

more than one nitrogen functional group¹⁶. In high molecular mass asphaltene samples, this is unlikely to be the case.

CONCLUSIONS

The combination of XPS and i.r. spectrometries with potentiometric titration has provided a unique method for identification and quantification of nitrogen functional group types in solid coal and soluble solids as well as liquid products. While XPS is used for solids, i.r. and potentiometric titration can only be applied quantitatively to soluble solids and liquids. Application of all three methods to soluble solid derivatives of coal has led to a method of nitrogen group determination which is self-consistent over the whole range of materials.

The distribution of nitrogen functional groups remains remarkably constant throughout the high molecular weight coal-derived fractions. This implies that any alteration of the nitrogen functional groups occurs after primary fragmentation of the coal structure, so that the products are found in the low molecular mass fragments.

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REFERENCES

- 1 'Energy and the Environment: Interactions' (Eds. L. Theodore and A. J. Buonicore), CRC Press Inc., Vol. I, Part A
- 2 Ford, C. D., Holmes, S. A., Thompson, L. F. and Latham, D. R. *Anal. Chem.* 1981, **53**, 831
- 3 Mills, G. A., Boedeker, E. R. and Oblad, A. G. *J. Am. Chem. Soc.* 1950, **72**, 1554
- 4 Bartle, K. D., Ladner, W. R., Martin, T. G. *et al. Fuel* 1979, **58**, 413
- 5 Wallace, S., Crook, M. J., Bartle, K. D. and Pappin, A. J. *Fuel* 1986, **65**, 138
- 6 Bartle, K. D., Perry, D. L. and Wallace, S. *Fuel Proc. Technol.* 1987, **15**, 351
- 7 Fieser, L. F. and Fieser, M. in 'Reagents for Organic Synthesis', Wiley-Interscience, 1967, p. 191
- 8 Moore, R. T., McCutchan, P. and Young, D. A. *Anal. Chem.* 1951, **23**, 1639
- 9 Briggs, D. and Riviere, J. C. in 'Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy' (Eds. D. Briggs and M. P. Seah), Wiley, New York, USA, 1984
- 10 Schwager, I. and Yen, T. F. *Anal. Chem.* 1979, **51**(4), 569
- 11 Wallace, S., Bartle, K. D., Perry, D. L. *et al.* in '1987 Int. Conf. on Coal Sci.' (Ed. J. Moulijn *et al.*), Elsevier, Amsterdam, The Netherlands, p. 9-12
- 12 Snyder, L. R. *Anal. Chem.* 1969, **41**, 314
- 13 Snyder, L. R. *Anal. Chem.* 1969, **41**, 1084
- 14 McKay, J. F., Cogswell, T. E., Weber, J. H. and Latham, D. R. *Fuel* 1975, **54**, 50
- 15 Green, J. B., Stierwalt, B. K., Green, J. A. and Grizzle, P. L. *Fuel* 1985, **64**, 1571
- 16 McKay, J. F., Harnsberger, P. M., Erickson, R. B., Cogswell, T. E. and Latham, D. R. *Fuel* 1981, **60**, 17

D.s.c. and TGA measurements of O₂ interaction with coal chars

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Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (TGA) were used to follow oxygen chemisorption on a series of coal chars when exposed to 0.1 MPa of O₂ at 373 K. Elovich plots correlated heat release and weight of oxygen chemisorbed as a function of reaction time. Rates of both heat release and weight increase generally decreased with increasing rank of original coal. Rates of heat release upon oxygen chemisorption also generally increased as rates of gasification of the chars at higher temperatures in air increased. Enthalpies of oxygen chemisorption, as a function of reaction time, were calculated for selected chars.

(Keywords: oxygen; coal char; d.s.c.)

