

Role of Carbon Active Sites in the Oxidation of Coal Chars

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INTRODUCTION

Over the last two decades there have been numerous coal char and carbon gasification studies that have determined relative rates of the carbon/gas reactions. It has been demonstrated, quite clearly, that the measured chemical reactivities of chars are functions of coal rank, pyrolysis severity, the presence of catalytically active species, and, of course, the reactant gas and the specific reaction conditions utilized. The goal of this, and other investigations is to attempt to rationalize this range of reactivities in terms of some fundamental parameter/property of the char. The specific aim is to determine if a fundamental rate constant can be obtained for, say, the carbon-oxygen reaction. It is felt that such an approach will lead, eventually, to a better understanding of char gasification in terms of theoretical and practical considerations.

Our approach has been to examine further the role that carbon active sites play in governing the reactivity of a wide range of chars and carbons. This concept was first put forward by Laine et al. (1,2) and has been extended by others (3,4,5). There appear to be relationships between reactivity and active site concentrations (as determined by oxygen chemisorption). The thrust of this study was to extend these types of reactivity studies and to examine, especially, the changes in active site concentration with degree of gasification (burn-off). An attempt has been made to develop a concept of "reactive" sites. That is, to consider sites that are actively participating in gasification reactions. The starting point of this concept is to define an equivalent reactive surface area (RSA) that can be utilized to normalize rates in terms of a pseudo Turn-over Number (TON).

EXPERIMENTAL

i. Materials

Five coals ranging from lignite to anthracite have been used throughout this study. In addition, a relatively "pure" carbon was prepared from Saran polymer (a copolymer of vinylidene and vinyl chloride). The coals are PSOC 833 - a Montana lignite; PSOC 465 - a Wyoming subbituminous A coal; PSOC 1099 - a HVA coal from Pennsylvania; PSOC 1133 - LV, Pennsylvania coal; and PSOC 868 - a Pennsylvania anthracite.

Samples of the raw coals were subjected to a range of pretreatments to alter, in a selective fashion, the inorganic constituents. These modifications were brought about by ion exchange and acid-washing procedures for the lignite (PSOC 833) and by acid-washing procedure for the other coals. Selected samples of all the coals were treated with calcium acetate solutions, varying from 0.001 M to 1.5 M, in order to change the calcium loading in the coals. Chars/cokes from the raw and treated coals were prepared either by slow heating (10°K/min) up to final temperatures of between 975 K and 1275 K, or by rapid pyrolysis (~ 10⁴ K/min) at 1275 K in an entrained flow reactor.

ii. Apparatus and Procedures

Isothermal and nonisothermal reactivities were determined in thermogravimetric analyzers (TGAs). Concentrations of CO and CO₂ in the product gas stream were measured by nondispersive infrared analyzers.

Nonisothermal reactivity measurements were performed using a small sample of coal (< 4 mg) placed in a TGA bucket and heated at a constant heating rate 5 K min⁻¹ to an ultimate final temperature in the reactant gas (air). The weight loss, and its first derivative were recorded. The parameter used to represent this reactivity is T_m, the temperature at which the maximum rate of weight loss (maximum of the first derivative) occurs. For isothermal reactivity measurements a sample of char is heated to the desired reaction temperature, in the absence of oxidizing gas, and then the reactant (air) gas was introduced. Weight change and its first derivative with time were determined directly by the thermogravimetric analyzer and also calculated from the composition of the gaseous products of reaction (CO and CO₂). Thus, the TGA reactivity is estimated from the following expression

$$R_{TGA} = 1/w \times \frac{dw}{dt}$$

where R_{TGA} is the reactivity (min⁻¹) at a given temperature and burnoff; w is the mass of the sample and dw/dt the instantaneous slope of the burn-off curve. The reactivity determined from the gas composition is calculated by a similar expression.

Reactive surface area (RSA) at any given level of burn-off is calculated from a knowledge of the quantities of CO and CO₂ evolved. It is assumed that each oxygen atom occupies 0.083 nm² (1). Using the values of Reactivity (R) and Reactive Surface Area (RSA), a Turn-over Number (TON) can be calculated (R/RSA). The units of TON are g/m² min.

