

OXYGEN CHEMISORPTION AS A TOOL FOR CHARACTERIZING "YOUNG" CHARS

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The introduction of the concept of active surface area (ASA) as measured by oxygen adsorption [N. R. Laine, F. J. Vastola, and P. L. Walker, Jr., J. Phys. Chem., **67**, 2030 (1963)] has led in recent years to various attempts to correlate char reactivity towards oxygen-containing gasification agents (e.g., CO₂). As may be seen from the literature, this approach has met with some, although not universal, success. Theories have been advanced which suggest that only a portion of active sites may participate in actual gasification reactions.

Hampering a fundamental understanding of what the role of active sites might be is lack of information on their nature. A wide variety of conditions has been suggested for measurement of ASA, generally involving temperatures in the range from 100°C to 350°C and oxygen pressures from fractions of a torr to atmospheric. Only in a few cases have these conditions been critically evaluated. In this paper, a series of experiments is reported upon, which seek to establish the importance of these conditions on determining the ASA of "young" chars (i.e., not heat treated for extended times).

1.0 Introduction

Gasification of carbonaceous solids has historically been and remains an area of significant scientific and technological interest (1-7). It has been well established that the reactivity of char to gasification generally depends upon three principal factors: (a) the concentration of "active sites" in the char; (b) mass transfer within the char; and (c) the type and concentration of catalytic impurities in the char. This paper is concerned with the nature of the active sites, and attempts to elucidate further what is normally being measured as active sites. It has been shown, or at least implied, by the results of various workers that active surface area (ASA) is a better predictor of char reactivity than is total surface area (TSA) (8-10). The most frequently employed technique for determining active sites in chars is oxygen chemisorption (8-16).

The gradual pyrolytic evolution of hydrocarbons (possibly including heteroatoms) to highly carbonaceous solids is accompanied by dramatic changes in the gasification reactivity of such materials. Here we are concerned with the gasification behavior of chars that have already undergone active pyrolysis in which most hydrocarbon gases and tars are evolved. The issues involved in transient high rate hydrogasification or steam reactivity during pyrolysis (e.g., 1, 17, 18) are not addressed here.

Active sites in relatively pure carbons are normally thought to be associated with various types of imperfections in the carbon structure. Work with graphite has suggested the important role of carbon crystallite edges or dislocations. The majority

of mechanistic theories of carbon gasification are based on the "pure-carbon-surface-imperfections" model. This is appropriate for chars that have been heat-treated at high temperatures for extended periods of time and thus have relatively low residual oxygen and hydrogen contents (i.e., "old" chars). Some caution must be exercised in applying results obtained from pure carbons to "young" chars. This point will be considered further below.

Carbon gasification theories are based largely upon chemisorption-desorption mechanisms (some also allow for surface diffusion of intermediates). There is some evidence to suggest that the same type of oxygen-carbon complexes are involved in oxygen, steam, and carbon dioxide gasification (2,19). A correlation has also been demonstrated between active sites involved in hydrogen gasification and those involved in carbon dioxide gasification, although there is no direct proof that the sites involved are indeed the same in both cases (1). There is, however, a legitimate concern that the concept of "active sites" may be too broad, and that active sites may in fact be quite different in "young" chars than in "old" chars. It is the issue of what exactly is being measured by oxygen chemisorption which will be addressed in this paper.

There exists a distinction between "active" sites that are reactive and those that are nonreactive at a given temperature. The reactive "active" sites are responsible for the release of surface carbon oxides, while the nonreactive "active" sites will chemisorb oxygen but will not release surface oxides at the temperature under consideration. Raising the temperature of the carbon converts some nonreactive to reactive "active" sites (5,8). This mechanism, combined with the expected Arrhenius-type enhancement of chemical reaction rates, results in increasing gasification rate with temperature.

The preceding effect, however, is not always observed, and thus other factors must also play a role. For example, it has been observed that the rate of carbon combustion normally increases with increasing temperature, up to about 1500K. In the 1500-2000K temperature range, however, it has often been noted that the rate of combustion actually decreases with increasing temperature (5, 20-23). One explanation for this behavior is known as "thermal annealing" (3,5, 24-26). This same effect has also been postulated as being responsible for a decrease in reactivity towards other gases as well (1, 27, 28). There is a trend towards lower reactivity with increased time and temperature of char heat treatment (1, 29-35). This behavior reflects a progressive and continuous ordering of the remaining carbon and is actually an extension of the pyrolysis process.

