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Reactivity of heat-treated coals in hydrogen

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Reactivities of eighteen 40 x 100 mesh U.S. coals charred to 1000°C have been measured in H_2 at 2·7 MPa and 980°C. The char—hydrogen reaction usually occurs in two stages: a slow induction period followed by a constant-rate region. Reactivities of various chars in the initial stage (R_i) decrease, in general, with increasing carbon content of the parent coals, whereas reactivities in the constant-rate region (R_c) are essentially independent of the rank of the parent coals. Reactivities of chars in H_2 differ markedly from those in air and CO_2. Results of surface-area measurements of chars and activation energies for the hydrogasification reaction suggest that during the induction period the reaction is diffusion-controlled whereas in the constant-rate region it is chemically controlled. Upon removal of mineral matter, R_i values generally decrease but R_c values show a random variation. Removal of mineral matter from coals prior to their carbonization brings about profound changes in surface area and porosity of chars. The effect of char particle size on reactivity is considered.

The reaction of coal chars with H_2 is an important part of the overall process for the production of substitute natural gas; consequently, it has received considerable attention[1-9]. The reaction of low-temperature chars with H_2 proceeds in two stages: a very rapid first-stage reaction and a slow second-stage reaction involving the gasification of the ·maining char which has a graphite-like (trigonally bonded) structure. Most workers have studied the reactivity of chars which have been pretreated at some fixed maximum temperature. Because the maximum temperature was usually reasonably low, the char had a certain amount of volatile matter remaining which resulted in a higher initial reactivity. In order to study the slow second-stage reaction, it would be better to work with a char prepared at a temperature at which volatile matter is essentially completely eliminated. In the present study, chars prepared at 1000°C have been used. The variables chosen for investigation were rank of the parent coal, mineral-matter content, particle size, reaction temperature and pressure.

Walker and coworkers[10,11] have recently studied the reactivities of various American coal chars in air at 500°C and CO_2 at 900°C. It was found that char reactivity was predominantly determined by the rank of the parent coal and mineral-matter composition. In the present study, reactivities of various chars in H_2 have been compared with those in air and CO_2.

EXPERIMENTAL

Char selection

The coals selected for the preparation of chars were the same as those used previously in air and CO_2 reactivity work[10,11]. All coals were rich in vitrinite. Table 1 presents alyses of the parent coals.

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Char preparation

The various coals were ground and 40 x 100 U.S. standard mesh fractions were used for the preparation of chars. Non-caking coals were carbonized in a fluidized-bed reactor, while the caking coals were carbonized in a horizontal tube reactor. In each case, coals were heated at a rate of 10°C/min to 1000°C. An inert atmosphere of N_2 was used during heat treatment. Samples were held at 1000°C for 2 h. Chars prepared from non-caking and weakly caking coals were used as such, whereas chars prepared from strongly caking coals (PSOC-171, 4 and 137) were re-ground and 40 x 100 mesh fractions used for reactivity determinations.

In order to study the effect of mineral-matter removal on reactivity, selected coals were acid-washed with 10 volume percent HCl and/or demineralized with a 1:1 HCl—HF mixture prior to carbonization. Samples of PSOC-127, a relatively unreactive low-volatile bituminous char, and PSOC-87, a highly reactive lignite char, were chosen for investigating the effect of particle size on reactivity. Different particle sizes chosen for this study were 40 x 100, 100 x 150 and 200 x 325 mesh fractions. The preparative methods used to produce acid-washed and demineralized chars, as well as chars with different particle sizes, were the same as described previously[11].

Temperature selection

Of all the carbon gasification reactions, the carbon—hydrogen reaction is thermodynamically the least favourable[12]. It is favoured at high pressures. In our experimental set-up described below, the maximum temperature attainable at 5·5 MPa was 800°C. Under these conditions, reactivities of chars were very low compared to those in air and CO_2[10,11]. In order to have higher gasification rates, it was essential to operate at higher temperatures and/or pressures. However, an increase in pressure above 5·5 MPa decreased

Table 1 Analyses of coals

PSOC Sample No.	ASTM rank	State	Ash (wt %, dry basis)	Ultimate analyses (wt %, daf)				
				C	H	N	S[a]	O (by diff.)
89	Lignite	N.D.	11·6	63·3	4·7	0·48	0·98	30·6
91	Lignite	Mont.	7·7	70·7	4·9	0·80	0·30	22·3
87	Lignite	N.D.	8·2	71·2	5·3	0·56	0·46	22·5
140	Lignite	Tex.	9·4	71·7	5·2	1·3	0·72	21·1
138	Lignite	Tex.	10·3	74·3	5·0	0·37	0·51	19·8
98	Sbb-A	Wyo.	8·4	74·3	5·8	1·2	1·1	17·7
101	Sbb-C	Wyo.	6·1	74·8	5·1	0·89	0·30	18·9
26	HVB	Ill.	10·8	77·3	5·6	1·1	2·3	13·6
22	HVC	Ill.	10·1	78·8	5·8	1·6	1·8	12·1
24	HVB	Ill.	11·8	80·1	5·5	1·1	2·3	11·1
67	HVB	Ut.	4·8	80·4	6·1	1·3	0·38	11·9
171	HVA	W. Va.	7·6	82·3	5·7	1·4	1·8	8·9
4	HVA	Ky.	2·1	83·8	5·8	1·6	0·66	8·2
137	MV	Ala.	7·1	86·9	4·8	1·5	0·81	5·9
114	LV	Pa.	9·8	88·2	4·8	1·2	0·62	5·2
127	LV	Pa.	5·7	89·6	5·0	1·0	0·52	3·9
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