RESULTS AND DISCUSSION

Nonisothermal reactivities for the five coals are listed in Table 1. It can be observed that the reactivity of the coals (T_m-temperature at which maximum weight loss occurs) inversely follows rank. That is, as the rank of coal increases the reactivity decrease (higher value of T_m). Significant differences in the T_m values (630 K to 800 K) are noted over the rank range examined for the raw coals. The values for the demineralized coals exhibit somewhat less variability (701 K to 809 K). It is important to note that the reactivities of the raw subbituminous and lignitic coals are significantly greater than those determined for the respective demineralized samples. However, for the higher rank coals, demineralization can actually produce a slightly more reactive material. Thus, we see that in the lower rank coals, and their chars, the presence of inorganic species does indeed dominate reactivity. In all cases (except raw lignite), heat treatment does reduce "reactivity." As would be anticipated, one also observes that increasing the heat treatment temperature for any given sample produces a less reactive carbonaceous material. These results, of course, show the influence of reduction in active site concentration and possible catalyst deactivation with increasing heat treatment. Overall, perhaps the most important observation to be made is that catalytic effects of inorganic matter in higher rank coals are less important than those found for lower rank coals. In addition, it is possible that during the demineralization process some closed porosity is opened, thus, increasing the overall accessibility to active area. It is also possible that acid treatment reduces the thermoplastic properties of the higher rank coal, which in turn leads to slightly higher reactivity.

It is interesting to note that for lignite the reactivities follow the level of calcium loading. However, loadings above some value of the raw sample (0.09 mmol/g) have relatively little additional influence on reactivity. It should be noted that the biggest changes in reactivity occur at the lower calcium loadings.

Typical isothermal reactivity plots for a char (PSOC 833; Demineralized + 0.3 MCa; rapid pyrolysis at 1275 K, 0.3 s) are given in Figure 1. In this figure one can see that the reactivity profiles, as a function of burn-off, for this sample are very similar for the IR and TGA methods. The major discrepancy occurs at high levels of burn-off. In this case, the instantaneous reactivity appears to be increasing to about 10% burn-off, it then levels off to a relatively constant value up to 40% burn-off, and continues to increase to about 80% conversion. If one uses the gas analysis data to calculate the RSA then one obtains the plot shown in Figure 2. Using these RSA values, a TON as a function of burn-off (at 677 K) can be estimated (Figure 3). The variation of TON with conversion is quite small and appears to remain at a value of about 1.3×10^{-4} g/m² min. The only exceptions in this plot are at low levels of gasification (< 5%). We have found that application of this approach yields a relatively narrow range of values for TON for approximately 5 to 85% burn-off from all the chars and carbons studied (prepared at all degrees of pyrolysis severity). As an example, Figure 4 shows the values of TON for all the demineralized, heat treated coals used in this study (reactions for this suite of samples were made at temperatures between 658 to 721 K). It should be noted that TON's for the higher rank coal demineralized chars (anthracite and LV) have values of around 1.45×10^{-4} g/m² min, whereas the values for the equivalent chars from the lower rank coals (HVA, Subbit and Lignite) are somewhat lower ($\sim 1.3 \times 10^{-4}$ g/m² min), and appear to decrease slightly with burn-off. A brief summary of the preliminary data is given in Table 2. These results do show a remarkable degree of constancy for all these materials being gasified in air.

CONCLUSIONS

Nonisothermal reactivity measurements, in air, indicate the influence of the severity of time/temperature history on the subsequent reactivity of chars derived from a wide rank range. Instantaneous reactivities can be normalized by use of a reactive site concept. The calculated TON is quite constant for several chars (and carbons), over a wide degree of conversion and reaction temperature.

ACKNOWLEDGEMENTS

This research was sponsored by the Gas Research Institute, Chicago. Special thanks is given to Dr. Charles Nelson for his continued interest in these studies.

REFERENCES

1. N. R. Laine, F. J. Vastola and P. L. Walker, *J. Phys. Chem.*, **67**, 2030 (1963).
2. N. R. Laine, F. J. Vastola and P. L. Walker, 5th Carbon Conf., p. 211, Pergamon Press, Oxford (1963).
3. L. R. Radovic, P. L. Walker, Jr. and R. G. Jenkins, *Fuel*, **62**, 849 (1983).
4. L. R. Radovic, K. Steczko, P. L. Walker, Jr. and R. G. Jenkins, *Fuel Processing Technology*, **10**, 311 (1985).
5. M. R. Khan, ACS (Fuel Chemistry Div.) Preprints, **32**(1), 298 (1987).