It would, therefore, seem logical to associate the temperature dependence of the annealing process in chars with the activation energies of the latter phases of pyrolysis; i.e., 100 to 200 kcal/mol typical for high temperature H₂ release (36) and graphitization (37), respectively. In fact, this range is consistent with the results of a few studies on pure, relatively graphitic carbons (21, 26). The values of annealing reaction activation energies derived from experiments with younger chars have been generally lower, however.

In the present study, we examine the chemisorption behavior of relatively young chars only, so in comparing this study to those on graphites or chars produced by prolonged heating at high temperature, caution must be exercised. In this study, the effects of temperature and oxygen pressure on chemisorption behavior are considered.

Experimental

Two different kinds of chars were examined in the course of this study. One was prepared from pyrolysis of a previously demineralized North Dakota lignite, the composition of which is shown in Table I. Demineralization was accomplished by washing the sample with HCl, followed by HF and again followed by HCl, according to the technique of Bishop and Ward (38). The residual mineral matter content of the lignite was determined to be approximately 0.8%. The other char which was examined was derived from a phenol-formaldehyde resin, carefully synthesized so as to avoid any cation contamination.

Table I

	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>Ash</u>	<u>O</u>
North Dakota Lignite ⁺	65.6	3.6	1.1	0.8	11.0	17.9
Phenolic Resin	73.9	5.5	0	0	0	20.6
Phenolic Resin Char*	87.2	1.6	0	0	0	11.2

All analyses on a weight percent, dry basis. Oxygen by difference.

⁺The analysis is for the as-received lignite, prior to demineralization.

*Pyrolysis as indicated in the text.

Both samples were pyrolyzed at similar conditions. Pyrolysis was performed under inert gas (helium). The resin samples were heated at a rate of 4 to 5°C/min to a maximum temperature of 950°C, held for about 2 hours at temperature, and then cooled to room temperature at a rate of 2 to 25°C/min. Samples were never permitted to contact oxygen while at high temperatures, except during the actual chemisorption experiments. The weight loss during pyrolysis was approximately 40%. The total surface area of chars produced this way was roughly 300m²/g. The lignite sample was heated at a rate of about 3°C/min to 1000°C, held at this temperature for 2 hours, and then cooled to room temperature at a rate comparable to the heating rate. The weight loss of the lignite during pyrolysis was 42.3%.

Prior to chemisorption, samples were always outgassed for about 2 hours at 950°C, under helium.

Generally, chemisorption was performed in a TGA type device. About 50-100 mg of powdered sample was placed in a quartz bucket, the system tared, and mass change followed as a function of time, at the desired oxygen partial pressure and temperature. Experiments were performed to assess the effects of oxygen pressure and temperature on oxygen chemisorption behavior.

Effect of Temperature on Oxygen Chemisorption Behavior

There exists a voluminous literature on low temperature oxidation of coals and a significant number of studies on low temperature oxidation of chars. Generally, the analysis of oxygen uptake in these systems has been analyzed in terms of the Elovich equation, expressed as

$$dq/dt = a \exp(-bq)$$

where q is the amount of oxygen chemisorbed per gram of char, and a and b are constants. Recent work on 550°C cellulose char has shown the data on oxygen uptake at temperatures between 74 and 207°C to be reasonably fit by this equation, and implies a linear increase in chemisorption activation energy from 13 to 25 kcal/mol with increasing extent of uptake (39). These data were interpreted, together with ESR data, to suggest that far more oxygen is chemisorbed than there are free radical sites initially available. A chain reaction via peroxy radicals was ruled out on the basis of the high activation energies. A Diels Alder reaction was postulated, but not vigorously supported. This is representative of the uncertainty concerning oxygen uptake mechanisms on chars. The mere fact that the Elovich equation fits data does little to establish mechanism; as has been pointed out, the Elovich equation may be consistent with several different types of sorption isotherms (5). Its validity in interpreting results from porous samples has been questioned as well (40).

