Energy

F
O
S
S
I
L

215-8475 (1)
6-26

DR-0159.7

DOE/PC/60800-T1
(DE84008908)

ACTIVE SITES IN CHAR GASIFICATION

First Quarterly Progress Report for September—December 1983

By
E. M. Suuberg
J. M. Calo
M. Wojtowicz
W. Lilly

Work Performed Under Contract No. FG22-83PC60800

Brown University
Providence, Rhode Island

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Active Sites in Char Gasification
(DOE Grant DE-FG22-83PC60800)

First Quarterly Progress Report
Period: September, 1983 - December, 1983

Submitted to: The U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940

Attn: Mr. Jack Walters

Submitted by: Brown University
Division of Engineering
Providence, R. I. 02912

Prepared by: E. M. Suuberg and J. M. Calo (Co PI's)
M. Wojtowicz and W. Lilly

Abstract

This report reviews the background and motivation for this work, and discusses some initial scoping studies on chars similar to the model compounds to be used in later phases of the work. Some preliminary synthetic methodologies for model compounds are presented.

1.0 INTRODUCTION

Gasification of carbonaceous solids has historically been and remains an area of significant scientific and technological interest (1-7). This project focuses on furthering the understanding of gasification reactivities of chars. 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. The present study primarily addresses the first factor.

1.1 The Nature of Active Sites.

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., 1,8,9) 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-with-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.

Carbon gasification theories are based largely upon chemisorption-desorption mechanisms (some also allow for surface diffusion of intermediates). The same type of oxygen-carbon complexes appear to be involved in oxygen, steam, and carbon dioxide gasification (2,10). 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 have been numerous attempts to measure active site concentrations in carbons and chars. In one such study (11), the total active surface area (ASA) was estimated by exposure of a char surface to oxygen at low temperatures (ca. 573K). Under these conditions, surface carbon oxides are not released, so all the absorbed oxygen was assumed to be chemisorbed on active sites. Heating the char to 1223K released the adsorbed oxygen, and the ASA was calculated assuming each oxygen released had been chemisorbed on an edge-type carbon atom of $8.3 \text{ \AA}^2$. In this manner, it was determined that the ratio of ASA to total surface area increased by about an order of magnitude during oxidation of a graphitized char. Another study suggested that the variation in this ratio was actually rather small during combustion of many heat-treated chars (12). Other work involving steam gasification of various chars pointed out that the preceding ratio might vary by an order of magnitude among different materials (13). This point is addressed further below.

1.2. Effect of Temperature on Active Site Concentration. 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 (5,11). 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 (5,14-17). One explanation for this behavior is known as "thermal annealing" (3,5,18-20). This same effect has also been postulated as being responsible for a decrease in reactivity towards other gases as well (1,21,22). There is a trend towards lower reactivity with increased time and temperature of char heat treatment (1,23-29). 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 (30) and graphitization (31), respectively. In fact, this range is consistent with the results of a few studies on pure, relatively graphitic carbons (15,20). The values of annealing reaction

activation energies derived from experiments with younger chars have been generally lower, however; in the case of annealing of chars with respect to gasification by hydrogen, activation energies have been reported in the range of 9-20 Kcal/mol (1,32,33). The same range has been observed for annealing with respect to oxidation reactions, but the activation energies for annealing of a given char with respect to oxygen attack are not always the same as for annealing with respect to hydrogen (33). Such low values of the activation energy for annealing may be an artifact of the model used to describe the annealing process. In almost all of the cases cited, annealing was treated as a simple single, first order chemical process (thus described by a single activation energy). More realistically, however, annealing in "young" chars involves a wide spectrum of pyrolytic reactions, ranging from those involving gas evolution to those responsible for graphitization. It is well known that modeling a set of independent, parallel chemical reactions by a single first order rate model can give rise to a pseudo-activation energy lower than any of the "true" activation energies in the set of reactions (e.g., see 34). Of course, there is no direct proof that this was the case in the studies cited. The issue is further complicated by the fact that in the case of chars derived from natural products, the annealing process may also be accompanied by changes in the form of catalytic impurities (33).