the maximum attainable temperature. It was observed in a few preliminary experiments that an increase in the reaction temperature increased char reactivity to a greater extent than an increase in pressure. Accordingly, we have determined the reactivities of chars at 980°C, which was attained at an H_2 pressure of 2·7 MPa. Temperatures higher than 980°C were not used because we wished to carry out reactivity studies at a temperature less than that used for char preparation (that is 1000°C). Even under the chosen experimental conditions, reactivities of most chars in H_2 were less than those in air at 500°C and CO_2 at 900°C.

The equilibrium $[CH_4]/[H_2]$ ratio for the reaction C + $2H_2 \rightarrow CH_4$, taking carbon as β-graphite, at 980°C and 2·7 MPa H_2 pressure was calculated (from data in reference 12) to be 0·24. This ratio will be higher for turbostratic carbons such as chars. The $[CH_4]/[H_2]$ ratio leaving the reactor for the most reactive char in the present study, PSOC-87, was calculated to be about 7×10^{-4}. Thus, under the experimental conditions used, that is 980°C and 2·7 MPa H_2 pressure, the char—hydrogen reaction was not limited by equilibrium considerations.

Reactivity measurements

A DuPont 951 TGA balance, in conjunction with a 990 Thermal Analyzer, was used to monitor weight changes during reaction. The balance was mounted in an autoclave. The details of the experimental set-up have been described previously[13]. About 10 mg of char contained in a platinum bucket were used for reactivity measurements. The autoclave was evacuated and then pressurized with N_2 to 2·7 MPa. Helium at 2·7 MPa was introduced into the reactor at a flow rate of 1·2 l/min (STP). After a period of 15 min, the furnace was activated to raise the sample temperature to 980°C at a heating rate of 20°C/min. The temperature was kept constant at 980°C for 15 min to ensure thermal stability. At this stage, helium in the reactor tube was replaced by H_2 at 2·7 MPa at the same flow rate.

Sample weight was then continuously recorded. The volume of the reactor tube was about 120 cm^3. Therefore, using a flow rate of 1·2 l/min (STP) or 41 cm^3/min at 2·7 MPa, it would take about 3 min to displace helium by H_2 over the char sample. Therefore, in all reactivity measurements, starting time for the reaction was considered to be when helium was displaced by H_2.

It was ascertained in a few preliminary runs that the use of a quartz bucket for a given char gave essentially the same weight losses at different reaction times as the use of a platinum bucket. This indicates that the platinum bucket did not catalyse the hydrogasification reaction. It was also ascertained that when sample weights up to 10 mg were used for reactivity measurements, there was minimal resistance to hydrogen diffusion down through the bed. That is, specific gasification rates were independent of the starting weight (height) of char used.

Surface area

Surface areas of chars 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[14]. Adsorption isotherms of N_2 and CO_2 were determined in a conventional volumetric apparatus. Prior to making an adsorption run, samples were outgassed at 500°C for 12 h at a pressure of $1·33 \times 10^{-3}$ Pa. For each adsorption point on the isotherm, an arbitrary adsorption time of 30 min was allowed. Surface areas of chars have been expressed on a dry-mineral-matter-containing basis.

RESULTS

In the present study, weight loss vs. time curves usually had a slow induction period followed by a rate increase, as was also reported for the reaction of chars with air[10], CO_2[11], H_2[8], and steam[8]. Jenkins et al.[10] found that the rectilinear
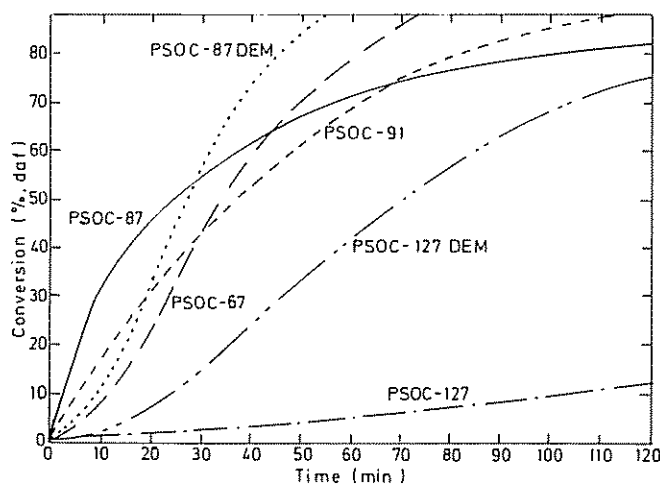
Figure 1   Burn-off curves in H_2 at 2·7 MPa and 980°C for selected chars produced from raw and demineralized coals

