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the science and technology of Fuel and Energy



Published by Butterworths

Importance of carbon active sites in the gasification of coal chars

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(Received 18 November 1982, revised 31 January 1983)

A demineralized lignite has been used in a fundamental study of the role of carbon active sites in coal char gasification. The chars were prepared in N_2 under a wide variety of conditions of heating rate (10 K min^{-1} to 10^4 K s^{-1}), temperature (975–1475 K) and residence time (0.3 s–1 h). Both pyrolysis residence time and temperature have a significant effect on the reactivity of chars in 0.1 MPa air, determined by isothermal thermogravimetric analysis. The chars were characterized in terms of their elemental composition, micropore volume, total and active surface area, and carbon crystallite size. Total surface area, calculated from CO_2 adsorption isotherms at 298 K, was found not to be a relevant reactivity normalization parameter. Oxygen chemisorption capacity at 375 K and 0.1 MPa air was found to be a valid index of char reactivity and, therefore, gives an indication, at least from a relative standpoint, of the concentration of carbon active sites in a char. The commonly observed deactivation of coal chars with increasing severity of pyrolysis conditions was correlated with their active surface areas. The importance of the concept of active sites in gasification reactions is illustrated for carbons of increasing purity and crystallinity including a Saran char, a graphitized carbon black and a spectroscopically pure natural graphite.

(Keywords: coal chars; gasification; active sites; carbon)

A fundamental understanding of the kinetics of coal gasification requires the knowledge of the role of carbon active sites, inherently present catalysts and diffusivity of the reactant and product gases within the pores of the devolatilized char¹. At the present time, however, a complete quantitative assessment of the relative importance of these three factors, and especially the first two, is still impossible to make. The pressing need for design data for the new generations of coal gasification processes probably justifies the great number of essentially empirical kinetic studies that provide useful correlations but in which the above factors are combined into overall parameters (e.g., reactivities), which cannot be related to measurable physical properties of the corresponding chars. The predictive capabilities of such correlations and the possibility of their extrapolation are uncertain at best. A parallel effort is needed to obtain more fundamental kinetic parameters.

Many coal researchers have not fully realized the relevance to the kinetics of coal gasification of studies performed on relatively pure and highly crystalline materials such as graphitized carbon blacks and graphite. A recent comprehensive review by Essenhigh² stresses the value of these studies in helping to understand coal reactions.

It has been emphasized, e.g., by Laine *et al.*³, that a fundamental rate constant for the carbon–oxygen reaction cannot be obtained on the basis of the total surface area (TSA) of the reacting carbon. A fundamental rate constant should depend only on the reaction temperature and not on the extent of reaction or, possibly, the type of carbon used. Laine *et al.*³ showed, in the case of a graphitized carbon black, that the rate 'constant' based on

TSA increased continuously with conversion (burn-off). However, when the constant was expressed per unit of active surface area (ASA), taking into account the formation of a stable carbon–oxygen complex, it was essentially unchanged with conversion. The importance of ASA in the gasification of carbons has been suggested or confirmed by other investigators^{4–6}. It is reasonable to expect that the wide spread in reported experimental values of reactivity per unit of total surface area (up to four orders of magnitude) of different carbons and chars⁷, obtained under presumably identical reaction conditions, is due, at least in part, to the different amounts of ASA in carbons (chars) with the same TSA⁸.

The purpose of the present Paper is to present experimental evidence for the usefulness (and, indeed, necessity of application) of the concept of active sites in understanding the gasification behaviour of coal chars. The role of catalysis is discussed in companion publications^{9,10}.

EXPERIMENTAL

Coal demineralization

The coal used in this study was a North Dakota lignite (PSOC-246) from the Hagel seam. It has already been thoroughly characterized^{11,12}. A 70 × 100 US mesh fraction of the raw coal (mean particle size $\approx 170\ \mu\text{m}$) was washed with HCl and HF to remove essentially all the inorganic constituents. About 40 ml of 5 N HCl were added to 6 g of coal in a plastic beaker (250 ml). The mixture was stirred for 1 h at 330–335 K. The coal was filtered off and mixed with 40 ml of full-strength (29N) HF. This mixture was also stirred at 330–335 K for 1 h, then

filtered and the coal residue mixed with full-strength (12 N) HCl for a third treatment at the same temperature for 1 h. Finally, the coal was filtered off, washed with warm distilled water until no chloride ion was detected in the filtrate (with 0.1 N AgNO₃), and dried in air at room temperature.

Coal pyrolysis

The demineralized (Dem) coal was devolatilized in a flow of N₂ (99.99% purity) by both slow and rapid pyrolysis. Slow pyrolysis (10 K min⁻¹) was carried out in a conventional horizontal-tube furnace at 975–1475 K and residence (soak) times up to 1 h at final temperature. Rapid pyrolysis ($\approx 10^4$ K s⁻¹) was carried out in an entrained-flow furnace at 1275 K. The residence time was varied between 0.3 s and 5 min. The details of the experimental set-up and procedures are given elsewhere^{8,13}.

Char reactivity measurements

Reactivities of the chars were determined by isothermal thermogravimetric analysis (TGA) in 0.1 MPa air. A Fisher TGA unit (model 360) was used. Air (20 kPa O₂) was chosen as the reactant gas because the high reactivity of carbon in O₂ allowed operation at low temperatures, typically 550–750 K. Under these conditions the concentration of active sites, created at higher temperatures (≥ 975 K), does not change significantly between the pyrolysis and gasification steps.

