POROSITY OF COALS AND COAL PRODUCTS

MASTER

Technical Report 7

Prepared by

O.P. Mahajan and P.L. Walker, Jr.

at

THE PENNSYLVANIA STATE UNIVERSITY

Date Published - March 1978

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. EX-76-C-01-2030

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

POROSITY OF COALS AND COAL PRODUCTS

by

O.P. Mahajan and P.L. Walker, Jr.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

PSU-TR-7

COAL RESEARCH SECTION
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

REA

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or 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 on privately owned rights.

ABSTRACT

Different experimental approaches for characterizing porosity of coals and coal products have been described. Results of densities, surface areas and pore volume distributions for coals of different rank and the manner in which they change upon heat treatment have been discussed.

True density, that is the density of the solid phase of coals, as measured by the displacement of helium, is rank dependent. It shows a shallow minimum at about 81% carbon and rises sharply as 90% carbon is approached. Particle densities of coals, as measured by the volume of mercury displaced, show the same kind of rank dependence as do the corresponding helium densities.

It has been concluded that adsorption of N_2 at 77°K measures the area of transitional and macropores, whereas CO_2 adsorption at 298°K measures essentially the total surface area of coals. Both N_2 and CO_2 areas show a dependence on coal rank. Coals with N_2 areas greater than $10 \text{ m}^2/\text{gm}$ fall in the carbon content range (daf basis) from 76 to 82%. Nitrogen areas of most coals on both sides of this carbon content range are usually less than $1 \text{ m}^2/\text{gm}$. Carbon dioxide surface areas of coals of all ranks are higher than $100 \text{ m}^2/\text{gm}$. There is a general decrease in CO_2 area with decrease in carbon content down to about 76% carbon and then an increase for coals of lower rank. It has been suggested that while reporting surface areas of microporous coals and chars the adsorbate, adsorption temperature, equilibrium time, particle size and cross-sectional area of the adsorbate used should be reported.

Surface areas of coals determined from water adsorption isotherms are invariably lower than the corresponding CO_2 areas. It has been concluded

that besides adsorption on inorganic impurities, sorption of water on coals involves adsorption at the oxygen functional groups.

Results of distribution of total open pore volumes for coals of different rank, in the pore diameter ranges less than 12A (micropores), 12-300A (transitional pores) and greater than 300A (macropores), shows that: (i) in coals with carbon contents less than about 75%, porosity is primarily due to the presence of macropores, (ii) in coals with carbon contents in the range 75-84%, porosity is predominantly due to the presence of transitional and macropores, and (iii) in coals varying in carbon content from 85 to 91%, microporosity predominates.

Surface areas and densities of coals undergo significant changes upon heat treatment. In general, the surface area first increases with increasing heat treatment temperature (HTT), passes through a maximum and decreases thereafter; the temperature at which the maximum occurs depends upon the starting coal. Results of density measurements on heat treated coals in fluids of different dimensions show that coals can be converted into molecular sieve materials by heat treatment, the character and extent of molecular sieving depending upon the rank of the starting coal and its HTT.

With increasing burn-off during gasification of a char, specific pore volume increases continuously, whereas specific surface area passes through a maximum. The process opposite to gasification, that is carbon deposition, decreases both the specific area and specific pore volume of a char.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	i
Table of Contents	iii
Preface	iv
I. Introduction	1
II. Densities of Coals and Chars	4
A. True Density	4
B. Particle Density	14
C. Apparent Densities in Liquids	19
D. Open Pore Volume and Porosity	21
III. Surface Area	22
A. Heat of Wetting	22
B. Adsorption of Gases	23
IV. Pore Size Distribution	36
A. Mercury Porosimetry	36
B. Capillary Condensation of Nitrogen	37
V. Selected Experimental Results	40
A. Helium and Mercury Densities of Coals	40
B. Surface Areas of Coals	42
C. Distribution of Total Open Pore Volume in Coals	45
D. Effect of Heat Treatment of Coal on Properties	47
E. Effect of Oxidation and Carbon Deposition on Properties of Chars	49
References	51

PREFACE

As part of the present contract, we have been assigned the responsibility of evaluating and developing methods to characterize the porosity in coals and coal products. This is an ongoing effort, but it did seem to be appropriate at this time to bring the reader up-to-date on our thinking as to what some of the problems are and what we consider to be the best approaches at characterizing porosity at this time.

It is not easy to characterize the porosity in coal. Coal, in essence, behaves as an aperture-cavity material, with a significant fraction of the apertures being of molecular dimensions. This means that very small differences between the dimensions of the molecule used to probe the porosity and the aperture size can have marked effects on the accessibility of the molecule into that porosity--and, hence, the final answers for surface areas and pore volumes.

Unfortunately, almost anything one does to prepare a coal or char for a measurement has a profound effect on the aperture size. Consider that coals contain significant amounts of functional groups at the edges of the aromatic and hydroaromatic building blocks. Many of the functional groups contain oxygen which makes them hydrophilic, that is they like to adsorb water from the atmosphere. Thus, one of the serious problems is the extent to which adsorbed water blocks or reduces the aperture sizes in coal. Normally one outgasses the coal above 100°C in an attempt to remove much of the water from the coal prior to making measurements. But the water is held more or less tightly to different functional groups on the coal, and the coal cannot be taken to a sufficient temperature to remove all water from all coals before

thermal degradation of some functional groups commences. Coals also shrink, more or less, upon removal of water depending upon coal rank.

One could go on at length about the interaction of water and oxygen from the air with coal and how this interaction drastically affects reported surface areas and porosities. The important message is that there is no one correct value for these parameters for a coal. The values determined depend upon the probing molecule, the particle size of coal on which the measurement is made, the preparation conditions such as outgassing temperature, pressure and time; the temperature at which the measurement is made, and the time allowed for the measurement. Therefore, the reader should always be sure to check out the conditions and before utilizing surface area and pore volume data found in the literature.

