Thermochimica Acta, 93 (1985) 737-740
Elsevier Science Publishers B.V., Amsterdam

STRUCTURAL CHANGES IN COALS DURING PYROLYSIS

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ABSTRACT

Derivative thermogravimetry (DTG), emanation thermal analysis (ETA), gas adsorption methods for surface area and microporosity measurements, helium pycnometry and mercury porosimetry have been used for the characterization of structural changes in two bituminous coals of British origin (Manvers Wath and Markham Main), during heating in argon up to 980 °C (heating rate 5 °C/min). The results are compared and advantages of the ETA for the assessment of the surface area and porosity changes in dynamical conditions of thermal treatment are demonstrated.

INTRODUCTION

A number of papers have appeared in recent years on the structure of coals and chars and their relationship to reactivity for gasification /1,2/. Pyrolysis of coal is complex. It yields water, tar and other volatiles and produces a semichar. Further heating with hydrogen evolution converts the semichar to a char /3/. We have studied the pyrolysis of two British bituminous coals by Derivative Thermogravimetry (DTG). Structural changes during pyrolysis were investigated by Emanation Thermal Analysis (ETA) /4-6/, in conjunction with measurement of micropores and mesopores by gas adsorption. Other porosity measurements were made using helium pycnometry and mercury porosimetry.

EXPERIMENTAL

The coals, Manvers Wath and Markham Main, were of National Coal Board ranks 602 and 702. The range of particle size used in all experiments was 500--850 μm. DTG curves (Fig.1) of both coals were made on a Stanton Redcroft 781 thermobalance under an argon flow rate of 20 ml/min and a temperature program of 5 °C/min up to 1100 °C. A series of char samples was prepared for each coal by heating in argon at 5 °C/min to 300, 500, 600, 800, 900 and 1100 °C on a Cahn 2000 Microbalance /7/. In situ measurements were performed to obtain microporosity and surface area data with a reproducibility of ±10 %.

Carbon dioxide isotherms at 195 K were measured and analysed according to the Dubinin-Radushkevich (D-R) equation /8/. BET nitrogen isotherms at 77 K were carried out after pre-adsorption of n-nonane /9/. Porosity was measured using a combination of helium pycnometry and mercury porosimetry.

Emanation thermal analysis measurements based on the release of radon ^{220}Rr from the coal samples labelled before the measurements by impregnation

Proceedings of ICTA 85, Bratislava

with traces of radon parent isotopes ^{228}Th and ^{224}Ra) have been performed using ETA apparatus described elsewhere /6/. ETA curves represent the dependences of the radon release rate from the coal samples during heating (heating rate 5 °C/min) in argon (flow rate 50 ml/min).

RESULTS AND DISCUSSION

At is follows from the gas adsorption measurements performed, the effect of temperature on the structure of coal was found to be similar for both Manvers Wath and Markham Main, resp. Pyrolysis patterns by DTG were also alike (see Fig.1)

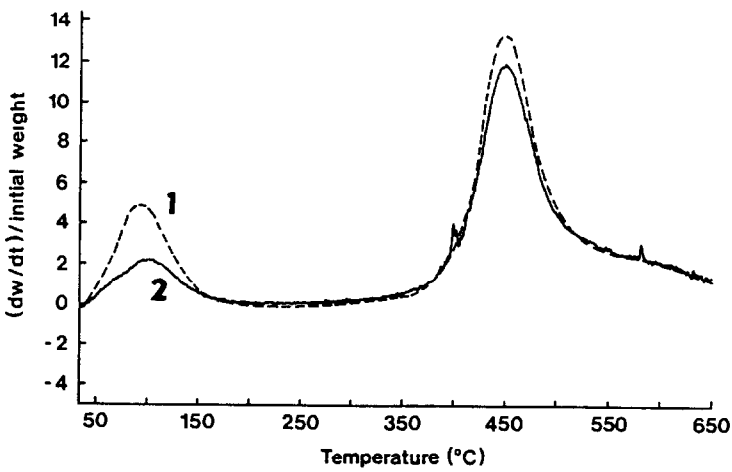

Fig. 1 DTG curves of coal pyrolysis in argon at 5 °C/min

curve 1 (dotted line) - Markham Main
curve 2 (full line) - Manvers Wath

Tables I and II show changes in micropore volume and associated surface area values obtained using Dubinin-Radushkevich equation /8/. The values increase during heating in argon up to 800 °C above which they begin to decline. Helium density values increase continuously with temperature.

Fig. 2 shows the changes in pore volume distribution with pyrolysis temperature for pores greater than 3 nm in diameter. Both investigated coals show a small increase in intermediate pores (20 – 2 nm) at 300 °C. At 500 °C the volume of macropores (> 20 nm) and mesopores increases considerably. Above 700–800 °C there is a slight reduction in these pores but the structure remains intact. This structural development follows the model proposed by Simons /10/ of pore evolution, preservation of pore size distribution and development of a "pore tree" structure.

