Thermochimica Acta, 160 (1990) 215–222
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DSC–TG STUDIES OF COAL STRUCTURE MODIFICATION BY THE INERT GAS HELIUM

P. STARZEWSKI and W. ZIELENKIEWICZ

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,
01224 Warsaw (Poland)*

(Received 29 August 1989)

ABSTRACT

The influence of the inert gases helium and argon on the thermal properties of coal have been studied using DSC and TG. The coals studied were high-volatile bituminous coal and anthracite. It has been stated that the heat capacity of coal is strongly influenced by helium. This phenomenon is especially distinct for high-volatile bituminous coal. The authors attempt to explain this phenomenon.

INTRODUCTION

Coal is an extremely complex heterogeneous solid [1]. Investigations into its structure have shown many specific features of its macromolecular structure.

Coal swells in liquids and vapours [2]; many physico-chemical phenomena occur during these processes: the change in specific volume [3], the heat effect involved [4,5] and the reduction of the temperature of glass transition in coal [6]. All these processes are called ‘swelling phenomena’.

Results of calorimetric determination have demonstrated that the values of enthalpy of helium adsorption on coals are much higher than expected (from -35 kJ mol^{-1} to -67 kJ mol^{-1} [7]. These results indicate that not only physical adsorption occurs. The estimated values of enthalpies of the physical adsorption of helium on coals may not exceed -10 to -15 kJ mol^{-1}. These results suggest that a broader investigation of the influence of inert gases on coal structure by application of DSC and TG would be appropriate.

Thermal analysis methods play an important role in determining the characteristics of coal structure [8–11], and its change with increasing temperature.

0040-6031/90/$03.50

EXPERIMENTAL

Materials, reagents, apparatus and procedure

Two Polish coals were studied: details of these coals, their origins and analyses, are shown in Table 1. The helium and argon gases used were reagent grade.

The heat capacities of the coals were determined using a DuPont 910 differential scanning calorimeter in the range 303–593 K. The measurements were made in open pans in order to avoid changes of pressure during sample heating. Specimen masses varied from 18.5 to 21.5 mg. The atmospheres used were helium or argon, each flowing at 6–8 l h^{-1}. For a few experiments, the samples in the calorimeter were initially dried at 363 K in a vacuum (0.1 Pa). The vacuum system was attached to the DSC module. The DSC system was calibrated by sapphire C_p measurements. The coal specimens were weighed before and after the experiments. A decrease in the weight of the samples of about 2% was observed above 373 K and related to the moisture loss. The heat capacity was calculated using the final mass of the samples (dry sample).

The measurements were repeated without opening or any change in the system. The coal samples were cooled to the starting temperature in the gas flow. The mean error of the DSC measurements was estimated to be less than ±5%.

The thermogravimetric measurements were made in the range 303–1173 K using a DuPont 951 thermogravimetric analyser with the argon or helium flowing at 8–10 l h^{-1}. All DSC and TG experiments were carried out with a linear heating rate of 5 K min^{-1}.

RESULTS

The heat capacity versus temperature curves in helium and argon atmospheres for high-volatile bituminous coal (hvb coal) are shown in Fig. 1. The

TABLE 1

Origins and analyses of coals used

Type	Origin	Moisture (wt.%)	Ash (wt.%)	Volatile (wt.%)	Carbon (wt.%) daf	Hydrogen (wt.%) daf	Sulphur org. (wt.%) daf	Nitrogen + oxygen daf (wt.%)
Anthracite	Walbrzych	1.0	4.1	5.6	90.9	3.3	–	–
High-volatile bituminous I	Pokoj	1.4	4.2	36.4	86.4	5.4	0.8	7.4

daf, Dry ash free.

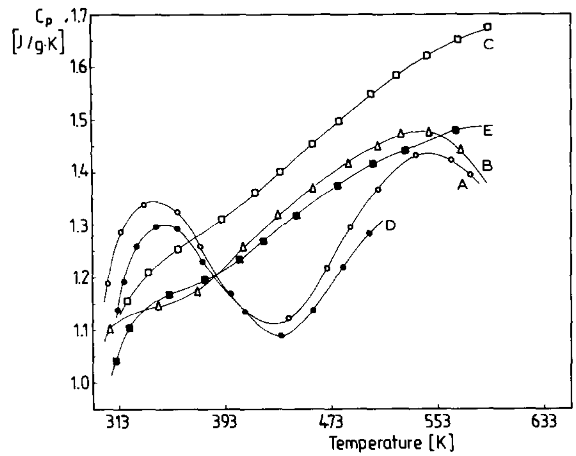

Fig. 1. Heat capacity of high-volatile bituminous coal: A, in helium, initial run; B, in helium, repeat run; and C, in helium, saturated for 10-h at 363 K and for 10 h at 303 K, after out-gassing in vacuum at 363 K; D, in argon, initial run; and E, in argon, repeat run.