I. INTRODUCTION

Coals are composed of aromatic and hydroaromatic building blocks containing more or less crosslinks between the building blocks and heteroatom functional groups at their periphery. Hirsch (1954), from an exhaustive x-ray study, has described a model which distinguishes between the three types of structures present in a wide range of coals (Figure 1). These structures may be described as follows:

(i) Open structure. This structure is characteristic of low rank coals in the range up to about 85% carbon. Coals in this range are highly porous; the lamellae are connected by crosslinks and are more or less randomly oriented in all directions.

(ii) Liquid structure. This structure is typical of bituminous coals in the range from about 85 to 91% carbon. In this range, the number of crosslinks has decreased considerably and the lamellae show some orientation with the formation of crystallites consisting of two or more of these lamellae. Pores are practically absent.

(iii) Anthracitic structure. This structure is common in higher rank coals with a carbon content of over 91%. In this structure the degree of orientation of the lamellae with regard to each other has increased greatly and the crosslinks have disappeared. As a result, high porosity is observed.

The pores in coals and chars vary in size from large cracks of micron dimensions to apertures which are even closed to helium at room temperature. It is the empty volume, known as pore volume, within the pores of any porous material that enables large volumes of gas or liquid to be adsorbed. A large pore volume need not always imply a large pore surface area because the latter is dependent upon the pore size distribution. In the case of

Figure 1

SCHEMATIC MODEL OF COAL STRUCTURE From Hirsch (1954)

porous adsorbents, Dubinin (1966) has suggested the use of the following classification, which is generally accepted for coals and chars as well, for distinguishing between pores of different sizes: (i) micropores--pores which have diameters less than 20A, (ii) transitional pores--pores which have diameters in the 20-200A range, and (iii) macropores--pores which have diameters greater than 200A.

The porosity in coals has a large influence on behavior during their mining, preparation and utilization. Unless coals are near outcrops or under light cover, they contain significant quantities of adsorbed methane in their natural state in the seam. A knowledge of the pore volume and pore size distribution of coals determines the extent and ease of diffusion of methane out of the pore structure during mining. Coal preparation for the market by the removal of mineral matter depends upon the specific gravities of the coal and minerals; the specific gravity of the organic phase of coals is partly dependent upon porosity. The porosity of coals has its greatest significance in utilization processes. In the liquefaction and gasification conversion processes and in the use of metallurgical coke, chemical reactions occur between gases (or liquids) and coal surfaces much of which is located in pores. Product molecules must be able to escape rapidly enough from the pores to permit access of fresh reactants. Since the conversion processes involve application of heat, a char is always an intermediate product of the process. Again, the rank of the coal precursor and nature of its pore structure permit a prediction of the type of porosity that will be developed during processing and, hence, an assessment of the suitability of the coal for a particular conversion process. Furthermore, a number of commercial activated carbons used for gas and water purification are produced by carbonizing coals in the absence of air and subsequently activating the char in an oxidizing

atmosphere. Knowledge of the porosity of the coal precursor can be helpful in predicting whether a suitable char and, hence, an activated carbon can be produced from the coal.

For the quantitative characterization of internal pore structure of coals and chars, one needs to estimate the pore volume, surface area and pore size distribution. Due to the physical and chemical complexity of coals, the techniques for characterizing their pore structure are numerous; and sometimes it is difficult to select the most suitable method(s) for this purpose. Since it is not possible to discuss all the methods (techniques) available for pore size characterization, emphasis will be laid on methods which are most commonly used for such characterization.

II. DENSITIES OF COALS AND CHARS

For porous solids, such as coals and chars, three different densities, that is true density, particle density and apparent density can be considered.

A. True Density

True density of a porous solid is the weight of a unit volume of the pore-free solid. To determine the true density of a porous solid, the pore structure must be completely filled with a fluid medium which does not interact with the porous material. As we will see, no fluid completely fills the pore volume of coals and chars so the term true density should be understood in this light.

1. Helium Density

Since helium is the smallest atom available, it has the best chance of penetrating all of the porosity in coals and chars. It was earlier believed (Franklin, 1949) that coals have no closed-off pores which are inaccessible to helium atoms. However, x-ray studies on anthracites have shown

the presence of some porosity which is closed to helium (Kotlensky and Walker, 1960). Therefore, the helium density of a coal will be lower than its true density.

a. Experimental Measurement of Helium Density. For measuring helium density, different apparatus designs can be considered. All of them are based on measurement of volume of helium occupying a sample holder in the presence and absence of a known weight of sample.

One apparatus was described by Spencer (1967). He found that the error in the measured density was dependent upon the weight of the sample used; for a sample weight of 6.5 gm and a helium density of about 2 gm/cm^3 , the error was about $\pm 0.005 \text{ gm/cm}^3$.

A second apparatus was described by Greenhalgh et al. (1966). They found that for a sample having a density of 2 gm/cm^3 , the error in helium density, using a 1 gm sample, was within $\pm 2\%$.

In the third type of apparatus (Howard and Hulett, 1924), the evacuated sample holder is separated from the measuring system by a stopcock. The system incorporates an arrangement for varying its volume by adding or removing a weighed quantity of mercury. For helium density measurements, the evacuated sample holder is isolated and the measuring system is filled with helium at a known pressure, p . The gas is then expanded into the sample holder by opening the stopcock. Following expansion, the pressure in the system falls. The pressure in the apparatus is restored to the initial pressure, p , by adding the required quantity of mercury. If the temperature in the apparatus is constant, then the volume of mercury added represents the dead volume of the sample holder.

Walker and his school have used a modified version of the Howard and Hulett apparatus for measuring helium densities. Since they have found it

to be quite satisfactory, it is described in some detail. The apparatus is mounted in a double-walled box constructed from 1/2 in. thick plywood. The space between the two walls is filled with about 2 in. thick fiber-glass insulation. The front side of the box is a hinged door in which a 3/16 in. thick pane of plexiglass is mounted. The door can be closed to form a tight seal. This construction is necessary to achieve minimum heat transfer between the inside and outside of the box. A thermoregulator and an electronic relay in conjunction with two electric light bulbs (40 and 60 watts), which serve as a source of heat, are utilized and maintain the box temperature at $30.50 \pm 0.02^{\circ}\text{C}$. A fan is utilized to circulate air in the box.