In this laboratory, the reactivity of coal chars has been studied in air¹, CO₂², H₂³, and steam⁴. In the case of the oxidizing gases (air, CO₂, and steam), reactivity decreased sharply with increasing rank of coal from which the chars were derived. The first step leading to overall char gasification is oxygen transfer to carbon surface active sites⁵, and it is therefore of interest to study this step in the absence of carbon gasification. This has been done in this study on chars for which gasification results are available, using differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Chars used

Seventeen chars, derived from coals varying in rank from anthracite to lignite, were used in this study, and Table 1 presents analyses of the coals. The coals were ground and sieved to 40 × 100 mesh (US sieve series), then carbonized in N₂ at 10 K min⁻¹ up to 1273 K and held for 2 h. Chars prepared from strongly caking coals (PSOC-171, 4, and 137) were reground to 40 × 100 mesh. Table 2 shows the ash contents and the concentrations of the major inorganic elements in the chars.

D.s.c. and TGA apparatus

A Dupont d.s.c. cell was used in conjunction with a cell base Module-II and a 990 thermal analyser. This apparatus and its calibration are described elsewhere^{6,7}. The major components of the TGA apparatus were a Cahn RG weighing mechanism placed in a glass vacuum bottle electrobalance, connected to a vertical Vycor tube. The TGA apparatus is also described elsewhere⁷.

Operating procedure

A known weight of char was charged inside the d.s.c. cell or TGA reactor. The sample was outgassed, flushed with 0.1 MPa N₂ at 45 ml min⁻¹, heated to 873 K and kept at this temperature for 30 min, and finally cooled

to room temperature. Following this pretreatment the char was held in flowing N₂ at 373 K ± 1.0 K for 45–90 min to allow the instruments to attain thermal stability. Oxygen at 0.1 MPa pressure and a flow rate of 45 ml min⁻¹ was then introduced to replace N₂, and the thermograms were started. Values of Q (cal g⁻¹ char) and W (mg g⁻¹ char) were determined for a 30 min chemisorption time, during which oxygen transfer to a fraction of the carbon surface active sites took place⁸. It has previously been shown⁷ that at 373 K physical adsorption of gas and char gasification in 0.1 MPa O₂ produce negligible changes in heat and weight compared with oxygen chemisorption. Thus, d.s.c. and TGA measurements give the heat evolved and the weight increase, respectively, as a result of oxygen chemisorption on the char.

RESULTS AND DISCUSSION

Kinetics of oxygen chemisorption

Dependence of Q on reaction time (t) is illustrated for the chars in Figures 1 and 2. In all cases studied, linearities were observed, indicating that the rate of heat release is decreasing exponentially with increasing Q .

$$dQ/dt = a \exp(-\alpha Q) \quad (1)$$

which upon integration is simplified to

$$Q = \frac{2.3}{\alpha} \log(\alpha Q) + \frac{2.3}{\alpha} \log(t) \quad (2)$$

where α (g char cal⁻¹) is a constant and a (cal g⁻¹ char min⁻¹) is the initial rate of heat release. This is the well known Elovich equation⁹, which frequently describes the kinetics of chemisorption of gases on solid surfaces. Values of α and a are listed in Table 3.

Dependence of W on reaction time is illustrated for a number of chars in Figure 3. For some of the chars, the TGA apparatus was not sufficiently sensitive to measure weight increases due to oxygen chemisorption. In all cases studied, linearities were observed for W versus $\log(t)$

