

ACTIVE SURFACE AREA ON CARBON REACTIVITY

K. Kuo and H. Marsh

Northern Carbon Research Laboratories, Department of Chemistry,
University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, U.K.

Introduction

Carbon reactions with oxidizing gases result in carbon being selectively and continuously removed. The overall reactivity ($\text{g g}^{-1} \text{s}^{-1}$) which is usually expressed in terms of "rate of mass burn-off" does not give a detailed understanding of these heterogeneous carbon/gas reactions and the influence of factors such as: (a) parent material e.g. cellulose to polycyclic hydrocarbons, giving a more or less defective constituent lamellar molecule structure; (b) the heat treatment temperature (HTT) of the carbon; increasing severity of heat treatment possibly results in a reduction of defect density and hence decreased reactivity; (c) accessible or total surface area (TSA); (d) catalysis by inorganic impurities.

Measured kinetic parameters should reflect the true chemical reactivity of the carbon surface if possible. The intrinsic reactivities of carbon-gas systems usually expressed on a surface area basis ($\text{g m}^{-2} \text{s}^{-1}$) are normalized with respect to either the geometric or Total Surface Area (TSA) or Active Surface Area (ASA).

Despite numerous studies of the carbon/oxidising gas reaction, quantitative intrinsic rate data are scarce. Smith (1) collected published data of intrinsic reactivities of a large variety of carbons with the objective of comparing one with another. Values of the intrinsic reaction rate based on TSA for different types of carbons, at a given temperature and otherwise constant conditions can differ by up to four orders of magnitude. It has long been recognised that TSA is a gross indicator of carbon reactivity and does not always correlate well with reactivity. TSA which is usually measured at very low temperature e.g. N_2 at 77 K and CO_2 at 273 K could sometimes give unrealistically low surface areas due to activated diffusion effects. This is especially so with carbons having significant contents of ultra- or micro-porosity. Reactant gases at gasification temperatures which are much higher (e.g. CO_2 at 1173 K) than adsorption temperatures would have access to more surface than the adsorbates. Hence the poor correlations of TSA with reactivity especially with low TSA carbons.

The use of low temperature oxygen chemisorption technique as a measure of ASA to correlate carbon reactivity originated with the work of Laine *et al.* (2). Although this technique of measuring ASA is essentially empirical due to the complexity of the carbon/oxygen interaction (3-6), there has been success with correlations of ASA with carbon reactivity (7-12).

Concept of Active Surface Area (ASA)

The concept of ASA, which attempts to rationalise differences in carbon reactivity can be described using Figures 1, 2 and 3. These figures are plots of three reactivity functions against TSA of carbons. TSA can range from $<0.1 \text{ m}^2 \text{ g}^{-1}$ to $>1000 \text{ m}^2 \text{ g}^{-1}$. Generally, anisotropic (graphitizable) carbons e.g. cokes have low surface areas and isotropic (non-graphitizable) carbons e.g. chars have high surface areas. In Figure 1, the overall reactivity R (s^{-1}) is plotted against the measured accessible total surface area (TSA) of the carbon. If all surfaces are comparable in terms of reactivity then there should be a linear relationship between R and TSA (solid line of Figure 1). However, most carbon surfaces could be either more or less reactive (broken lines) or could be more randomly distributed.

Figure 2 is a plot of the intrinsic reactivity R' ($\text{g m}^{-2} \text{s}^{-1}$) based on TSA against the measured accessible total surface (TSA) of the carbon. If all surfaces are comparable in terms of reactivity then they should all have the same reactivity (solid horizontal line of Figure 2). Differences between surfaces will be indicated by deviations from this line. For example, significant catalysis or possibly inaccurate low surface area measurements give data points above the horizontal line.

Figure 3 uses the intrinsic reactivity R'' ($\text{g m}^{-2} \text{s}^{-1}$), based on ASA plotted against the measured accessible TSA of the carbon. If all surfaces have equal densities and type of active sites (and hence reactivity) then they should have the same reactivity value (horizontal line AB of Figure 3). Again, differences between the active sites of carbons will be indicated by deviations from this line. Points D, E and F could describe carbons with contained mineral matter which is catalytic. The line BC describes solid carbon surfaces of increasing surface area but where the percentage of defects or active sites increases with increasing surface area. Position C is for carbons of high heat treatment temperature and Position B is for carbons of low heat treatment temperature.