The gas flow rate was 300 cm³ (s.t.p.) min⁻¹. About 1–5 mg of the char were placed in a platinum bucket suspended from the Cahn balance within a quartz hang-down tube. The reactant gas was preheated by flowing downwards through the outer concentric tube before contacting the sample in upward flow through the inner tube. The furnace was preheated to the reaction temperature and then raised to surround the hangdown tube in which a flow of dry, O₂-free N₂ (99.999% purity) was maintained. After a period of ≈ 15 min, in which the recorded sample temperature and weight reached constant values, the flow of N₂ was switched to dry air. Weight changes were recorded continuously as a function of time. Additional details of the experimental procedure are given elsewhere⁸.

Char characterization

Elemental analyses (C, H, N) were performed on the Dem-chars to determine the extent of their devolatilization. The amounts of potential gasification catalysts still present in the chars were determined by emission spectroscopic analysis of the high-temperature ash (HTA) from the Dem-coal. X-ray diffraction (XRD) patterns were also obtained from the Dem-chars to determine the size of the carbon crystallites formed during pyrolysis. A Rigaku diffractometer (Geigerflex D/max; 40 kV, 20 mA, CuK α radiation) was used. The samples were mounted into a hollow aluminium holder (20 \times 17 \times 2 mm) provided with a glass slide on the bottom. A silicon internal standard was used.

In an attempt to measure the concentration of carbon active sites, oxygen chemisorption capacity of the chars was determined. A quartz bucket with ≈ 0.05 – 0.10 g of char was placed on top of a thermocouple sheath in a double-walled quartz reactor. Before and after chemisor-

ption, the system was outgassed at 375 K to a pressure of $\leq 10^{-4}$ Pa. Chemisorption was carried out at 375 K and 0.1 MPa air for ≈ 12 h. The furnace temperature was then raised to 1225 K and held constant for 3 h to release the chemisorbed oxygen³ as CO and CO₂. A liquid N₂ trap was used to freeze out CO₂ and prevent its reaction with the char sample. The total quantity of gases evolved was measured with a Baratron differential manometer. Gas analyses were carried out with a mass spectrometer.

Physical adsorption of CO₂ at 298 K on the various Dem-chars was also measured to obtain values for their micropore volume and total surface area. A conventional volumetric apparatus was used¹⁴. Usually adsorption equilibrium was reached within 1 h in the entire pressure range used.

THEORETICAL

As a TGA apparatus was used in this study for determining reactivities, it is convenient to express the observed rates (R), which are intensive properties, in terms of unit mass of solid reactant. Thus, by definition:

$$R \equiv -\frac{1}{m_c} \frac{dm_c}{dt} \quad (1)$$

where m_c is the mass of carbon (dry, ash-free char) at time t . Defining conversion of carbon, X_c in conventional terms:

$$X_c \equiv (m_{c,0} - m_c)/m_{c,0} \quad (2)$$

where $m_{c,0}$ is the initial mass of carbon, Equation 1 becomes:

$$R \equiv \frac{1}{1 - X_c} \frac{dX_c}{dt} \quad (3)$$

At a constant temperature, in isothermal TGA studies, and in the absence of catalysis, the rate is a function of the concentration of reactants. Assuming first-order dependence on carbon concentration and pseudo-zero-order dependence on gas concentration (flow system, excess gas present):

$$R \equiv \frac{1}{1 - X_c} \frac{dX_c}{dt} = kC_c \quad (4)$$

where k is the rate constant (pressure dependent, if the rate is not zero-order in gas concentration); C_c is the concentration of carbon active sites. Thus:

$$\frac{dX_c}{dt} = kC_c(1 - X_c) \quad (5)$$

The term dX_c/dt represents the slope of the TGA plot, i.e., conversion *versus* time. It is seen that it depends on the variation of C_c with conversion. If $C_c \neq f(X_c)$, dX_c/dt is expected to decrease continuously from some maximum value at $X_c = 0$ to zero at $X_c = 1$. However, in general:

$$C_c = f(X_c) \quad (6)$$

The nature of this functional relationship is the key to the determination of fundamental rate constants³. For coal chars it is unknown at the present time and equation cannot be integrated to determine the rate constant k . Therefore, a simplified approach was adopted in this study. The concentration of carbon active sites (ASA) was

Table 1 Spectroscopic analysis of ash from Dem-coal (% HTA = 0.22) and amounts of potential gasification catalysts in Dem-char

Compound	Content in ash (wt %)	Content in Dem-char (wt %)
SiO ₂	7.5	n.a. ^a
Al ₂ O ₃	17.5	n.a.
TiO ₂	5.6	≈0.02
Fe ₂ O ₃	18.5	≈0.06 ^b
MgO	2.0	n.a.
CaO	9.8	≈0.04
SrO	<1	<0.005
BaO	15.9	≈0.07
Na ₂ O	<1	<0.005
K ₂ O	<1	<0.005
Total	≈77 ^c	-- ^c

^a n.a. = not applicable (no significant catalysis expected from clays¹⁵ or MgO¹⁶)

^b Assuming that Fe is present as FeS₂

^c The remaining 23% are principally sulphur oxides and are not thought to contain any significant amount of potential catalysts

Table 2 Elemental analysis of raw and Dem-coal and selected Dem-chars prepared at 1275 K