The helium density apparatus, shown in Figure 2, is constructed from Pyrex glass. Two 1-liter helium bulbs are connected to both sides of the manifold. These reservoirs are isolated from the rest of the system by high vacuum stopcocks through which helium is admitted into the system. Stopcocks S_1 and S_2 are manipulated from outside the box by control rods extending through its side. The section of glass tubing between B and F is of precision bore of 1/4 in. diameter.

For helium density determinations, generally 7 gm of oven-dried (110°C) sample are placed in the sample holder. The volume of the empty sample holder is calibrated with mercury. The sample is again outgassed at 110°C for 12 hr under a vacuum of 10^{-5} torr, obtained by the combination of a rotary vacuum pump and a mercury diffusion pump. The sample is then cooled to the measurement temperature (30.5°C). The level of mercury in the gas burette is raised to coincide with a given etch mark on the capillary tube connecting bulbs of known volume. The level of mercury in the precision bore tubing is noted using a cathetometer. With stopcock S_3 closed, helium is introduced into the apparatus at a known pressure in the range 200-450 torr (helium density

Figure 2

HELIUM DENSITY APPARATUS

is essentially independent of pressure in this range). The pressure is measured by a Barocell electronic manometer having a precision of 0.001 torr. Helium is then expanded into the sample holder by opening stopcock S_3 . After a constant pressure within the system is attained[†], mercury levels in the gas burette and precision bore tubing are appropriately raised till the pressure is restored to the starting value. The helium density of the sample is calculated from the ratio of its weight to the dead volume obtained from the above experiment.

Nelson (1977) checked the precision of helium density; for five runs on a HVA bituminous coal, the helium density was found to be $1.320 \pm 0.002 \text{ gm/cm}^3$. He also checked the accuracy of helium density for a non-porous spectrographic grade natural graphite. He determined its density to be 2.267 gm/cm^3 , which is in excellent agreement with the theoretical value of 2.269 gm/cm^3 for graphite.

b. Helium Adsorption. When determining densities of carbonaceous solids by helium displacement, it is assumed that the gas is not adsorbed at room temperature. However, this is not always true (Maggs et al., 1960; Kini and Stacy, 1963; Kipling et al., 1966). Kini and Stacey (1963) showed that at 25°C adsorption of helium varied with the nature of the carbon and increased, in general, with increasing surface area and 'true' density of the sample. However, Maggs et al. (1960) have reported that at room temperature helium is not adsorbed on coals appreciably enough to cause significant errors in the densities. As will be discussed shortly, helium, water and methanol densities of chars measured at room temperature are in close agreement

[†]For measuring helium densities of 40 x 70 mesh fractions of coals, Nelson (1977) arbitrarily allowed 45 min for pressure equilibration. Equilibrium was attained well within this period; longer periods had no noticeable effect on pressure and, hence, helium density.

with one another (Youssef, 1976). This agreement suggests the absence of significant helium adsorption on chars.

Because of the possibility of adsorption of helium at room temperature, it has been recommended (Kipling et al., 1966) that measurement of helium density, particularly for the highly adsorptive carbons, be made at 300°C. However, this cannot be done for raw coals because they may undergo structural changes at this temperature.

c. Density Correction for Mineral Matter. Coals of all ranks invariably contain different amounts and types of mineral impurities which usually have high densities. The densities ('true', particle and apparent) are corrected for the mineral matter by the following equation:

$$\frac{X}{\rho_m} + \left(\frac{1-X}{\rho_c} \right) = \frac{1}{\rho} \quad (1)$$

where ρ_m is the density of mineral matter, ρ_c is the corrected density of the organic phase of coal (or char), ρ is the original uncorrected density and X is the fractional mineral matter content by weight. The density of mineral matter present in coals has been reported to differ little from that of the ash itself (Tschambler and de Ruiter, 1963). When the ash density is not determined experimentally, average ash densities of 2.7 or 3 gm/cm³ have been used (van Krevelen, 1961).

2. Water Density in the Presence of a Wetting Agent

Determination of helium density involves an elaborate vacuum system and a reasonably cumbersome and time consuming procedure. Attempts were made in the past (Tschambler and de Ruiter, 1963) to determine densities of coals by the pycnometric method (to be described shortly) using liquids of small molecular dimensions such as methanol and water. Methanol densities of coals are generally higher than the helium densities due to specific interactions, as will be discussed later. For the lower rank coals,

the water densities, like methanol densities, are higher than the corresponding helium densities whereas for higher rank coals, the water densities are lower (Tschambler and de Ruiter, 1963). The lower values have been attributed to the hydrophobic character of higher rank coals as a result of which water cannot completely displace air present in the pores.

Ettinger and Zhupakhina (1960) suggested that water penetration into the coal structure can be increased with the help of a wetting agent. They used a wetting agent composed of a mixture of polyethyleneglycol and mono-alkylphenyl ethers. The molecules of the wetting agent, which have hydrophobic hydrocarbon radicals attached to hydrophilic polar surface groups, undergo orientation in water. Ettinger and Zhupakhina suggested that in the case of hydrophobic coals, the polar groups of the wetting agent are turned into the water and the nonpolar groups towards the coal surface. Therefore, subject to penetration by the wetting agent itself, water molecules can penetrate into the coal structure quickly and more completely.

The experimental technique of Ettinger and Zhupakhina involves the following steps. Three-gm coal samples (-60 mesh) are transferred into a 100 cm³ measuring flask with the help of a funnel. A very thin coal film which is difficult to wash down with water is left on the funnel. To remove it, 20 drops of 1:1 solution of the wetting agent in water are poured directly on the funnel. Care should be taken that no foam formation occurs on addition of the wetting agent. The flask is then half-filled with distilled water after which it is placed in a boiling water bath for 30 min and later filled with water up to a graduated mark. The flask is then cooled for 30 min in a thermostated water bath maintained at 20°C after which it is weighed. A blank run, without any sample, is also made by weighing the flask filled at 20°C with water containing the same amount of wetting agent as used with coal. Ettinger and Zhupakhina determined the helium and water

densities of fourteen coals having volatile matter contents (daf) in the 1.7-44.5% range. With three exceptions, the difference between the two methods was less than 1%.