portion, after an induction period, extended over a range in which about 40% of the char was gasified They calculated the reactivity parameter by the following equation:

$$R_o = -\frac{1}{W_o} \cdot \frac{dW}{dt}$$

where W_o is the initial weight of the char on a dry-ash-free basis (mg) and dW/dt is the maximum rectilinear weight loss (mg h^{-1}). For the char–hydrogen reactivity plots, the rectilinear region was considerably shorter than that for reaction in air and CO_2. On the other hand, the rate calculated on the basis of unreacted char remained constant for a longer period. Therefore, the reactivity parameter R has also been expressed as

$$R = -\frac{1}{W} \cdot \frac{dW}{dt}$$

where W is the weight of char unreacted at time t. Two parameters R_i and R_c were calculated by this equation: R_i represents the initial rate at $t = 0$ and R_c expresses the constant rate in the region where the kinetics follow a first-order rate expression with respect to the unreacted char.

Reactivity profiles

Reactivity profiles for a few representative chars during the hydrogasification reaction are shown in *Figure 1*. It is seen that PSOC-91 and 87 chars show no induction period. For chars which show an induction period, its duration varies in each case. Variations of reaction rates with conversion calculated from the plots in *Figure 1* are illustrated in *Figure 2*. Chars PSOC-87 and 127 show some peculiar characteristics. The reaction rate for PSOC-87 char decreases sharply with conversion. On the other hand, for PSOC-127 char, the rate is very low and increases monotonically even after 5 h of reaction, when only 25% of the char is gasified. Obviously, R_c values (as we define R_c) do not exist for these two chars. For the sake of convenience, maximum reactivities of these chars have been taken as R_c values. The remainder of the chars in *Figure 2* exhibit a normal behaviour during gasification; that is, for these chars reaction rate attains a constant R_c value after some induction period.

Correlation of char reactivity with coal rank

Values of reactivity parameters R_i, R_c and R_o for all the chars produced from raw coals, together with their surface areas, are listed in *Table 2*. Percentage carbon conversions corresponding to the onset of R_c values for various chars are given in parentheses in *Table 2*. R_i and R_c values for various chars are plotted as a function of carbon content of the parent coals in *Figure 3*. It is seen that there is some correlation between R_i values and carbon content of the parent coals. R_i values for various chars vary from 0·05 to 2·6 mg h^{-1} mg^{-1}, generally increasing as the rank of the parent coal decreases. However, R_c values show no correlation with coal rank. For example, the reactivity of a Pennsylvania anthracite char (PSOC-81) is larger than that of most chars of lower rank. With a few exceptions, R_c values for various chars vary from 0·7 to 2·3 mg h^{-1} mg^{-1} (*Table 2*). In this context, Feldkirchner and Linden[3] also observed a similarity in hydrogasification rates of the residual portions of three coal chars with greatly different initial properties. The fact that values of R_c are essentially independent of parent coal rank suggests that following an induction period, most chars, irrespective of the rank of their parent coals, can be gasified at about the same rate. In this study, the chars which were notable exceptions to this finding (that is, PSOC-137, 114, and 127) were produced from MV or LV coals. There is no correlation between carbon conversions corresponding to the onset of R_c values for various chars and rank of the parent coals.
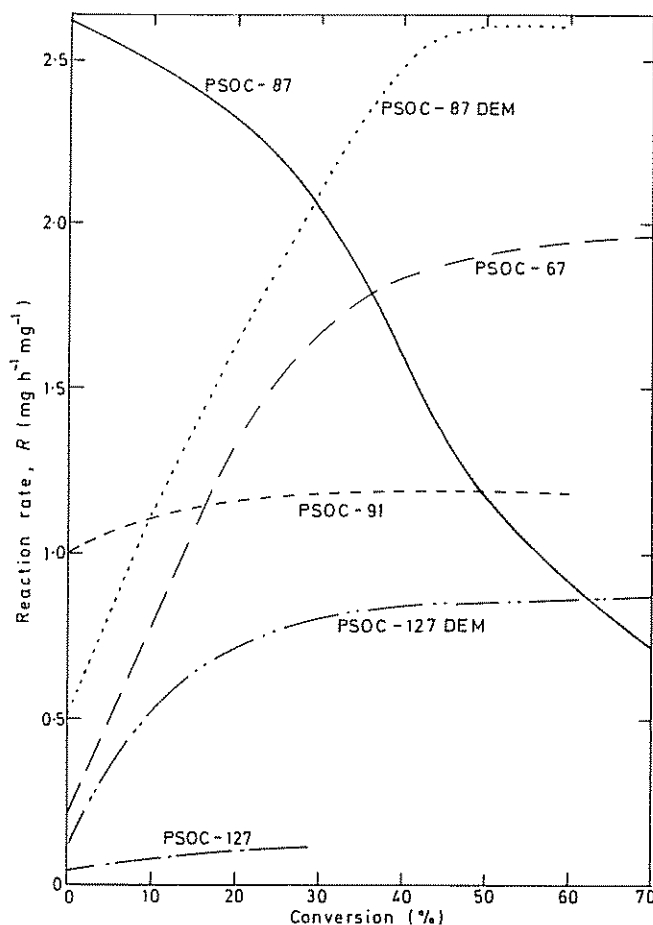
Walker and coworkers[10,11] have recently studied the