The accurate prediction of thermal annealing rates depends upon having a proper model of the processes involved. While a single first order reaction model may be quite adequate for predictive purposes within a narrow range of heating rates, it may perform quite unsatisfactorily when applied to situations in which heating rates are quite different. Recently, there has been increased interest in the reactivity of chars

produced at high heating rates. These studies have shown that as heating rate is increased, char reactivity increases (23,35), possibly by the promotion of more chaotic crystallite growth.

The annealing reactions can affect the activation energy of gasification reactions (36). When corrected for mass transfer effects, the activation energy for oxidation reactions seems to decrease with increasing char pretreatment temperature (5), thereby suggesting a shift in the stability of the remaining active sites.

1.3. The Relationship Between Precursor Material and Active Sites

There exists unequivocal evidence that the nature of the parent hydrocarbon material has a major influence on both the concentration and the nature of active sites for gasification. The differences are greatest during the early phases of pyrolysis, thereafter decreasing as the carbon increases in purity as a result of heat treatment. In the case of coals, there is a marked trend towards decreased hydrogasification activity with increasing rank (1) (a similar trend has been reported in another study, but with more scatter; 37). This effect is at least partially attributable to the variation of available surface area with rank, although also to differences in inherent reactivity of the carbons. The rates of steam, carbon dioxide, and oxygen gasification are likewise known to depend to some extent upon the parent material of the char (1, 13, 23-25, 38). It is important to account separately for variations in total surface area, catalytic effects due to impurities, and the chemical nature of precursor material (e.g., see review 39).

The ratio of active to total surface area has been previously noted to be a function of the type of char (13). This ratio may vary from a few percent (11) to near unity for thin layers of pyrolytic carbon (40).

It has been established that during low temperature oxidation of coal, the non-aromatic sites are attacked preferentially (41). Exactly how long, during the course of pyrolysis, these originally non-aromatic sites retain their identity as active sites, has not been established. In the case of graphites, it is well known that the formation of etch pits reflects a preferential attack on edge atoms (e.g., see review 42). The carbon atoms on the edges of the large parallel layers in graphite are considerably more reactive with respect to oxidation than those in the middle of the basal plane (at temperatures of 1000K and above; 43). Non-graphitic carbons are generally comprised of a mixture of crystallographically-ordered aromatic regions and disordered carbon. It has been observed that during oxidation of carbon blacks and partially graphitized carbons, the disordered regions are the most reactive (review 44).

Thus, it is clear that differences exist in the reactivity of different physical regions in the char. The question of whether or not these differences correlate with particular chemical features of the char precursor has not been thoroughly explored. Among the few examples are suggestions of correlations between char reactivity and organic oxygen content (45,46). The amount and chemical nature of oxygen in the char is unquestionably related to the structure of the parent materials. The problem of understanding and predicting char reactivity is thus closely related to the study of the formation of carbons by pyrolysis (e.g., review 47; the role of mesophase, 48; graphitization, 31, 49; ESR studies, 50; general physical properties of non-crystalline carbons, 51). The work being carried out here focuses on the role of precursor material on subsequent gasification reactivity by using phenol-formaldehyde resins and

related polymers as model compounds.

1.4. Changes in the Nature and Concentration of Active Sites With Gasification.

In only a relatively few cases is it known exactly how the nature of active sites changes with extent of gasification. It has been observed that graphites oxidize or gasify primarily via edge atom attack. For carbons containing both ordered and disordered regions, the disordered regions usually burn off first (44). The same conclusion may be inferred from data on oxidation of pyrolyzed phenol-formaldehyde resins (52). The reported crystallite dimensions of the chars (an indicator of the average size of the ordered regions) was not observed to change even up to 40% burn-off. This implies that the reaction occurred primarily in the disordered regions. This same study (52) also sheds some light on the annealing process. As expected, char reactivity was observed to decrease with increasing preparation temperature. The fact that this decrease was not accompanied by large changes in either the size of the ordered regions or the total surface area suggests that annealing probably involves processes in the disordered regions (perhaps a "shifting" of carbon from disordered to ordered regions, with a preferential average crystallite size). Unfortunately, the fraction of carbon in disordered versus ordered regions was not reported.

