon monoxide, and nitrogen show considerable similarity. The results in all four gases are depicted in Figs. 3 and 4. Figure 3 contains the results for the initial runs in all atmospheres other than air; Fig. 4, the repeat runs in the same atmospheres. These results are discussed in more detail below.

4. DISCUSSION OF EXPERIMENTAL RESULTS

The difference in behavior between initial and subsequent runs is remarkable, if not surprising. A comparison of Figs. 3 and 4 shows that the overall effect occurring in the temperature region of these measurements is exothermic, although both endothermic and exothermic trends are noted in the thermal curves. It has been shown that thermograms for coals depend greatly on operating parameters and the thermal history of the specimens [11].

The measurement referred to in this paper as the immediate rerun is believed to represent the true heat capacity of the coal since it no longer has a heat of reaction superimposed on the heat capacity, as in the initial run. These data can be fitted by the model without difficulty. Richardson

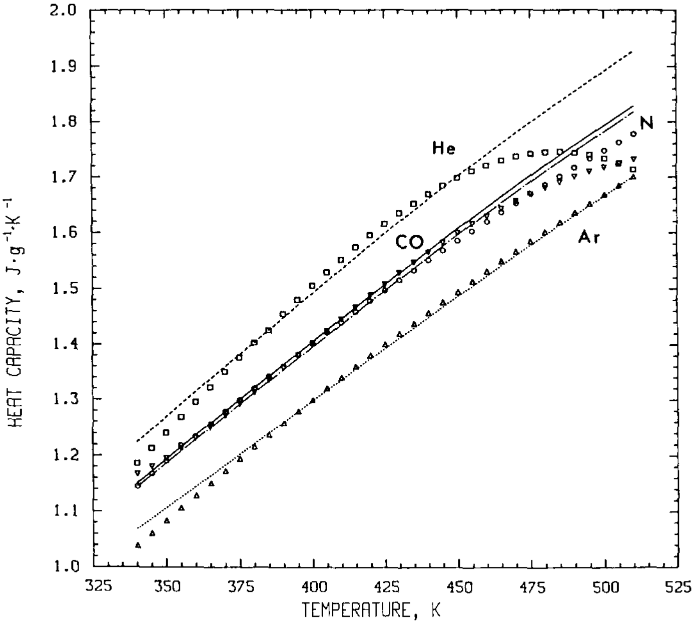

Fig. 4. Heat capacity and modeling fit of repeat runs of coal (PSOC 854) in various atmospheres. Lines, fitted data; symbols, experimental points. Nitrogen, —·—, ○; argon, ····, △; helium, ----, □; carbon monoxide, ——, ▽. Theory: N_2, $\theta_1 = 710$ K, $\theta_2 = 1950$ K; Ar, $\theta_1 = 730$ K, $\theta_2 = 2100$ K; He, $\theta_1 = 700$ K, $\theta_2 = 1830$ K; CO, $\theta_1 = 680$ K, $\theta_2 = 1900$ K.

[12] and Singer and Tye [13] have noted similar effects for initial and repeat measurements and also do not consider the initial measurement to represent the heat capacity of coal.

The cause of the behavior observed during the initial runs is not clear. One possible explanation of the thermogram observed was that water was released from the mineral species in an exothermic reaction; this water was later desorbed with endothermic energy requirements. Merrick's model for heat capacity of coal during carbonization had not allowed any breakdown until above 573 K. Modification of the model by MacDonald to allow for evolution of species below that temperature showed that release of water, alone, could explain the results [14]. None of the specimens showed any significant mass loss. It could be surmised, then, that the water released did not escape from the specimen cell but remained there to react. Thus the phenomenon we are observing is at least partially caused by the desorption and readsorption of inherent moisture. In discussions of the thermal analysis of raw coals, Glass [15] and Berkowitz [16] describe both exothermic and endothermic trends. Our thermogravimetric measurements give no evidence of a general breakdown of the coal structure. The strong exotherm observed may result from a readsorption of water on a coal surface that has been altered as it was heated and is under somewhat increased pressure. Barton et al. [17] found the heat of adsorption of water on coal to be exothermic. Norden and Bainbridge [18] report that heats of adsorption can be exothermic or endothermic, depending on the moisture content of the coal. The heat of interaction of coal and water has been shown to increase with increasing oxidation [17, 19].

In air, whatever reaction occurs appears to be slowly reversible, as scans run 2 or 3 days later show virtually identical behavior. In nitrogen, only a trace of the initial behavior was observed a month later. No evaluation was made of reversibility in the other gases.