Figure 2   Variation of reaction rate in H_2 at 2·7 MPa and 980°C with conversion of various chars produced from raw and demineralized coals

Table 2 Surface areas and reactivities in H_2 of $1000°C$ 40 × 100 mesh chars

Parent coal PSOC No.	Surface area ($m^2 g^{-1}$)		Reactivity ($mg\,h^{-1}\,mg^{-1}$)		
	N_2	CO_2	R_i	R_c	R_o
89	290	630	0·73[a]	1·0 (10)	0·75
91	31	420	1·0 [a]	1·2 (15)	0·91
87	93	260	2·6 [a]	2·6 [b]	2·2
140	120	640	0·55	1·7 (20)	1·0
138	120	560	0·62[a]	1·5 (10)	1·1
98	11	340	0·34	1·0 (15)	0·73
101	62	400	1·2 [a]	1·2 [b]	1·1
26	10	86	0·37	1·0 (25)	0·63
22	19	330	0·38	2·0 (20)	1·3
24	25	370	0·50	2·3 (25)	1·2
67	4	110	0·17	1·9 (40)	1·1
171	2	19	0·08	0·64 (20)	0·43
4	1	39	0·13	1·7 (35)	0·86
137	4	45	0·21	0·28 (20)	0·26
114	2	46	0·22	0·39[b]	0·37
127	2	12	0·05	0·09[b]	0·07
81	1	39	0·13	2·0 (40)	0·81
177	<1	40	0·06	0·73 (35)	0·38

[a] Little or no induction period
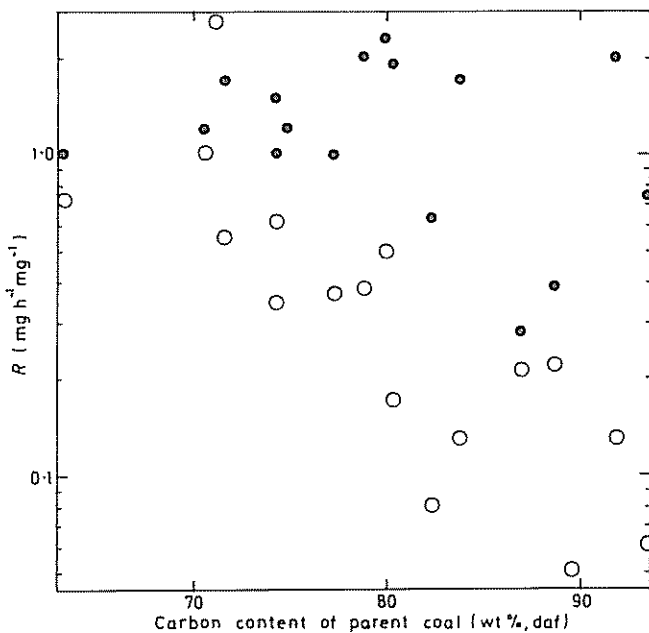[b] No constant rate region (see text)

Figure 3 Variation of reactivity in H_2 at 2·7 MPa and 980°C of chars produced from raw coals of different carbon contents ● R_c; ○ R_i

reactivities of chars, prepared from the same set of coals as those used in the present study, in air at 500°C and CO_2 at 900°C. They observed that R_o values for given chars were essentially the same in air and CO_2 and that in both atmospheres char reactivity decreased with increasing carbon content of the parent coal. However, R_o values in H_2 do not show a correlation with coal rank (*Table 2*). Furthermore, the spread in R_o values in H_2 for various chars is much less than that in air and CO_2 [10,11]. It is thought pertinent to point out that except for the chars which do not give con-

stant R_c values, there is a fair correlation between normalized values of R_o and R_c for various chars reacted in H_2. Different reactivities of various chars in H_2 and air (or CO_2) are further exemplified by the fact that while PSOC-91 char is the most reactive char in air and CO_2 [10,11], the highest reactivity in H_2 is shown by PSOC-87 char.

Effect of mineral matter on reactivity

Removal of mineral matter profoundly affects reactivity profiles of chars. This is illustrated by results of PSOC-87 and 127 chars (*Figures 1* and *2*). The demineralized chars show both an induction period and a steady state rate (R_c), whereas the chars produced from the raw coals do not show such behaviour.