Direct measurements of the ratio of active to total surface area have been performed as a function of extent of gasification or burn-off (11,53). In both these cases, the ratio appears to increase with increasing extent of gasification. In the case of highly graphitized chars, this behavior can be explained in terms of an increase in the fraction of edge atoms with burn-off, or alternatively, by the "co-operative effect" (i.e., edge atoms

becoming more reactive with increasing depth of the etch pit; 54, 55). In chars with small crystallite regions and much disordered structure, the decrease in reactivity with loss of disordered carbon might be compensated for by changes promoting greater reactivity in the remaining carbon.

1.5. Summary and Scope of Present Work

Thus it may be concluded that two main factors influence the concentration and nature of (non catalytic) active sites: the structure of the parent hydrocarbon, and the time-temperature history of the precursor material and the char. This study focuses on both of these factors and their interrelationships.

2.0 Work This Quarter

2.1. General Background on Model Polymers

The chars proposed for study will be produced by pyrolysis of polymers of the phenol-formaldehyde family. These polymers share the general structure:

where Ar denotes an aromatic unit of arbitrary size, X represents a substituent on an aromatic ring (e.g., -OH, -H, -CH₃), and CH₂ is a methylene bridge. Our specific interest in coal gasification led to this choice since coal in general is known to incorporate similar structural features.

The pyrolysis of phenol-formaldehyde resins (where Ar=benzyl and X=OH) has been extensively studied (reviews 56 and 57; work with labeled resins, 58; crosslinking effects, 52,63,64). The chars produced upon pyrolysis of

these materials are normally glassy carbons of relatively low surface area (ca. $1 \text{ m}^2/\text{g}$), that readily develop high surface areas at very low burnoffs (e.g., $854 \text{ m}^2/\text{g}$ at 10% burnoff; 52). Isotope studies have revealed that both ring and methylene carbons survive in the char upon pyrolysis. Under a variety of preparation conditions the chars are always observed to contain crystallites on the order of $25\text{-}30 \text{ \AA}$ (i.e., L_a). Considerably less work has been performed with polymers in which $X=\text{H}$, or in which Ar is larger than a single benzene ring. Nevertheless, pyrolysis mechanisms have been proposed for polybenzyl (Ar = benzyl, $X = \text{H}$; 56,65). Some general characteristics of pyrolysis of analogous materials with larger Ar groups have also been reported (64).

The materials to be used in this study will be synthesized in our laboratory. Well known techniques (58,64,65) will allow the labeling of key carbon groups with C^{13} (e.g., methylene C^{13} bridges with C^{12} rings). These synthesis techniques are reported to be reliably specific (e.g., 58,64). The fraction of labeled carbon present will be verified by total combustion in the TGA apparatus and subsequent mass spectrometric analysis of the resultant product gases.

Once synthesized, the model compounds will be pyrolyzed at variable heating rates (on the order of 1000K/s to 100K/min or less). Two separate experimental systems will be used for this purpose: low heating rate runs will be carried out in a conventional ceramic tube furnace with a maximum temperature of about 2000K ; while the high heating rate runs will be performed in-situ in the same quartz gradientless pyro-gasifier reactor in which the transient kinetic studies will be conducted. Of course, the effects of the important parameters such as heating rate, heat treatment time, and peak temperature will be systematically examined.

A conscious effort will be made throughout the sample synthesis and preparation work to minimize impurity levels. Since absolutely impurity-free chars are impossible to achieve, spot checks will be conducted using existing analytical capability in our laboratories (e.g., standard ashing and atomic absorption) to identify typical impurities and their concentrations. Where impurity levels are determined to be a problem, standard acid washing techniques will be employed.

The resultant sample chars will be characterized with respect to elemental composition (in a Perkin-Elmer 240 elemental analyzer), total surface area by CO₂ adsorption, active surface area by oxygen chemisorption (11) in a TGA apparatus connected to a mass spectrometer, and for crystallographic parameters by X-ray diffractometry (47).