Measurements made in nitrogen, argon, and carbon monoxide show similar behavior. This might be expected from the similarity of molecular diameters, heat capacity, and thermal conductivity of these gases. At the temperatures encountered in this study, none of these gases would be expected to be reactive. Our measurements gave no evidence of enhanced reactivity as suggested by Klabunde [8] for carbon monoxide in the presence of calcium-bearing carbonaceous surfaces. Data obtained in argon are about 8% lower than those obtained in nitrogen or carbon monoxide; helium data, 6–7% higher. These differences exceed the experimental variation in average values by a factor of two. Calculation of the contribution to the total measured heat capacity of the coal and the gas shows that the differences observed with the different gaseous atmospheres cannot be explained by the differences in the heat capacity of the gas contained in the specimen cell. The differences in interaction energy of the various gases with coal may be a factor here. Furlong et al. [20] report differences in adsorption energy for nitrogen and argon fur rutile (TiO_2) and silica surfaces.

Air and helium both exhibited distinctive behavior. The oxygen in air could be expected to have an effect on the chemical structure even though there is no wholesale breakdown of the structure. Because helium can penetrate the pore structure so effectively, the differences observed with helium do not seem unreasonable.

Mahajan et al. [21] have studied coals of various ranks in a helium atmosphere at 5.6 MPa. They report only endothermic trends for bituminous coals. There are several differences between their work and that reported here. They used open pans in a pressurized atmosphere; their specimens sustained mass losses, for which corrections were made. This work was done in sealed cells with pressures of less than 0.3 MPa. No mass loss was observed. Thus any inherent moisture given off during heating remained in contact with the coal surface and could react with it. More important, however, is the fact that they show initial thermal curves; we compare heat capacities obtained in initial and subsequent runs. The exothermic effects we discuss are noted by comparison of these two runs rather than in a single initial run. It is important to note also that the coals we used were oxidized. Guttierez-Rodriquez and Aplan [22], in a study of the flotability of coal, report that severe oxidation causes coals to exhibit behavior expected for lower-rank coals.

The differences in the magnitudes of the heat capacities or thermal effects (second and initial runs, respectively) for coals sealed in nitrogen 2 years apart was surprising. The difference in the values of the heat capacities in Ref. 14 and those in this paper varies from about 7.5 to 10%, depending on the temperature. The exothermic effects observed on the later initial runs are markedly larger. A probable explanation of this lies in the increased oxidation. In the 2-year interval between the preparation of the two sets of samples, the coal was stored at room temperature in contact with the atmosphere. Thus oxidative, or weathering, processes continued during that time. The fact that the coal had been ground to 150 μm would accelerate oxidation significantly. From evidence of the effects of oxidation on calorific value, it is reasonable to suppose that the difference in heat capacities has been caused by the increased oxidation that had occurred before the specimens were prepared [23–25]. The investigations into the causes of these differences is not complete. Variations in sample preparation and running procedures and deterioration of the sample stored in air with time are contributing factors. It is hoped that further measurements on PSOC-854 and on premium coals, now available, will shed light on this question.

5. MODELING

The model developed by Merrick has been modified by MacDonald to allow release of water below 573 K, in accord with observation. A description of the application of this model has been published [14].

A linear combination of the heat capacity of the water released and that of the coal substance (char) remaining is used to represent the total heat capacity of the specimen. The experimental heat capacity data are fitted by adjusting characteristic temperatures, θ_1 and θ_2, in a two-term Einstein formulation for the heat capacity of the char. This representation was selected by Merrick because it provided better agreement with experimental data than a one-term function and was computationally simpler than a Debye representation. In addition, it is reasonable in view of the combination of the stronger in-plane and weaker out-of-plane bonds in coal.

The results of fitting the true heat capacity data, i.e., what has been referred to here as the rerun data, with this model are shown in Fig. 4. The lines represent the prediction from the model; the points, the experimental data. Values obtained for θ_1, shown here, are considerably higher than those obtained in the earlier results in nitrogen, where $\theta_1 = 500$ K [14]. This is consistent with the lower heat capacities obtained in the recent measurements compared to those obtained earlier. These differences emphasize that no physical significance should be attached to the values of these characteristic temperatures. In this work they are fitting parameters only.

Figure 5 shows the correlation of the heat capacity of coal and chars obtained by using Merrick's algorithm with analytical data for PSOC-854 and characteristic temperatures appropriate for a nitrogen atmosphere. Results for Merrick's coal C are also shown [3]. Our experimental results, which are far more extensive than those available to Merrick at the time of his original study, show good agreement with his model.

When fitting data from the initial runs, however, where water is allowed to escape from the coal, parameters in addition to the charac-

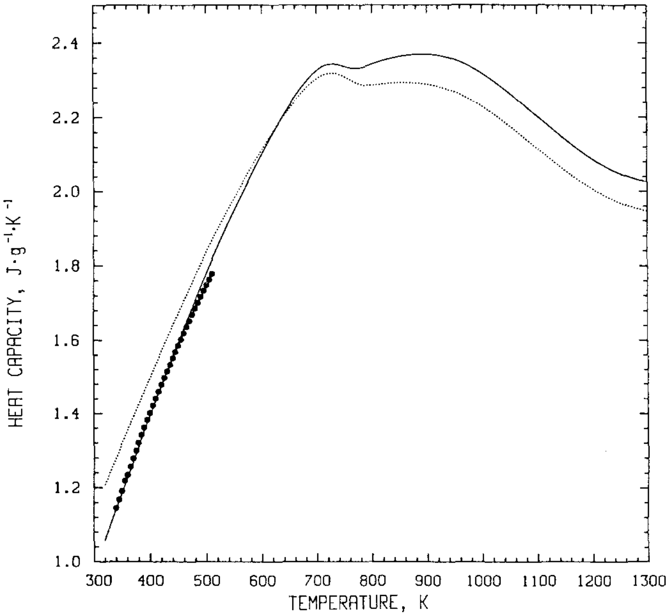

Fig. 5. Predicted heat capacity of coals and chars using Merrick algorithm. Experimental, ●. Predicted: this work, 42.5% volatile matter, ——; Merrick, 35% volatile matter, ·····.