Sample	Content (wt %, dry)					Atomic H/C
	C	H	N	Ash	O+S ^a	
Coal						
Raw	64.1	4.4	1.4	9.7	20.4	0.82
Dem	66.8	4.5	1.2	≈0.2	27.3	0.81
Char ^b (Dem)						
R-0.3 s	89.6	2.0	1.3	≈0.4	6.7	0.27
R-1.8 s	92.4	1.1	1.2	≈0.4	4.9	0.14
R-5 min	91.5	0.6	1.3	≈0.4	6.2	0.08
S-30 min	90.6	1.3	1.3	≈0.4	6.4	0.17
S-1 h	94.7	0.7	1.2	≈0.4	3.0	0.09

^a By difference

^b R, rapid pyrolysis; S, slow pyrolysis

measured in the absence of gasification and the rate constant k was determined from the initial slope of the TGA plot, i.e., at $X_c \rightarrow 0$:

$$k = (dX_c/dt)_0 / C_c \quad (7)$$

RESULTS

Pretreatment of lignite with HCl and HF is quite effective in removing the inorganic constituents, the ASTM ash content being reduced from 9.7 wt% (dry) in the raw coal to ≈0.2%. Table 1 gives the results of the emission spectroscopic analysis of the ash obtained from the Dem-coal, as well as the maximum amounts of potential gasification catalysts present in the Dem-chars, calculated assuming 50% organic weight loss upon devolatilization.

Table 2 gives the elemental analyses of the starting raw and demineralized lignite and of selected Dem-chars. For sample designation here and throughout this paper, R refers to rapid pyrolysis and S to slow pyrolysis. The letter R or S is followed by the pyrolysis residence time. Unless otherwise indicated in parentheses, the lignite chars studied throughout the paper were prepared at 1275 K. For the raw lignite chars, when the kinetics were followed

by the ash-tracer technique, pyrolysis appeared essentially complete¹³ after ≈0.5 s at 1275 K; weight loss was ≈50% daf coal, and the char had a H/C atomic ratio of ≈0.3. As seen in Table 2, after 0.3 s at 1275 K the Dem-char had a similar H/C ratio. However, as was shown to be the case also for chars loaded with calcium⁹ and raw chars¹³, hydrogen evolution from the Dem-char is a slow process. There is a substantial decrease in the H/C ratio with increasing pyrolysis residence times past 0.3 s. The oxygen contents (together with sulphur) are given for completeness. These values are not thought to be reliable because they were obtained by difference. Also, they included the oxygen chemisorbed on the chars at room temperature upon exposure to air after pyrolysis.

The effect of pyrolysis conditions on the subsequent gasification reactivity ($R = dX_c/dt$) of Dem-chars in 0.1 MPa air is shown in Figures 1 and 2. A typical normalized TGA plot¹⁷ is given in Figure 3. In most cases, especially for the rapidly heated chars, the plots were essentially linear up to ≈50% conversion and subsequently exhibited a decrease in slope. For these chars the initial (maximum) slope was used in the calculation of rate constants according to Equation 7. In some cases, especially for the chars prepared by slow pyrolysis, an induction period was observed¹⁷. This portion of the burn-off plot of increasing slope could be eliminated in most cases by decreasing the reaction temperature. Therefore, it is attributed to initial diffusional limitations and

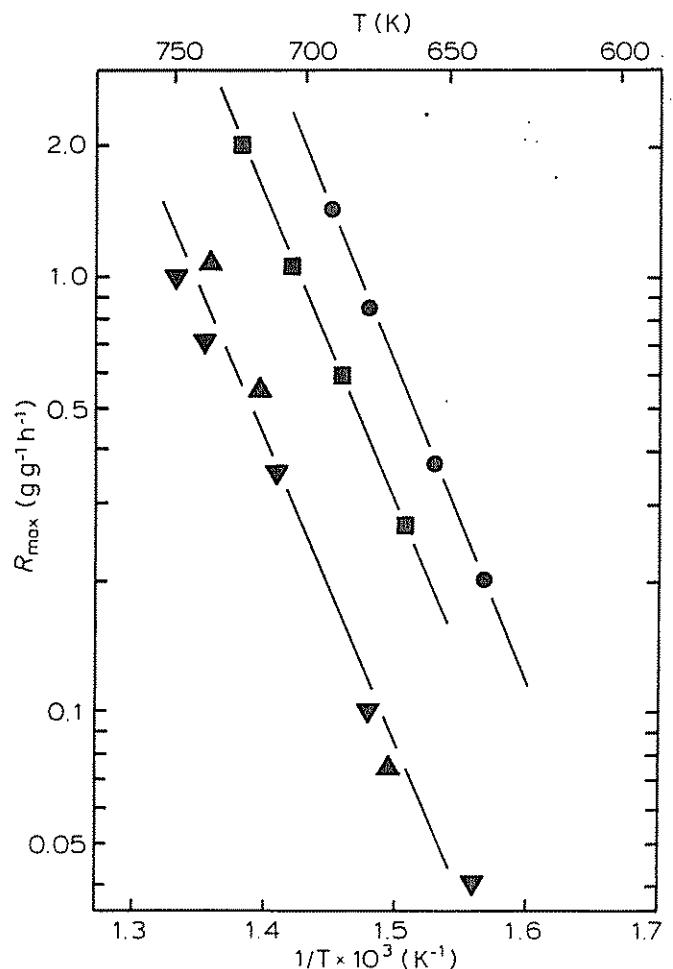


Figure 1 Effect of pyrolysis residence time at 1275 K on the reactivity of demineralized lignite char. ●, R-0.3 s; ■, R-1.8 s; ▲, R-5 min; ▼, S-1 h