Reactivity parameters for various chars prepared from raw as well as acid-washed (AW) and demineralized (DEM) coals are listed in *Table 3*. It is seen that in most cases R_i values decrease upon mineral-matter removal, whereas R_c values show a random variation; that is, they increase in some cases (PSOC-91 and 87 chars) and decrease in other cases (PSOC-138, 101 and 81 chars). In the case of the PSOC-127 char, both R_i and R_c values increase significantly upon demineralization.

It is noteworthy that in most cases demineralized chars have lower N_2 surface areas and higher CO_2 areas than do the corresponding chars produced from raw coals (*Table 3*). This effect is most pronounced for PSOC-87 char. In this case, the N_2 surface area, upon demineralization, decreases from 93 to 1·0 m^2/g whereas the CO_2 area increases from 260 to 600 m^2/g. This suggests that the removal of mineral matter from coals prior to their carbonization markedly affects the carbonization process and, hence, the pore size distribution and surface area of chars.

It is also noteworthy that in the case of PSOC-89, 91, 87, 138 and 101 chars, which have relatively large N_2 surface areas (*Table 2*), there is little or no induction period; and

Table 3 Surface areas and reactivities in H_2 of 1000°C 40 x 100 mesh chars produced from acid-treated coals

Parent coal PSOC No.	Surface area ($m^2 g^{-1}$)		Reactivity ($mg h^{-1} mg^{-1}$)	
	N_2	CO_2	R_i	R_c
91	31	420	0·96	1·2
91 AW	—	—	0·55	1·4
87	93	260	2·6	2·6[a]
87 AW	11	610	0·36	1·0
87 DEM	1	600	0·51	2·6
138	120	560	0·67	1·5
138 AW	4	680	0·57	1·2
138 DEM	47	115	0·23	0·82
101	62	400	0·86	1·2
101 AW	3	670	0·38	1·1
127	2	12	0·05	0·09[a]
127 DEM	4	37	0·11	0·83
81	1	39	0·13	2·0
81 AW	—	—	0·12	1·6
81 DEM	1	56	0·08	1·2

[a] No constant rate region

Table 4 Effect of particle size on reactivity of chars in hydrogen

Mesh size	Reactivity, R_o ($mg h^{-1} mg^{-1}$) of chars from coals			
	87	87 DEM	127	127 DEM
40 x 100	2·1	1·5	0·11	0·51
100 x 150	2·7	1·6	0·12	0·54
200 x 325	1·3	1·8	0·16	1·11

the constant rate region commences at conversions less than 20%.

Effect of particle size on reactivity

Reactivity measurements were made on three particle sizes of chars prepared from raw and demineralized samples of PSOC-127 and 87. As mentioned earlier in this paper, true R_c values were not obtained for the two raw chars. Therefore, R_o values (as defined earlier) are reported for different particle sizes (*Table 4*). Considering first the results for the chars produced from the raw coals, for PSOC-87 R_o increases by about 30% upon reduction in particle size from 40 x 100 to 100 x 150 mesh. However, reactivity of the 200 x 325 mesh fraction is about one-half of that of the other two size fractions. Reactivity of PSOC-127 char increases slightly with decrease in particle size.

Reactivity of the char produced from demineralized PSOC-87 is almost independent of particle size. Reactivities of the 40 x 100 and 100 x 150 mesh particle sizes are lower than reactivities of the corresponding particle sizes of the raw chars, whereas reactivity of the 200 x 325 mesh parcle size is appreciably higher for the demineralized char. Reactivity of the PSOC-127 char, for each particle size, is seen to increase appreciably upon mineral-matter removal.

Reactivity of the PSOC-127 demineralized char is about the same for the 40 x 100 and 100 x 150 mesh particle sizes but increases about two-fold upon reduction in particle size to 200 x 325 mesh.

Effect of hydrogen pressure on reactivity

The dependence of reaction rate (R_c) on hydrogen pressure in the 0·7–2·8 MPa range was determined for PSOC-91 char. The rate was found to be proportional to the first power of H_2 pressure, as is also reported in the literature[3,4,6,8].

Effect of temperature on reactivity

Reactivities of a few representative chars were determined at three different temperatures: 875, 925 and 980°C. The reactivity of each char increased with temperature, as expected. Pseudo-activation energies were calculated for various chars as a function of conversion. Results are given in *Table 5*. Typical Arrhenius plots for one of the chars, PSOC-67, for various conversions are shown in *Figure 4*. It is seen that the pseudo-activation energy increases from 150 kJ/mol at the beginning of the reaction to 213 kJ/mol when the rate attains a steady state value. Similar variations in activation energy are also observed for PSOC-91, 87 (DEM), and 127 (DEM) chars (*Table 4*). Zielke and Gorin[1] have also reported that the pseudo-activation energy for the hydrogasification reaction increased with conversion and tended to level off towards an asymptotic value at higher burn-offs.

