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Unification of coal-char gasification reaction mechanisms

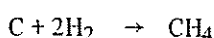
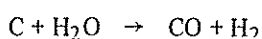
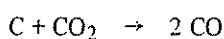
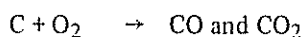
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Shapes of burn-off versus time (t) plots for various chars reacted in different gases are quite similar. These plots can be normalized into a single characteristic curve using a dimensionless time scale such that $t/\tau_{0.5}$ equals one at a fractional burn-off (BO) of 0.5. The shape of the characteristic curve has been explained qualitatively on the basis of changes in porosity and surface area occurring during gasification of microporous chars. For each gasification medium, BO versus $t/\tau_{0.5}$ data for different chars, up to a maximum BO of 0.7, can be correlated by a cubic equation of the form: $BO = a(t/\tau_{0.5}) + b(t/\tau_{0.5})^2 + c(t/\tau_{0.5})^3$. Up to a BO of 0.7, different char gasification reactions can also be described reasonably well by a first-order equation. However, the correlation is not as good as that provided by the cubic model.

In the conversion of coal chars to gaseous fuels, the four important gasification reactions are:



We have studied extensively in this laboratory these reactions on coal chars produced from a complete spectrum of American coals from anthracite to lignite¹⁻⁴. For each reaction we have found a major increase in char reactivity with decreasing rank of the coal from which the char is produced. Such increase has been explained in a manner consistent with the three important parameters which control gasification rates of microporous chars. That is, as chars are produced from coals of decreasing rank under fixed conditions of charring, the concentration of carbon sites active to gasification increases, the accessibility of reactant gases to these active sites increases, and the specific activity of inorganic impurities towards catalysis of gasification increases.

In calculating reactivities in the past we have used the simple expression

$$R = \frac{1}{w} \cdot \frac{dw}{dt}$$

where either w is the starting weight of dry, ash-free char and dw/dt is the maximum value found as burn-off proceeds or w represents char weights remaining at various values of time t and dw/dt represents slopes at corresponding times. Usually R is found to be constant over some burn-off range. It was noted that even though there were major differences in char reactivity (R) as the rank of the parent coal from which chars were produced was changed, the shape of the burn-off versus reaction time plots appeared to be quite similar. If this is so, it should be possible to normalize all

reactivity plots using an adjustable time parameter, τ , which can conveniently be used as a measure of differences in reactivity for a wide spectrum of chars. This paper concerns itself with examining the feasibility of such a normalizing procedure.

EXPERIMENTAL

Char preparation

U. S. coals ranging in rank from anthracite to lignite of 40×100 U. S. mesh size were used for the preparation of chars. Table 1 presents analyses of the parent coals. The chars were prepared by heating coals in an atmosphere of N_2 at a rate of $10^\circ C/min$ to $1000^\circ C$. Soak time at $1000^\circ C$ was 2 h. Details of the experimental procedure have been described previously³.

Reactivity measurements

The TGA technique was used to measure continuous weight changes during gasification of various chars in air (1 atm*) at $405^\circ C$, CO_2 (1 atm) at $900^\circ C$, steam (0.022 atm) at $910^\circ C$, and H_2 (2.76 MPa or 27.2 atm) at $980^\circ C$. Experimental details are described elsewhere¹⁻⁴. The reaction conditions selected reflect the fact that the rates of carbon gasification (R) in the four reacting gas media at similar conditions of temperature and pressure are: $R_{air} \gg R_{H_2O} \approx R_{CO_2} > R_{H_2}$ ⁵. Gasification rates were measured using a shallow bed of char particles so that mass transport resistance to diffusion of reactant gas molecules down through the bed was minimal.