A few suitable X-ray machines are available in the Division of Engineering. For the present studies we plan to use an instrument available in the Materials Science group of the Division of Engineering. Of particular interest are measurements of the resultant crystallite dimensions of the chars at various degrees of pyrolysis and gasification, as well as interlayer spacings, and the fraction of carbon in disordered versus ordered regions.

2.2 Actual Preparation of Polymers

Two methods have been found to work well in preparing samples of phenol-formaldehyde resin and its non-hydroxylated analogs for char studies. Various curing regimens have been tried and the resultant resins were analyzed with a Perkin-Elmer model 240B elemental analyzer. Initial attempts to analyze thin films of the cured resins with a Perkin-Elmer

model 735B infrared spectrometer were unsuccessful due to difficulty in controlling film thickness and the brittle nature of the cured resins. Now, however, the resins are analyzed by coating onto silver chloride windows.

Preparation of phenol-formaldehyde resins was conducted using the method described by Bossert and Brode to obtain phenol/formaldehyde and naphthol/formaldehyde resins. This method, the curing regimens, and the resultant analyses are outlined below.

Starting materials:

3.00 g phenol (0.032 mole)

10. ml formaldehyde 40% soln (0.135 mole)

1.5 ml conc ammonium hydroxide soln (catalyst)

Procedure:

The starting materials were mixed in an 18 x 150 mm test tube which was then fitted to a 0.6 x 100 cm glass reflux tube in a cork stopper. The test tube was immersed into a 100°C water bath and the mixture refluxed until a milky, yellowish appearance was present in the mixture for five minutes. The solution was then removed from the water bath and treated with 5 drops of glacial acetic acid to neutralize the base catalyst. After cooling the mixture in an ice bath to increase the viscosity of the product, the aqueous layer was decanted. The remaining product was reheated in the water bath and transferred to an aluminum weighing pan for curing.

Curing regimens and analyses:

At 85°C for 16 hours in air at 1 atm

<u>ELEMENT</u>	<u>COMPOSITION (%)</u>
carbon	75.4
hydrogen	6.3
nitrogen	4.6
other (mainly oxygen)	13.7

At 85°C for 16 hours in air at 1 atm

At 100°C for 64 hours in air at 1 atm

At 210°C for 2 hours in air at 1 atm

<u>ELEMENT</u>	<u>COMPOSITION (%)</u>
carbon	75.7
hydrogen	5.8
nitrogen	4.7
other (mainly oxygen)	13.7

The unacceptably high nitrogen levels have led to efforts to scale back the amount of catalyst required. These methods will be finalized during the next quarter. Infrared spectra will also be extensively used to ascertain that all oxygen is in the appropriate phenolic position, and that there are no carbonyl or alcoholic oxygens present in the sample (nor any free phenol).

The preparation of a naphthol-formaldehyde resin (in which Ar is a naphthalene ring) has also been attempted and seems promising. The methods used are outlined below.

Starting materials:

- 2.00 g β -naphthol (0.014 mole)
- 10. ml formaldehyde 40% soln (0.135 mole)
- 1.5 ml conc ammonium hydroxide soln (catalyst)

The above procedure was used to prepare these samples. The reddish brown product begins precipitating at room temperature shortly after the mixture is combined. The reaction goes very smoothly at 100°C and the product is much more viscous than its phenolic counterpart.

Curing regimens and analyses:

At 100°C for 64 hours in air at 1 atm

<u>ELEMENT</u>	<u>COMPOSITION (%)</u>
carbon	83.0
hydrogen	5.6
nitrogen	2.7
other (mainly oxygen)	8.6

At 100°C for 64 hours in air at 1 atm

At 210°C for 2 hours in air at 1 atm

Product was highly oxidized (burnt); no analysis performed

This material requires further testing to determine its nature before it is considered an acceptable model compound.

Finally, a phenanthrene-formaldehyde resin (containing no hydroxyl groups) was prepared by a method described by Lazarov and Angelova⁽⁶⁹⁾.