It is against this background of uncertainty in mechanism that the data on the effect of temperature on chemisorption are analyzed. Generally, a fresh young char surface, when first exposed to oxygen, rapidly picks up oxygen and then continues to pick up oxygen at an ever decreasing rate for many hours subsequently (consistent with the form of the Elovich equation).

The effect of temperature on the amount of oxygen chemisorbed by a char has been studied to a limited extent previously. An Australian brown coal char pyrolyzed for more than 10 hours at 1000°C showed a trend of increasing oxygen capacity with increasing temperature of chemisorption between 25 and 200°C (41). Experiments with a higher rank coal char prepared at similar temperatures showed that oxygen capacity increased with temperature only up to about 100°C (16), while a 550°C cellulose char showed increasing oxygen uptake with increasing temperature up to at least 207°C (39). An activated graphon (highly graphitized carbon black) showed increasing chemisorption capacity with increasing temperature up to at least 550°C (13). The actual temperature dependence of saturation amounts of uptake was seen to be quite complex (12).

As a result of the uncertainty concerning the effect of temperature on chemisorption behavior, several tests were performed with the chars of interest in this study. In both series of experiments, chars with initially clean surfaces were subjected to "staircase" temperature profiles under an atmosphere of dry air. Figure 1 shows the results of these tests. In the case of the resin char, there is evidence for increased capacity with increasing temperature up to 300°C, at which temperature the mass begins to decrease due to decomposition of the surface oxides. In the case of the lignite char, the effect of temperature is much less pronounced and mass loss becomes evident at 250°C.

Thus, it must be concluded that the effect of temperature on chemisorption may vary widely from char to char, and there is a legitimate question as to what exactly is being measured at any arbitrary condition. Depending upon the situation, the maximum uptake may be an artifact due to competing processes of continued chemisorption and desorption of complexes. In the case of the resin char, the apparent activation energy for the high temperature decomposition process is 29 kcal/mol.

Effect of Oxygen Pressure on Chemisorption Behavior

The effect of oxygen pressure on chemisorption behavior has also been

studied to only a limited extent previously. It was found for 1000°C Australian brown coal char that both reversibly sorbed and chemisorbed oxygen increased in amount with increasing pressure of oxygen (from 161 torr to 760 torr) (41). On the other hand, a sample of higher rank coal char which had been pyrolyzed at 1000°C showed no variation in oxygen chemisorption capacity for pressures ranging from about 7.6 torr to 760 torr (16). In another study, a graphon sample displayed oxygen chemisorption capacity which was markedly pressure dependent in the pressure range 0.5 torr to 700 torr (13). The increase in oxygen chemisorption with oxygen pressure was also observed at high temperatures (615°C, 42).

In seeking to better characterize oxygen chemisorption as a diagnostic technique, a series of experiments was conducted in the present study at various partial pressures of oxygen. The results of these tests are shown in Figure 2. It is apparent that the partial pressure of oxygen has a marked influence on the rate of uptake of oxygen, and apparently, on the ultimate oxygen capacity of the sample.

Conclusions

The obvious conclusion that can be drawn from this work is that oxygen chemisorption can hardly be termed a site-specific analytical technique, at least when applied to typical young chars. The fact that apparent oxygen capacities are sensitive to temperature and pressure does not necessarily imply that oxygen chemisorption is not useful as a correlative tool; it has been shown that active site concentrations, as measured by chemisorption of oxygen, do correlate reasonably well with char reactivity in several cases (e.g., 8,9). Still, the solid evidence for the relationship between chemisorbed oxygen complexes and gasification have come mainly from a series of very careful studies on very "old" chars, oxidized at moderate temperatures (8,11-15).

This raises the question as to what value oxygen chemisorption techniques are in characterizing young chars. Clearly, as a characterization technique, chemisorption is difficult enough so as to make actual gasification reactivity tests look more attractive, if this is the information which is actually desired. At present, when applied to young chars, the oxygen chemisorption technique must derive its value from being a tool for studying the actual mechanism of gasification of these materials.

