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STRUCTURAL CHANGES IN COAL CHARS DURING GASIFICATION

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ABSTRACT

Two bituminous coal chars of the same rank were gasified at atmospheric pressure with CO_2 at 980 C. Porosities and reaction rates were measured at different degrees of carbon burn-off. Comparison of changes in porosity and reactivity with per cent burn-off indicates that total surface area is a significant parameter for reactivity but cannot be regarded as the major controlling factor.

INTRODUCTION

As reserves of natural gas and oil began to decline, interest in coal gasification to produce substitute natural gas, and in coal characterisation has increased. In particular, the British Gas Corporation has developed and proven the BGC-Lurgi Slagging Gasifier for a wide range of coals. The process used in the gasifier is the steam-oxygen gasification of coal where the following reactions take place :

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (2)$$

$$C + CO_2 \rightarrow 2CO \qquad (3)$$

The rate determining step of the steam-oxygen reaction(1) is considered the same as that in the carbon-carbon dioxide reaction(2,3). Therefore, as the carbon-carbon dioxide reaction is also the simplest of the heterogeneous gasification reactions, it was chosen as the reaction to be studied here.

The reactivity of a coal char will depend, among other things, on the number of active sites(4,5), and the pore structure of the char, as well as on char pretreatment and the nature and concentration of mineral matter. Although the number of active sites is the most important parameter where the reaction is chemically controlled, the development of pore structure with carbon burn-off may well determine the accessibility of reactants to active sites and, hence, determine reactivity.

Measurement of surface areas and microporosity(4,5,6,7) of coal chars is complex. A commonly used equation (D-R) is that of Dubinin and Radushkevich(8)

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based on the earlier Dubinin Polanyi Theory of Volume Filling of Micropores$^{(9,10)}$. It has the form :

$$w = w_0 \exp \{-B(T/\beta)^2 \log^2 (p_0/p)\} \qquad (4)$$

where w is the amount of adsorptive taken up at pressure, p, and w_0 is the total micropore volume.

The object of this paper is to show how micropore volume and specific surface area of two bituminous coal chars of the same rank change as the chars are burned away and to see if these changes correlate with changes in reactivity.

EXPERIMENTAL

Reactivity Measurements

Two British bituminous coals were used in this work : Markham Main and Manvers Barnborough. Both belong to the NCB 702 classification; this rank being the most abundant in the U.K. They were first converted to chars by pyrolysis, under nitrogen, at temperatures of 860°C and 910° respectively.

Ultimate analysis of the chars showed the Markham char to have a carbon content of 87.2% (as received basis) and the Manvers to contain 89.4% carbon. Thermogravimetric analysis then revealed a volatile carbon content of 7% and 2%, respectively.

Ten gram samples of the chars were then placed in a differential fixed bed reactor at atmospheric pressure. They were brought up to reaction temperature (980°C) in a stream of N_2 prior to gasification with CO_2. The cross-sectional gas flow across the 3 cm deep char bed was about 450 moles min^{-1} m^{-2}. Traces of oxygen were removed upstream of the char bed by an oxygen trap and gas products were analysed downstream by gas chromatography.

The reaction of carbon dioxide with carbon produces only carbon monoxide (equation 3). Therefore, the gasification rate of the coal char (R) is half the rate of production of CO (R_{CO}), which can be calculated directly from analysis of the outlet gas composition and flow rate.

The amount of carbon burned off the char surface (B) at any time (t) is found from :

$$B = \Sigma \frac{R_i + R_{(i-1)}}{2} (t_i - t_{(i-1)}) \qquad (5)$$

The specific gasification rate (R_s), which is defined as the gasification rate per gram of solid carbon available for reaction at any time (t), is :

$$R_s = C/(C_F - B) \qquad (6)$$

where C_F = total amount of fixed carbon in the original char.

Whilst the carbon lost from the char, measured as the percentage of the original carbon content burned off the char (%B) is :

$$\%B = \frac{100B}{C_F} \tag{7}$$

Reaction rates were found to be reproducible to within ±10% for the same reaction conditions in all cases.

Surface Area Measurements

Seventy-five milligram samples of the same chars with particle size 500 - 850 μm were placed in a platinum mesh bucket within a silica hangdown flowtube on a Cahn 2000 Electrobalance. They were gasified with CO_2 under the same conditions as in the differential reactor except that the reaction was stopped at different percentages of burn-off in order to measure the changes in surface porosity.

After samples were gasified on the Electrobalance, they were outgassed overnight at 730°C to about 10^{-5} bar. This was to remove any oxygen complex formed on exposure of the char to air which would block the micropores. A carbon dioxide isotherm was then carried out at 195 K.