Nelson (1977) has recently determined densities of eight 40 x 70 mesh coals varying in carbon contents (daf) from 70.9 to 89.5% by helium displacement, as well as by the Ettinger and Zhupakhina technique. He used Triton X-100 (iso-octyl phenoxy polyethoxy ethanol) as the wetting agent. This wetting agent is similar in structure to that used by Ettinger and Zhupakhina. The results listed in Table I show that with the exception of one sample, PSOC-318, the helium and water densities for the remainder of the samples differ significantly from each other.

3. Water and Methanol Densities of Coals and Chars

Also listed in Table I are the pycnometric water densities (25°C) of the eight coals determined in the absence of any wetting agent (Youssef, 1976). Densities of coals in liquids normally show 'drifts' with time. The water densities listed in Table I are the 'equilibrium' values obtained after five days. That is, after five days the densities did not show any further drift or variation with time. The water densities of all the coals investigated, irrespective of the rank, are invariably higher than the corresponding helium densities. The higher water densities are indicative of specific interactions between water and oxygen-containing surface complexes present on coal surfaces and/or imbibition of water by coals.

Youssef (1976) also determined the helium, water and methanol densities of thirteen char samples prepared from two lignite chars by (i) depositing different amounts of carbon by the cracking of methane, and (ii) activation of the raw and carbon deposited (CD) samples to different levels of carbon burn-off. The two chars, referred to above, were prepared by carbonizing a

Table I
Densities of Coals (from Nelson, 1977)

PSOC No.	%(daf)	Density, gm/cm ³ (dmmf)		
		Helium	Water-wetting agent	Water
318	89.5	1.326	1.326	1.526
254W	87.2	1.301	1.288	1.465
268	85.9	1.285	1.316	1.371
223	81.3	1.297	1.363	1.400
212	79.0	1.326	1.380	1.432
248	75.2	1.343	1.418	1.556
242	73.9	1.340	1.373	1.648
246	70.9	1.373	1.510	1.563

North Dakota lignite (40 x 100 mesh) at 855 and 1000°C. Carbon deposition and activation were carried out in the manner described elsewhere (Kamishita *et al.*, 1977).

The helium and 'equilibrium' water and methanol densities (determined at 25°C after five days of contact time) of various char samples are given in Table II. The water and methanol densities represent the average of two determinations for each sample. It is seen that the three densities for each sample are in close agreement with one another.

Youssef (1976) found that for nine determinations, 95% confidence intervals on the mean methanol and water densities of a given char were 1.667 ± 0.015 and 1.663 ± 0.015 gm/cm³, respectively.

It is concluded that while the 'true' densities of chars can be determined by using the displacement of helium, methanol or water, 'true' densities of coals can only be determined by helium displacement.

Table II
Densities of Chars (from Youssef, 1976)

Sample		Density, gm/cm ³ (dmmf)		
		Helium	Methanol	Water
<u>CD Series</u>				
	<u>CD, % (daf)</u>			
855°C Char	0	2.07	2.06	2.00
	1.0	1.86	2.05	1.95
	1.7	1.97	2.04	1.99
	2.6	1.83	1.86	1.88
1000°C Char	0	2.08	2.08	2.05
	3.6	2.00	2.01	1.98
<u>Burn-off Series</u>				
	<u>Burn-off % (daf)</u>			
855°C Char	0	2.07	2.06	2.00
	1.1	2.03	2.07	2.01
	2.3	2.03	2.07	2.03
	10.2	2.13	2.10	2.08
	33.6	2.14	2.14	2.06
855°C Char- 2.6% CD	0	1.83	1.83	1.90
	1.7	2.00	2.00	1.99
	3.7	1.96	2.02	2.01
	29.1	2.02	1.99	2.02

B. Particle Density

Particle density is the weight of a unit volume of the solid including pores and cracks. Particle density can be determined by three techniques, namely (1) mercury displacement, (2) gas flow and (3) silanization.

1. Mercury Displacement

The maximum pressure, p , required to force mercury into a cylindrical pore of radius, r , is given by the Washburn equation (1921):

$$p = - \frac{2\gamma \cos\theta}{r} \quad (2)$$

Where γ is the surface tension of mercury, and θ is the contact angle between mercury and the pore wall. If it is assumed that θ is 140° (which is close to the value for a wide variety of solids) and γ is 480 dynes/cm, equation (2) simplifies to

$$r = \frac{106}{p} \quad (3)$$

where p is in lb/in.^2 and r is in microns. Thus, when an outgassed solid is immersed in mercury at atmospheric pressure, according to equation (3), mercury cannot enter into pores smaller in radius than $7 \mu\text{m}$.

Various commercial porosimeters are available for determining particle density and pore size distribution of porous solids. For measuring mercury density, the following procedure is utilized. About 1 gm of a sample is oven-dried at 110°C for 2 hr and placed in a penetrometer of known weight. The capillary stem of the penetrometer is graduated. The penetrometer is inserted into a glass filling device and evacuated for 90 min. Mercury is then introduced by tilting the glass filling device until the tip of the penetrometer is about 0.5 cm within the mercury pool. By carefully opening the stopcock to the atmosphere, air is admitted until atmospheric pressure is reached at which point the penetrometer is completely filled with mercury. The mercury-filled penetrometer is removed from the glass filling device,

weighed and transferred to the high pressure vessel. The mercury density of the sample is determined from the volume of mercury displaced at a given pressure (the exact pressure depends upon the particle size used, as will be discussed shortly). The volume of mercury displaced is calculated from the following equation:

$$V_s = V_p - \frac{(W_p + W_s + W_{Hg}) - (W_p + W_s)}{\rho_{Hg}} - \Delta V_{Hg} \quad (4)$$