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Table 1 Analysis of coals

PSOC sample no.	ASTM rank	State	Ash (% dry basis)	Ultimate analysis (wt%, daf)				
				C	H	N	S ^a	O ^b
89	Lignite	ND	11.6	63.3	4.7	0.48	0.98	30.5
91	Lignite	MT	7.7	70.7	4.9	0.80	0.30	22.3
87	Lignite	ND	8.2	71.2	5.3	0.56	0.46	22.5
140	Lignite	TX	9.4	71.7	5.2	1.30	0.72	21.1
138	Lignite	TX	10.3	74.3	5.0	0.37	0.51	19.8
98	Sbb. A	WY	8.4	74.3	5.8	1.20	1.1	17.7
101	Sbb. C	WY	6.1	74.8	5.1	0.89	0.30	18.9
26	HVB	IL	10.8	77.3	5.6	1.10	2.3	13.6
22	HVC	IL	10.1	78.8	5.8	1.60	1.8	12.1
24	HVB	IL	11.8	80.1	5.5	1.10	2.3	11.1
67	HVB	UT	4.8	80.4	6.1	1.30	0.38	11.9
171	HVA	WV	7.6	82.3	5.7	1.40	1.8	8.9
4	HVA	KY	2.1	83.8	5.8	1.60	0.66	8.2
137	MV	AL	7.1	87.0	4.8	1.50	0.81	5.9
114	LV	PA	9.8	88.2	4.8	1.20	0.62	5.2
81	Anthracite	PA	7.8	91.9	2.6	0.78	0.54	4.2
177	Anthracite	PA	4.3	93.5	2.7	0.24	0.64	2.9

^a Organic sulphur^b By difference

Table 2 Concentration of inorganic impurities in the chars

PSOC char no.	Ash content (%)	Concentration (expressed as oxides (%))				
		Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
89	—	—	—	—	—	—
91	11	0.13	3.77	1.44	0.009	0.032
87	13	0.96	2.73	0.79	0.052	1.50
140	12	1.13	1.35	0.24	0.057	0.067
138	16	1.48	1.30	0.26	0.083	0.077
98	12	1.25	2.27	0.35	0.088	0.029
101	8	0.43	2.67	0.58	0.004	0.053
26	20	12.8	0.97	0.076	0.19	0.052
22	23	2.45	2.05	0.26	0.50	0.080
24	14	3.76	0.14	0.11	0.32	0.043
67	5	1.11	0.85	0.037	0.011	0.11
171	11	2.77	0.68	0.17	0.19	0.18
4	2	0.51	0.12	0.026	0.005	0.039
137	19	9.09	0.24	0.17	0.28	0.047
114	12	0.20	0.098	0.084	0.31	0.041
81	6	0.33	0.14	0.082	0.047	0.010
177	5	0.37	0.04	0.023	0.037	0.033

plots, indicating that the rate of oxygen chemisorption is decreasing exponentially with increasing amount of oxygen chemisorption, or that the Elovich equation is again obeyed. Values of α and a are again listed in Table 3.

Relation of Q_{15} to properties of chars

It is convenient to measure the amount of heat released over some period of time. For the experimental conditions used, the rate of heat released after an exposure time of about 20 min becomes so small that it becomes difficult to measure. Arbitrarily, the amount of heat released after an exposure time of 15 min, Q_{15} , has been used to correlate with various properties of the chars and starting coals. As seen in Figure 4, Q_{15} shows a linear correlation with the initial rate of heat release (a) for the bituminous and anthracite coals. However, for most of

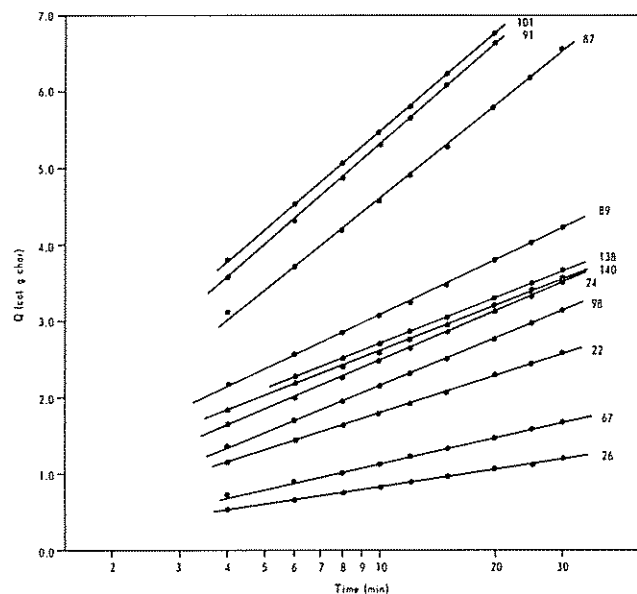


Figure 1 Heat released upon exposure of coal chars to 0.1 MPa O₂ at 373 K

the lignites Q_{15} values are less than the values predicted from the initial rates of heat released.

