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Effect of carbon deposition on porosity and reactivity of a lignite char

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(Received 24 September 1976)

Carbon deposition from the cracking of methane into the pores of a lignite char occurs at a significant rate at temperatures between 815 and 855°C. The maximum amount of carbon deposited is much less than the amount of open pore volume within the char which is potentially available to accommodate carbon. Removal of the inorganic impurities from the char by acid washing significantly reduces the extent of carbon deposition. Carbon deposition reduces surface area and open pore volume of the char and accessibility of methane into the pore structure. Deposition of carbon has a large and lasting adverse effect on the subsequent reactivity of the char to air. This has been attributed both to a decrease in active surface area, and deactivation of catalytic inorganic impurities due to coating with carbon. Deposited carbon is much less reactive to air than the lignite char. Results indicate that in order to maximize subsequent char reactivity to oxidizing gases, carbon deposition from volatiles during the conversion of coal to char should be kept to a minimum.

For the production of low- and high-CV gases by coal gasification, it is desirable to maximize gasification rates. The major factors which control the reactivity of carbonaceous solids to O_2, H_2O and H_2 are[1,2]:
(1) concentration of active carbon sites located at the edges of layer planes, (2) presence of catalytic inorganic impurities, and (3) diffusional limitations on how rapidly the reactant gas molecules can reach the active sites. The complex dynamic changes in char properties occurring during gasification have recently been discussed by Tomita *et al.*[3] Since devolatilization (pyrolysis) precedes the gasification step, it is probable that methane (released as a constituent of volatile matter) while diffusing out of the microporous structure into the main gas stream may crack on the carbon surface depositing carbon. The phenomenon of chemical vapour deposition resulting from the cracking of methane on various surfaces has been reported widely in the literature[4-6]. Carbon deposition (CD) or carbon deposited (CD) on the char surface may adversely affect the three factors, referred to above, that control char reactivity. To the authors' knowledge, the effect on the aforementioned factors of CD on a char surface has not previously been studied. This paper describes the effect of CD within the pore volume of a lignite char on changes in the porosity, the rate at which reactant molecules can diffuse into (or product molecules can diffuse out of) the internal pore structure, and subsequent reactivity of the char during gasification.

The authors realize that the conditions selected in the present study for the char preparation, for the CD process, and for subsequent gasification are arbitrary; in any study of this type such selections are necessary. It is felt, however, that principles have been demonstrated by this study — principles that have significance to those concerned with the practical question of understanding coal-char structure and reactivity.

EXPERIMENTAL

Sample selection

A North Dakota lignite coal (PSOC-87) was selected for

the present study. Proximate and ultimate analyses of the coal are given in *Table 1*.

A commercial activated carbon (BPL, 12 x 30 U.S. mesh, supplied gratis by Calgon Corporation, Pittsburgh) was also used in a few studies. This carbon is reported to have a mercury density of 0.85 g/cm^3, a helium density of 2.1 g/cm^3 and an open pore volume of 0.70 cm^3/g.

Char preparation

About 30 g of raw coal (40 x 100 U.S. mesh) were taken in a graphite boat. The boat was placed in a tube furnace. Prepurified N_2 was flushed through the tube furnace for 1 h. Following this, the coal was heated to the desired maximum temperature at a rate of 10°C/min. Soak time at maximum temperature was 2 h. The char was subsequently cooled in N_2 to room temperature.

In order to study the effect on CD of inorganic impurities associated with the char, the char, prior to CD, was treated with 10 vol % HCl close to its boiling point (about 100°C) for 3 h. The char was then washed free from chloride ions with hot distilled water. This treatment decreased the ash yield of the char, on a dry basis, from 11.5 to 6.6%.

Carbon deposition

For studying the kinetics of CD on the char and activated carbon, a Fisher TGA unit, Series 300, was used. A mixture of methane and N_2 at a total pressure of 100 kPa and a me-

Table 1 Proximate and ultimate analyses of raw coal

Constituent	(wt %)
Proximate Analysis	
Ash (dry basis)	11.5
Volatile matter (daf)	54.2
Fixed carbon (daf)	45.8
Ultimate Analysis (daf)	
C	71.2
H	5.3
N	0.56
S	0.46
O (by difference)	22.5

* Present address: Kawasaki Steel Corporation, Chiba, Japan

thane partial pressure of 6.5 kPa was used for CD. For TGA runs, about 4 mg of char were taken in a platinum pan. After flushing out the whole system with prepurified N_2 (flow rate of 300 cm^3/min) for 2 h, heating was started at the rate of 10°C/min. As soon as the desired CD temperature was attained, it was held constant until the sample weight became constant. At this stage, N_2 was replaced by the methane—N_2 mixture at the same flow rate. Weight changes due to CD were recorded as a function of time.