After completion of the CO_2 isotherm, samples were outgassed overnight at 730°C. They were then saturated at room temperature with n-nonane according to the method of Gregg and co-workers(11,12). Saturation was judged to be complete when uptake of nonane ceased, generally after 5 - 16 hours. This was followed by degassing to 10^{-4} bar, also at room temperature, to remove excess nonane. It is assumed that the long nonane molecules not only fill all the micropores in the system but also strongly resist desorption from the micropores at room temperature by reason of their shape. A nitrogen isotherm was then determined at 77 K and the BET surface area measured was considered to be the surface area of mesopores only.

RESULTS AND DISCUSSION

Reactivity Curves

One potential problem with heterogeneous reactions at high temperature is that of rate limitation by bulk diffusion. However, Bradshaw et al(13) showed that at atmospheric pressure and up to 1000°C bulk diffusion effects did not restrict the reaction of carbon with CO_2 in a thermobalance flow system. In their system the Manvers char used was from the same batch as used in this work. It was of particle size 15 - 180 μm and had a maximum reaction rate, at 980°C, of 9.5×10^{-4} moles min^{-1} g^{-1}, whilst in this work, using a different reaction system and a different particle size, the maximum reaction rate under the same conditions was 8.5×10^{-4} moles min^{-1} g^{-1}.

Plots of reactivity vs. carbon burn-off at 980°C are shown in Figure 1 for both coal chars. As can be seen, the Markham is by far the more reactive at all values of measured burn-off. The general shape of the two plots are also distinctly different. Both show an initial rise in reactivity which may possibly be attributed to carbon burn-off opening up closed pores, or removal of carbon behaving like debris initially blocking the structure(14). However, above about 20% burn-off the Manvers shows a more or less constant reactivity up to 80%, whilst the Markham shows a steady increase in reactivity up to about 50%, followed by a sharp fall above 60%.

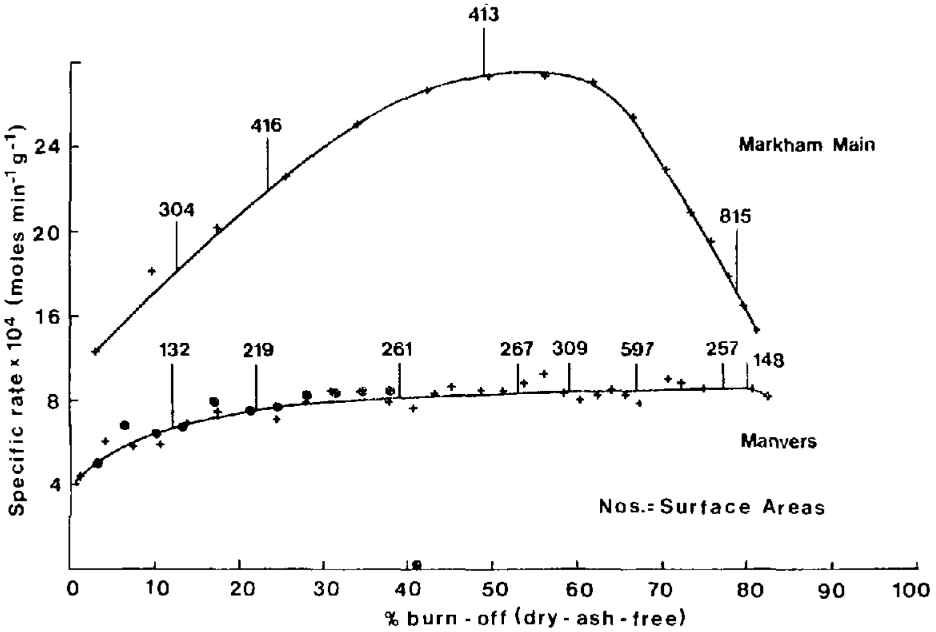

FIG.1 REACTIVITY VS % BURN - OFF

At 100% burn-off the reaction will clearly cease since there will be no more carbon to react. However, the definition of reactivity adopted in this work means that it is a differential quantity, with the weight of carbon remaining as the denominator, so there is no fundamental reason why the rate should fall before 100% burn-off is reached. From these results, there is no evidence one way or the other but the fall-off in reactivity of Markham may be due to effects of residual mineral matter or to a genuine decrease in activity at high carbon burn-off. However, a point to be borne in mind is that the carbon burn-offs are calculated indirectly during reactivity measurements by mass balance and that errors in flow rates of the product gas are cumulative so that errors arise in the higher values of carbon burn-off. This in turn affects the specific rate values which depend on the amount of solid carbon remaining. This is the probable cause of the slight fall in the reactivity of Manvers above 80% burn-off. From this point of view, the gravimetric method of determining reactivity is superior because the amount of carbon gasified and the amount of carbon remaining are obtained directly by the same single measurement.