curves A (helium) and D (argon) represent C_p versus temperature for raw samples (not dried and not initially saturated by gases). The typical maxima for raw samples observed at 303–393 K are related to the moisture desorption [9]. The minima at 393–473 K are qualitatively the same as those observed by many investigators [9,10,12]. Both these phenomena are independent of the inert atmosphere and were observed in the initial runs only. For the repeat runs (curves B in helium and E in argon, Fig. 1), the heat capacities increase smoothly. Above 550 K, curves A and D, and B and E are distinctly different. In this region, C_p for helium-atmosphere measurements decreases by about 8.5% from the value at 550 K.

Prolonged initial helium saturation markedly changes the heat capacity. Figure 2 shows the results of heat capacity measurements for hvb coal samples which were initially saturated in helium for 10 h at 370 K, and then for 5 h at 300 K. Curve A represents the first run, and B and C are the succeeding experiments.

After each experiment, the sample was saturated with helium for about 2 h. In these experiments, the observed decrease in recorded C_p is important. The heat capacity decreases for A experiments (Fig. 2) from 400 K. In subsequent experiments (B and C, Fig. 2) the heat capacity values increase and the temperature at which the C_p decrease begins is also observed.

Helium saturation of hvb coal at temperatures above 410 K does not induce heat capacity changes. Prolonged helium saturation of a sample of hvb coal initially dried under vacuum at 360 K is more efficient: the heat capacity reaches the 'equilibrium curve' (Fig. 1C), the same curve for the repeat experiments. The heat capacity value from the 'equilibrium curves' is 10% higher than that measured in argon. In argon atmosphere, a constant C_p

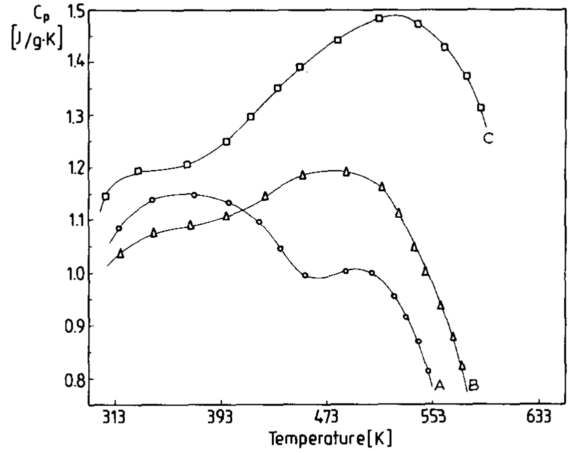

Fig. 2. Heat capacity of high-volatile bituminous coal, helium saturated for 10 h at 363 K and for 5 h at 303 K: A, initial run; B, repeat run; and C, repeat run.

value, the 'equilibrium curve' (Fig. 1E), is obtained in all cases as early as the second run.

The reproducibility of the C_p measurements for partially saturated hvb coal samples is low. Figure 3 shows C_p curves of partially saturated samples. The shape of the C_p curves is dependent on sample preparation methods (drying) and the time and temperature of gas saturation. When hvb coal is partially saturated by helium, C_p is essentially depressed. The shape of these curves as a temperature function is difficult to define.

Figure 4 shows the results of the DSC measurements for anthracite using the same methods as for hvb coal (Fig. 1). There are small differences, about

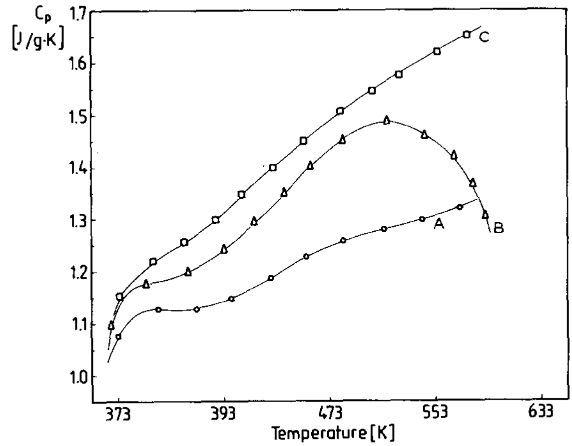

Fig. 3. Comparison of heat capacities of high-volatile bituminous coal in helium: A, saturated for 2 h at 363 K after out-gassing in vacuum at 363 K; B, curve C from Fig. 2; and C, curve C from Fig. 1.