DISCUSSION

Introduction

The major factors which control the reactivity of carbonaceous solids to O_2, CO_2, H_2O, and H_2 are known[12]. They are: (1) concentration of active sites, (2) presence of inorganic impurities which act as catalysts, and (3) diffusion limitations on how rapidly the reactive gas can reach active sites. Accepting the above, there are still two major problems to be faced if we are really to understand the reactivity of coal chars. First, we have the necessity of being able to characterize chars sufficiently well to be able to relate, quantitatively, their reactivity to measurable parameters. Secondly, we need to understand how to prepare chars from different organic precursors (coals in this case) which possess optimum properties so as to result in a maximization of their gasification rates.

Table 5 Pseudo activation energy for the hydrogasification reaction of selected 40 x 100 mesh chars

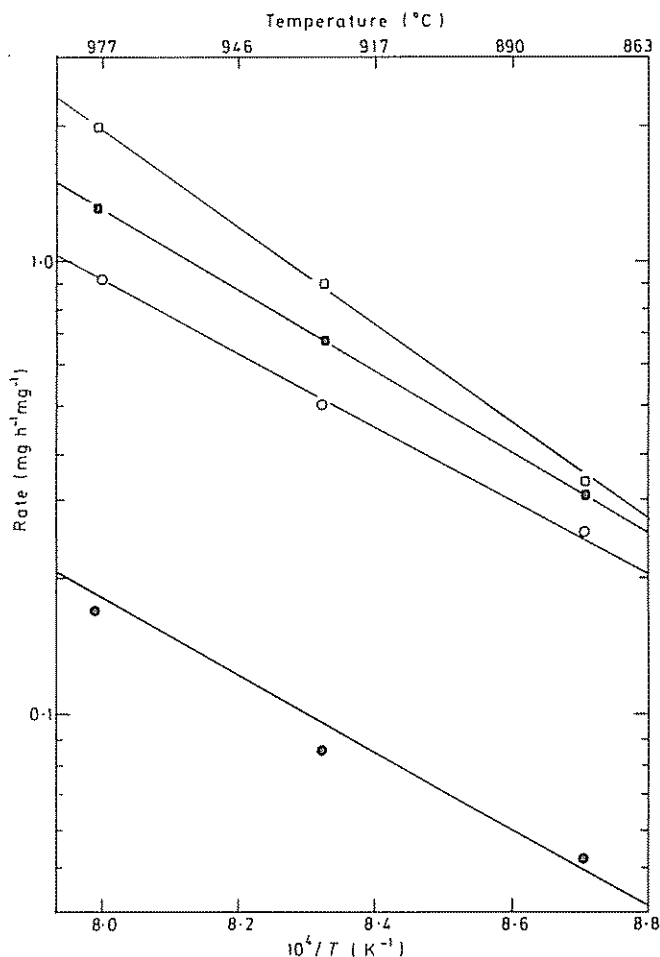| Parent coal PSOC No.	Activation energy (kJ/mol)	
	From R_i	From R_c
91	130	201
87	217	—
87 DEM	121	184
67	150	213
127	67	—
127 DEM	59	184

Temperature (°C)

Figure 4 Arrhenius plots for hydrogasification of char produced from raw coal PSOC-67 at different conversions. ● 0%; ○ 10%; ▣ 20%; □ 40—70%. Activation energies calculated from plots are 150, 150, 176, and 213 kJ/mol, respectively, with increasing conversion

The problem is more complex since it involves dynamic changes in char properties during its gasification. Consider the above three factors. As gasification proceeds, the concentration of active sites (ASA) can change as a result of opening of closed porosity and enlarging of existing porosity. Or on a microscopic scale, gasification enlarges boundaries between crystallites and enlarges defect sizes (vacancies, for example) within crystallites. ASA is generally measured by chemisorption of oxygen or hydrogen onto active carbon sites[15,16]. The extent of change in ASA with carbon burn-off depends in complex ways upon such variables as: the starting structure of the char, gasification temperature, reactive gas, nature and dispersion of inorganic impurities present, and the level of burn-off itself. The effect of some of these variables is just now being appreciated and clearly indicates the need for much future research.

As gasification proceeds, rates of diffusion of reactants to active sites and products away from active sites increase. This results in a progressive decrease in the limitations imposed on gasification rates by mass transport processes. Coal chars generally have a trimodal pore distribution of macro, transitional, and micropores. The majority of the ASA is located in the micropore system. Which pore system offers the limiting resistance to diffusion depends upon the diffusion coefficient (D_{eff}) and the average pore length (L) in each pore system. As we go from the larger

to the smaller pore system, both D_{eff} and L decrease. However, D_{eff} generally decreases more sharply than does L, resulting in the micropore system usually presenting maximum resistance to diffusion. Since most of the micropores in coal chars (prior to their gasification) are very small or of a size comparable to that of the reactive molecules, diffusion is activated[17]. Consequently, diffusion rates increase very sharply with small amounts of gasification. For example, we have shown in this laboratory that the gasification of an anthracite char in air from 6·9 to 9·1% burn-off changes the diffusion of methane from activated diffusion (activation energy of 27·5 kJ/mol) to Knudsen diffusion[18]. Thus it is clear that if one is going to evaluate, quantitatively, the role of mass transport in char gasification, diffusion parameters need to be measured as a function of char burn-off.