Figure 5 shows the relationship between Q_{15} and the carbon content of the parent coal from which the char was produced. As the carbon content of the parent coal increases, Q_{15} generally decreases; this decrease is rapid at first within the range of the lignitic and subbituminous coal chars. The marked exception is the char derived from PSOC 89, which has been omitted from Figure 5. This coal has a carbon content (daf) of 63.3% (the lowest of all coals) and yet a Q_{15} of only 3.5 cal g⁻¹ char. Unfortunately, only limited data, such as analysis of inorganic impurities and surface areas, are available for this char.

It is known¹⁰ that the specific surface areas of chars change with the rank of coal from which they are produced. It is also known that coal chars are molecular sieve materials¹¹, exhibiting different surface areas in N₂ (77 K) and CO₂ (298 K). Figures 6 and 7 show the relationships between Q₁₅ and the N₂ and CO₂ surface areas of the coal chars. For the higher rank coal chars, there is a general increase of Q₁₅ with increasing N₂ surface areas. However, the plot goes through a clear maximum for the lower rank coal chars. For the relationship between Q₁₅ and CO₂ surface areas, again there is a general increase in Q₁₅ with increasing surface area for the higher rank coal chars. Again, for the coal chars of lower rank, there is no correlation between Q₁₅ and surface area. Some of the low rank coal chars exhibit Q₁₅ values considerably higher than would be predicted from the broad correlation. Since coal chars are molecular sieve materials, it is expected that surface areas measured in CO₂ at 298 K are more representative of surface areas accessible to O₂ at 373 K than the areas

measured in N₂ at 77 K. If CO₂ areas do closely represent areas accessible to O₂ at 373 K, clearly this indicates that more than just the specific surfaces of chars determine heat release upon oxygen chemisorption. It suggests that other factors such as the geometric configuration of the char surface (the nature of carbon bonding on the surface) and the presence of inorganic species in the surface also affect significantly Q₁₅.

Relation of Q₁₅ to char gasification rates

It has previously been shown¹² that reactivity plots for coal chars in different gases (i.e. fractional burn-off versus reaction time) have a characteristic shape.