For measurement of surface area, helium and mercury densities as well as diffusion parameters, relatively larger quantities of samples are needed. Since CD on such quantities cannot be carried out in a conventional TGA unit, an alternate experimental approach was used for this purpose. About 4 g of char were taken in a graphite boat which was placed in a tube furnace. The system was purged with prepurified N_2 for 1 h. Heating was then started at a rate of 10°C/min. The sample temperature was raised to the desired CD temperature. Soak time at this temperature was 1 h. Following this, N_2 was replaced by the methane—N_2 mixture. The extent of CD was estimated from the weight increase of the sample after the run.

Although every effort was made to prepare the CD samples in the tube furnace and TGA unit under essentially the same experimental conditions, it was not possible to have exactly the same extent of CD on the samples.

Reactivity measurements

Reactivity of chars to 100 kPa of air before and after CD was determined in the TGA unit. About 4 mg of sample were taken in a platinum pan. It was ascertained in a few preliminary experiments that under the chosen experimental conditions, char reactivity was independent of bed height (weight). That is, resistance for diffusion of reactant gas molecules down through the bed was minimal. Prior to making reactivity runs, the system was flushed with N_2 (300 cm^3/min) for 30 min to displace the air present. The sample was then heated to the desired gasification temperature at a rate of 10°C/min. Heating was continued at this temperature until the sample weight became constant. Following this, N_2 was replaced by air at the same flow rate. The decrease in sample weight during gasification was recorded continuously as a function of time.

Surface area

Surface areas of various samples were determined from N_2 adsorption at 77 K using the BET equation and from CO_2 adsorption at 298 K using the Polanyi—Dubinin equation[7]. Adsorption isotherms were determined in a conventional volumetric apparatus.

In the present study, a considerable time elapsed between the preparation of various char samples and their surface area measurements. In a few preliminary runs, it was found that heat treatment/outgassing conditions prior to surface area measurements profoundly affected the surface area values, particularly the N_2 surface areas. The higher the heat treatment/outgassing temperature, the larger was the surface area. The following reasoning seems to be plausible for explaining these results. The chars are turbostratic carbons. Therefore, they are expected to have a reasonable concentration of carbon sites located at the edges of layer planes. These sites can potentially chemisorb oxygen on exposure to air even at ambient temperature[8,9]. Therefore, when a freshly prepared char is exposed to atmosphere (air), it can chemisorb oxygen. Since most of the area of chars is located

in micropores, the chemisorption of oxygen is expected to decrease the micropore size to an extent that some of the micropores initially present in the char will become inaccessible to adsorbate molecules. Since the minimum dimension of a N_2 molecule (0.364 nm) is larger than that of a CO_2 molecule (0.33 nm), the chemisorption of oxygen is expected to adversely affect the N_2 area to a greater extent than the CO_2 area. Heat treatment (or outgassing) of a char at progressively increasing temperatures will desorb increasing amounts of chemisorbed oxygen. Therefore, porosity of a char will increase with increasing heat-treatment temperature provided the temperature does not exceed that seen by the char during its preparation. With increase in porosity, accessibility of pores to the adsorbate molecules will increase. This in turn will result in an increase in surface area. Therefore, in order to avoid any ambiguity in the surface area values, the following procedure was used. Before making an adsorption run, the sample was heated in a tube furnace for 2 h in a prepurified N_2 flow at a temperature 50°C below that seen by the sample during its preparation. Thereafter, the sample was cooled in N_2 to room temperature. A known amount of the sample was immediately transferred to a sample holder which was then attached to the adsorption equipment. Prior to measuring the surface area, the sample was again outgassed at 500°C for 8 h. For each adsorption point on the N_2 and CO_2 isotherms, an arbitrary adsorption time of 30 min was allowed.

Helium and mercury densities

True and apparent densities of various samples were determined by helium and mercury displacements, respectively, in the manner described previously[7]. These densities were used to calculate the open-pore volumes and percentage porosities[7].