The details are as follows:

Starting materials:

- 4.00 g phenanthrene (.022 mole)
- 0.92 g p-formaldehyde (0.29 mole)
- 0.89 g zinc chloride dissolved in 7.75 ml gl. acetic acid (catalyst)

Procedure:

The starting materials were mixed and refluxed at 100°C, as described above, until a constant greenish-yellow appearance was present for 30 minutes. The reaction mixture was then removed from the water bath, cooled to room temperature, transferred to a glass separatory funnel, and extracted three times with 50 ml aliquots of distilled water to remove the catalyst. The remaining product-bearing solution was transferred to an aluminum weighing pan and the solvent was evaporated at 110°C under vacuum at 29 inches Hg.

Curing regimen and analysis:

At 185°C for 16 hours under vacuum at 30 inches Hg

<u>ELEMENT</u>	<u>COMPOSITION (%)</u>
CARBON	94.7
HYDROGEN	5.3
nitrogen	trace
other (mainly oxygen)	0.0

With this type of resin, which requires preparation with zinc chloride as a catalyst, it will be particularly important to determine how much potentially catalytic metal is left in the resin.

Some refinements of all of the methods described are currently under investigation. Refluxing the reaction mixtures under nitrogen and reducing the amount of ammonium hydroxide catalyst appear to reduce the concentrations of nitrogen and other contaminants (largely oxygen) in uncured samples. The vacuum oven was not available at the time the initial samples of phenolic and naphtholic resins were prepared, hence their curing was performed in air. Future curing of these resins will be performed

under vacuum (preflushed with nitrogen) to minimize oxidation. Analysis of the aqueous layer by gas chromatograph to determine the amounts of unreacted starting materials is planned. A pellet press has been purchased to facilitate the manufacture of KBr pellets to be used in future infrared characterizations of the resins. Atomic absorption analyses of the resins are also planned.

2.3. Preliminary Study of the Surface Area Change in Oxidation of Char

Derived from Bakelite

In an effort to quickly develop the techniques of sample pyrolysis and characterization to be used with the actual model substances, some preliminary work was performed with Bakelite samples (commercial phenol-formaldehyde resin). An analysis of a typical commercial material is shown below.

<u>ELEMENT</u>	<u>COMPOSITION (wt%)</u>
carbon	64.2
hydrogen	5.6
nitrogen	3.5
other (mainly oxygen)	19.3
ash	7.4

Clearly, these materials contain high levels of nitrogen contaminants and inert fillers, and are thus of little interest in a quantitative sense. Nevertheless, their gross behavior should mimic that of the more carefully prepared model substances. Consequently, they were used to explore various facets of the pyrolysis characterization work.

Samples of commercial Bakelite were crushed to a size of -2 mm and pyrolyzed in a boat inserted into a tube furnace heated from room

temperature to 700°C in a period of two hours. The furnace was purged with nitrogen throughout. Upon reaching 700°C, the furnace heating system was switched off, but the nitrogen purge maintained until the system again reached room temperature.

Samples of char were analyzed for surface area using a commercial (Quantasorb) gas absorption system. Nitrogen was used as the adsorbate in this work, and relative pressures of 0.1, 0.2 and 0.3 were studied. All samples were outgassed at 200°C for 1 hour prior to examination. The surface area of the char was calculated from these data by use of the B.E.T. equation (see appendix I).

Following the initial surface area determination, samples were oxidized in-situ (in the Quantasorb sample cell) at a temperature of 300°C. The oxidizing medium was air, which was passed continuously through a sample bed of char (typically 0.8g of char were contained in the cell). The degree of oxidation (burnoff) was determined by periodically switching from air to nitrogen as the purge gas, cooling the cell, and weighing the contents. Then the surface area was redetermined as outlined, and the cycle repeated.

It is known the phenolic resins give glassy chars upon pyrolysis, and that the surface area is a strong function of heat treatment temperature (52). In that study, it was noted that the lower the temperature of pyrolysis, the greater the change of surface area with burnoff; above 1400°C pyrolysis temperatures, no major effect of burnoff on surface area was noted. For pyrolysis temperatures of 1000°C, it was noted that the surface area was approximately linear in burnoff. In the present study, this low temperature pyrolysis behavior was examined more thoroughly, through the experiments described above.