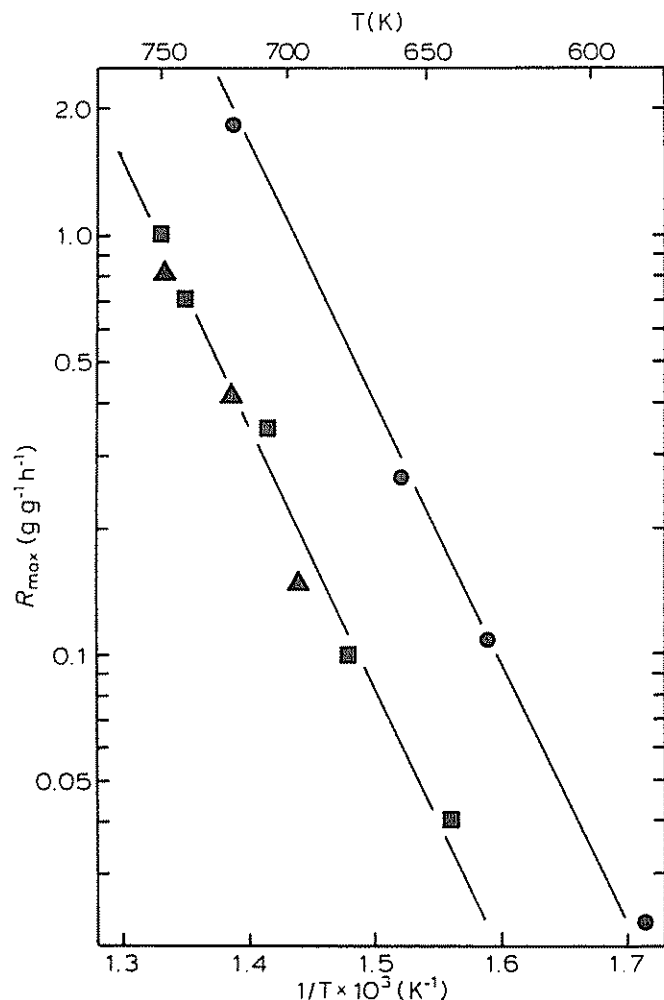


Figure 2 Effect of pyrolysis temperature at 1 h residence time on the reactivity of demineralized lignite char. ●, 975 K; ■, 1275 K; ▲, 1475 K

opening of the previously partially closed pores in the aperture-cavity pore system of these chars. For this type of char, the maximum slope was taken as the observed reactivity (R_{max}) in Figures 1 and 2, and it was used in the calculation of rate constants in Equation 7, assuming that the concentration of carbon active sites did not change appreciably. Also shown in Figure 3 are the predictions of the Simons' model¹⁸ for different values of initial porosity of the char.

It is seen in Figures 1 and 2 that both residence time at 1275 K and temperature have a significant effect, the reactivity decreasing with increasing severity of pyrolysis conditions. The reported reactivities were independent of gas flow rate and sample bed weight (or height) and were thus free from external heat and mass transfer limitations⁸. They were also independent of char particle size between 60 and 170 μm . However, in reactions of microporous solids, such as lignite chars, the insensitivity of the rate to changes in particle size is only a necessary, but not sufficient, condition for the absence of limitations of intraparticle mass transfer. The accessibility of the reactant gas to the micropores (< 2 nm), where most of the reactive surface is located, may not be improved significantly upon grinding even to particles of the order of 1 μm . However, theoretical predictions are uncertain because of the difficulties in estimating the effective gas diffusivity and diffusion distance in the porous solid⁸.

Additional experimentation was therefore necessary to show that the reported reactivities are intrinsic, chemically controlled rates.

It was reasoned that, as the reaction temperature is increased, a solid possessing a homogeneous microporous structure with no feeder (macro- and transitional) pores, such as a Saran char,* would enter partial diffusion control (Zone II in Ref.19) before a lignite char with its extensive feeder pore system²⁰. Figure 4 shows the Arrhenius plots for the two chars in the same range of reaction rates, used consistently throughout this study, between 0.02 and 5.0 $\text{g g}^{-1} \text{h}^{-1}$. The activation energies for both the Saran char and the Dem-chars are $\approx 130 \text{ kJ mol}^{-1}$ and constant in the entire range of rates. If it is assumed that for the very low rates, say below 0.05 $\text{g g}^{-1} \text{h}^{-1}$, the diffusivity of O_2 is high enough to achieve a uniform concentration throughout a char particle, then the constancy of activation energy implies the absence of Zone II conditions for the Saran char and, consequently, for the lignite chars. Indeed, Ismail²¹ also found that below $\approx 3 \text{ g g}^{-1} \text{h}^{-1}$, the reactivities of a similar Saran char were measured in the chemically controlled regime.