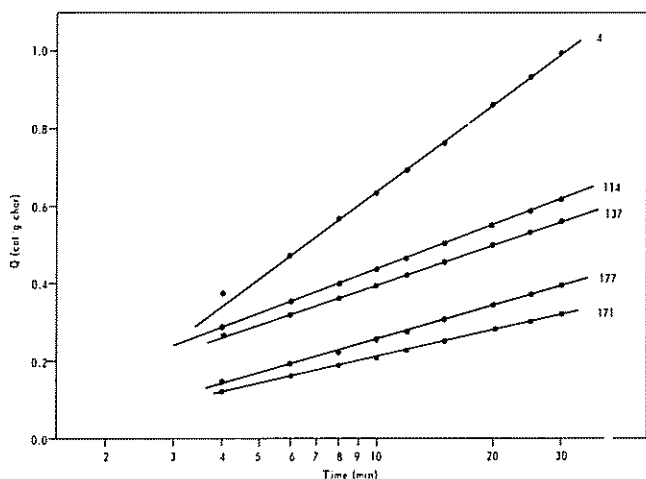


Figure 2 Heat released upon exposure of coal chars to 0.1 MPa O₂ at 373 K

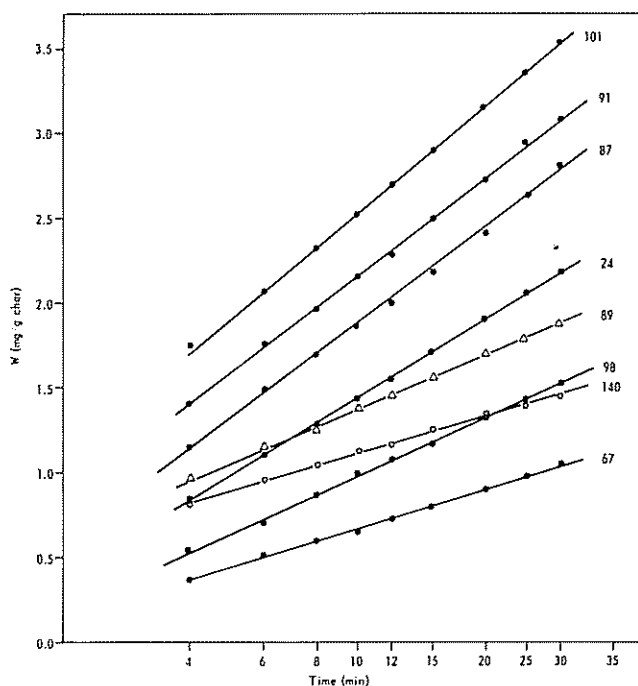


Figure 3 Weight gain due to oxygen chemisorption upon exposure of coal chars to 0.1 MPa O₂ at 373 K

Table 3 Elovich parameters α and a for coal chars

PSOC char number	From d.s.c.		From TGA	
	α (g char cal ⁻¹)	a (cal g ⁻¹ char min ⁻¹)	α (g char mg ⁻¹ O ₂)	a (mg O ₂ ⁻¹ g char min ⁻¹)
89	0.96	2.04	2.14	0.88
91	0.53	3.11	1.22	1.13
87	0.58	2.46	1.24	0.82
140	1.18	1.81	3.22	1.07
138	1.15	1.92	—	—
98	1.12	1.04	2.01	0.36
101	0.53	3.46	1.11	1.48
26	3.07	0.42	—	—
22	1.40	0.90	—	—
24	1.07	1.37	1.54	0.61
67	2.04	0.51	3.15	0.26
171	10.00	0.08	—	—
4	3.05	0.24	—	—
137	6.58	0.20	—	—
114	7.20	0.20	—	—
177	7.90	0.09	—	—

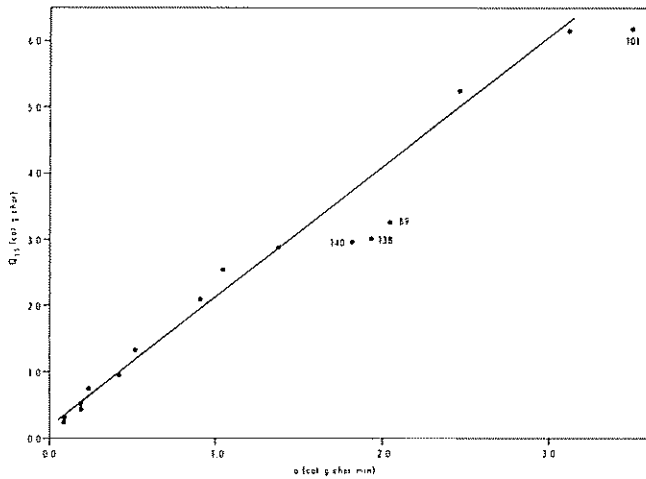


Figure 4 Relation between heat released (Q_{15}) and the Elovich parameter (a) upon oxygen chemisorption on chars