Figure 1 shows that the surface area is indeed proportional to burnoff, for samples pyrolyzed at 700°C. Furthermore, the extent of burnoff with time (Fig. 2) is linear at low burnoffs, in contrast to the results reported in the literature (52). This seems to imply that the ratio of active sites to total surface area is unchanged by low extents of burnoff. This issue will of course be much more extensively studied in the future.

3.0 Plans for the Upcoming Quarter

The previously described improvements in resin procedures will be used to produce lower residual nitrogen resins. Curing will be carried out in vacuua, will be taken of the resins to assure their purity. The degree of crosslinking of the resins will be determined by standard solvent swelling techniques.

Upon obtaining a satisfactory phenolformaldehyde resin, the pyrolysis and active site determination phases of the project will begin. The thermogravimetric analyzer (TGA) is presently being modified to permit mass spectrometric sampling of the desorbed carbon oxide species, in order to permit the measurement of carbon isotope ratios.

Concurrently with the above activities, work is continuing on the preparation of a non-oxygen-containing resin. The intent is to determine what role oxygen substituents play in the formation of active sites during pyrolysis.

4.0 Financial Status of the Project

The project is on the proposed expenditure schedule, except for capital expenditures. Major items of capital equipment which have been

Figure 1. Surface area change with oxidation level for char heat-treated at 700°C.

Figure 2. Oxidation of char heat-treated at 700°C.

acquired during this quarter include:

1. The Cahn Model 113 Absorption Balance
2. The Quantasorb Surface Area Analyzer
3. The Secondary Electron Multiplier for the Mass Spectrometer

It was felt necessary that the Quantasorb device be purchased now, rather than in year 2, inasmuch as many of the active surface area results would be much more easily interpreted given a knowledge of the total surface area (as provided by the Quantasorb). The effect of purchasing this instrument earlier than budgeted is to cause a deficit in year one, which will be offset in year 2, at no net change in the total for the program.

Appendix I - B.E.T. Surface Area Determination

Measurements of surface area were based on the Brunauer-Emmett-Teller (B.E.T.) equation:

$$\frac{1}{X(P_0/P-1)} = \frac{C-1}{X_M C} \left(\frac{P}{P_0} \right) + \frac{1}{X_M C}$$

where:

X = the mass of adsorbate at relative pressure P/P₀.

P = the partial pressure of adsorbate

P₀ = saturation vapor pressure of the adsorbate

X_m = the mass of adsorbate at a coverage of one monolayer

C = a constant, related to the heats of condensation and adsorption of the adsorbate.

This equation contains two unknowns, X_m and C, requiring at least two points (X) to be determined at different values of (P/P₀). The mass of

adsorbate is actually not directly determined in the present technique, but rather, is calculated from:

$$X = (A/A_C) \cdot V_C \cdot (P_A M / RT) \quad (2)$$

where:

V_C = a known volume of calibration gas (the adsorbate)

A_C = the signal given by introduction of V_C into the measurement system

A = the signal given by complete desorption of the adsorbate at a particular P/P_0

= ambient pressure

M = molecular weight of adsorbate

T = temperature (K)

R = gas constant

Plotting $1/X (P_0/P-1)$ vs. P/P_0 yields a straight line of slope $(C-1)/X_M C$, and intercept $1/XC$. From these two quantities, X_M is easily determined, and the total surface area(s) of the sample is given by:

$$S = X_M N A_{CS} / M \quad (3)$$

where

N = Avogadro's number ($=6.023 \times 10^{23}$).

A_{CS} = the cross sectional area of an adsorbate molecule ($16.2 \times 10^{-20} \text{ m}^2$ for nitrogen).

Here, the usual convention of reporting surface areas on a specific

basis is followed, which involves dividing the value of S by the number of grams of sample.

It has been noted that (1) is normally only followed in the range of P/P_0 from 0.05 to 0.35. Significant variations in linearity invalidate the approach. For the Bakelite samples studied, reasonably linear behavior has been observed in this range.