Methane diffusion

The desorption technique described by Walker and coworkers[10,11] was used to measure the diffusion parameter for methane. The apparatus as well as the experimental and computational procedures used to calculate the diffusional parameter $D^{1/2}/r_0$ (where D is the diffusion coefficient and r_0 is the diffusion path length) have been described by Nandi and Walker[11].

Prior to making a diffusion run, the char sample was subjected to the same heat treatment cycle as was used for surface area measurements. The sample was then equilibrated with about 0.5 MPa methane for 24 h. This time was ascertained in a few exploratory runs to be sufficient for the attainment of equilibrium. The volume of methane desorbed after different time intervals was determined in the manner described previously[11]. The following equation, applicable far from equilibrium, was used to calculate the diffusion parameter[10,11]:

$$\frac{V_t - V_0}{V_\infty - V_0} = \frac{6}{\sqrt{\pi}} (Dt/r_0^2)^{1/2}$$

where V_∞, V_t and V_0 are the volumes of methane desorbed after time $t = \infty$, $t = t$ and $t = 0$, respectively. The volume of methane desorbed after 24 h was taken as V_∞. Plots of ($V_t - V_0$)/($V_\infty - V_0$) against $t^{1/2}$ gave straight lines; the slopes were used to calculate diffusion parameters.
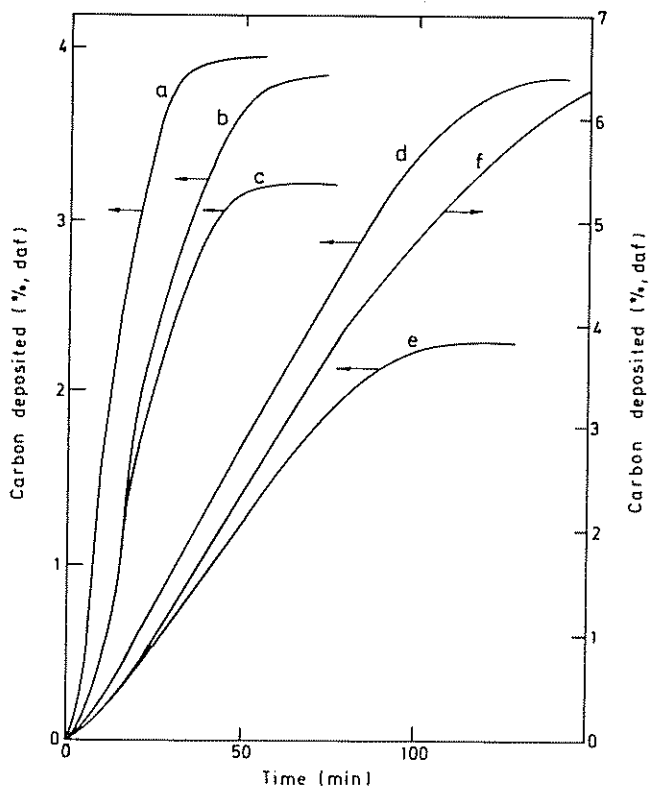
Figure 1 CD on the 855°C char and activated carbon. Raw char: a, 855°C; b, 825°C; c, 815°C. Acid-washed char: d, 845°C; e, 815°C. Activated carbon: f, 815°C

RESULTS

Carbon deposition

Amounts of CD on the 855°C char at 815, 825 and 855°C as a function of time are plotted in *Figure 1*. In each case the rate of CD first increases gradually with time to a maximum, then gradually decreases with time until finally the remaining rate falls abruptly to essentially zero. The maximum amount of CD increases with increasing reaction temperature.

Acid washing of the char decreases the extent, as well as the rate, of CD (*Figure 1*). The amounts of CD at 815°C on the raw and acid-washed chars show that the removal of mineral matter by acid treatment decreases the extent of total CD by about 30%. Furthermore, the limiting constant CD on the acid-washed sample is attained after about 115 min compared to only 50 min for the raw char.

Carbon deposition was next studied on the activated carbon. The results are also plotted in *Figure 1*. At 815°C, maximum CD on the activated carbon is twice that found on the 855°C lignite char. However, when the rates of CD are considered on a fractional basis, that is, ratio of amount of CD at a given time to the maximum amount of CD, the rate is faster in the case of the raw char.