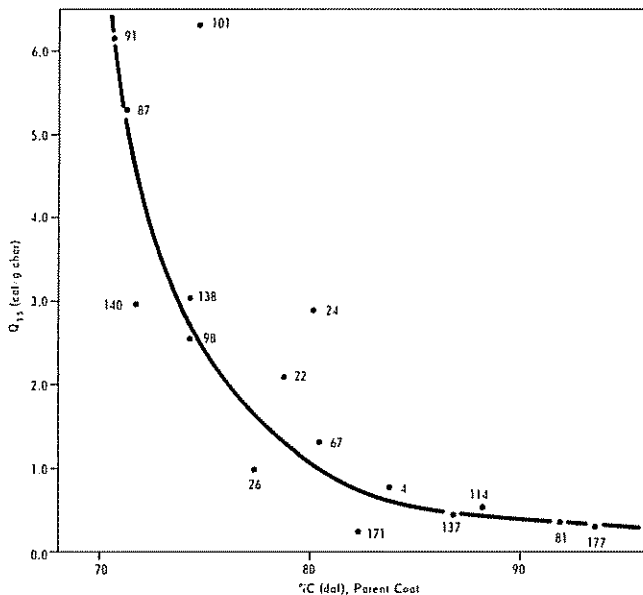


Figure 5 Variation of heat released upon oxygen chemisorption on chars with carbon content of the parent coals

Independent of char reactivity, the plots can be normalized to one curve by dividing experimental reaction times by the reaction time, $t_{0.5}$, to attain a fractional burn-off of 0.5. Thus values of $t_{0.5}$ can be used as a measure of char reactivity. Figure 8 shows the correlation between Q_{15} and $t_{0.5}$ for the char-air reaction. The correlation is essentially linear, and the more heat released in 15 min upon oxygen chemisorption at 373 K on the chars, the greater the char gasification rates in air at 678 K.

It is notable, however, that the char produced from lignite PSOC 140 falls substantially below the line in duplicate d.s.c. runs. This cannot be explained by ΔH for oxygen chemisorption showing an unusually low value, but the char may have unusual molecular sieve properties that exclude O₂ from a significant number of active sites at 373 K, only to be opened up to air upon gasification. Alternatively, oxygen chemisorption at apertures may effectively block access of O₂ to a significant fraction of surface active sites.

Enthalpy of oxygen chemisorption

Results presented in Figures 1-3 can be used to calculate values of ΔH ($\Delta H = 32Q/W$), which are plotted in Figure 9 as a function of time. At fixed values of reaction time, ΔH values for the chars produced from bituminous coals are significantly lower than those produced from the low rank lignite and subbituminous coals. However, there are also large differences in ΔH for the low rank coals. Further, there are wide differences in the way ΔH changes with reaction time for the chars. The majority of the chars shows decreasing values of ΔH with increasing time or increasing coverage with chemisorbed oxygen. Two chars show essentially no

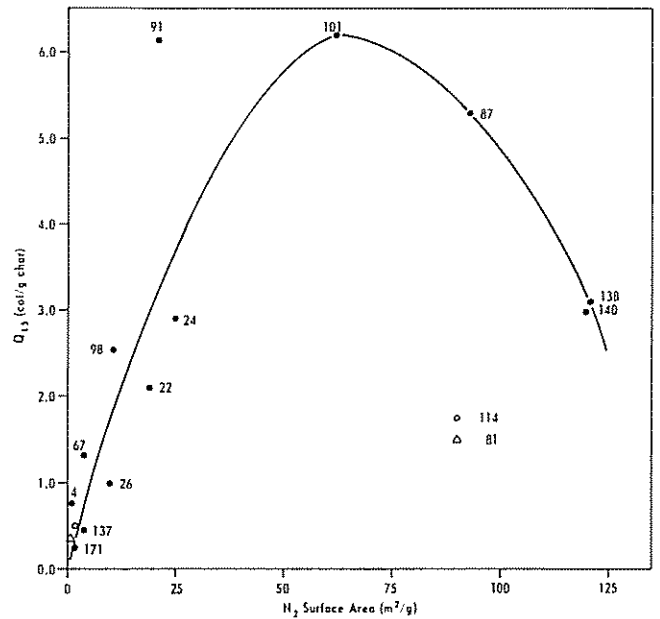


Figure 6 Relation between heat released upon oxygen chemisorption on chars and N₂ surface area of chars