TABLE 1

VALUES OF TEMPERATURE OF MAXIMUM WEIGHT LOSS (T_m) FOR NONISOTHERMAL REACTIVITIES IN AIR AT 5 K MIN⁻¹ FOR ALL COALS AND THEIR RAPID AND SLOWLY PYROLYZED CHARs

Sample	No Pyrolysis	T_m (K)		Rapid Pyrolysis 1215 K (0.3 s)
		Slow Pyrolysis 975 K (1 h)	1275 K (1 h)	
<u>Lignite</u>				
Raw	630	630	697	593
Demin	723	755	829	744
Demin + 0.01 Ca	639	660	760	624
Demin + 0.1 Ca	630	613	741	574
Demin + 0.5 Ca	613	622	743	568
Demin + 1.0 Ca	608	619	748	570
<u>Subbit</u>				
				1275 K (0.3 s)
Raw	648	--	809	--
Demin	701	750	809	709
Demin + 0.1 Ca	--	735	--	588
Demin + 0.5 Ca	--	720	--	541
<u>HVA</u>				
Raw	711	--	846	--
Demin	686	790	811	725
Demin + 0.1 Ca	--	701	--	709
<u>LV</u>				
Raw	735	--	846	--
Demin	704	765	818	730
Demin + 0.1 Ca	--	738	--	728
<u>Anth</u>				
Raw	800	--	853	--
Demin	809	823	851	794
Demin + 0.1 Ca	--	774	--	780

TABLE 2
EXAMPLES OF CALCULATED TON'S AT 50% BO

Sample	Reaction Temp. K	Ton x 10 ⁴ g/m ² .min
Saran Char	683	1.52
"	702	1.49
"	710	1.50
"	721	1.53
"	732	1.51
Lignite - Demin (1275, 1 h)	720	1.49
Lignite - Demin + 0.3 Ca (1275, 1 h)	677	1.30
Subbit - Demin (1275 K, 0.3 s)	654	1.38
HVA - Demin (1275, 0.3 s)	635	1.35
LV - Demin (1275, 0.3 s)	638	1.36
Anth. - Demin (1275, 0.3 s)	738	1.50

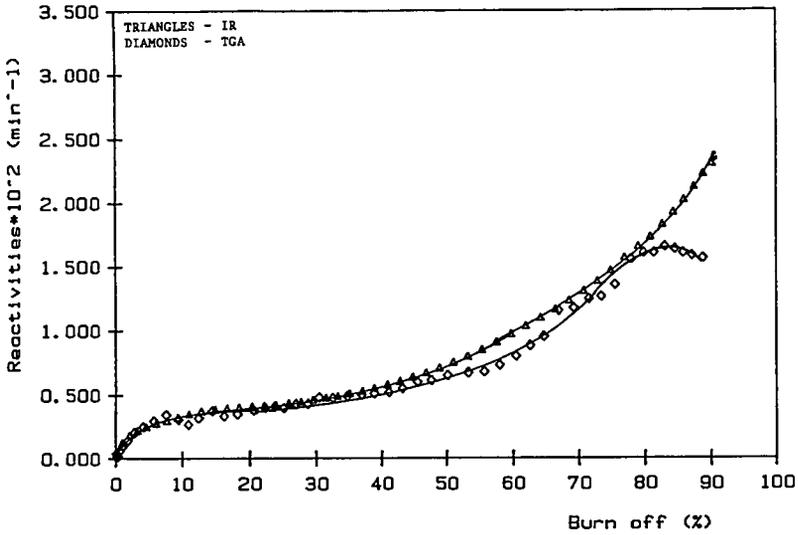


FIGURE 1. TGA and IR Reactivities at 677 K vs. Burn-off for PSOC 833 (DEN + 0.3 Ca) Heated to 1275 K (1 h)