teristic temperature are required. These are the concentration of water released, x, and the associated excitation energy, ε. Physically unrealistic values of these parameters are required to fit the very low values observed during the initial runs on the latest series of coal specimens.

The prediction of the behavior on the initial runs is a desirable goal because the energies involved are significant, as is their contribution to the heat balance of systems utilizing raw coal. No simple modification of our heat capacity model appears to allow for these predictions.

6. SUMMARY

Good agreement has been obtained between experimental measurements of the heat capacity of raw coals and a model representing the heat capacity. The initial heating of the coal shows a heat of reaction superimposed on the heat capacity. As the coal has become more seriously oxidized during its storage in the laboratory, the model is no longer able, with physically realizable parameters, to represent the behavior of the coal during the initial heating. In an attempt to understand the reaction occurring initially, measurements were made on specimens sealed in various atmospheres. The reaction observed may be explained by desorption/adsorption of water as the coal is heated in sealed cells. It is possible, also, that carbon dioxide may be released from the coal surface in amounts not detected by the methods used here. Efforts are under way in this laboratory to determine the energy involved in the initial reaction(s) and to identify the reactions themselves.

ACKNOWLEDGMENTS

The authors thank D. Merrick and C. T. Ratcliffe for helpful discussions during the studies reported here and the preparation of the manuscript.

REFERENCES

1. J. E. Callanan, National Bureau of Standards (U.S.), NBSIR 82-1666 (1982).
2. J. E. Callanan and S. A. Sullivan, Recommended Procedures for Measuring the Heat Capacity of Coal (in press).
3. D. Merrick, *Fuel* **62**:534 (1983); **62**:540 (1983).
4. D. Merrick, Thesis (University of London, London, 1977).
5. B. J. Filla and J. E. Callanan, *Rev. Sci. Instr.* **56**:592 (1985).
6. D. A. Ditmars, S. Ishihara, S. S. Chang, and G. Bernstein, *J. Res. Natl. Bur. Stand. (U.S.)* **87**:159 (1982).
7. J. E. Callanan and S. A. Sullivan, Development of Standard Operating Procedures for Differential Scanning Calorimeters, *Rev. Sci. Instr.* **57** (1986).

8. K. Klabunde, *Fuel Process. Technol.* **4**:73 (1981).
9. C. T. Ratcliffe, In press.
10. R. W. Carling, R. W. Mar, and A. S. Nagelberg, *ACS Fuel Div. Preprints* **28**:223 (1983).
11. N. I. Voina and D. N. Todor, in *Analytical Methods for Coal and Coal Products, Vol. 2*, C. Karr, Jr. ed. (Academic Press, New York, 1978), pp. 619–648.
12. M. J. Richardson, *Anal. Proc.* **22**:46 (1985).
13. J. M. Singer and R. P. Tye, Bur. Mines RI 8364 (1979).
14. R. A. MacDonald, J. E. Callanan, and S. A. Sullivan, *High Temp. High Press.* **17**:387 (1985).
15. H. D. Glass, *Econ. Geol.* **49**:294 (1954).
16. N. Berkowitz, *Fuel* **36**:355 (1957).
17. S. S. Barton, M. J. B. Evans, J. Holland, and J. E. Koresh, *Carbon* **22**:265 (1984).
18. P. Norden and N. W. Bainbridge, *Fuel* **62**:619 (1983).
19. E. A. Sondreal and R. C. Elllman, Bureau of Mines RI 7887 (1974).
20. D. N. Furlong, F. Rouquerol, J. Rouquerol, and K. S. W. Sing, *J. Chem. Soc. Faraday I* **76**:774 (1980).
21. O. P. Mahajan, A. Tomita, and P. L. Walker, Jr., *Fuel* **55**:63 (1976).
22. J. A. Gutierrez-Rodriquez and F. F. Aplan, *Colloids Surfaces* **12**:27 (1984).
23. L. G. Benedict and W. F. Berry, BCR, Inc., publication, 300 Hochberg Rd., Monroeville, Pa. (1964).
24. R. R. Ducher, M. E. Gunter, J. C. Crelling, and W. E. Brouer, GRI Report, NTIS PB86-103876.
25. J. F. Fryer and A. J. Szladow, *Alberta Sci. Council Info. Ser.* **66**:1 (1973).

Printed in Belgium