The approach adopted in this study is: (a) to create a range of carbons of quite different structures from the same parent materials which have relatively low impurity contents; (b) to relate reactivities of these 'pure' model carbons of different structures to surface areas (TSA, ASA); (c) to relate reactivities of coal chars of the same heat treatment temperature to the standard reactivity line of the 'pure' carbons. It is not unrealistic to assume that for 'pure' model carbons, values of the intrinsic reactivity based on ASA do not change much. Hence any wide variations from the standard reactivity line would be due to catalysis.

Experimental

Carbons (coke/chars) with different sizes of optical texture or structure were prepared by carbonization in a horizontal tube furnace under flowing nitrogen of the phenolic resin, Alnovol and by co-carbonization of Alnovol with increasing amounts of petroleum pitch, Ashland A500 (0-100 wt%). The carbons were found to have relatively low impurity contents (Table 1). Other parent materials used in this study to make cokes/ chars include a coal tar pitch (CTP 104), a commercial polymer polyvinylidene chloride (PVDC), a synthesized in-house polymer polyfurfuryl alcohol (PFA) (13) and a rank series of 6 bituminous coals from the Lower Kittanning seam supplied by Southern Illinois University, Illinois. All systems were carbonized to 1173 K, at a heating rate of 5 K min^{-1} , with a soak period of 1 h, except for the coal tar pitch which was carbonized to 1223 K at 4 K min^{-1} with a 0.5 h soaking period.

Carbon Reactivity Measurements

The reactivities of resultant carbons (size range 38-106 μm) to carbon dioxide at 1173 K were measured using a STA 780 Stanton Redcroft Thermal Analyser. This involves heating 10 $\text{mg} \pm 0.5 \text{ mg}$ sample in a stream of dry nitrogen in the TGA apparatus to 1173 K at 50 K min^{-1} . Once at this temperature the nitrogen is changed to carbon dioxide at the same gas flow rate (50 $\text{cm}^3 \text{ min}^{-1}$). The sample was allowed to burn-off isothermally until less than 50 wt% of the sample remained.

Under the conditions selected, the "burn-off" plots have a rectilinear portion which is indicative of the region of maximum reactivity. The reactivity parameter, R was calculated using Equation 1:

$$R = -\frac{1}{W_0} \cdot \frac{dW}{dt} \quad (1)$$

where R is the maximum reactivity at temperature, T K ($\text{g g}^{-1} \text{ s}^{-1}$), W_0 = initial mass of the carbon sample (ash free; g) and dW/dt is the maximum rectilinear weight loss (g s^{-1}).

Carbon Characterization

Elemental analyses (C,H,N) were performed on the cokes/chars to determine the extent of their devolatilization (Tables 2 and 4). The reflectance measurements ($R_0\%$) of the raw coals were taken from Skorupska N.M. (14). The resultant cokes/chars were mounted in resin, polished and examined for optical texture (15) to determine their degree of anisotropy (order). X-ray diffractions (XRD) were obtained from the carbons using a Phillips X-ray diffractometer (Phillips 1730) and CuK α radiation. The crystallite height, L_c , and diameters, L_a , were estimated from the (002) and (10) diffraction peaks, respectively, using the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where λ = the wavelength of the X-rays; θ = the Bragg angle; β = the corresponding peak width at half-maximum intensity and $K = 0.9$ (L_c) and 1.84 (L_a).

The Total Surface Area (TSA) of the resultant cokes/chars apart from the coal tar pitch CTP 104 coke and petroleum pitch A500 coke were determined from the adsorption isotherms of carbon dioxide at 273 K at pressures up to 0.1 MPa ($p_0 = 3.4$ MPa; $p/p_0 = 0.03$) using a McBain Spring Apparatus. From Dubinin- Radushkevich (DR) plots, the TSA as well as the gradient D were calculated. The gradient D can be used as a semi-quantitative indicator of average pore size distributions. Lower or higher values of the gradient represent narrower or wider micropores, respectively. The TSA of the two cokes (CTP 104 and A500) were determined from the nitrogen adsorption (BET) at 77 K using a low surface area volumetric apparatus. The oxygen chemisorption capacities (ASA) of the carbons were determined by two methods (a) oxygen chemisorption and (b) desorption of the chemisorbed oxygen. The sample (~250 mg) in a quartz bucket was 'cleaned' by outgassing to $<10^{-2}$ Pa and heated to 1173 K for 3.1 h. Chemisorption was carried out at 423 K and 22 kPa oxygen for 24 h. Weight gains were continuously recorded and used to calculate ASA:

$$ASA = n \times \sigma \times 10^{-18} \text{ m}^2 \text{ g}^{-1} \quad (3)$$

where n = no. of oxygen atoms

and σ = area of chemisorbed oxygen atom = 0.083 nm^2

Extents of chemisorption can also be calculated from equivalent amounts of carbon monoxide and carbon dioxide desorbed on heating to 1173 K. A multirange micromanometer which is attached to the vacuum rig was used to monitor the partial pressure of carbon monoxide by first trapping carbon dioxide in liquid nitrogen, and then evacuating the carbon monoxide and measuring the partial pressure of the evaporated carbon dioxide.

Results and Discussion

Table 1 shows the carbons to have very low inorganic impurities. The elemental analysis and carbon yields are in Table 2. The increase in carbon yield with increasing wt % A500 was an additive effect produced by incorporating increased amounts of A500 which has a higher carbon yield compared with that of Alnovol.

Optical microscopy and Transmission Electron Microscopy (TEM) show that the Alnovol resin produced an isotropic char which has a highly disordered microstructure whereas the petroleum pitch, A500, produced an anisotropic coke which has a more ordered microstructure.

With mixtures of the two, the resultant carbons showed some anisotropic texture the percentage of which roughly reflected the percentage of resin in the sample.

Table 3 shows that both the crystallite height, L_c (0.91 to 1.49 nm) and the diameter, L_a (3.70 to 4.45 nm) increase with increasing amounts of A500 present in the Alnovol:A500 mixture. This provides further semi-quantitative evidence to indicate the gradual change in microstructure of the carbons from disorder to order with increasing amounts of A500 added. An increase in both L_c and L_a is indicative of a decrease in the ratio of edge carbon atoms to basal carbon atoms. The chemisorption capacity of the carbons which decreased significantly from $41 \text{ m}^2 \text{ g}^{-1}$ for Alnovol chars to $4 \text{ m}^2 \text{ g}^{-1}$ for 25% Alnovol: 75% A500 carbon (Table 3) provide further quantitative evidence to support the theory that a more ordered 'pure' carbon would have less active sites. Although the trend is similar, the ASA calculated by desorption of chemisorbed oxygen complexes (CO and CO_2) is larger. The differences between the two ASA values vary from carbon to carbon. It is possible that for certain reactive carbons there is gasification occurring during oxygen chemisorption; hence the lower ASA values calculated by oxygen chemisorption.

Changes in adsorption properties are reflected by a decrease in the TSA ($570 - 1.11 \text{ m}^2 \text{ g}^{-1}$) and an increase in the gradient D of the DR plot (0.1-0.2) which is indicative of an increase in the average pore size (Table 3).

Table 4 shows the % Reflectance, % Carbon yield and elemental analysis of the raw coals and their chars. The reflectance measurement (14) as well as the % carbon yield increase with increasing rank of coals (from SIU 1439 to SIU 1467). It is shown in Table 5 that the oxygen chemisorption capacity and the TSA of the coal chars decreases with increasing rank of coal. Figures 4, 5 and 6 show the reactivities (R , R' and R'') of all the carbons plotted against TSA. The observed overall reactivity, R decreased by a factor of 60 between the highest reactivity value of SIU 1439 coal char ($210 \times 10^{-6} \text{ s}^{-1}$) and the lowest reactivity value of A500 coke ($3.5 \times 10^{-6} \text{ s}^{-1}$). The calculated TSA is found not to be a relevant reactivity normalization parameter. ASA on the other hand seemed to be a good reactivity parameter; a factor in overall reactivity of 60 is reduced to only $7(0.57 \times 10^{-6} \text{ to } 3.85 \times 10^{-6} \text{ g m}^{-2} (\text{ASA})\text{s}^{-1})$ when the reactivity is expressed in terms of ASA.