Effect of carbon deposition on reactivity

The effect of CD on char reactivity to air at 375°C was studied for the 855 and 1000°C chars. Burn-off curves for the raw and acid-washed chars, before and after CD, are plotted in *Figures 2* and *3*. Each curve has an initial induction period. Thereafter, an essentially rectilinear region associated with a maximum reactivity is found. Finally, the reacti-

vity decreases continuously until the sample has been gasified. Following the suggestion of Jenkins *et al.*[12], the reactivity parameter (*R*) was calculated from the following equation:

$$R = \frac{1}{W_0} \frac{dW}{dt}$$

where W_0 is the starting weight of the char on a dry-ash-free (daf) basis and dW/dt is the maximum rectilinear rate of weight loss. In the present study, time corresponding to 50% burn-off (τ) has also been used as an index of char reactivity. Obviously, the smaller the τ value, the larger will be the char reactivity. Values of R and τ for various samples are listed in *Table 2*.

The plots in *Figures 2* and *3* and R and τ values in *Table 2* show that the 1000°C char is significantly less reactive than the 855°C char. The reactivity decreases appreciably upon CD as well as upon mineral matter removal (by acid washing). Both the R and τ values indicate that the acid-washed char following 3.8% CD is about one-eighth as reactive as the corresponding raw char.

It was found that the reactivity of the activated carbon to air was too small to measure at 375°C. Therefore, reactivity was measured at 500°C. Reactivity plots (*Figure 3*), as well as the R and τ values (*Table 2*) for the as-received and 9.3% CD samples, indicate that the reactivity of the activated carbon also decreases following CD.
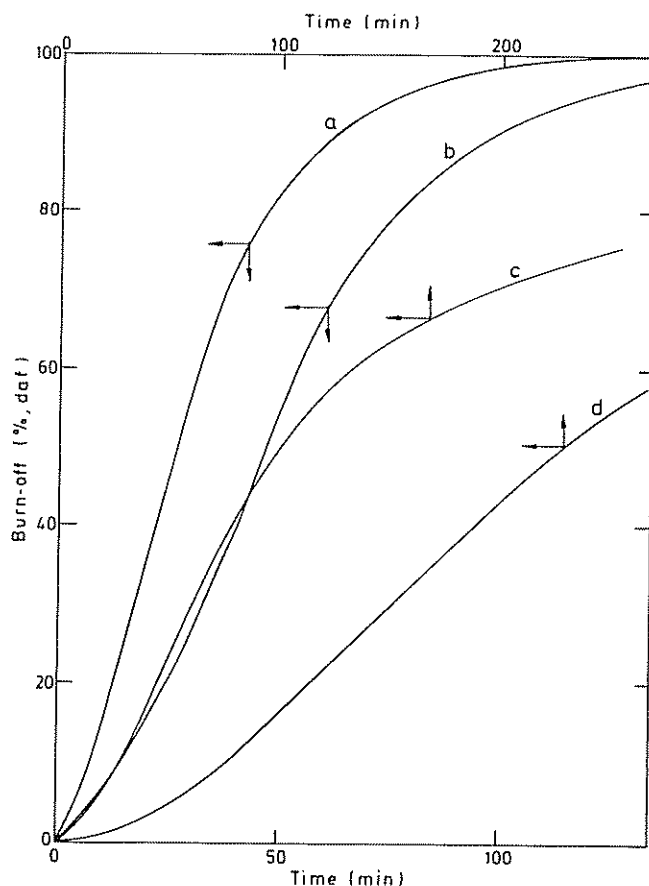

Figure 2 Burn-off curves in air at 375°C for 855°C raw and acid-washed chars before and after CD. a, raw char; b, raw char:2.6% CD; c, acid-washed char; d, acid-washed char:3.8% CD

Densities and porosity

Helium and mercury densities, total open pore volumes and open porosities of various samples are listed in *Table 3*. Porosity decreases following CD and increases upon activa-

tion. It is noteworthy that gasification to about 30% burn-off produces an open porosity in the raw char of 49.3% but only 38.4% within the 2.6% CD char.

Surface area

The N_2 and CO_2 surface areas of various samples are given in *Table 3*. The areas of the chars decrease progressively with increasing amounts of CD. The effect of gasification on surface area is different for the raw and CD chars. In the former case, N_2 area increases whereas CO_2 area decreases with increasing carbon burn-off. However, gasification of the CD samples results in an increase in both N_2 and CO_2 areas. It is noted that even after the 2.6% CD char is activated to 29.1% burn-off, the N_2 and CO_2 areas are not 'restored' to the areas of the raw char.