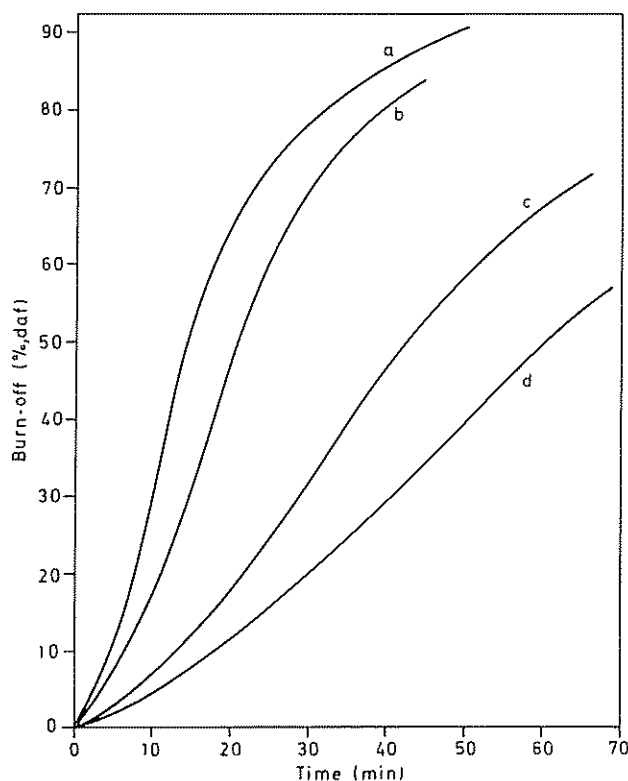
RESULTS AND DISCUSSION

The principle of normalizing reactivity plots is shown in Figures 1 and 2. Figure 1 shows burn-off versus time plots for the lignite char, PSOC-91, reacted in various partial pressures of O_2 at a total O_2-N_2 pressure of 1 atm. As expected

* 1 atm = 0.1013 MPa

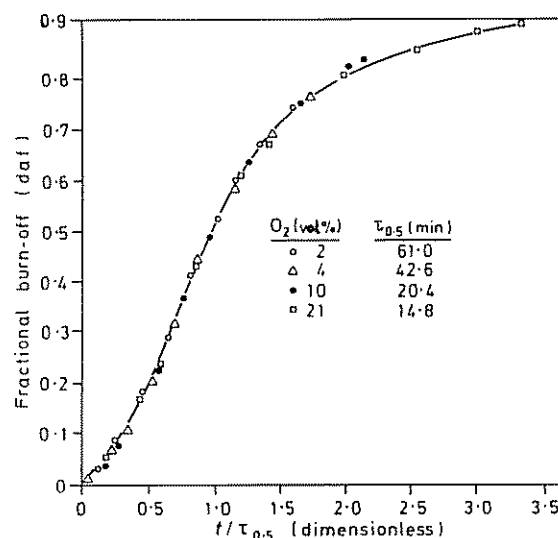
Table 1 Analyses of coals

PSOC Sample No.	ASTM rank	State	Ash (wt %, dry basis)	Ultimate analyses (wt %, daf)			
				C	H	N	Org. S
89	Lignite	N. D.	11.6	63.3	4.7	0.48	0.98
91	Lignite	Mon.	7.7	70.7	4.9	0.80	0.30
87	Lignite	N. D.	8.2	71.2	5.3	0.56	0.46
140	Lignite	Tex.	9.4	71.7	5.2	1.30	0.72
138	Lignite	Tex.	10.3	74.3	5.0	0.37	0.51
98	Subb. A	Wyo.	8.4	74.3	5.8	1.20	1.1
101	Subb. C	Wyo.	6.1	74.8	5.1	0.89	0.30
26	HVB	Ill.	10.8	77.3	5.6	1.10	2.3
22	HVC	Ill.	10.1	78.8	5.8	1.60	1.8
24	HVB	Ill.	11.8	80.1	5.5	1.10	2.3
67	HVB	Ut.	4.8	80.4	6.1	1.30	0.38
171	HVA	W. Va.	7.6	82.3	5.7	1.40	1.8
4	HVA	Ky.	2.1	83.8	5.8	1.60	0.66
114	LV	Pa.	9.8	88.2	4.8	1.20	0.62
81	Anthracite	Pa.	7.8	91.9	2.6	0.78	0.54
177	Anthracite	Pa.	4.3	93.5	2.7	0.24	0.64


 Figure 1 Influence of oxygen concentration on reactivity of PSOC-91 char at 405°C. a, 21% O₂; b, 10% O₂; c, 4% O₂; d, 2% O₂

ted, the gasification rate decreases sharply with decreasing O₂ pressure. Figure 2 shows that these individual reactivity plots can be well normalized using a dimensionless time scale such that $t/\tau_{0.5}$ equals one at a fractional burn-off of 0.5. Values of $\tau_{0.5}$, or the times to reach a fractional burn-off of 0.5, decrease from 61.0 min to 14.8 min as the percentage O₂ in the reactant mixture is increased from 2 to 21%.