Figure 4 shows the overall reactivity, R of the Alnovol:A500 carbon increases with increasing Alnovol present (i.e. equivalent to increasing TSA) (cf Figure 1). The slightly higher overall reactivity, R of the coal tar pitch coke, CTP 104 ($4.8 \times 10^{-6} \text{ s}^{-1}$) compared to the petroleum pitch coke, A500 ($3.5 \times 10^{-6} \text{ s}^{-1}$) is to be expected since coal tar pitches are known to be more heterogeneous and contain more impurities. The coal chars which contained more catalytic impurities (Table 4) exhibit higher overall reactivities R . However, the overall reactivity, R increases with decreasing coal rank (i.e. equivalent to increasing TSA).

Figure 5 is a plot of the intrinsic reactivity R' (per unit TSA) against the TSA of the carbon (cf Figure 2). For Alnovol:A500 cokes/chars with a TSA $>200 \text{ m}^2 \text{ g}^{-1}$ surfaces seem to be comparable in terms of reactivity, i.e. there is little variation in the intrinsic reactivity R' . However, deviations start to occur for low TSA carbons (cokes) ($<200 \text{ m}^2 \text{ g}^{-1}$) which have a high intrinsic reactivity, (R') and is due to activated diffusion effects giving inaccurately low TSA. This illustrates the inadequacy of using TSA as an indicator of carbon reactivity and is especially so when one is working with low TSA carbons. However, for a 'pure' carbon with relatively large TSA e.g. PVDC and PFA (no activated diffusion problems), intrinsic reactivities, R' fall on the same line as the Alnovol:A500 carbons. The intrinsic reactivity, R' of the coal chars deviates from the model carbons which is indicative of the significant effect of catalysis.

Figure 6 is a plot of the intrinsic reactivity R'' (per unit ASA) against the TSA of the carbon (cf Figure 3). For the Alnovol:A500 model carbons, there appears to be very little variation in the intrinsic reactivity, R'' for carbons ranging from low TSA to high TSA. The intrinsic reactivity, R'' of the other 'pure' model carbons, PFA and PVDC fall within the same region as the Alnovol:A500 carbons but the coal chars deviates from this region. This indicates that for 'pure' carbons with little or no catalytic impurities, most of their surfaces have equal densities and type of active sites and hence they have almost similar reactivity value. In contrast heterogeneous carbons like coal chars with contained catalytic mineral matter have different densities and type of active sites and hence the deviations.

Conclusions

In order to develop the concept of Active Surface Area a series of closely related but different carbons have been prepared with the same final heat treatment temperature. These carbons have been characterized in terms of optical texture, X-ray diffractions, total surface area (TSA) and Active Surface Area (ASA) as measured both by weight uptake of chemisorbed oxygen and by volume measurement of oxides of carbon desorbed from the carbon surface. The reactivities of these carbons to carbon dioxide at 1173 K and 0.1 MPa pressure have been measured. Reactivities are described as R , i.e. $g\ g^{-1}\ s^{-1}$ (weight loss data), as R' , ($g\ m^{-2}\ s^{-1}$) i.e. an intrinsic reactivity parameter based on total surface area (TSA) measured from adsorption isotherms, and as R'' ($g\ m^{-2}\ s^{-1}$) based on active surface area (ASA) measured from chemisorption of oxygen. Differences in R are progressively reduced when R' and R'' are the describing parameters. Differences in R'' can be attributed to the uses of too low a value of TSA, due to activated diffusion effects operating at physisorption adsorption temperatures. The carbons of different origins of relatively low inorganic impurities do not exhibit significantly large variations in reactivity.

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Table 1
Neutron Activation Analysis of
Parent Materials used and the
Resultant Cokes/Chars.