Surface Area and Micropore Volumes

Values for the micropore volume, w_0, determined from the simplified D-R equation, and values of "surface area" determined from them are shown in Table 1 for both chars.

TABLE 1

% Burn-off	Spec. Rate (moles min^{-1} g^{-1} x 10^{-4}	Mesoporous N_2 Surface Area m^2/g	D-R w_0 cm^3/g	Total D-R Surface Area m^2/g	Spec. Rate/D-R Surface Area (mol.$min^{-1}m^{-2}$ x 10^6)
Manvers Barnborough Char (Carbon Content 89.4%)					
12.01	6.6	29.34	0.0569	132	5.0
22.43	7.4	45.68	0.094	219	3.4
23.35	7.45	-	0.0979	228	3.3
39.12	7.95	76.62	0.1123	261	3.1
53.19	8.25	166.00	0.1148	267	3.1
59.36	8.35	-	0.1328	309	2.7
67.76	8.50	445.00	0.2566	597	1.4
77.45	8.50	-	0.1104	257	3.3
80.00	8.50	257.00	0.0638	148	5.7
Markham Main Char (Carbon Content 87.2%)					
12.89	13.5	40.64	0.1308	304	4.4
23.64	18.0	47.50	0.1785	416	4.3
23.55	18.05	-	0.1724	401	4.5
48.93	23.4	191.50	0.1775	413	5.7
78.78	13.05	384.00	0.3506	815	1.6

The problems of measuring surface areas of microporous carbons have been discussed before(4,5,6,7). Our choice of CO_2 adsorbed at 195 K was based on the need to use sufficiently high a temperature to allow diffusion of CO_2 along the very small micropores at an acceptable rate. At the same time we wished to work as near $P/p_0 = 1$ as was possible, with a non-pressurised apparatus, to see whether there was any tendency to multilayer formation at these higher partial pressures. One problem that arises is the value of p_0 to adopt. We have followed the use of Sing and his co-workers(15) in using that of the liquid extrapolated down to 195 K. The value is 1.86 bar and this means that effectively values of $P/p_0 > 0.6$ cannot be attained. The cross-sectional area of CO_2 was taken as 0.17 nm.

The isotherms (shown in Figure 2) are essentially of Type I, although values for $P/p_0 > 0.5$ could not be reached, as discussed above, so that it is difficult to say whether they have any Type II character. However, most of the D-R plots were linear over the range of $P/p_0 = 0.25$ only and showed upward deviations for higher values of P/p_0. This suggests that the pore filling model accounts for most of the adsorption observed but that there is a significant contribution from a BET-like multilayer formation.