The specific activity of different inorganic impurities for the catalysis of char gasification depends upon their chemical form, degree of dispersion, and possible internal porosity[19]. Relative activity of the same impurity also changes, depending upon which gasification reaction is being catalysed. For example, iron is more active than nickel for catalysing the gasification of carbon by O_2 or steam; nickel is more active than iron for catalysing the gasification of carbon by H_2 [12,20]. The specific activity of inorganic impurities can change dramatically (increase or decrease) with carbon burn-off, depending upon the reactive atmosphere and the chemical and physical state of the impurity in the unreacted char[19]. As an example of a chemical effect, consider iron, cobalt, and nickel. In the metallic state, these elements are active catalysts for carbon gasification. In the oxidized state, they are inactive catalysts. Thus what changes the specific catalytic activity of these elements undergo during char gasification will depend upon their oxidation state in the original char and the particular atmosphere in which gasification is occurring. That is, is the atmosphere oxidizing or reducing to these elements at reaction temperatures and pressures?

So far as physical effects are concerned, these primarily involve the extent of dispersion of the impurity in the carbon, that is the fraction of total atoms which are at the surface of the impurity and thereby accessible to the reactant gas. This is particularly important in the case of coal chars since there can be a very wide range in the dispersion of impurities. Most of the inorganic impurities present as discrete minerals have a rather low dispersion; and their degree of dispersion is expected to change little during carbon gasification. On the other hand, most of the inorganic impurities within the carbon matrix or associated with functional groups at the edges of the carbon matrix are highly dispersed. This degree of dispersion would be expected to decrease markedly during gasification. The extent will depend upon the impurity, its original degree of dispersion, the reactant atmosphere, and reaction temperature. These parameters determine the degree of impurity mobility and, therefore, the possibility of coalescence into larger particles[21].

It is clearly important to understand also what variables affect the physical and chemical properties of chars and their inorganic impurities. The rank of the starting coal, its possible pretreatment at low temperatures, and the nature of the heat treatment conditions to maximum charring temperature can be important. Indeed, the importance of some of these parameters is evident in this study.

With this introduction, interpretation of some of the more significant results found in this research can be con-

sidered. It is obvious, however, that a quantitative explanation of char reactivity on the basis of char character is an ambitious objective. It has not been accomplished in this paper.

Initial reactivities

One thing which makes it difficult to talk about char reactivity is that the reactivity can change with char burn-off, in some cases increasing and in other cases decreasing. This means that one should be very careful to understand on what basis and at what burn-off reactivity is being expressed. As is seen from *Figure 3*, initial char reactivities tend to increase with decreasing rank of the coal from which the char was produced. This is as expected on the basis of the three major factors affecting reactivity. First, the lower-rank coals have smaller average layer sizes, as measured from X-ray diffraction, than do the higher-rank coals[22]. This means that they have a greater concentration of edge sites which are expected to be active sites for gasification[12]. This correlation is expected to carry over to the chars produced from coals of different rank.

Secondly, the lower-rank coals generally have a greater concentration of macro and feeder pores than do the higher-rank coals[14]. This concentration is further enhanced upon their conversion to chars since the higher the volatile matter loss the more porosity is generally created. A larger concentration of macro and transitional pores again usually means a shorter diffusion distance (L) within the micropores. Hence, diffusional resistance to gasification is expected to be less in the chars derived from lower-rank coals. Indeed, this is generally confirmed by values of N_2 surface areas of chars given in *Table 2*. That is, larger N_2 areas are associated with larger values of area in the macro and transitional pores[14]. It is seen that many of the lower-rank coals have ·ubstantial N_2 areas, while N_2 areas of the chars produced rom the higher-rank HVB to anthracite coals are very small. Larger release of volatile matter from the lower-rank coals also results in enlargement of the boundaries between small trigonally bonded crystallites and, hence, easier access of reactant gas to active sites. This is reflected in increasing values of surface area in micropores as measured by CO_2 adsorption. That is, the chars produced from lower-rank coals have much higher CO_2 areas than those produced from the higher-rank coals, as seen in *Table 2*.

Thirdly, lower-rank coals have significant concentrations of inorganic species which are highly dispersed. The prime example is the association of cations with the carboxyl groups in lignites. These cations have exchanged with the hydrogen on the carboxyl groups over a period of years. Similar association is thought to occur with phenolic hydroxyl groups when they are involved in the formation of chelate structures. Upon thermal treatment of these coals, the functional groups decompose leaving behind in the chars inorganic species which are thought to be highly dispersed. In such a highly dispersed state, these species would be expected to have high specific activities for catalysing char gasification. In the higher-rank coals, by contrast, little or no association of inorganic species with functional groups located at the edges of planar regions is thought to occur. Dispersion of the inorganic fraction, which is primarily present as mineral matter, is poor.