SAMPLE	Sodium/ mg kg ⁻¹	Potassium/ mg kg ⁻¹	Iron/ mg kg ⁻¹
Phenolic resin, Alnovol	12.1 ± 0.7	10 ± 2	19 ± 4
Petroleum pitch Ashland A500	7 ± 1	<7	23 ± 8
Coal tar pitch CTP 104	37.1 ± 0.7	8 ± 2	61 ± 6
Alnovol char (NTT 1173 K)	39 ± 2	54 ± 5	130 ± 10
75% Alnovol:25% A500 (NTT 1173 K)	182 ± 4	73 ± 7	60 ± 9
50% Alnovol:50% A500 (NTT 1173 K)	46 ± 2	130 ± 9	100 ± 10
25% Alnovol:75% A500 (NTT 1173 K)	76.1 ± 0.8	107 ± 7	101 ± 8
A500 (NTT 1173 K)	19.8 ± 0.9	33 ± 3	81 ± 9
Poly(furfuryl) alcohol (NTT 1173 K)	6.6 ± 0.7	<7	25 ± 5
CTP 104 (NTT 1223 K)	101 ± 2	19 ± 2	160 ± 4

Table 2
% Carbon Yield and Elemental Analysis of
Cokes/Chars prepared at 1173 K, 5 K min⁻¹,
with 1 h soak.

SAMPLE	C/wt%	H/wt%	N/wt%	Atomic C/H	wt% Carbon Yield
Alnovol	95.7	0.6	0.4	13.6	56
87.5 Alnovol:12.5 A500	97.2	0.6	0.3	13.2	58
75 Alnovol:25 A500	96.7	0.6	0.1	12.7	60
62.5 Alnovol:37.5 A500	97.3	0.6	0.1	12.8	62
50 Alnovol:50 A500	94.6	0.6	0.3	12.4	65
37.5 Alnovol:62.5 A500	95.8	0.7	0.5	12.3	67
25 Alnovol:75 A500	98.3	0.6	0.1	13.1	69
12.5 Alnovol:87.5 A500	98.7	0.7	0.1*	12.6	74
A500	98.3	0.7	0.1	11.5	78
PVDC	95.1	0.6	0.8	14.5	26
PFA	96.9	0.6	0.1	13.8	49
CTP 104	97.1	0.4	1.1	20.4	46

TABLE 3
Crystallite dimensions, TSA and ASA of Alnovol:A500 carbons prepared at
1173 K, 5 K min⁻¹ and 1 h soak.

SAMPLE	ASA / m ² g ⁻¹									
	XRD		DR PLOT (CO ₂ , 273K)		ADS (423K, 27Pa O ₂)		DESORPT. (1173K, 3.1 h)			
	l.c./nm	l.a./nm	TSA/m ² g ⁻¹	DX10 ⁻²	ASA (adj.) m ² g ⁻¹	ASA/ TSA	mol CO ₂ /g X10 ⁻⁴	mol CO ₂ /g X10 ⁻⁴	ASA** m ² g ⁻¹	ASA/TSA**
Alnovol	0.91	3.7	570	10.1	4.1	0.07	8.43	2.58	68	0.12
87.5% Alnovol 12.5% A500	0.95	3.65	540	11.2	3.8	0.07	9.28	2.57	72	0.13
75% Alnovol : 25% A500	1	3.94	480	11.2	3.3	0.07	7.31	2.28	59	0.11
62.5% Alnovol 37.5% A500	1.02	3.75	410	12.2	2.9	0.07	7.15	2.13	57	0.14
50% Alnovol : 50% A500	1.16	3.5	310	11.1	2.5	0.08	5.55	1.8	46	0.15
37.5% Alnovol 62.5% A500	1.22	3.51	210	7.2	1.8	0.08	2.48	1.14	24	0.11
25% Alnovol : 75% A500	1.42	4.2	55	18.3	4	0.07	2	0.43	14	0.26
12.5% Alnovol 87.5% A500	1.46	4.2	9	19.2			1.94	0.27	12	1.59
A500	1.49	4.45	1.1							

Table 4
% Reflectance, % Carbon Yield and Elemental
Analysis of Coals and Coal Chars prepared at
1173 K, 5 K min⁻¹ with 1 h soak.