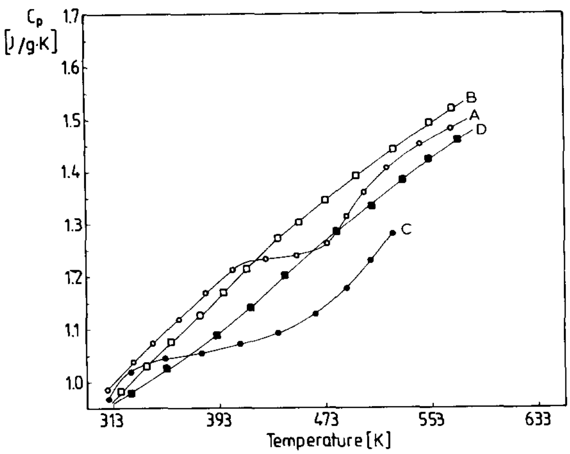

Fig. 4. Heat capacity of antracite: A, in helium, initial run; and B, in helium, repeat run; C, in argon, initial run; and D, in argon, repeat run.

5%, between the helium and argon measurements. The saturation of this coal does not change the C_p value.

To compare the results of the DSC experiments with the TG measurements, the samples from the DSC module were placed directly in the TG system and investigated by thermogravimetry. Figure 5 shows the relation of mass loss and temperature for hvb coal (curve D, sample in argon; C, after the DSC experiment shown in Fig. 3A; B, after the DSC experiment shown in Fig. 2B; and A, after the DSC experiment shown in Fig. 1E and Fig. 3C). There are considerable differences in mass loss for samples of hvb coal

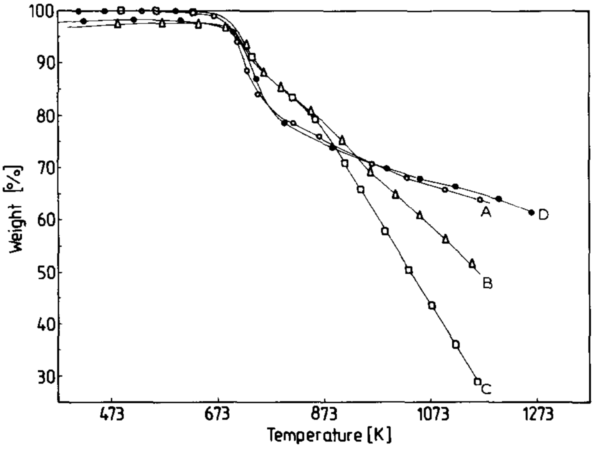

Fig. 5. Thermogravimetric heating curves for high-volatile bituminuos coal: A, after experiment C from Fig. 1 (helium); B, after experiment C from Fig. 2 (helium); C, after experiment A from Fig. 3 (helium); and D, after experiment E from Fig. 1 (argon).

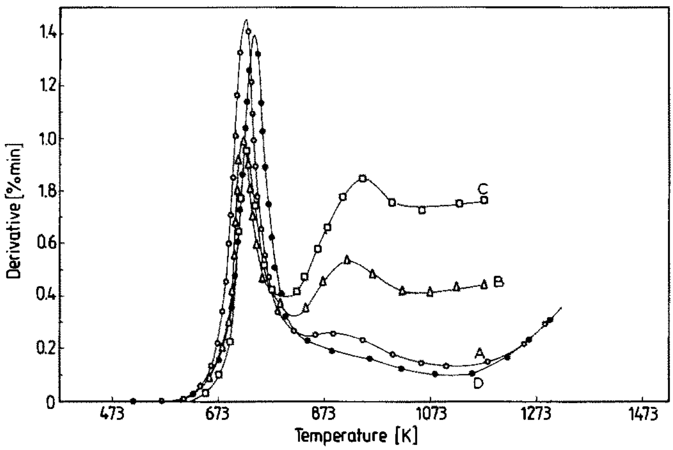

Fig. 6. The derivatives of curves from Fig. 5.

partially saturated by helium. The derivatives of the curves in Fig. 5 are shown in Fig. 6.

DISCUSSION

The results of the DSC and TG measurements for hvb coal and anthracite may be interpreted by means of the model for helium sorption on coal [7]. This two-step sorption model treats coal as a porous solid composed of rigid, graphite-like domains. The arrangement of the domains is a function of coalification. Between these domains are inclusions of low molecular weight organic compounds. This structure is not thermodynamically stable, especially for bituminous coals. Small, weakly-interacting helium atoms can easily penetrate the coal structure. The helium acts as a ‘molecular grease’. These small inert atoms discharge the localised stresses between the graphite-like domains in the coal structure. This process is exothermic; thus, an apparent decrease in heat capacity is observed for helium-saturated coal. The preliminary step of this process is the physical adsorption of helium on the porous surface of the coal. The energy of the physical adsorption of helium on hvb coal is about -4 to -5 kJ mol^{-1} [7]. Therefore, at temperatures above 390 K, the kinetic energy of gaseous helium is sufficiently high to eliminate the physically adsorbed helium from the coal. This means that the helium saturation of coal above 390–410 K is not efficient. Therefore, the heat capacities of hvb coals not initially saturated in argon or helium are approximately the same.