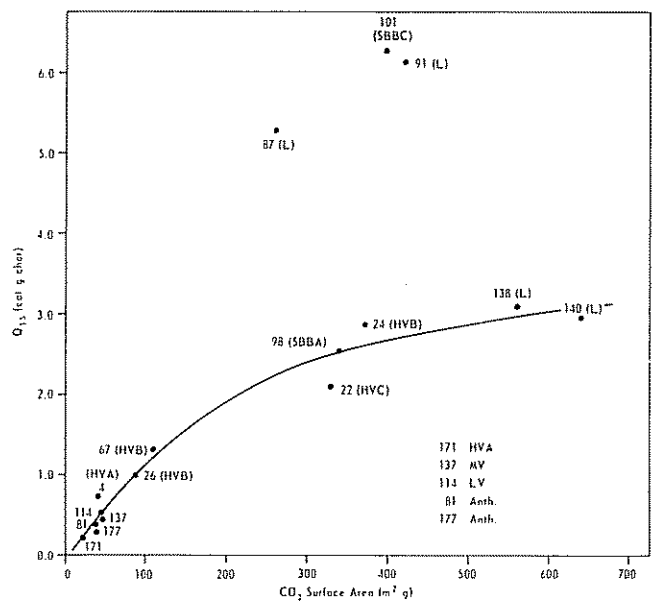


Figure 7 Relation between heat released upon oxygen chemisorption on chars and CO₂ surface area of chars

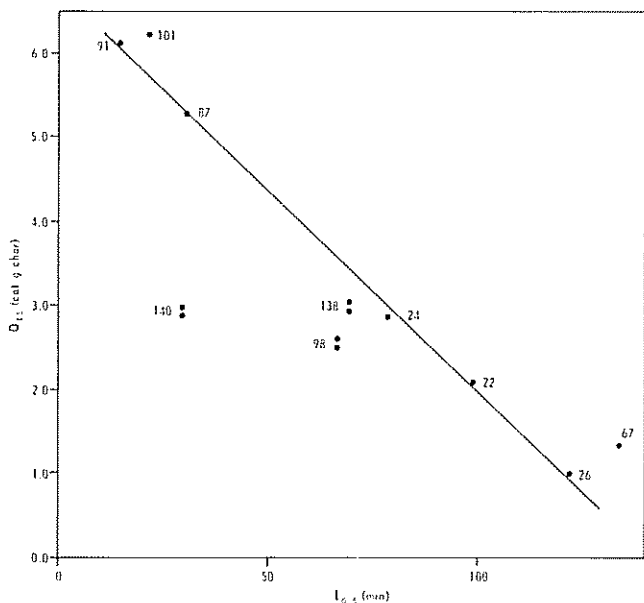


Figure 8 Relation between Q_{15} and time required to gasify 50% of chars in air at 678 K

change in ΔH with time, and one coal shows a slight increase in ΔH with time.

As discussed by Boudart¹³, ΔH frequently decreases with increasing coverage during chemisorption because of *a priori* and/or induced heterogeneity. *A priori* heterogeneity is attributed to the surface of the solid being terminated with different crystallographic planes and/or different chemical species. Induced heterogeneity is attributed to increased interaction of chemisorbed species with each other with increasing coverage and/or a change in the work function of the solid as chemisorption proceeds, even on a homogeneous surface. Previous studies with Saran char⁶ have shown that ΔH for oxygen chemisorption depends on the temperature to which the char is heated before oxygen chemisorption at 373 K. In this study, the chars were heated at 873 K in flowing N₂ for 30 min. A temperature of ≈ 1250 K under ultra high vacuum is required to remove essentially all oxygen complexes from carbon surfaces as CO and CO₂^{8,9}. From studies on Saran char⁶, it is estimated that oxygen already covered $\approx 60\%$ of the carbon sites before chemisorption on the coal chars. The fraction of inorganic mineral matter and well dispersed metal oxide sites (derived from carboxylate groups in the low rank coals) covered by oxygen prior to commencing chemisorption runs is uncertain. Obviously, ΔH values for oxygen chemisorption on coal chars can be affected by many variables.