Figure 2 is more or less typical of the shape of burn-off versus $t/\tau_{0.5}$ plots found for all chars reacted in all gases. That is, at low values of $t/\tau_{0.5}$ there is an increase in slope of the plot as $t/\tau_{0.5}$ increases. The plot then goes through a maximum in slope, followed by a lengthy region of slowly decreasing slope as fractional burn-off approaches one. Because of the complexity of the nature of char-gasification


 Figure 2 Normalized plot for reaction of PSOC-91 char at 405°C in different concentrations of O₂

reactions, it is difficult, at this stage, to offer a quantitative explanation for the 'characteristic' shape of the burn-off versus $t/\tau_{0.5}$ plots. One of the prime factors governing gasification rates of carbonaceous solids is the concentration of active sites (ASA), that is, carbon atoms located at the edges of layer planes^{5,6}. From fundamental studies on pure carbon surfaces, it is known that the first step in the overall gasification process is the dissociative chemisorption of the reactant gas at the active sites resulting in the formation of two types of heteroatom surface complexes, namely (1) an unstable or 'fleeting' surface complex which decomposes into the products of the gasification reaction, and (2) a stable surface complex whose build-up retards the formation of the 'fleeting' surface complex^{5,6}. At any stage during the gasification reaction, a part of the total ASA is covered with the stable complex. As a result, gasification rates are controlled by the concentration of ASA unoccupied by stable complex (UASA). Laine *et al.*⁷ have discussed the importance of UASA on the gasification rates of Graphon (a highly graphitized non-porous carbon black devoid essentially of all impurities) in O₂. They found that the rate constants for the formation of CO and CO₂, based on total surface area of the carbon, increased monotonically and sharply

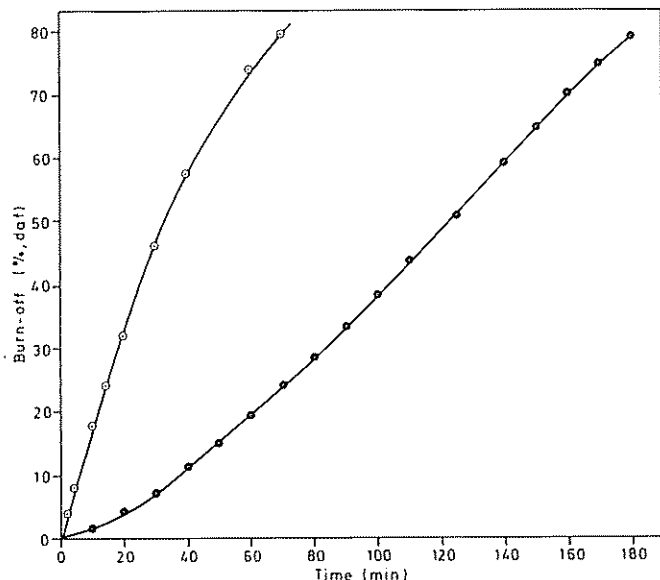


Figure 3 Effect of catalytic inorganic impurities on the shape of the reactivity plot of PSOC-87 char reacted in O_2 at $405^\circ C$. \circ , raw; \bullet , acid washed

with prior burn-off given to Graphon. In contrast, the rate constants based on UASA were essentially constant over the 0–35% burn-off range studied.