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References

- (1) Johnson, J. L., Kinetics of Coal Gasification, Chapter I, Wiley, 1979.
- (2) Laurendeau, N. M., Prog. Energy Combust. Sci., **4**, 221 (1978).
- (3) Von Fredersdorff, C. G., and Elliott, M. A., in Chemistry of Coal Utilization, Supplementary Volume, (H. H. Lowry, Ed.), Chapter 20, Wiley, 1963.
- (4) Walker, P. L., Jr., Rusinko, F., Jr., and Austin, L. G., in Advances in Catalysis, XI, 133 (1959).
- (5) Essenhigh, R. H., in Chemistry of Coal Utilization Second Supplementary Volume, (M. Elliott, Ed.), Chapter 19, Wiley, 1981.

- (6) Field, M. A., Gill, D. W., Morgan, B. B., and Hawksley, P. G. W., Combustion of Pulverized Coal, BCURA, Leatherhead, England (1967).
- (7) Mulcahy, M. F. R., and Smith, I. W., Rev. Pure Appl. Chem., **19**, 81 (1969).
- (8) Laine, N. R., Vastola, F. J., and Walker, P. L., Jr., J. Phys. Chem., **67**, 2030 (1963).
- (9) Radovic, L. R., Walker, P. L., Jr., and Jenkins, R. G., Fuel, **62**, 849 (1983).
- (10) Tong, S. B., Pareja, P., and Back, M. H., Carbon, **20**, 191 (1982).
- (11) Vastola, F. J., Hart, P. J., and Walker, P. L., Jr., Carbon, **2**, 65 (1964).
- (12) Hart, P. J., Vastola, F. J., and Walker, P. L., Jr., Carbon, **5**, 363 (1967).
- (13) Lussow, R. O., Vastola, F. J., and Walker, P. L., Jr., Carbon, **5**, 591 (1967).
- (14) Bansal, P. C., Vastola, F. J., and Walker, P. L., Jr., J. Coll. and Int. Sci., **32**, 187 (1970).
- (15) Phillips, R., Vastola, F. J., and Walker, P. L., Jr., Carbon, **8**, 197 (1970).
- (16) Canston, P.I, and McEnaney, B., Fuel, **64**, 1447 (1985).
- (17) Suuberg, E. M., Peters, W. A., and Howard, J. B., Fuel, **59**, 405 (1980).
- (18) Graff, R., and LaCava, A., U.S.D.O.E. Report FE-2340-9, 1978.
- (19) Ergun, S., and Mentser, M., in Chemistry and Physics of Carbon, **1**, (P. L. Walker, Jr., Ed.), Chap. 4, Dekker, 1965.
- (20) Eucken, A., Z. Angew. Chem., **43**, 986 (1930).
- (21) Strickland-Constable, R. T., Trans. Faraday Soc., **40**, 333 (1944), also Nagle, J., and Strickland-Constable, R. T., Proc. 5th Conf. on Carbon, Vol. p. 154, Pergamon (1962).
- (22) Meyer, L., Z. Phys. Chem., **17(B)**, 385 (1932).
- (23) Duval, X., J. Chim. Phys., **47**, 339 (1950) and **58**, 3 (1961).
- (24) Duval, X., Ann. Chim. (Paris), **10**, 903 (1955).
- (25) Spokes, G. N., and Benson, S. W., Fundamentals of Gas-Surface Reactions, p. 318, Academic Press, (1969).
- (26) Blyholder, G., Binford, J. S., Jr., and Eyring, H., J. Phys. Chem., **62**, 263 (1958).
- (27) Moseley, F., and Patterson, D., J. Inst. of Fuel, **38**, 378 (1965), also **40**, 523 (1967).
- (28) Zahradnik, R. L., and Glenn, R. A., Fuel, **50**, 77 (1971).
- (29) Walker, P. L., Jr., in Scientific Problems of Coal Utilization, (B. R. Cooper, Ed.), p. 237, U.S.D.O.E., 1978.
- (30) Jenkins, R. G., Nandi, S. P., and Walker, P. L., Jr., Fuel, **52**, 288 (1973).
- (31) Hippo, E., and Walker, P. L., Jr., Fuel, **54**, 245 (1975).
- (32) Blackwood, J. D., and McTaggart, F. K., Aust. J. Chem., **12**, 533 (1959).
- (33) Blackwood, J. D., Cullis, B. D., and McCarthy, D. J., Aust. J. Chem., **20**, 1561 (1967).
- (34) Gray, J. A., Donatelli, D. J., and Yavorsky, P. M., ACS Div. Fuel Chem. Prep., **20** (4), 103 (1975).
- (35) Blake, J. H., Bopp, G. R., Jones, J. F., Miller, M. G., and Tanbo, W., Fuel, **46**, 115 (1967).
- (36) Chermin, H. A. G., and Van Krevelen, D. W., Fuel, **36**, 85 (1957).
- (37) Fischbach, D. B., in Chemistry and Physics of Carbon, **2**, (P. L. Walker, Jr., Ed.), p. 1, 1971.
- (38) Bishop, M., and Ward, D. L., Fuel, **37**, 191 (1958).
- (39) Bradbury, A., and Shafizadeh, F., Carbon, **18**, 109 (1980).
- (40) Harris, J., and Evans, D., Fuel, **54**, 276 (1975).
- (41) Allardice, D., Carbon, **4**, 255 (1966).
- (42) Phillips, R., Vastola, F., and Walker, P., Carbon, **7**, 479 (1969).