To set the reactivities of lignite chars into perspective, Figure 4 also shows the Arrhenius plots obtained in this study for carbons of increasing purity and crystallinity: a carbon black (CB, Monarch 700, Cabot Corp.), a graphitized carbon black (GCB, V3G, Cabot Corp.) and a spectroscopically pure natural graphite (SP-1, Union Carbide Corp.). Their activation energies for gasification in air were ≈ 145 , 200 and 200 kJ mol^{-1} , respectively. It is seen that at 700 K a difference in reactivity of about five orders of magnitude exists between the least reactive SP-1 graphite and the most reactive short-residence-time Dem-char.

* Saran (Dow Chemical Company) is a copolymer of vinylidene chloride and vinyl chloride in a mole ratio of $\approx 9:1$. The char was prepared by heat treatment in N_2 at 1175 K for 3 h

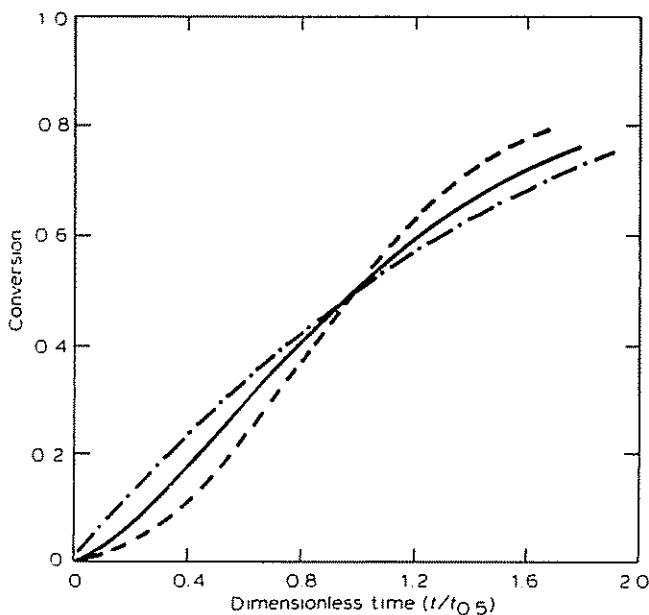


Figure 3 Normalized TGA plots for S-1 h (975 K) Dem-char at 720 K. (θ_0 , initial porosity). — Experimental curve (and curve predicted¹⁸ for $\theta_0 = 0.05$); --- curve predicted for $\theta_0 = 0.0$; -·- curve predicted for $\theta_0 = 0.5$

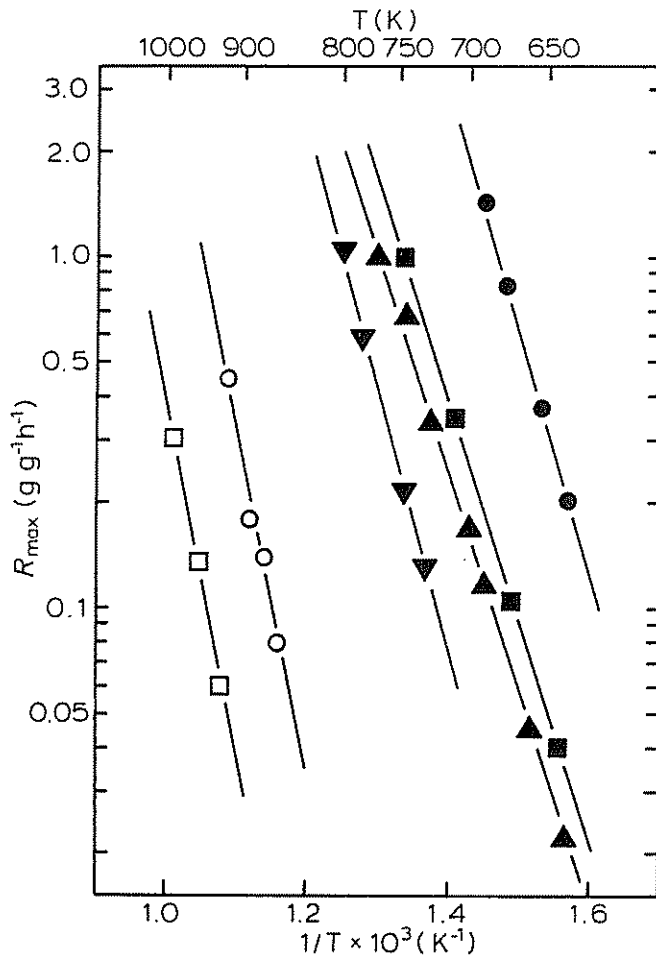


Figure 4 Arrhenius plots of reactivity for chars and carbons of various degrees of crystallinity and purity. ●, R-0.3 s; ■, S-1 h; ▲, Saran char; ▼, carbon black (Monarch 700); ○, graphitized carbon black (V3G); □, SP-1 graphite

Figure 5 shows the XRD patterns obtained for the starting Dem-coal and the short-residence-time chars prepared at 1275 K. The broad (002) and (10) carbon peaks at ≈ 23.5 and 43.5° (2θ), respectively, are characteristic of highly disordered carbonaceous materials. Crystallite height, L_c , and diameter, L_a , were estimated from the (002) and (10) diffraction peaks, respectively, using the Scherrer equation:

$$L = \frac{K\lambda}{B \cos\theta'} \quad (8)$$

where λ = the wavelength of the X-rays; θ = the Bragg angle; and B = the corresponding peak width at half-maximum intensity. For L_c and L_a determination²², $K = 0.9$ and 1.84 respectively. Crystallite sizes are shown in Table 3.