where V_a = displacement volume, cm^3

V_p = internal volume of the empty penetrometer, cm^3

W_p = weight of empty penetrometer, gm

W_s = weight of sample, gm

W_{Hg} = weight of mercury, gm

ρ_{Hg} = density of mercury, gm/cm^3

ΔV_{Hg} = deviation from complete filling, cm^3

In order to get meaningful mercury densities of coals and chars, it is essential to determine the minimum pressure needed to fill the interparticle void volume. Gan et al. (1972) used the following approach for this purpose. They used 40 x 70 mesh fraction of coals for mercury density determinations. They determined the filling pressure for a 40 x 70 mesh fraction of non-porous glass spheres. Significant amounts of mercury were forced into the voids between glass particles at pressures below 20 psi, followed by much less penetration between 20 and 60 psi. Above 60 psi, negligible further penetration occurred. To establish this point further, a similar run was made with an anthracite sample (40 x 70 mesh). Mercury penetration occurred up to 60 psi; between 60 and 500 psi, penetration was negligible. Since anthracites are essentially devoid of transitional and macropores and contain only micropores (Gan et al., 1972), it was concluded that at 60 psi the

interparticle voids would be filled with mercury and any further mercury penetration at higher pressures would be due to the presence of pores.

The size of the voids between the particles will vary as a function of coal particle size. The smaller the particle size, the smaller will be the void size and hence, according to equation (3), the larger will be the pressure needed to fill the interparticle void volume. Thus, the interparticle void volume for a given size fraction of coal should be estimated at a pressure at which the void volume between glass particles of the same size fraction as the coal sample used is filled with mercury. Caution should be exercised in using anthracites instead of glass spheres for such studies. Even though anthracites possess little or no macroporosity, macro cracks or fissures may develop upon grinding to finer sizes. Since the cracks act as macropores, it is difficult to distinguish these 'macropores' from the interparticle voids. Thus, it will be virtually impossible to estimate the pressure needed to fill only the interparticle void volume.

The precision of mercury density for ten runs made on a HVA bituminous coal was found to be $1.250 \pm 0.003 \text{ gm/cm}^3$ (Nelson, 1977).

2. Gas Flow Method

Ergun (1951) determined particle densities of a series of coal cokes using the principle of gas flow through beds of particles packed to different bulk densities. From measurements of pressure drop through the beds as a function of gas flow rate, Ergun determined the coefficients a and b of the linear form of the pressure drop equation (Ergun and Orning, 1949):

$$\frac{\Delta p}{LU_m} = a + bG \quad (5)$$

where Δp is the pressure drop, L is the height of the bed, U_m is the average linear gas velocity based on the cross-section of the empty column, G is the mass flow rate of the gas, and a and b are represented by:

$$a = \frac{2\alpha\mu S_v^2 (1-\epsilon)^2}{\epsilon^3} \quad (6)$$

$$b = \frac{\beta S_v (1-\epsilon)}{8\epsilon^3} \quad (7)$$

where μ is the absolute viscosity of the gas, S_v is the specific surface of the particle, ϵ is the fractional void volume of the bed and α and β are the statistical constants.

The particle density was obtained by the method of least squares as the intercept of either of the following linear relationships derived by Ergun and Orning (1949):

$$\rho_B = \rho - C_1 \sqrt[3]{\frac{\rho_B^2}{a}} \quad (8)$$

$$\rho_B = \rho - C_2 \sqrt[3]{\frac{\rho_B}{b}} \quad (9)$$

where ρ_B and ρ are bulk density and particle density, respectively, C_1 is a constant for the gas employed and the particle used and C_2 is a constant for the particles involved.

Ergun (1951) determined particle densities of sieve fractions varying from 8-16 to 100-140 mesh. The particle density increased monotonically with a decrease in particle size, as progressively smaller voids were removed from the particles as a result of continuing comminution.

The apparatus used by Ergun consisted of a glass tube, two flow meters and three manometers. The glass tube had an inside cross-sectional area of 7.24 cm^2 and was 80 cm long; its ends were gradually reduced. The tube was fitted with a coarse porous glass disk at a distance of 20 cm from the bottom. It had two pressure taps--one about 4 cm below the disk and the other 40 cm above. The cross-sectional area of the tube was calibrated gravimetrically

using distilled water. The pressure drop through the porous disk was determined as a function of gas flow rate to be applied later as a small correction to the total pressure drop.

The experimental procedure involved the introduction of a known weight of pulverized material of a narrow size fraction into the tube, packing it to different bulk densities and measuring pressure drop for each packing as a function of N_2 flow rate. After packing the bed, N_2 was introduced below the disk at a rate sufficient to expand the bed. The bulk density was varied by varying the rate of upward flow of N_2 . Each sample was packed to six to twelve different bulk densities.

3. Silanization Method

Ettinger and Zhupakhina (1960) determined the particle densities of coals by the silanization method, that is, by covering the coal surface with a thin film of an organosilicon compound. The thin film is impervious to water and has practically no influence on the coal volume.

Ettinger and Zhupakhina used the following experimental procedure. Three gm of -60 mesh fraction of coal were taken in a glass dish which was placed in a desiccator containing water. The dish was then put into another desiccator containing dimethyl dichlorosilane. After 10 min the dish was removed and the contents dried in an oven at 110°C for 2-3 hr. The sample was then cooled to room temperature. The 'silanized' coal was transferred into a measuring flask (50 cm^3 capacity) and was covered with a very dilute solution of pyridine in water--this solution was prepared by adding 1 drop of pyridine per 100 cm^3 of water. The flask was then filled with the pyridine solution and the contents were weighed at 20°C . Knowing the weight of pyridine solution filling the measuring flask, the particle density of coal could be calculated. Ettinger and Zhupakhina found that for fourteen

coals having volatile matter contents (daf) in the 2.1 to 48.6% range, the difference in particle density by the silanization technique and by geometric measurements on cubes of coals was less than 1%.