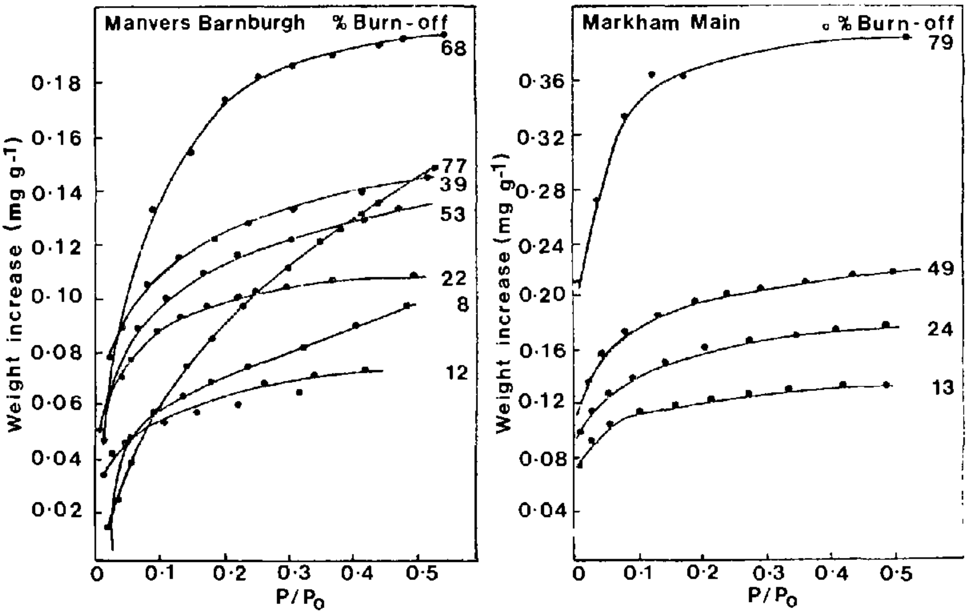

FIG. 2 COAL CHAR CO_2 ISOTHERMS AT DIFFERENT CONVESION LEVELS

A feature of the adsorption process was its slowness at 195 K suggesting that difficulties arising from activated adsorption and slow diffusion in narrow pores are not completely overcome even at relatively high temperature. Similar slow adsorption at relatively high temperatures on microporous carbons have been found by Koresh and Soffer(14) and attributed by them to carbon 'debris' in the pores slowing down diffusion of the adsorbed phase along the pores. However, Nandi et al(16) also found that a longer period of time is usually required to establish equilibrium when adsorbing CO_2 onto bituminous coals. Nevertheless, the problem was particularly troublesome at low values of carbon burn-off and was the reason why no adsorption was carried out on reacted chars. It was alleviated by increasing burn-off which suggests that carbon debris is increasingly removed as reaction proceeds.

Combined n-nonane and N_2 Adsorption

If larger pores were present, it would, in principle, be possible to use the method of Gregg and his co-workers to block off the genuine micropores (d < 2nm) by pre-adsorbing nonane. The surface area associated with the larger pores could be determined by adsorption of N_2 at 77 K in the usual way). Results for BET areas obtained by this procedure are given in Table 1, column 3. They show that at low values for carbon burn-off the mesopores contribute relatively little to the total surface area. However, as reaction proceeds and the D-R surface area increases, so too does the mesopore surface area.

However, some caution is needed in interpreting these results. The uptake of N_2 in some instances was very slow, indicating the problem of activated diffusion. Moreover, t-plots(17) of N_2 adsorbed on the nonane-filled char surfaces were quite anomalous giving plots in some cases with negative intercepts. In the results of Gregg and co-workers, the removal of the Type I component by filling micropores with nonane gives a simple Type II N_2 isotherm which in theory gives a linear t-plot passing through the origin.

We surmise that the method may break down in the present case because the coal char has a surface that is highly heterogeneous and in which there is a broad spread of pore size ranging continuously from molecular sized pores on one extreme to the mesopore region and up to the macropore region on the other.

Correlation of Reactivity and Surface Area

Markham char, besides having the greater reactivity does generally have a higher D-R surface area than Manvers. On the other hand, the reactivity per unit area is still widely different for the two chars (Table 1, column 6). However, there is a reasonable correlation of surface area with reactivity up to burn-off values of about 50%. Thereafter, the two parameters diverge sharply. These phenomena are illustrated in the reactivity plot of Figure 1 which also shows values for surface area at different values of carbon burn-off. Table 1 (column 2) shows values for specific rate using the D-R surface area. The most notable anomaly is seen for the Markham char where reactivity is falling off sharply at high values of burn-off while surface area is still increasing.

It is possible that the concept of active surface area (ASA)(18) with accessibility to active sites controlled by mesopores may be more rewarding and it is one that we shall pursue for future work.

Thus, with the limited evidence presented here, it is not possible to be definitive about correlation between micropore surface area and reactivity. Some limited correlation does occur for the earlier part of the reaction but does not hold over complete burn-off.

SUMMARY AND CONCLUSIONS

- Two coal chars of the same rank have remarkably different reactivities. Markham Main is almost twice as reactive as Manvers Barnborough.
- Different shapes of the reactivity plots indicate differences in structure. Markham with a more closed structure than Manvers, reaches its maximum later at about 45 - burn-off.
- Changes in reactivity plots are only partially paralleled by surface area changes for both chars. It seems that active surface areas (ASA) may be more important in controlling reactivity.
- The constant plateau of reactivity of Manvers after the maximum is reached indicates a constant dispersion of active sites.
- The decrease in reactivity of Markham after the maximum is reached indicates either : 1) a decrease in active site dispersion; or 2) a decline in activity of active sites with burn-off.
- Finally, ambiguity in porosity results, especially towards the end of gasification indicates a complexity of interaction between structure and reactivity and other effects such as the catalytic effect of mineral matter. Also, there appears to be a continuum of all types of pores throughout the chars up to nearly full conversion. Ambiguity also reflects the difficulty in characterising a complex material such as coal which has a flexible(19) structure. Nevertheless, the results are interesting and show that more studies are needed on coal chars especially on active surface area in relation to reactivity.

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