Table 3 also gives the results of oxygen chemisorption measurements for selected Dem-chars, as well as values of micropore volume of selected Dem-chars, obtained from CO_2 adsorption experiments²³ using the y -intercept of the Dubinin-Radushkevich plots and taking the density of liquid CO_2 at 298 K as 1.0 g cm^{-3} . Volumes are relatively high and of the same order of magnitude as found for typical²³ carbonaceous adsorbents (≈ 0.3 – $0.4 \text{ cm}^3 \text{ g}^{-1}$).

Table 4 gives the values of surface area and reactivity for selected Dem-chars prepared under a wide variety of

pyrolysis conditions. Total surface areas (column 2) were calculated by assuming that micropore volume is approximately equal to the BET monolayer capacity¹⁴. A value of 25.3 nm^2 for the surface area of the CO_2 molecule was assumed¹⁴. Values of active surface area, i.e., surface area occupied by dissociatively chemisorbed oxygen atoms (column 3), were calculated assuming a value of 0.08 nm^2 for the area occupied by each oxygen atom³. The reactivity values at 700 K in column 4 were obtained by interpolation from Figures 1 and 2. Rates per unit TSA (column 5) were obtained from columns 2 and 4. The rate

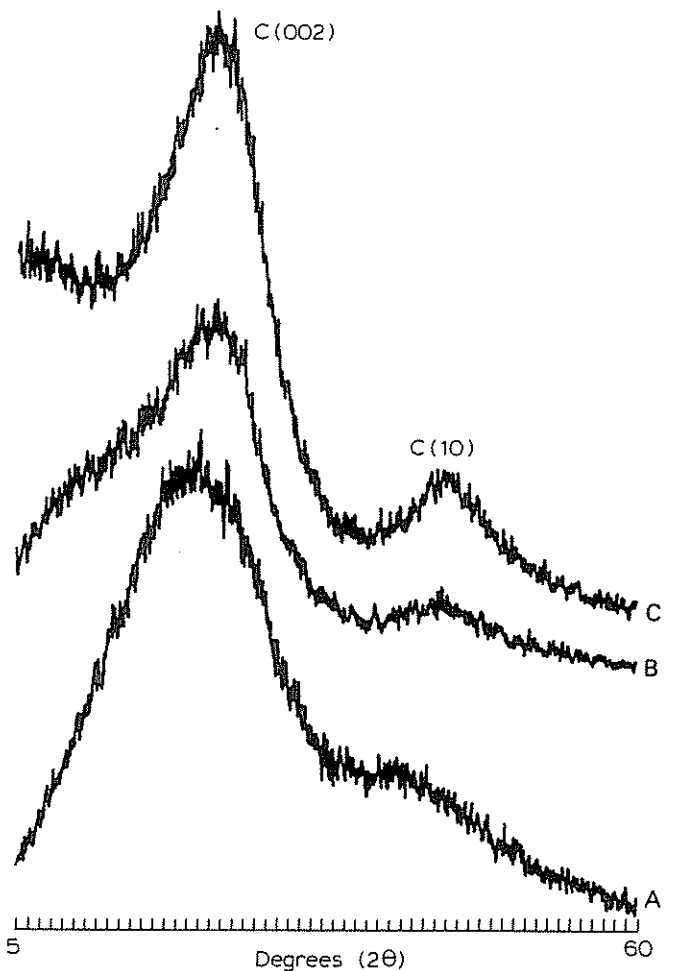


Figure 5 XRD patterns for Dem-coal and short-residence-time chars prepared at 1275 K. A, Coal; B, R-0.3 s; C, R-1.8 s

Table 3 Oxygen chemisorption capacities, micropore volumes and crystallite dimensions of selected Dem-chars

Sample ^a	Oxygen content (wt %)	Micropore volume ($\text{cm}^3 \text{ g}^{-1}$)	L_c (nm)	L_a (nm)
R-0.3 s	7.2	0.18	0.7	2.2
R-1.2 s	5.4	0.19	n.d.	n.d.
R-1.8 s	4.3	0.21	0.7	2.7
R-5 min	2.3	0.21	1.0	3.2
S-30 min	n.d. ^b	0.19	n.d.	n.d.
S-1 h	1.6	n.d.	1.0	3.0
S-1 h (975 K)	3.4	n.d.	n.d.	nd
S-1 h (1475 K)	0.72	n.d.	1.0	3.5

^a R, rapid pyrolysis; S, slow pyrolysis

^b n.d., not determined

Table 4 Surface areas and reactivities of Dem-chars and carbons of increasing purity and crystallinity

Sample ^a	TSA (m ² g ⁻¹)	ASA (m ² g ⁻¹)	R_{700} (g g ⁻¹ h ⁻¹)	R_{700} (g m ⁻² (TSA) h ⁻¹)x10 ³	k_{700} (g m ⁻² (ASA) h ⁻¹)x10 ³
R-0.3 s	630	225	1.8	2.9	8.0
R-1.8 s	730	133	0.94	1.3	7.1
R-5 min	710	73	0.30	0.42	4.1
S-30 min	665	n.d. ^b	0.28	0.42	n.d.
S-1 h	n.d.	50	0.25	n.d.	5.0
S-1 h (975 K)	n.d.	108	1.2	n.d.	11
S-1 h (1475 K)	n.d.	25	0.15	n.d.	6.0
Saran char	1224 ^c	50 ^c	0.15	0.12	3.0
CB-Monarch 700	206	n.d.	0.05	0.24	n.d.
GCB-V3G	63 ^c	<1 ^c	≈0.0002 ^d	0.0032	>0.2
SP-1 Graphite	1.8 ^e	<0.1 ^e	≈0.00002 ^d	0.011	>0.2

^a R, rapid pyrolysis; S, slow pyrolysis

^b n.d., not determined

^c Data taken from Taylor²⁴

^d Extrapolated value

^e Data taken from Walker *et al.*²⁵

constants (at 20 kPa O₂) in column 6 were obtained according to Equation 7, i.e., by dividing the values in column 4 by those in column 3. Also shown in Table 4 are the corresponding values of surface area and reactivity for carbons of increasing purity and crystallinity.