Nelson (1977) determined the particle densities of 40 x 70 mesh fractions of eight coals varying in carbon contents (daf) from 75.3 to 91.3% by the mercury displacement and silanization methods. He found that for one sample (a HVC bituminous coal) the difference in the two densities was 1.2%, whereas for the remainder of the seven samples the difference showed a random variation from 1.6 to 7.3%.

C. Apparent Densities in Liquids

Apparent densities are normally determined by the pycnometric method. In the simplest case, weight of the liquid filling a pycnometer at a constant temperature is determined. A known amount of the oven-dried coal or char sample is weighed into the dry pycnometer which is then filled with the liquid. The pycnometer with its contents is again weighed. The pycnometer densities show 'drifts' with time. This behavior is characteristic of microporous adsorbents. In such solids, air present in micropores may not be completely displaced by the liquid. In order to circumvent this difficulty, the solid is outgassed. Without exposing the outgassed sample to air, it is contacted with the liquid in which the apparent density is to be determined. A schematic diagram of the apparatus used by Toda (1972) for apparent density determinations is given in Figure 3. A sample bottle (1), about 4 cm³ in volume and containing about 1.5 gm sample (28 x 60 mesh), is connected with the vacuum system through a capillary tube (3). After outgassing for about 1 hr at 100-110°C, the sample bottle is taken off the vacuum system at a glass joint (4) and weighed precisely. The bottle is again connected to the vacuum system at 100-110°C until a pressure of 10⁻⁴ torr

Figure 3

APPARATUS FOR MEASURING APPARENT DENSITIES

1, sample bottle; 2, glass joint; 3, capillary tube; 4, glass joint; 5,6, greaseless vacuum stopcock; 7, vacuum stopcock; 8, cork sealed with paraffin wax; 9, bottle for dilatometric liquid; 10, line for level adjustment.

From Toda (1972)

is obtained. The greaseless vacuum stopcock (5) is closed and the vacuum stopcock (6) is opened to admit the organic liquid into the sample bottle. The sample bottle (1) and capillary tube (3), which connects the sample holder to the vacuum system, are detached from the apparatus and placed in a thermostated bath maintained at $25 \pm 0.2^\circ\text{C}$. The liquid level is adjusted to a fixed mark (10) with an injector. Following this, the weight of the sample bottle and capillary tube assembly is determined. Since the weight and the free space of the sample bottle and of the capillary tube and the density of the dilatometric liquids are known, the apparent densities of coals can be calculated. Toda (1972) found that the densities were reproducible to 0.005 gm/cm^3 .

A porous material may have several apparent densities depending upon its particle size, range of pore diameters in the material, molecular dimension of the fluid, its degree of interaction with the material (that is, surface effects and swelling), and time allowed for penetration of the fluid. Too small coal particles are undesirable for density measurements because of the possibility of their floating on the measuring liquid. It has been suggested (Tschambler and de Ruiter, 1963) that particles of 0.1 to 0.3 mm diameter are best for measuring apparent densities.

D. Open Pore Volume and Porosity

Total open pore volume (V_p) of the organic phase of coal (or char) is calculated from the relationship

$$V_p = \left(\frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}} \right) \quad (10)$$

where ρ_{Hg} and ρ_{He} are the mercury and helium densities (daf), respectively.

Porosity (P) of a coal is calculated from the following relationship

$$P = 100 \rho_{\text{Hg}} \left(\frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}} \right) \quad (11)$$

By determining the apparent density of coal in fluids of different, but known dimensions, it should be possible to find the pore size-pore volume distribution. Open pore volume (V) accessible to a given fluid is calculated from

$$V = \left(\frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_a} \right) \quad (12)$$

where ρ_a is the apparent density in the given fluid.

III. SURFACE AREA

A. Heat of Wetting

When an outgassed sample is immersed in a liquid which wets its surface, a rise in temperature of the system results. The temperature increase is proportional to the total area of surface wetted by the liquid and the heat (h) released on wetting a unit area of the adsorbent.

A good wetting agent should have the following properties: (i) its molecular size should be small so that it is accessible to even the smallest pores in the system, (ii) it should have good wetting properties, and (iii) its volatility should be a minimum at room temperature. The three properties are characteristic of a polar organic liquid. Because of the size considerations, heat of wetting in methanol has been used extensively in the past for determining surface areas of coals. However, adsorption of methanol on coals involves specific interactions between the hydroxyl group of methanol and oxygen functional groups present on coal surfaces (Marsh, 1965; Spencer, 1967). It has been shown that in the case of coals, h in methanol is a function of the concentration of oxygen functional groups

and, hence, of coal rank (Robert and Brusset, 1965; Robert and Pregermain, 1963).

Several calorimeters have been described in the literature for determining heats of immersion. However, due to inherent limitations associated with the use of methanol as a wetting agent, the heat of wetting method is now of only historical importance and, therefore, will not be discussed further.

B. Adsorption of Gases

1. General

For determining surface area by gas* adsorption, one needs to find out the monolayer capacity, that is, the number of molecules necessary to cover the surface of the adsorbent with a complete monolayer. This quantity when multiplied by the area occupied by a single adsorbed molecule gives the surface area. The monolayer capacity is conventionally determined by the Brunauer-Emmett-Teller (BET) equation. Derivation of this equation is described elsewhere (Brunauer et al., 1938). For surface area measurements the equation is used in the following form:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{p}{p_0} \quad (13)$$

where V = volume adsorbed at equilibrium pressure p

p_0 = saturation vapor pressure of the adsorbate at the adsorption temperature

V_m = monolayer capacity

$C = \exp[(E_1 - E_\infty)/RT]$

*For the sake of convenience, the terms gas and vapor have been used interchangeably in the text.

where E_1 is the heat of adsorption in the first layer and E_ℓ is the heat of liquefaction of the adsorbate. Thus, C represents the 'net' heat of adsorption. A plot of $p/V(p_0 - p)$ against p/p_0 should yield a straight line of slope $(C-1)/V_m C$ and intercept $1/V_m C$.