Except in the case of the 855°C char activated to 33.6% burn-off, which has about the same N_2 and CO_2 areas, the N_2 areas for the remainder of the CD and activated char
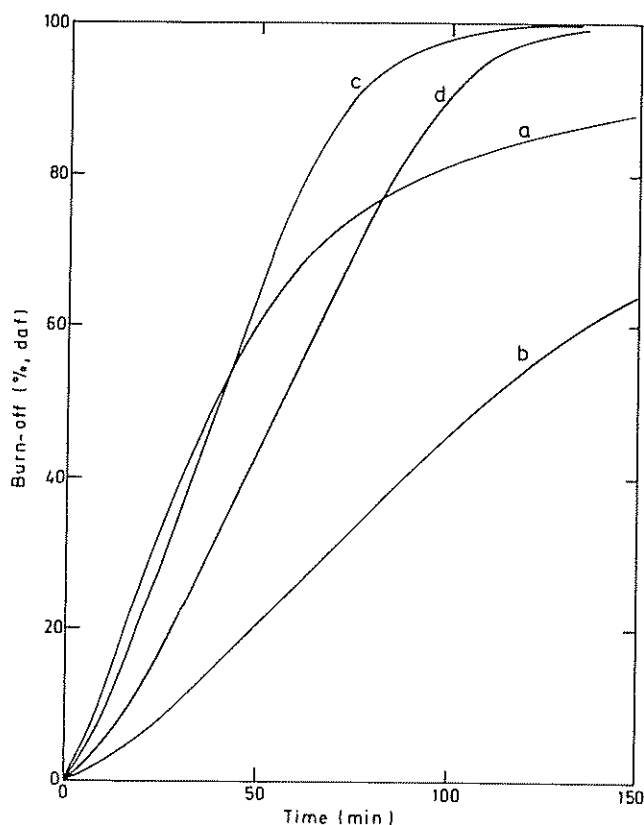

Figure 3 Burn-off curves in air at (i) 375°C for raw and CD 1000°C lignite char, and (ii) 500°C for as-received and CD activated carbon. 1000°C char: a, raw char; b, raw char:3.6% CD. Activated carbon: c, as-received; d, as-received: 9.3% CD

Table 2 Reactivity results for various chars and activated carbon samples

Sample	Reactivity parameter (R) (mg h^{-1} mg^{-1})	τ (min)
855°C-char		
Raw char	1.21	28
Raw char: 2.6% CD	0.85	47
Acid washed	0.45	99
Acid washed:3.8% CD	0.16	228
1000°C-char		
Raw char	0.87	39
Raw char:3.6% CD	0.31	108
BPL Activated Carbon		
As-received	0.85	39
As-received:9.3% CD	0.62	56

Table 3 Area, density and porosity data for various samples

Sample	Surface area (m^2/g(daf))		Helium density (g cm^{-3} (daf))	Mercury density (g cm^{-3} (daf))	Open pore volume (cm^3 g^{-1} (daf))	Open porosity (%)
	N_2	CO_2				
CD Series						
855°C-char	CD (%(daf))					
	0	241	960	2.05	1.32	0.270	35.6
	1.7	76	771	1.94	1.37	0.214	29.3
	2.6	33	249	1.80	1.37	0.174	23.8
1000°C-char	0	130	681	2.06	1.36	0.250	34.0
	3.6	31	457	1.98	1.35	0.236	31.9
BPL Carbon	0	1296	838	2.1	0.85	0.700	59.5
	2.4	1030	745	—	—	—	—
	5.2	916	726	—	—	—	—
	13.3	807	679	—	—	—	—
Burn-off Series						
855°C-char	Burn-off (%(daf))					
	0	241	960	2.05	1.32	0.270	35.6
	1.1	336	799	2.01	1.28	0.284	36.3
	2.3	385	800	2.01	1.26	0.296	37.3
	10.2	484	747	2.10	1.25	0.324	40.5
	33.6	695	699	2.09	1.06	0.465	49.3
855°C-char:2.6% CD	0	33	249	1.80	1.37	0.174	23.8
	1.7	43	339	1.98	1.31	0.258	33.8
	3.7	124	361	1.97	1.28	0.270	34.6
	29.1	160	369	1.98	1.22	0.314	38.4

samples are less than the corresponding CO_2 areas. The lower N_2 areas are presumably due to activated diffusion into the microporous structure[13] in such a way that more of the ultrafine micropores are inaccessible to N_2 than CO_2.