References

- (1) Johnson, J. L., Kinetics of Coal Gasification, Chapter 1, 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) Suuberg, E. M., Peters, W. A., and Howard, J. B., Fuel, 59, 405 (1980).
- (9) Graff, R. and LaCava, A., U. S. D. O. E. Report FE-2340-9, 1978.
- (10) Ergun, S. and Mentser, M. in Chemistry and Physics of Carbon, 1, (P. L. Walker, Jr., Ed.), Chap. 4, Dekker, 1965.
- (11) Laine, N. R., Vasola, F. J. and Walker, P. L., Jr., J. Phys. Chem. 67, 2030 (1963).
- (12) Tyler, R. J. and Smith, I. W., Fuel, 54, 99 (1975).
- (13) Otto, K. and Shelef, M., "Catalytic Steam Gasification of Carbons", Paper B47, Sixth Int. Congress on Catalysis, London (July, 1976).
- (14) Eucken, A., Z. Angew. Chem., 43, 986 (1930).

- (15) Strickland-Constable, R. T., Trans. Faraday Soc., 40, 333 (1944),
also Nagle, J. and Strickland-Constable, R. T., Proc. 5th Conf.
on Carbon, p.154, Pergamon (1962).
- (16) Meyer, L., Z. Phys. Chem., 17(B), 385 (1932).
- (17) Duval, X., J. Chim Phys., 47, 339 (1950) and 58, 3 (1961).
- (18) Duval, X., Ann. Chim. (Paris), 10, 903 (1955).
- (19) Spokes, G. N. and Benson, S. W., Fundamentals of Gas-Surface
Reactions, p.318, Academic Press, (1969).
- (20) Blyholder, G., Binford, J. S., Jr. and Eyring, H., J. Phys. Chem.,
62, 263 (1958).
- (21) Moseley, F. and Patterson, D., J. Inst. of Fuel, 38, 378 (1965) also
40, 523 (1967).
- (22) Zahradnik, R. L. and Glenn R. A., Fuel, 50, 77 (1971).
- (23) Walker, P. L. Jr. in Scientific Problems of Coal Utilization,
(B. R. Cooper, Ed.), p.237 U. S. D.O.E., 1978.
- (24) Jenkins, R. G., Nandi, S. P. and Walker, P. L., Jr., Fuel, 52,
288 (1973).
- (25) Hippo, E. and Walker, P. L., Jr., Fuel, 54, 245 (1975).
- (26) Blackwood, J. D. and McTaggart, F. K. Aust. J. Chem., 12 533 (1959).
- (27) Blackwood, J. D., Cullis, B. D. and McCarthy, D. J., Aust. J. Chem.,
20, 1561 (1967).
- (28) Gray, J. A., Donatelli, D. J. and Yavorsky, P. M., ACS Div. Fuel
Chem. Prepr., 20 (4), 103 (1975).
- (29) Blake, J. H., Bopp, G. R., Jones, J. F., Miller, M. G. and Tanbo, W.,
Fuel, 46, 115 (1967).
- (30) Chermin, H. A. G. and Van Krevelen, D. W., Fuel, 36, 85 (1957).