The BET surface areas of porous and non-porous adsorbents are conventionally determined from N_2 adsorption isotherms measured at 77°K. For N_2 adsorption on most adsorbents, the value of constant C in equation (13) is high. Therefore, $(C-1)/C \approx 1$ and $1/V_m C \approx 0$ so that equation (13) can be approximated as

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m} \cdot \frac{p}{p_0} \quad (14)$$

In other words, when C is high, the BET plot passes through the origin and its slope is inversely proportional to V_m . Thus, for evaluation of V_m , only one adsorption point is needed.

The main advantage of the single point method is that it permits rapid determination of surface areas. It should be used for making only routine surface area measurements, where one is primarily interested in comparative rather than absolute surface areas. However, caution should be used in selecting a reasonable relative vapor pressure at which adsorption is measured. Although Brunauer et al. (1938) used a relative pressure of 0.3, the BET plots for many microporous adsorbents, including coals and chars, are not linear up to $p/p_0 = 0.3$. If, on the other hand, too low a relative pressure is used, the results may be erroneous. It is known (Lamond and Marsh, 1964; Mahajan and Walker, 1969) that for microporous adsorbents, adsorption at low relative pressures is governed primarily by pore size of the adsorbent rather than by the magnitude of its surface.

Having determined V_m , the next step is to assign a correct value for the cross-sectional area of the adsorbed molecule. Emmett and Brunauer (1937) calculated the molecular area (σ_m) from the following equation assuming that the adsorbed molecules were hexagonally closepacked spheres.

$$\sigma_m = 3.464 \times 10^{16} \left(\frac{M}{4\sqrt{2}N_A\rho_s} \right)^{2/3} \quad (15)$$

where M is the molecular weight of the adsorbate, N_A is Avogadro's number and ρ_s is the density of the adsorbed phase, which was assumed to be the same as that of the bulk liquid or solid at adsorption temperature.

There is a definite uncertainty as to the area an adsorbed molecule occupies in pores of molecular dimensions such as those present in coals and chars. In such pores, the appropriate molecular area could be up to four times that found from adsorption on a flat surface. Since pores in coals are slit-shaped (Franklin, 1949; Walker et al., 1966), a molecular area from two to three times that found on a conventional flat surface is probably more reasonable.

The N_2 surface areas of coals are considerably lower than those expected. It has been suggested (Anderson et al., 1965; Walker and Geller, 1956) that at -196°C the micropore system in coals is not completely accessible to N_2 molecules due to an activated diffusion process and/or shrinkage of pores. Adsorption of N_2 at -196°C is considered to measure the area of the macropores, transitional pores and the larger micropores in coals and chars (Walker and Geller, 1956; Anderson et al., 1965).

There is another drawback associated with N_2 adsorption at -196°C . Lamond and Marsh (1964) have suggested that when the pores are several times the diameter of a N_2 molecule, then N_2 at -196°C fills these pores at very low relative vapor pressures resulting in reversible capillary condensation

before the apparent monolayer capacity is reached. Therefore, the areas in such cases are unrealistically high.

Due to inherent limitations associated with the use of N_2 adsorption at -196°C , it was realized that in order to obtain surface areas of microporous coals, it was essential to measure adsorption of gases at as high a temperature as possible. Attempts were made to determine surface areas of coals from adsorption of neon at room temperature (Bond and Spencer, 1957), hydrocarbon gases at or near room temperature (Vander Sommen, 1955; Gregg and Pope, 1959) and Kr and Xe at -78 and/or 0°C (Ahuja *et al.*, 1961; Kini, 1963, 1964). However, none of these methods gave the total surface area of coals. Walker and Kini (1965) measured surface area of coals from adsorption of N_2 (-196°C), Kr (-78°C), CO_2 (-78 and 25°C) and Xe (0°C).[†] Since the saturation vapor pressures of CO_2 at 25°C and of Kr and Xe at the selected adsorption temperatures were considerably in excess of atmospheric, their isotherms were determined in a high pressure adsorption system. Walker and Kini concluded that adsorption of Xe at 0°C and of CO_2 at -78°C should usually measure essentially the total surface area of coals, whereas CO_2 adsorption at 25°C should always measure essentially the total surface area of coals.

The Polanyi-Dubinin (P-D) equation, given below, has been used by Marsh and Siemieniowska (1965) to calculate surface areas of coals from CO_2 adsorption measured at 0 and 20°C :

[†]Walker and Kini used the following values for the cross-sectional areas (A^2): N_2 (-196°C) 16.2, Kr (-78°C) 21.7, CO_2 (-78°C) 20.7, Xe (0°C) 22.0 and CO_2 (25°C) 25.3.

$$\log V = \log V_0 - \frac{0.434 BT^2}{\beta^2} \left[\log \left(\frac{p_s}{p} \right) \right]^2 \quad (16)$$

where V = amount adsorbed at equilibrium pressure p

V_0 = micropore capacity

p_s = saturation vapor pressure of the adsorbate

β = affinity coefficient of the adsorbate relative to N_2 or benzene

B = a constant which is a measure of the micropore size

The intercept of the plot between $\log V$ and $[\log (p_s/p)]^2$ gives the micropore capacity V_0 which, when multiplied by the cross-sectional area of an adsorbed molecule, gives the micropore surface area. The P-D equation is usually applicable over the relative vapor pressure range of 1×10^{-5} to 0.2. The unique feature of the P-D equation is that it permits the evaluation of micropore capacity and, hence, surface area from adsorption data obtained below 1 atm pressure in a conventional volumetric apparatus.

Walker and Patel (1970) found excellent agreement between surface areas of a number of coals calculated by the BET and P-D equations from adsorption of CO_2 measured at $25^\circ C$ in two different pressure ranges. The micropore surface area (from the P-D equation) approximates closely the total surface area (from BET equation) in coals because of the large percentage of microporosity existing in coals (Gan et al., 1972).