DISCUSSION

The presence of abundant exchangeable cations (mainly Ca²⁺) on the carboxyl groups in lignites makes possible a very high initial dispersion of inherent catalysts (principally CaO) on the char surface during gasification. It was shown in other parts of this study⁸⁻¹⁰ that lignite char gasification should be treated as a catalytic gas-solid reaction, with catalyst dispersion being the relevant reactivity parameter. Therefore, an attempt to understand the role of carbon active sites becomes meaningful only in the absence of these *in situ* catalysts, wherein lies the purpose of the demineralization step. A demineralized lignite should be considered as the most convenient 'model compound' for studying uncatalysed coal char gasification reactions at a fundamental level. It contains ≈2000 ppm of impurities, which is still a relatively high level of potential catalysts when compared to carbons of higher purity²⁴, also used in this study: SP-1 graphite (<6 ppm), V3G (<120 ppm) and Saran char (<100 ppm). Pyrite is known not to be removed effectively by treatment with HCl and HF, which is reflected in its relatively high content in the Dem-char. However, it is expected to be poorly dispersed, and it rapidly loses catalytic activity in oxidizing atmospheres²⁶. Thus, the principal catalysts of concern in the Dem-char are Ca- and Ba-containing species, potentially highly dispersed.

A comparison of the reactivity results shown in Figures 1 and 2 with those obtained for Ca-containing chars (Dem+Ca)⁸⁻¹⁰ indicates that overall char deactivation is significantly reduced in the absence of Ca. For example, between 975 and 1475 K, at a pyrolysis residence time of 1 h, the reactivity of Dem-char decreases by a factor of about six, while that of Dem+Ca-char decreases by a factor of ≈100. However, deactivation of the Dem-char is initially faster than that of the Dem+Ca-char. An increase in residence time from 0.3 to 1.8 s at 1275 K results in essentially no decrease in reactivity of Dem+Ca-char; for Dem-char, however, a twofold decrease is

observed. The above discussion suggests that two fundamentally different processes govern the observed deactivation of Dem- and Dem+Ca-chars.

Researchers in the past have treated the commonly observed process of char deactivation with increasing heat-treatment severity either qualitatively²⁷⁻²⁹ or empirically³⁰⁻³². The problem with the empirical approach, from a fundamental standpoint, is that it combines all the factors responsible for char deactivation into an overall parameter (such as, for example, the energy of thermal deactivation used by McCarthy^{30,31}) that cannot be related to measurable physical properties of the char. The approach taken in this investigation represents an attempt to quantify the fundamental physical properties, changes of which during heat treatment are responsible for the decrease in char reactivity, i.e., the concentration of carbon active sites and catalyst dispersion.

The XRD patterns in Figure 5 and crystallite size data in Table 3 provide a qualitative argument in support of the contention that the deactivation of Dem-char is due to the decrease in the concentration of carbon active sites. An enhancement of the (10) XRD peak of carbon after lignite pyrolysis of 0.3-1.8 s at 1275 K is evident in Figure 5. It correlates well with the observed char deactivation (Figure 1). In principle, if the crystallite height either does not change appreciably, or increases, an increase in crystallite diameter causes a decrease in the ratio of edge (active) carbon atoms to basal (inactive) carbon atoms. Although a clear distinction between basal and edge sites becomes uncertain for carbons of highly disordered and defective structure with very small crystallites, such as lignite chars ($L_c \approx 2$ nm), it is suggested here that the development of a relatively pronounced (10) carbon peak is an indication of a decrease in active site concentration. The oxygen chemisorption results given in Table 3 provide quantitative evidence. It is seen that the chemisorption capacity of the chars also decreased significantly as pyrolysis residence time increased from 0.3 to 1.8 s at 1275 K. Additional increases in heat-treatment severity cause a further decrease in ASA, as suggested both by the oxygen chemisorption capacity decrease and the crystallite diameter increase, also shown in Table 3.

It is shown in Table 4 that the calculated TSA is not a relevant reactivity normalization parameter. For example, at 1275 K the observed rate decreases by a factor of

six between 0.3 s and 5 min. However, TSA increases in this range of pyrolysis residence time. This conclusion is confirmed in the case of carbons of increasing purity and crystallinity; a difference in observed rates of four orders of magnitude is reduced only by about two orders of magnitude when TSA is taken into account. However, it is seen that a difference in observed reactivities of Dem-chars of a factor of 12 is reduced to within a factor of three when the rate constants are expressed per unit ASA according to Equation 7. The value of ASA for the Saran char was obtained under conditions similar to those used in this study²⁴. It is seen that the rate per unit carbon active site is very similar to the rate constants for the Dem-chars. In the case of V3G, chemisorption was carried out at 575 K and 65 Pa O₂, also in the absence of gasification. It is assumed that the value of oxygen chemisorption capacity thus obtained is also a measure of ASA. It is seen that the difference in observed reactivities of almost three orders of magnitude between Saran char (and also Dem-chars) and V3G is reduced to within one order of magnitude when their ASAs are taken into account. The same is true for SP-1 graphite; a difference in observed reactivities of about four orders of magnitude is also reduced to within a factor-of-ten difference in rate constants.