The situation with microporous coal chars, in contrast to Graphon, is far more complicated. For such materials, gasification rates are controlled not only by ASA but also by two other factors, namely (1) diffusional limitations or the extent ASA located in micropores is accessible to reactant molecules, and (2) amount, chemical form and particle size (degree of dispersion) of catalytic inorganic impurities^{5,6}. The three major factors governing gasification rates undergo complex dynamic changes during gasification³. These changes govern the shape of the burn-off versus $t/\tau_{0.5}$ plots. In the case of coal chars, it is not possible to monitor quantitatively these changes over the entire range of carbon burn-off. In order to understand the 'mechanism' of char gasification and, hence, the shape of the reactivity plots, it is imperative first to study the mechanism for a relatively pure microporous carbon which has a structure similar to the coal-derived chars. In this laboratory we have recently initiated such a study using a microporous polymer carbon. The burn-off versus $t/\tau_{0.5}$ plot for this carbon in air is similar in shape to that shown in Figure 2. The polymer carbon will be gasified (in the absence of any diffusional effects) to different levels of carbon burn-off and the changes occurring in total (BET) surface area and UASA will be measured in the manner described by Laine *et al.*⁷. At a later stage, in order to simulate the behaviour of 'impure' chars containing catalytic inorganic impurities, platinum dispersed on the polymer carbon will be used as a gasification catalyst. The use of platinum makes it possible to follow experimentally the quantitative changes in its degree of dispersion over the entire range of carbon burn-off. The results of such an investigation will be reported in a subsequent publication.

Although the characteristic shape of the burn-off versus $t/\tau_{0.5}$ plot (Figure 2) cannot be explained quantitatively at this time, we now endeavour to offer at least a qualitative explanation on the basis of what is known about the development of porosity and surface area in microporous chars as they undergo gasification. Before gasification, these chars contain closed porosity, that is porosity inaccessible even to

helium. With the onset of gasification, two important phenomena occur: (1) enlarging of pores that were open in the unreacted char, and (2) opening up of closed pores. Since the total number of pores is increased as well as their average radius, specific pore volume and specific surface area increase with increasing carbon burn-off. The specific surface area increases sufficiently rapidly as $t/\tau_{0.5}$ increases so that the product of specific area and char weight remaining, that is total area remaining, increases. The result is an increasing slope of the burn-off versus $t/\tau_{0.5}$ plot. At some point, depending upon the pore structure of the individual char, walls between existing pores are gasified away; and the total number of open pores commences to decrease. This leads to the specific surface area ultimately going through a maximum as burn-off proceeds. This results in the slope of the burn-off versus $t/\tau_{0.5}$ plot going through a maximum value and continuing to decrease to complete burn-off.

The aforementioned qualitative explanation ignores the effect which catalysis by inorganic impurities can have on the shape of the burn-off curve. For example, if a catalyst is initially very active but as burn-off proceeds become less active owing to sintering (that is, increase in particle size) or change in chemical state, the $t/\tau_{0.5}$ region over which the gasification rate is increasing can be shortened or indeed removed completely. This is graphically illustrated by the burn-off versus time plot for the lignite char, PSOC-87, reacted in air at $405^\circ C$ (Figure 3). It is noteworthy that for this char the maximum rate is observed immediately, as gasification commences. It is reasonable to conclude that in this case the catalytic effect of inorganic impurities on gasification is overshadowing the effect of increase in specific surface area. This view is supported by the fact that upon removal of catalytic impurities from the raw char (by acid washing with 10 volume % HCl at $60^\circ C$), the burn-off curve (Figure 3) is similar in shape to that shown in Figure 2. It is noted that the burn-off versus time plots for raw and acid-washed PSOC-87 chars when reacted in H_2 at $980^\circ C$ at a pressure of 2.76 MPa (27.2 atm) have previously been reported by Tomita *et al.*³ to be essentially of the same shape as those obtained for the corresponding char samples in air (Figure 3).