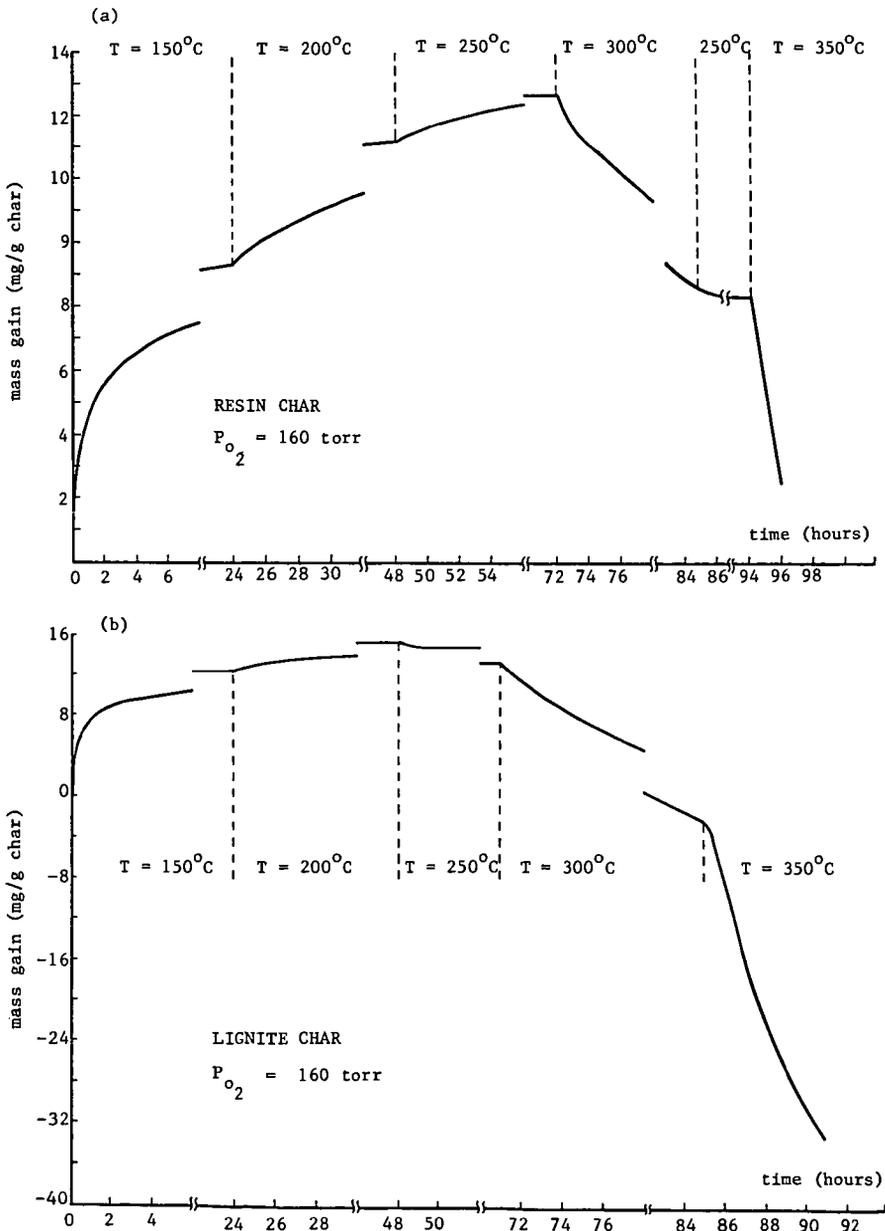


Figure 1. Effect of Temperature Changes on Oxygen Chemisorption Behavior
 (a) Resin Char (b) Lignite Char