The N_2 and CO_2 areas of the activated carbon also decrease upon CD (*Table 3*). The decrease in area upon carbon deposition is less pronounced for the activated carbon than for the char samples. For instance, 2.6% CD on the 855°C char decreases the CO_2 area from 960 to 249 m^2/g, whereas 13.3% CD on the activated carbon decreases the CO_2 area from 838 to only 679 m^2/g. For the activated carbon, N_2 areas are higher than the CO_2 areas at each level of CD. This phenomenon has previously been reported for various microporous carbons[14]. The higher N_2 areas have been attributed to reversible filling of micropores. It has been argued that such N_2 areas are often meaningless[14].

Diffusion parameter

It was observed in a few preliminary runs that in the case of the 855°C char activated to more than 2% burn-off and for the 2.6% CD char activated to 29.1% burn-off, diffusion of methane was so rapid that diffusion parameters could not be estimated. Therefore, diffusion paramters could only be estimated for selected samples. Diffusion of methane from some samples was also measured as a function of temperature in order to obtain information on whether diffusion was activated.
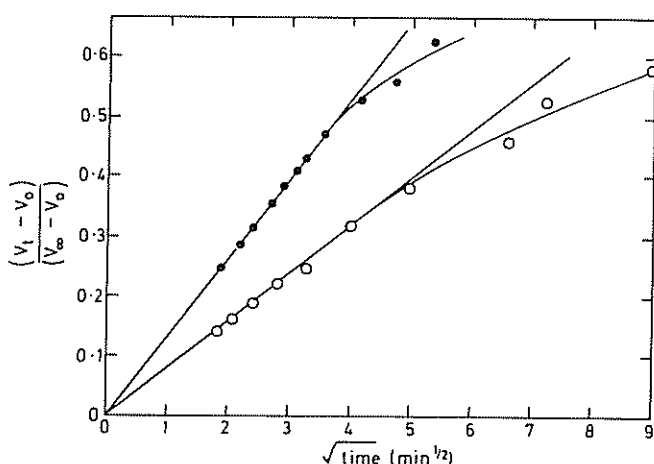

Figure 4   Methane desorption diffusion plots for raw and CD 1000°C chars. ●, raw char: ○, raw char: 3.6% CD

Typical methane diffusion plots are shown in *Figure 4*. Diffusion parameters are listed in *Table 4*. To calculate D values, the average particle radius (that is, 0.142 mm) was arbitrarily taken for r_0. These data indicate that deposition of carbon on the char reduces the diffusion parameter, whereas gasification of the raw as well as the CD chars increases the diffusion parameter. Furthermore, diffusion is non-activated on the 855°C char but is activated on the char following either CD to 2.6% (that is, 19.7 ± 4.5 kJ/mol) or CD to 2.6% and burn-off to 3.7% (that is, 9.6 ± 4.0 kJ/mol).

DISCUSSION

The broad question of how coals, upon thermal treatment, are converted to carbonaceous solids is an intriguing one from both academic and practical viewpoints. As coals are thermally treated, they lose volatile matter. The removal of volatiles opens up the microporosity in coals making the structure subsequently more accessible to oxidizing gases and H_2. To maximize subsequent char reactivity, if one wishes to convert the char to low- or high-CV gases, it is desirable to have the structure as open as possible. Two factors can lead to the reduction of porosity in coal chars. One is heating the char to too high a temperature; concurrent with the loss of volatiles some crosslinks are broken which allow the aromatic regions to align better and result in loss of porosity. At lower temperatures, up to about 700 to 900°C, the loss of volatiles predominates and results in an overall opening up of the structure. But as temperature is further raised and as volatile release becomes small, breakage of crosslinks, crystallite alignment, and pore-volume loss become significant. This study has not concerned itself with this phenomenon. Rather, it has concerned itself with the other phenomenon which can lead to porosity decrease in chars. It is known that surfaces catalyse the cracking of hydrocarbons leading to the production of hydrogen and deposited carbon. This is an important chemical vapour-deposition reaction which has a number of practical applications in the production of pyrolytic carbon.