The small amount of helium adsorbed during the first stage of the experiments (from 303 K to 390 K) enables the initiation of the structure modification above 550 K. Prolonged helium saturation of hvb coal at 370 K supplies sufficient helium to initiate the structure modification at lower temperatures (Fig. 3). The non-recurrent C_p curves obtained for intermediate saturation steps are caused by the difficulty in reproducing the same saturation of the coal structure.

The possible production of a surface layer of modified coal is important. This layer can hinder the penetration of the coal structure by helium atoms. A decrease in the helium sorption on partially helium-saturated coal samples has been observed in calorimetric experiments [7].

The dependence of the preliminary vacuum out-gassing on the modification process is obvious. The empty pore-system is easily accessible for helium penetration.

The helium structure-modification manifests itself in the DSC experiments in two effects: the first is the discharge of the stresses between the graphite-like domains which gives the apparent decrease in heat capacity (exothermic effect); in the second, the presence of helium atoms between the domains gives a higher mobility (grease effect) which causes an increase in the heat capacity of fully saturated samples of hvb coal.

This explains why coal modified by helium has a higher heat capacity than that treated in argon atmosphere, where this effect is not observed. The small differences in heat capacity observed for anthracite samples in helium and argon show that the modification of this more organised structure is much smaller.

This proposed model of helium interaction with the coal structure explains the abnormal C_p versus temperature curves reported by Callanan et al. [12] for hvb coal saturated by inert gases.

It is more difficult to explain the results of the TG experiments. Comparing Fig. 3 with Figs. 5 and 6 shows that the decrease in heat capacity (Fig. 3A,B) is related to the faster decomposition of the samples (Fig. 5B,C). The sample of partially saturated hvb coal (Fig. 5B) is 75% decomposed at 1173 K when the fully saturated samples (Fig. 5A) and the unsaturated samples (Fig. 5D) are only decomposed 30% and 35%, respectively. These differences are related to the three-times higher energy of activation for the second step of hvb-coal decomposition (Fig. 6C and D, from 820 to 970 K) calculated from the Arrhenius plot.

The rapid decomposition of partially saturated samples may be the result of the presence of a two-phase system (phase modified and raw).

The same effects but approximately ten times smaller, i.e. a decrease in the first decomposition step (Fig. 6B and D, 670–770 K) related to an increase in the second step (Fig. 6B and D, from 820 K) were observed by Serageldin and Wei-Ping Pan for the catalytic (Li_2CO_3) decomposition of coal [13].

Differences in the second step of the thermogravimetric experiments show that helium modifies the coal structure which is broken at this stage of the TG experiment. Coal with a well organised structure such as anthracite does not undergo major structural changes during helium saturation.

The important changes in heat capacity and decomposition rate of the coal caused by helium saturation suggest a possible new way of modifying the structure of coal. This process occurs very easily under normal conditions. These facts provide the motivation for future studies into the mechanism of coal structure-modification by inert gases.

REFERENCES

1 M.L. Gorbaty, J.W. Larsen and I. Wender, (Eds.), Coal Science, Academic Press, New York, 1982.
2 R.M. Meyers, (Ed.), Coal Structure, Academic Press, London, 1982.
3 J.N. Nelson, Om.P. Mahajan and P.L. Walker, Jr., Fuel, 59 (1982) 831.
4 J.O. Glanville, K.L. Newcomb and J.P. Wightman, Fuel, 65 (1986) 485.
5 Y. Grillet and P. Starzewski, Fuel, 68 (1989) 55.
6 L.M. Lucht, J.M. Larson and N.A. Peppas, Energy and Fuels, 1 (1986) 56.
7 P. Starzewski and Y. Grillet, Fuel, 68 (1989) 375.
8 W.A. Kneller, Thermochim. Acta, 108 (1986) 357.
9 M.J. Richardson, Anal. Proc., 22 (1985) 46.
10 R.A. MacDonald, J.E. Callanan and K. McDermott, Energy and Fuels, 1 (1987) 535.
11 J.M. Singer and R.P. Tye, Bur. Mines RI, (1979) 8364.
12 J.E. Callanan, S.A. Sullivan and R.A. MacDonald, Int. J. Thermophys. 8 (1987) 133.
13 M.A. Serageldin and W.-P. Pan, Thermochim. Acta, 76 (1984) 145.