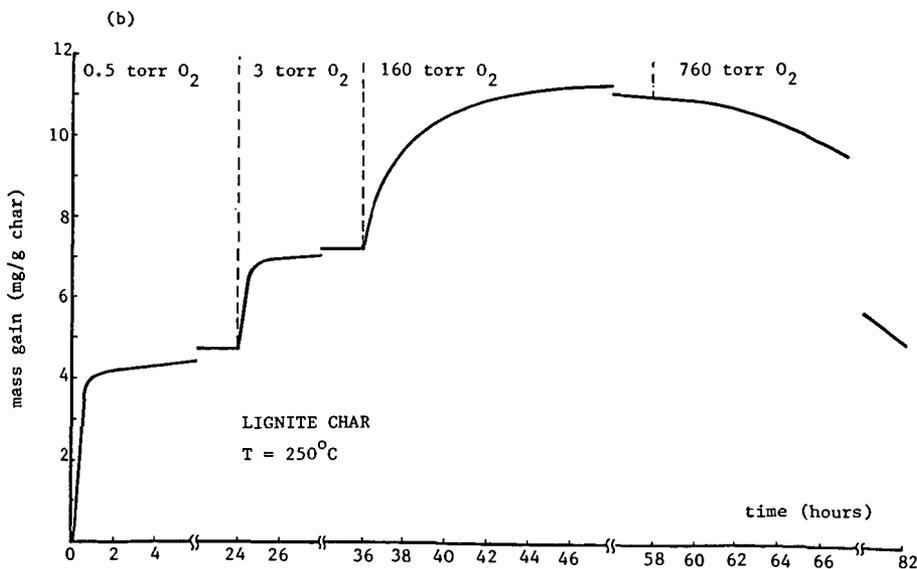
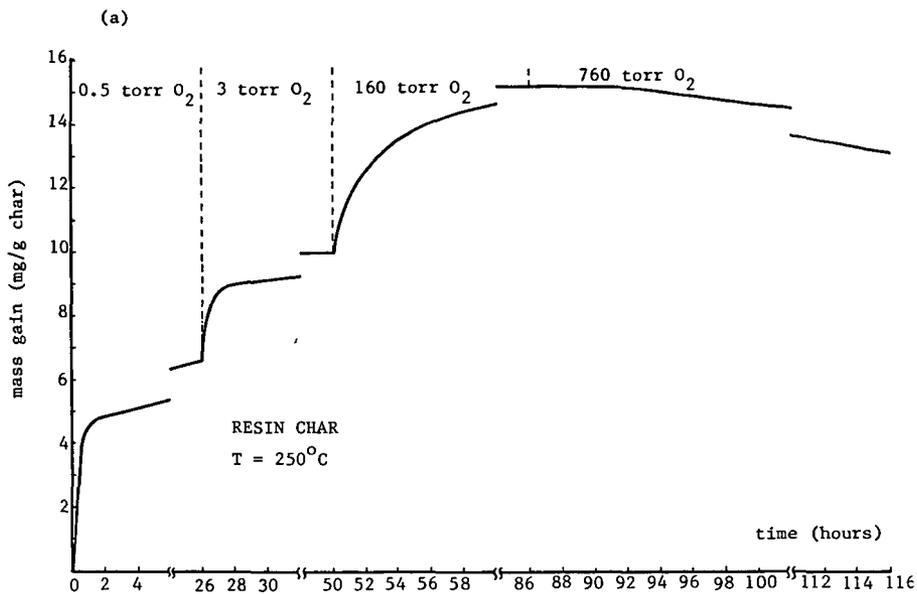


Figure 2. Effect of Oxygen Partial Pressure Changes on Oxygen Chemisorption Behavior

(a) Resin Char (b) Lignite Char