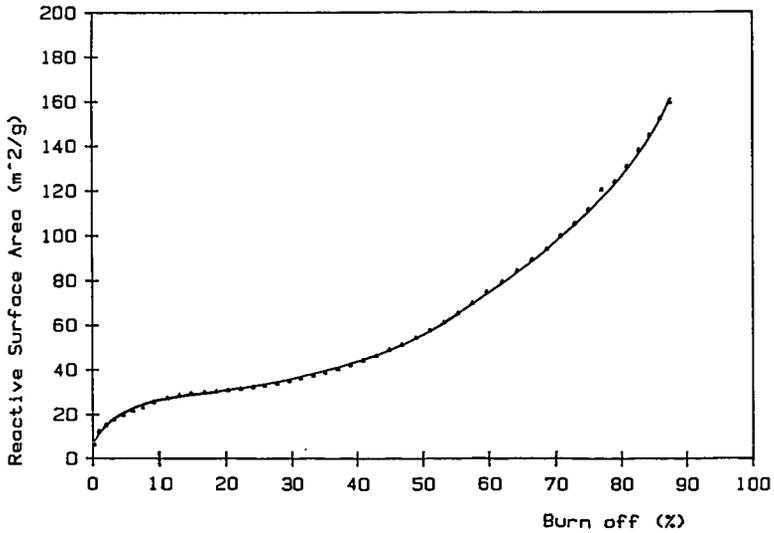


FIGURE 2. RSA vs Burn-off (677 K) for PSOC 833 (Dem + 0.3 Ca), 1275 (1 h)

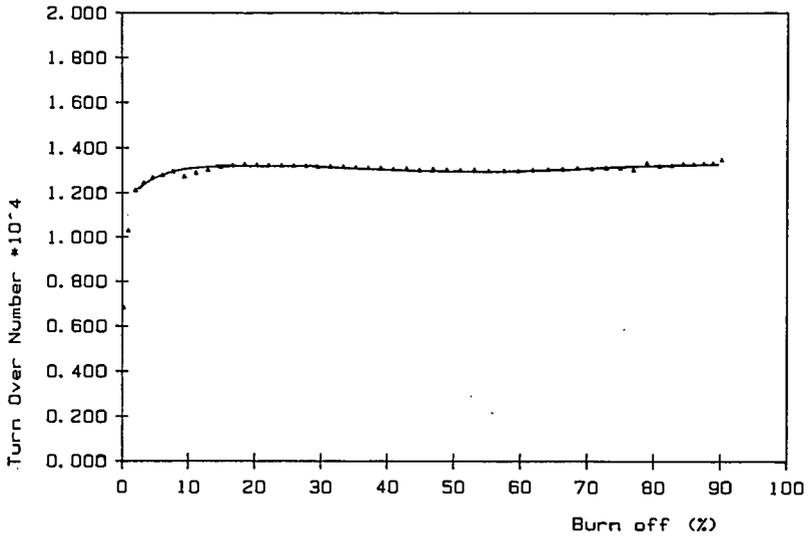


FIGURE 3. TON vs Burn-off (677 K) for PSOC 833 (Dem + 0.3 Ca), 1275 (1 h)

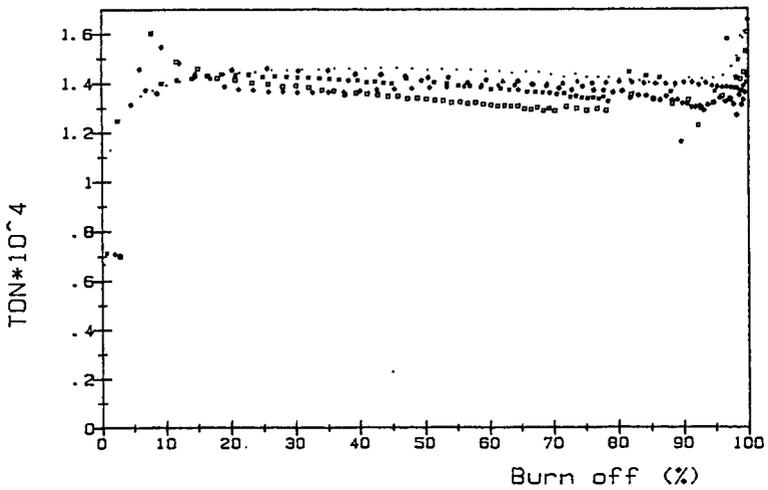


FIGURE 4. TON vs Burn-off for Demineralized Coal Chars (Rapidly Heated)