Thermochimica Acta, 93 (1985) 741-744
Elsevier Science Publishers B.V., Amsterdam

Table I: Surface area and porosity characteristics of Manvers Wath Coal

Temp. °C	D-R w_o cm^3/g	D-R Surface m^2/g	BET Surface m^2/g	He ∂ g/cc	HG Bulk ∂ g/cc	T.O.P. Vol.	% Porosity
Virgin	0.039	90	54	1.41	1.04	0.2523	26.24
300°	0.049	114	54	1.41	1.237	0.0976	14.29
500°C	0.1024	238	181	1.60	1.026	0.3525	35.87
700°				1.83	1.062	0.3946	41.93
800°	0.1187	276	228				
900°	0.0527	123	71	1.825	1.257	0.2504	31.11
1-76°	0.0117	27	50				

Table II: Surface area and porosity characteristics of Markham Main Coal

Temp. °C	D - R w_o cm^3/g	D-R Surface m^2/g	BET Surface m^2/g	He ∂ g/cc	HG Bulk ∂ g/cc.	T.O.P. Vol.	% Porosity
Virgin	0 0706	164	28	1.47	1.156	0.1893	21.89
300°				1.44	1.19	0.1457	17 32
500°	0.0968	225	116	1.56	0.815	0.5850	47.52
600°				1.735	0.823	0.6387	52.56
800°	0.1276	297	166				
900°	0.0568	132		1.937	1.027	0.4610	47.00
1100°	0.0097	23	60				

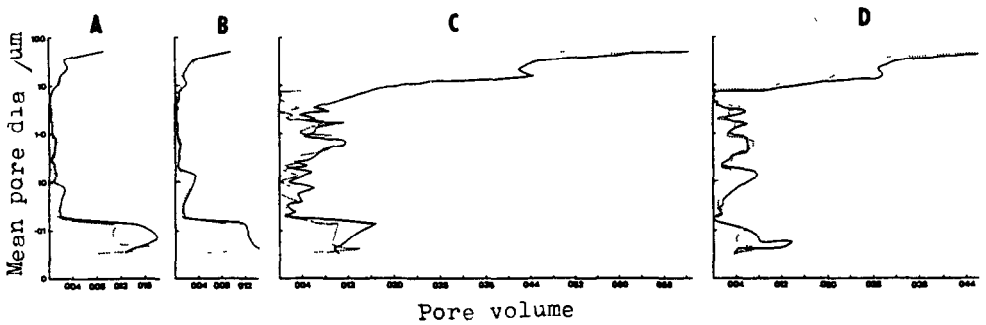

Fig. 2 Pore volume distribution of two coal samples treated in argon at 5 °C/min
A (virgin), B (heated to 300 °C), C (heated to 500 °C), D(heated to 800 °C)
Full line - Markham Main Coal, Dotted line - Manvers Wath Coal

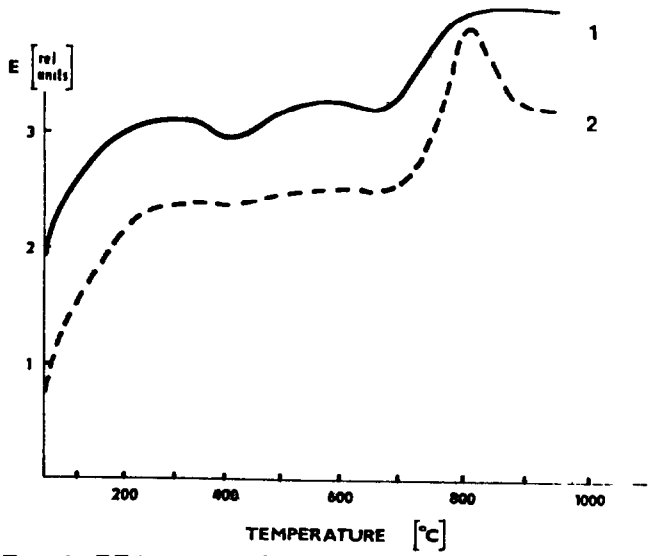

Fig. 3 ETA curves of coal pyrolysis in argon at 5 °C/min. Curve 1 - Manvers Wath Coal, curve 2 - Markham Main Coal

The ETA curves in Fig. 3 characterize changes of pore structure and diffusivity of the coal samples directly during heating in argon, without the necessity to interrupt the thermal treatment.

The sharp increase of radon release rate starting at 650–800 °C indicates the evolution of surface area and open porosity. These effects are in good agreement with surface and porosity measurement made by gas adsorption.

Differences in the behaviour of the coals studied are indicated by ETA at temperatures above 800 °C.

CONCLUSION

It was shown that the development of microporosity occurs by pore opening and generation of new pores. Larger pores increase due to enlargement of existing pores and combination of small pores. Pore volume distributions show changes in the macro and transitional structure through the plastic range /11/ to final full development of the char. The ETA reflects the evolution of the micropore structure of the coals studied to its maximum development at 800 °C. The ETA can be recommended for rapid information about the structural changes in coals during pyrolysis.

Acknowledgement. The authors would like to thank Dr. S.G. Williams for his comments and advice.

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