As hydrocarbons are produced upon heat treatment of coal, they will only be measurable following diffusion from the internal porosity of the particles into the main gas stream. Diffusion out of the particles can take more or less time depending upon such variables as particle size, pore size, and tortuosity of the pores. Collision with pore walls occurs a large number of times before the molecules escape from the particle. The collision can be with a carbon surface or with

Table 4   Diffusion results at various measurement temperatures

Sample	$D^{1/2}/r_0 \times 10^3$ (s$^{-1/2}$) −15°C	$D \times 10^9$ (cm^{2}s^{-1})	$D^{1/2}/r_0 \times 10^3$ (s$^{-1/2}$) 0°C	$D \times 10^9$ (cm^{2}s^{-1})	$D^{1/2}/r_0 \times 10^3$ (s$^{-1/2}$) 25°C	$D \times 10^9$ (cm^{2}s^{-1})	$D^{1/2}/r_0 \times 10^3$ (s$^{-1/2}$) 40°C	$D \times 10^9$ (cm^{2}s^{-1})
855°C raw char	6.21	7.80	6.48	8.49	6.40	8.28	—	—
1.7% CD	—	—	—	—	3.00	1.82	—	—
2.6% CD	—	—	2.05	0.85	2.58	1.55	3.51	2.49
1.1% burn-off	—	—	—	—	8.92	16.1	—	—
2.6% CD: 1.7% burn-off	—	—	—	—	2.77	6.97	—	—
2.6% CD: 3.7% burn-off	5.72	6.62	6.17	7.70	7.81	12.3	—	—
1000°C raw char	—	—	—	—	4.95	4.94	—	—
3.6% CD	—	—	—	—	3.00	1.82	—	—

an inorganic (mineral matter) surface. Collision may lead to hydrocarbon cracking and deposition of carbon. It is obvious that such deposition can lead to the loss of porosity in the resultant char. That such CD occurs during the heating of coal has been strongly suggested by the well-known phenomenon that the weight loss of coal, in taking it to a final temperature, is dependent upon the rate of heating to the final temperature. The more rapid the heating, generally the greater is the resulting weight loss. It is suggested that as heating rate increases the pressure build-up within the particle increases to a higher level as a result of the inability of the volatiles to escape from the particle rapidly enough. Indeed, this pressure build-up is sometimes sufficient to lead to decrepitation of the particle. The point is that the greater pressure gradient from the centre to the outside of the particle leads to a higher rate of volatile escape from the particle, thereby providing less time for the CD process to occur. The result is a greater weight loss the more rapid the rate of heating. It is interesting that in this laboratory it has just been reported that rapid heating ($\approx 10^4$°C/s) of a lignite char results in considerably higher surface areas than heating at rates used in this study (N. Nsakala and J T. Ashu, unpublished results, 1976).

Recently, Anthony and co-workers[15] showed that increases in the particle size of coal and helium pressure also decrease the amount of volatiles produced upon rapid heating and pyrolysis of coal. They attribute this to an increase in the percentage of reactive volatiles which polymerize and/or crack on hot coal surfaces, thereby depositing solid material.

Rate of carbon deposition on lignite char

According to the data of Palmer and Cullis[4], the rate of homogeneous cracking of methane at the maximum temperature used in this study (855°C) would be low. In this laboratory, W. Hoffman has recently shown (unpublished results, 1976) that a carbon surface is a catalyst for the decomposition of propylene to carbon, ethylene and methane and, further, that inorganic impurities in the carbon are still better catalysts. Therefore, it was expected that a significant rate of CD from methane would be found at 815–855°C over the lignite char and that this rate would be reduced following acid treatment of the char to remove some inorganic impurities. What was not predictable was the amount of carbon that would be deposited on the char. As seen in *Figure 1*, CD stops abruptly on both the raw and acid-washed chars. We have no explanation for the observed difference in the total CD occurring on the raw and acid-washed chars at different reaction temperatures. Assuming that the density of the deposited carbon is essentially the same as that of the carbon in the raw lignite char, the maximum amount of CD is substantially less than that which could be accommodated within the open pore volume of the char. The raw char had an open porosity of 35.6% (*Table 3*) but maximum carbon deposited at 855°C was only about 4% (*Figure 1*).

There are at least two explanations for these results. First, the inorganic impurities are the active sites for methane cracking and when they are covered, significant methane decomposition stops. Second, the apertures in the lignite char are closed sufficiently by CD so that methane no longer has access into the microporosity within the char. Support for this conclusion comes from the nitrogen surface-area results. Addition of 2.6%, by weight, of deposited carbon to the 855°C lignite char reduced the N_2 surface area

from 241 to 33 m²/g (*Table 3*). Deposition of 4% carbon would be expected to result in a further significant decrease in nitrogen area. Since the kinetic diameter of methane is larger than N_2, that is, 0.380 nm compared to 0.364 nm, accessibility of the porosity to methane would be expected to be still less than that found for N_2[16].