For the results discussed above emphasis should not be unduly placed on the absolute values of the reported ASAs or rate constants. It is thought that this analysis primarily demonstrates trends and illustrates the principles involved in the kinetics of carbon gasification in general and coal char gasification in particular. It is well known, for example, that the oxygen chemisorption capacity is a function of both temperature and pressure³³ and is also dependent on whether it is measured in the presence or absence of gasification³⁴. Consequently, the concept of carbon active sites is being extended to include a more or less wide distribution of site activities with different heats of chemisorption. For example, in coal chars, intuitively speaking, they would include sites as diverse as those bonded to heteroatoms (principally H), nascent sites, i.e., sites created during pyrolysis and gasification, dangling carbon atoms (singly bonded), edge carbon atoms (doubly bonded) and, finally, trigonally bonded basal carbon atoms. However, from the standpoint of gasification reactivity (as opposed to chemisorption activity), by analogy with heterogeneous catalysis³⁵, it is the optimum sites that are important, i.e., sites that are both active and available. Very active sites are probably unavailable for reaction because of the formation of a stable carbon-oxygen complex. Sites of lower activity have difficulty in forming the carbon-oxygen reaction intermediate. It is, therefore, not unreasonable to expect that the somewhat arbitrary chemisorption conditions used in this study (375 K, 0.1 MPa air) give at least a relative indication of the concentration of carbon active sites in the various carbons or chars. They certainly provide an index of their gasification reactivity, as shown in *Table 4*.

It is of interest to examine to what extent catalysis, especially by CaO and BaO (see *Table 1*), plays a role in the gasification of Dem-chars. Dispersion of CaO has been measured in the case of Dem+Ca-chars prepared under the same pyrolysis conditions used in this study^{8,10}. It is worth noting that the chars shown in *Table 4* with somewhat higher rate constants are the ones that were

shown to contain highly dispersed CaO (and probably BaO), i.e., the short-residence-time and low-temperature chars. It is suggested that for these chars catalysis is more important, i.e., the catalysed reaction contributes significantly to the overall rate. With increasing severity of pyrolysis and increasing purity (Dem-char < Saran char \approx V3G < SP-1) the rate constants become smaller. This also suggests a decreasing contribution of the catalysed reaction to the overall rate. If the above qualitative analysis is taken into account, the spread in rate constants shown in *Table 4* becomes even smaller, thus providing an additional argument for the fundamental nature of these constants.

It was emphasized previously that to predict (or explain) the entire range of a TGA plot, such as the one shown in *Figure 3*, one needs to determine the variation of ASA with conversion. Several attempts have been made in the past to achieve this^{3,24}. However, much work has been done, especially in recent years, to predict char gasification behaviour on the basis of changing porosities and total surface areas^{18,36-47}. Models of varying degrees of sophistication have been proposed. The number of adjustable parameters in these approaches usually varies accordingly. Only in a few of them can these parameters be easily related to measurable physical properties of the chars. One such model is Simons' 'tree (or river)-system' model^{18,38-41}. In the present study an attempt has been made to use it to compare theoretical predictions with experimentally observed behaviour. The results for the Dem-char prepared at 975 K for 1 h, reacted at 720 K in 0.1 MPa air, are given in *Figure 3*, as a typical illustration. In the chemically controlled régime, assumed here, the input variable (from experiment) is the time necessary to reach a conversion of 50%. The adjustable parameter is the initial porosity (θ_0) of the char. It is seen that the value of $\theta_0 = 0.05$ gives the best fit to the experimental curve. However, this is an unrealistically low value for this highly porous char. The point of this illustration is to suggest that models of purported general applicability should (inevitably) address the effects of catalysis and carbon active sites in char and carbon gasification.

SUMMARY AND CONCLUSIONS

A demineralized lignite char was taken as the 'model compound' for studying the uncatalysed char gasification at a fundamental level. The total surface area of a char calculated by assuming that the micropore volume is approximately equal to the monolayer capacity was shown *not* to be a relevant reactivity normalization parameter. The oxygen chemisorption capacity of chars at 375 K and 0.1 MPa air was shown to be a good index of their gasification reactivity at higher temperatures and thus gives an indication, at least from a relative standpoint, of the concentration of carbon active sites. The commonly observed coal char deactivation brought about with increasing severity of pyrolysis conditions can be correlated with a decrease in the active surface area of the chars.

ACKNOWLEDGEMENTS

This work was supported by a grant from the Gas Research Institute, on Contract No. 5014-363-0235. Initial

financial support for L.R.R., in the form of a Fulbright Scholarship, was provided by the Yugoslav-American Commission for Educational Exchange. Elemental analyses were carried out by the staff of the Mineral Constitution Laboratory, Pennsylvania State University. The coal samples were obtained from the Coal Research Section, Pennsylvania State University.

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