Change in reactivities with carbon burn-off

As seen in *Figure 3*, the spread in reactivities of chars

once a constant rate, R_c, is reached is much less than the spread in initial reactivities, R_i. This again is as expected. Carbon burn-off enlarges pore sizes and, thereby, reduces diffusional resistance. Carbon burn-off also enlarges boundaries between crystallites and, thereby, increases access to edge or active sites. Further, removal of carbon atoms by gasification would be expected to reduce the pinning of small inorganic species at the surface, thereby increasing their mobility and accelerating a decrease in their dispersion as they coalesce. In some cases a H_2 atmosphere has also been reported to enhance the decrease in dispersion of inorganic species supported on substrates[21,23]. A maximum decrease in diffusional resistance, a maximum increase in accessibility to active sites, and a minimum change in extent of dispersion of inorganic species would be expected for the chars produced from higher-rank coals upon carbon burn-off. Thus, it would be expected that their reactivity would approach the reactivity of chars produced from the lower-rank coals.

It is of interest that the activation energy for char gasification increases with carbon burn-off as seen in *Table 5* and *Figure 4*. Zielke and Gorin have reported a similar finding and attributed the increase to a preferential gasification of the more disordered char structure first, leaving behind a less reactive structure which progressively more resembles a well ordered carbon structure[1]. If this were the explanation, we would expect the activation energies calculated from R_i values to be higher for the chars produced from the higher-rank coals. But this is not the case; for example, the activation energy for gasification of char from PSOC-87 coal is much greater than that for gasification of the char from PSOC-127, as seen in *Table 5*. Rather, we feel that an increase in activation energy with carbon burn-off can be attributed to a reduction in diffusional control of gasification rates[12] and/or a decrease in the extent to which gasification is catalysed by impurities[19]. The latter effect would be a result of decreasing impurity dispersion as burn-off proceeds.

Effect of coal pretreatment on subsequent char reactivities

A number of coals were acid-washed with HCl or demineralized with a HCl—HF mixture prior to their charring, with the intention of studying the effect of mineral-matter removal on reactivity. However, acid-washing appears to have resulted in something more subtle (and perhaps even more interesting) taking place. That is, as is seen in *Table 3*, the surface area of chars as measured by N_2 and CO_2 adsorption is markedly affected by prior acid-washing of the coals. In some cases areas increase; in other cases areas decrease.

Major effects of acid-washing on char reactivities are seen. Consider two examples, that is chars from PSOC-87 and 127. The char produced from raw PSOC-87 has the highest initial reactivity R_i of any sample. Acid-washing of PSOC-87 in HCl and HF produces a major decrease in reactivity, probably as a result of a significant decrease in inorganic (catalyst) content[10,11]. Upon burn-off, the reactivity of the char from raw PSOC-87 decreases sharply and continuously, while the reactivity of the char from demineralized PSOC-87 increases sharply before reaching a constant R_c value. Indeed, the plots cross over each other at a burn-off of about 30% and at an R value of about 2.0 mg h^{-1} mg^{-1}, as seen in *Figure 2*. The decrease in R with burn-off for the char from raw PSOC-87 has been dis-

cussed previously and has been associated with a decrease in catalyst dispersion. The fact that R values for the char from the demineralized coal are higher at higher burn-offs than R values for the char from the raw coal is interesting and, perhaps, expected from CO_2 surface areas. That is, the CO_2 area for the demineralized char is substantially greater than that for the raw char. The reason for this large area difference is not understood at this time, but emphasizes the possibility that acid treatment of coals can markedly affect the charring process — or the dehydrogenation and condensation reactions which occur as a coal proceeds to a char.

The effect of acid treatment of coal PSOC-127 on subsequent char reactivity was as expected on the basis of prior studies of this effect on the char—air[10] and char—CO_2[11] reactions. That is, it was suggested previously that since acid-washing markedly lowers inorganic impurity content, where these impurities would be expected to be primarily large discrete mineral-matter particles in this coal, macro and transitional porosity would be introduced. This, in turn, would sharply lower diffusional resistance to gasification in this char and, thereby, increase reaction rate. However, results in *Table 4* on the effect of particle size reduction on reactivity shed doubt on this interpretation for the char—H_2 reaction. That is, for the raw-coal char R increases relatively little with decreasing particle size, suggesting then a minimum effect of diffusional resistance on gasification rates. Rather it appears, as with PSOC-87, that prior acid-washing of PSOC-127 significantly affected the charring process. Both the N_2 and CO_2 surface areas of the demineralized char are significantly higher than values for the raw char.

The situation is further complicated by the possibility that the chars still retain some chlorine and/or fluorine. That is, following treatment of the coals with acids, chlorine and fluorine ions are difficult to desorb upon subsequent washing with water. Some may be chemisorbed. It is known that chemisorbed chlorine is not completely desorbed from carbon upon heat treatment in an inert atmosphere up to 900°C [24]. However, chemisorbed chlorine is quantitatively removed from carbon upon treatment with H_2 at temperatures above 800°C, producing HCl and an H atom. In turn, the H atom would be expected to have a high reactivity with carbon sites leading to the formation of methane.

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