- (31) Fischback, D. B. in Chemistry and Physics of Carbon, 7, (P. L. Walker, Jr., Ed.), p.1, 1971.
- (32) Blackwood, J. D., McCarthy, D. J. and Cullis, B. D. Aust. J. Chem., 20, 2925 (1967).
- (33) McCarthy, D. J., Carbon, 19, 297 (1981).
- (34) Juntgen, H. and Van Heek, K. H., Fort. der Chem. Forsch., 13, 601 (1970).
- (35) Ashu, J. T., Nsakala, N., Mahajan, O. P., and Walker, P. L., Jr., Fuel, 57, 250 (1978).
- (36) Gregg, S. J. and Tyson, P. F. S., Carbon, 3, 39 (1965).
- (37) Tomita, A., Mahajan, O. P. and Walker, P. L., Jr., ACS Div. Fuel Chem. Prepr., 20(3), 99 (1975).
- (38) Smith, I. W., Fuel, 57, 409 (1978).
- (39) Walker, P. L. Jr., Shelef, M., and Anderson, R. A., in Chem & Phys. of Carbon, 4, (P. L. Walker, Jr., Ed.), Dekker, p.287 (1968).
- (40) Tong, S. B., Pareja, P. and Back, M. H., Carbon, 20, 191 (1982).
- (41) Van Krevelen, D. W., Coal, p.241, Elsevier (1961).
- (42) Thomas, J. M. in Chem. & Phys. of Carbon, 1, (P. L. Walker, Jr., Ed.), p.121, Dekker (1965).
- (43) Acharya, T. R. and Olander, D. R., Carbon, 11, 7 (1973).
- (44) Donnet, J. B., Carbon, 20, 267 (1982).
- (45) Sears, J. T., Muralidahara, H. S. and Wen, C. Y., I & EC Proc. Des. & Dev., 19, 358 (1980)
- (46) Blackwood, J. D., Aus. J. Chem., 12, 14 (1959).
- (47) Fitzer, E., Mueller, K., and Schaefer, W., in Chemistry and Physics of Carbon, Vol 7, P. L. Walker, Jr., Ed., p.237, Dekker, 1971.

- (48) Marsh, H. and Walker, P. L., Jr., in Chem. & Phys. of Carbon
Vol.15, P. L. Walker, Jr. and P. A. Thrower, Eds., p.230,
Dekker, 1979.
- (49) Pacault, A., Chem. and Physics of Carbon, Vol 7, (P. L. Walker,
Jr., Ed). p.107, Dekker, 1971.
- (50) Lewis, I. and Singer, L. in Chem. & Phys. of Carb., 17, (P. L.
Walker, Jr., and P. A. Thrower, Ed.), p.1, Dekker, 1981.
- (51) Delhaes, P. and Carmona, F., Chem. & Phys. of Carb. 17, (P. L.
Walker, Jr. and P. A. Thrower, Eds.), p.90, Dekker, 1981.
- (52) Chang, H. W. and Rhee, S. K., Carbon, 16, 17 (1978).
- (53) Mentser, M. and Ergun, S., U. S. Bureau of Mines Bulletin No.
664 (1973).
- (54) Wong, C. and Yang, R. T., Carbon, 20, 253 (1982).
- (55) Evans, E. L., Griffiths, R. J. M., and Thomas, J. M., Science,
171, 1974 (1971).
- (56) Conley, R. T. Thermal Stability of Polymers, Vol.1, Chap. 11,
Dekker, 1970.
- (57) David, C. in Comprehensive Chem. Kinetics, Vol.14, (C. H. Bamford
and C. F. H. Tipper, Eds.), pp.114-121, Elsevier (1975).
- (58) Yamashita, Y. and Ouchi, K., Carbon, 19, 89 (1981).
- (59) Fitzner, E. and Schafer, W., Carbon, 8, 353 (1970).
- (60) Ouchi, K. and Honda, H., Fuel, 38, 429 (1959).
- (61) Kobayashi, K., Sugawara, G., Toyoda, S., and Honda, H., Carbon,
6, 359 (1968).
- (62) Yamashita, Y. and Ouchi, K. Carbon, 17, 365 (1979).
- (63) Markovic, V. and Marinkovic, S., Carbon, 18, 329 (1980).

- (64) Wolfs, P. M., J., Van Krevelen, D. W., and Waterman, H. I.,
Fuel, 39, 25 (1960).
- (65) Haas, H. C., Livingston, D. I., and Sanders, M., J. Poly. Sci.,
15, 503 (1955).
- (66) Reid, J., Garside, B. K., Shewchun, J., El-Sherbiny, M., and
Balik, E. A., Appl. Opt., 17, 1806 (1978).
- (67) Suuberg, D. M., Peters, W. A., and Howard, J. B., IEC Proc. Des.
Dev., 17, 37 (1978).
- (68) Blackwood, J. D. and Ingeme, A. J., Austral. J. Chem., 13, 134
(1960).
- (69) Lazarov, L and Angelov, S., Fuel, 59, 55 (1980).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.