Deposition of carbon from methane over a commercial activated carbon was also studied to see if a large difference in total open-pore volume would have an effect on the amount of carbon which could be deposited. As shown in *Figure 1*, there is a marked effect. The activated carbon with an open-pore volume of 0.70 cm³/g, compared to 0.27 cm³/g for the lignite char, was infiltrated with 6.2% carbon at 815°C, with deposition still continuing, while the lignite char could only accommodate about 3.2% carbon.

Effect of carbon deposition on porosity within char

Microporous carbon solids appear to be without exception aperture-cavity type meterials[16]. Results on the effect of CD on open porosity in the lignite char are consistent with this conclusion. As seen in *Table 3*, deposition of 2.6%, by weight, carbon leads to a reduction in open porosity from 35.6 to 23.8%. It is obvious that some apertures are being reduced in size by CD to the extent that helium no longer can pass through at room temperature. Thus, the accessibility of helium to the larger cavities existing behind the apertures has been removed, leading to a reduction in porosity considerably in excess of the total volume of carbon which has been deposited. Extensive subsequent gasification of the CD raw char does not open up porosity to the extent that is found for gasification of the raw char. Again, as seen in *Table 3*, gasification to about 30% burn-off produces an open porosity in the 855°C raw char of 49.3% but only 38.4% within the CD-raw lignite char. This is consistent with the reactivity of the deposited carbon being significantly less than that of the lignite-char carbon, as will be discussed shortly.

The diffusion results support the porosity changes (discussed above) resulting from CD and carbon burn-off. The diffusion coefficient decreases and activation energy for diffusion increases following CD owing to reduction in aperture sizes. The enlargement of apertures following carbon burn-off results in an increase in the diffusion coefficient and a decrease in the activation energy. That the deposited carbon is less reactive during gasification than the base lignite-char carbon is indicated by a lower diffusion coefficient for the 2.6% CD–3.7% burn-off char, representing a net burn-off of 1.1%, compared to that for the 1.1% burn-off raw char. Any changes in diffusion coefficient resulting from CD are expected to affect the utilization factor during subsequent gasification of the char[1].

Effect of carbon deposition on reactivity of char to air

Of particular interest is the marked retarding effect which CD has on the reactivity of the lignite char. As is seen from *Figure 2*, 2.6%, by weight, deposited carbon on the 855°C lignite char affects the whole burn-off curve. Carbon deposition can retard subsequent char reactivity by covering inorganic impurity sites which can act as catalysts and by reducing the surface area available for the reaction.

That small amounts of CD have such pronounced effects on lignite-char reactivity is instructive. Two extreme situations can be considered. On the one hand, the deposited carbon can be much more reactive to air than is the lignite-char carbon. In this case, in the limit, the initial burn-off

will be totally accounted for by the deposited carbon and the original microporous structure in the lignite char quickly restored. Experimental results show clearly that this was not happening. On the other hand, the deposited carbon can have a much lower reactivity than the base lignite-char carbon. Surface area development by char gasification resulting in the enlargement of apertures (and increasing gasification rates) will be small since deposited carbon will block apertures. In fact, experimental results suggest that the truth lies more closely to the latter extreme situation. Surface area development in the char as a result of gasification is sharply reduced by prior CD, as discussed earlier. As the data in *Table 3* show, burn-off of the 855°C raw char to about 30% increases N_2 surface area to about 695 m^2/g. By contrast, burn-off of the 2.5% CD raw char sample to about 30% only increases the N_2 surface area to about 160 m^2/g. It is, therefore, clear that CD on the lignite char is undesirable if one wishes to maximize surface area development and concurrent char reactivity.

Reactivity of carbons is dependent upon, among other variables, the concentration of active sites in the carbon[1,2]. The concentration increases with decrease in crystallite size, decrease in crystallite orientation, and increase in defect concentration in the basal plane. Since pyrolytic carbons normally show reasonable crystallite alignment with their basal planes parallel to the substrate surface on which deposition has occurred, it is concluded that the deposited carbon has a smaller active-site concentration than the turbostratic lignite-char carbon. It should be possible by tracer studies, using tagged C-13 in the methane, to follow quantitatively the relative reactivities of C-12 carbon in the lignite char and C-13 carbon in the deposited carbon.

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