SAMPLE	*R/%	C/wt%	H/wt%	N/wt%	Atomic C/H	% Ash	% Carbon Yield
<u>Coal</u>							
SIU 1439	0.47	62.6	4.7	1.3	1.12	10.2	
SIU 1444	0.66	66.5	4.7	1.3	1.18	10.7	
SIU 1436	0.86	72.6	5.0	1.4	1.22	13.3	
SIU 1445	1.01	70.6	4.4	1.3	1.33	14.2	
SIU 1458	1.24	75.5	4.3	1.2	1.48	9.9	
SIU 1467	1.75	69.6	3.6	1.3	1.64	18.0	
*(Ref 14)							
Char (HTT 1173 K, 5 K min ⁻¹ 1 h soak)							
SIU 1439		78.0	0.4	1.3	15.97	16.4	61%
SIU 1444		80.0	0.4	1.0	14.93	17.3	66%
SIU 1436		83.0	0.5	1.2	14.21	22.7	70%
SIU 1445		77.9	0.4	1.1	15.20	17.9	72%
SIU 1458		83.3	0.4	1.1	15.54	13.6	76%
SIU 1467		78.1	0.4	1.1	15.99	34.4	85%

Table 5
Crystallite dimensions, TSA and ASA of Cokes and Chars.

SAMPLE	XRD		ASA / m ² g ⁻¹								
			DR PL0T (CO ₂ , 273K)		AOS (423K, 77Pa O ₂)		DesORP (1173K, 3 h)				
	Lr/nm	Ln/nm	TSA/m ² g ⁻¹	OX10 ⁻²	ASA (adg.) m ² g ⁻¹	ASA/ TSA	mol CO/g x10 ⁻⁴	mol CO ₂ /g x10 ⁻⁴	ASA** m ² g ⁻¹	ASA/TSA**	
CIP 104			0.75								
PFA	0.81	3.11	346	8.5	41	0.11		8.82	2.68	71	0.18
PVOC	0.84	3.19	750	12	40	0.05		7.47	1.96	56	0.07
SIU 1439			250	32.1							
SIU 1444			240	6.9	52	0.22		8.18	2.84	87	0.36
SIU 1436			160	7.7	22	0.14		4.23	1.6	50	0.32
SIU 1445			110	6.9	26	0.24		4.48	1.82	51	0.48
SIU 1458			52	9.8	11	0.22		2.44	0.72	23	0.45

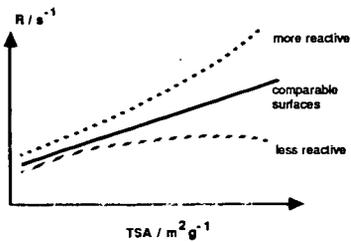


FIGURE 1 Overall Reactivity, R , vs TSA

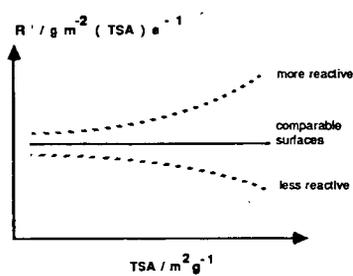


FIGURE 2 Intrinsic Reactivity, R' , vs TSA

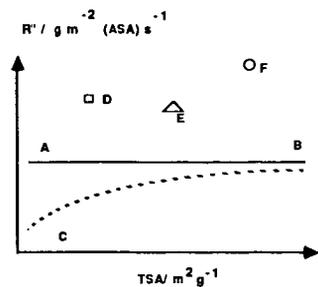


FIGURE 3. Intrinsic Reactivity, R'' , vs TSA

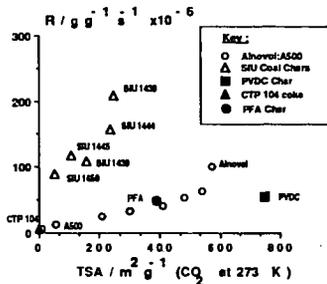


Figure 4. Overall Reactivity, R , vs TSA.

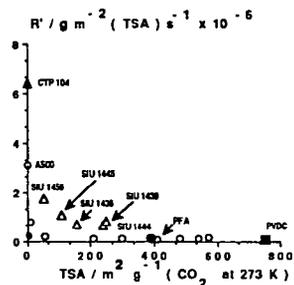


FIGURE 5. Intrinsic Reactivity, R' , vs TSA.

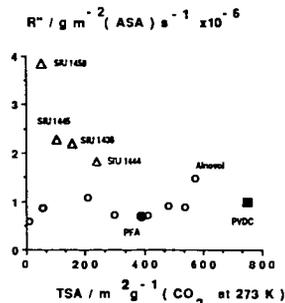


FIGURE 6. Intrinsic Reactivity, R'' , vs TSA.