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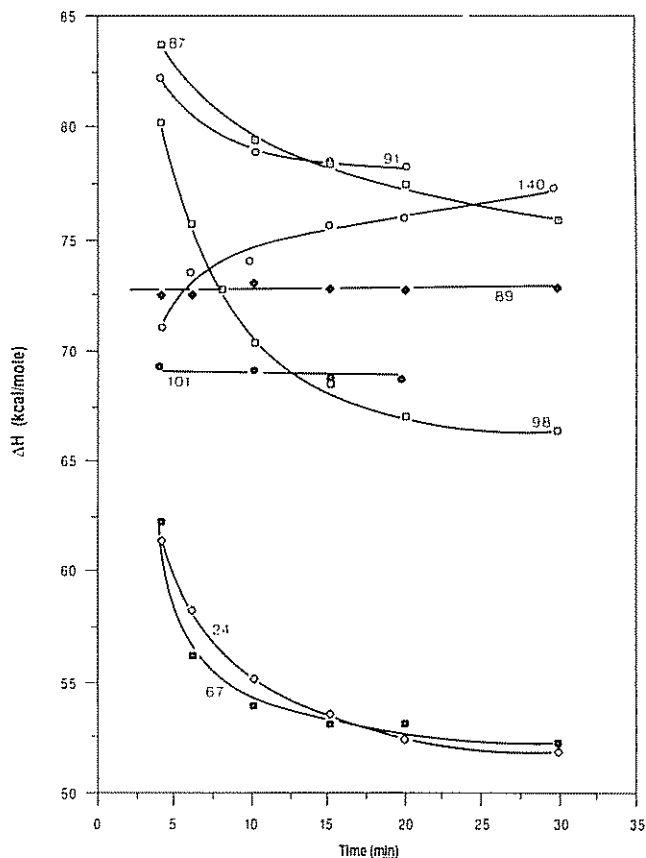


Figure 9 Change of ΔH with reaction time for oxygen chemisorption on coal chars

REFERENCES

- Jenkins, R. G., Nandi, S. P. and Walker, P. L. Jr. *Fuel* 1973, 52, 288
- Hippo, E. and Walker, P. L. Jr. *Fuel* 1975, 54, 245
- Tomita, A., Mahajan, O. P. and Walker, P. L. Jr. *Fuel* 1977, 56, 137
- Linares-Solano, A., Mahajan, O. P. and Walker, P. L. Jr. *Fuel* 1979, 58, 327
- Walker, P. L. Jr., Rusinko, F. Jr. and Austin, L. G. in 'Advances in Catalysis' (Eds. D. D. Eley, P. W. Selwood and P. B. Weisz), Vol. 11 Academic Press, New York, USA, 1959, pp. 133-221
- Ismail, I. M. K. and Walker, P. L. Jr. *J. Colloid Interfac. Sci.* 1980, 75, 299
- Ismail, I. M. K. *Ph.D. Thesis* The Pennsylvania State University, USA, 1978
- Walker, P. L. Jr., Bansal, R. L. and Vastola, F. J. in 'The Structure and Chemistry of Solid Surfaces' (Ed. G. Somorjai), Wiley, New York, USA, 1969, pp. 81: 1-81: 16
- Bansal, R. C., Vastola, F. J. and Walker, P. L. Jr. *J. Colloid Interfac. Sci.* 1970, 32, 187
- Mahajan, O. P. and Walker, P. L. Jr. *Fuel* 1979, 58, 333
- Nsakala, N. Y., Essenhigh, R. H. and Walker, P. L. Jr. *Fuel* 1978, 57, 605
- Mahajan, O. P., Yarzab, R. and Walker, P. L. Jr. *Fuel* 1978, 57, 643
- Boudart, M. *J. Am. Chem. Soc.* 1952, 74, 3556