With these points in mind, it is of interest to see the extent to which one equation, with $\tau_{0.5}$ being the only adjustable parameter, can unify all the char reactivity data obtained in this paper. Computer correlation of data for each gasifi-

Table 2 $\tau_{0.5}$ values for gasification runs

PSOC Sample No.	$\tau_{0.5}$ for different reacting gases (min)			
	Air	Steam	CO ₂	H ₂
89	—	—	5.5	43.5
91	14.8	10.6	5.0	36.5
87	30.0	11.4	—	24.0
140	29.6	19.6	10.3	34.0
138	69.5	28.0	17.0	32.0
98	66.4	—	26.0	50.0
101	21.6	13.6	7.0	37.5
26	121	138	200	59.0
22	99.0	64.0	54.0	33.5
24	78.5	51.0	30.0	32.0
67	134	152	220	34.5
171	—	260	—	96.5
4	—	114	—	49.0
114	—	—	—	126
81	—	255	270	51.5
177	—	330	—	110

Table 3 Unification of coal-char gasification reactions

Reactant	No. of reactant-char combinations	Cubic model				First order	
		a	b	c	r ² (%)	Slope	r ² (%)
Air	10	0.317	0.367	-0.182	96.0	0.756	94.1
CO ₂	11	0.436	0.189	-0.122	99.2	0.728	78.4
H ₂ O	13	0.375	0.276	-0.148	99.1	0.761	87.4
H ₂	16	0.349	0.283	-0.144	96.6	0.693	88.6
All	50	0.368	0.277	-0.147	98.2	0.727	87.5

fication medium was conducted, as well as computer correlation of data for all gasification media. Burn-off versus time data for a fractional burn-off up to 0.7 were used in all cases. The suitability of the following equations to correlate the data was tested: a linear equation between burn-off and $t/\tau_{0.5}$, an equation involving first and second power terms in $t/\tau_{0.5}$, an equation involving first and third power terms in $t/\tau_{0.5}$, and an equation involving first, second, and third power terms in $t/\tau_{0.5}$. The last equation gave the best correlation of the data.

Tables 2 and 3 summarize the results. For the char produced from coal PSOC-140, ten reactivity runs were made with steam. For the ten determinations, a 95% confidence interval on the mean value of $\tau_{0.5}$ was found to be ± 0.8 min. Table 2 shows the wide variation of $\tau_{0.5}$ values found for the chars in each reaction medium as the rank of coal from which the chars were produced changes. Generally, $\tau_{0.5}$ values for each reactant gas fall in the same order, but there are exceptions, as expected, which reflect the uniqueness of each reaction. For example, values of specific catalytic activity of impurities for each reaction are not expected to fall in the same order.

Table 3 presents the best values for coefficients in the cubic equations between fraction burn-off and $t/\tau_{0.5}$ for each reactant, as well as for all reactants. r^2 values give how much of the variance, assuming no correlation between burn-off and $t/\tau_{0.5}$, can be removed by the particular cubic equation. It is obvious that for each individual reactant and also for all reactants the equations given result in a high correlation of results for burn-off versus $t/\tau_{0.5}$.

The success of the cubic equation to further correlate reactivity data was studied for other reaction conditions. It was successful in correlating data for the char-steam and char-CO₂ reactions as the partial pressure of the reactant gas and reaction temperature were varied.

As discussed earlier, each char-reactant gas mixture shows some region of $t/\tau_{0.5}$ over which the reaction rate is first order in amount of char remaining unreacted. This region of $t/\tau_{0.5}$ was found to vary with the nature of the char as well as the reactant gas, but in no case was the first-order obeyance observed over the entire range of carbon burn-off. Because of the observed first-order dependence of various char gasification reactions over some range of burn-

off, computer correlations were also made with the first-order model, $\ln[1/(1 - BO)] = k(t/\tau)$, where BO is fractional burn-off. These results are also summarized in Table 3. A necessary but not sufficient condition for the data obeying a first-order model is that k must equal 0.693 since $t/\tau_{0.5} = 1.0$ at $BO = 0.5$. Different reactions are seen to be more or less closely described, over a fractional burn-off range up to 0.7, by a first-order equation. A reasonably good correlation is found for the char-air reaction, and a low correlation is found for the char-CO₂ reaction.

From these studies, it is concluded that a good parameter to use to correlate char reactivity data is the time required to reach a fractional burn-off of 0.5. When this parameter is used, it is also shown that our char gasification data can be successfully normalized into burn-off versus $t/\tau_{0.5}$ plots of almost similar shape. Since each char-reactivity run also exhibits some $t/\tau_{0.5}$ region where the rate is first order in weight of char remaining, it probably is desirable to report first-order rate constants in order to adhere to the more conventional treatment of kinetic data.

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