The use of CO_2 for surface area measurements has been objected to on the grounds that its adsorption may be influenced by the quadrupole moment of the CO_2 molecule. It has been reported that the amount of CO_2 adsorbed per unit surface area (as measured from N_2 adsorption) increased with increase in the concentration of hydroxyl groups present on the carbon surface (Deitz et al., 1964). However, Ramsey (1965) irradiated an anthracite in air with γ -rays and found that although the irradiation increased the oxygen content by about 40%, the CO_2 area increased by only 5%. He concluded

that CO_2 adsorption can be used for surface area measurements of not only anthracites but also oxygenated coals. The fact that surface areas measured by Xe at 0°C are in reasonably good agreement with those measured by CO_2 at -78 and 25°C (Walker and Kini, 1965) strongly suggests the absence of any significant chemical interaction of the CO_2 molecule with oxygen functional groups present on coal surfaces.

Walker et al. (1968) have suggested that when reporting surface areas of coals, the adsorbate, adsorption temperature, equilibrium time, coal particle size and the cross-sectional area of the adsorbate used should be reported.

The concept of surface area of microporous adsorbents has often been criticized. For one thing, one cannot assign a definite value for the cross-sectional area of the adsorbate molecule, as discussed earlier. Further, in the case of microporous adsorbents, Dubinin (1966) disagrees with the concept of layer-by-layer filling of pores, as is envisaged in the BET equation (Brunauer et al., 1938). Dubinin has suggested that due to an adsorption force field in the entire volume of micropores, adsorption results in volume filling of the pores. According to Spencer and Bond (1966), surface areas of coals should not be reported. Instead, they have suggested reporting monolayer volumes or total volumes of sorbate uptake.

2. Experimental Methods for Adsorption Measurements

There are three general methods used for adsorption measurements, namely (a) volumetric, (b) gravimetric and (c) thermal conductivity methods.

a. Volumetric Method. This is the most commonly used method for adsorption measurements and is most suited for adsorbates having boiling points below room temperature. In this method, the pressure, volume and temperature of a given quantity of an adsorbate are measured and the number

of moles present is calculated. The adsorbate is then brought into contact with the adsorbent. After equilibrium is attained with respect to pressure, the number of moles in the gas phase is again calculated. The difference between the number of moles present initially and after contacting with the adsorbent represents the amount adsorbed.

Although many types of volumetric apparatus have been described in the literature, they all have essentially the same basic features. A typical volumetric apparatus is shown in Figure 4. An adsorbent bulb is connected by capillary tubing to a mercury manometer and a gas burette, which consists of five bulbs of progressively decreasing volumes. The bulbs are separated from each other by short capillary sections which have reference marks etched on them. The volume of each bulb between successive reference marks is calibrated with mercury. The gas burette is surrounded by a constant-temperature water jacket. The left-hand limb of the manometer, with the exception of the bottom 10 cm length and the connecting tubes, are capillary tubings. Before taking a pressure reading, the mercury meniscus in the left-hand limb is brought to a fixed mark, X. A meter scale attached to the manometer is used to record the pressure.

A known weight of the sample is taken into the sample holder. The weight of the sample to be used varies with the nature of the adsorbate gas and the adsorption temperature used. For adsorption of N_2 at $-196^\circ C$, the weight of the sample should be enough to represent a total surface area of 2 m^2 (Emmett, 1941). When surface area of the adsorbent is low, a large sample holder must be used. This increases the dead space. As a result, there is a loss of precision.

There is some controversy about the temperature at which a coal sample should be dried before adsorption measurements. The situation is more complex

Figure 4

VOLUMETRIC APPARATUS FOR MEASURING GAS ADSORPTION

with lignites and brown coals. In our laboratory, the practice is to outgas a coal sample at 110°C overnight (about 16 hr) under a vacuum of 10^{-5} torr. It has been reported (Franklin, 1949; Malherbe, 1951) that under these conditions the coal surfaces are freed from adsorbed water and other gases.

Surface areas of chars can be markedly affected by the heat treatment/outgassing conditions used prior to adsorption measurements. Kamishita et al. (1977) have reported that if the chars prepared at high temperatures are stored in an air atmosphere for an extended period of time before measuring their surface areas, then the heat treatment/outgassing conditions prior to adsorption measurements have a marked effect on monolayer capacity. Kamishita (1976) found that the N_2 surface areas of a 1000°C lignite char measured following outgassing for 8 hr (i) at 105°C, (ii) at 500°C, and (iii) at 950°C were 59, 179 and 553 m^2/gm , respectively. Kamishita et al. (1977) have suggested that freshly prepared chars can chemisorb oxygen on exposure to air at room temperature. The chars, like coals, are aperture-cavity type materials. The chemisorption of oxygen can reduce the aperture size to an extent that N_2 molecules will not enter through them into the cavities in which a large surface area is located. Kamishita et al. suggested that in order to get the 'true' surface area of a char either the area be measured soon after its preparation or the char, prior to adsorption measurements, be heated in an inert atmosphere (or outgassed) at a temperature close to but lower than the temperature seen by the char during its preparation.

Following outgassing/heat treatment at the desired temperature, the sample is cooled to room temperature in the absence of oxygen. The sample holder is then surrounded by a constant temperature jacket maintained at the desired adsorption temperature. Before adsorption measurements can be made,

it is essential to calibrate the volume of the system enclosed by stopcocks S_1 and S_3 , the uppermost etch on the burette and mercury manometer up to mark X. It is done in the following manner. With stopcocks S_1 and S_3 closed and the mercury level in the gas burette adjusted to coincide with the uppermost etch, helium is introduced into the system. After adjusting the mercury level in the left limb of the manometer to mark X, the gas pressure is noted. Subsequently for the same helium dosage, gas pressures are measured with mercury levels adjusted to each burette etch mark. Since the volumes of the burette bulbs are known, it is easy to calculate the 'unknown' volume by the application of simple gas laws. This volume is referred to as V_1 in the text. The next step involves the measurement of the free volume (known as dead space) of the sample bulb containing the sample up to stopcock S_1 . This is determined by expanding the same dose of helium, which is previously used for determining V_1 , into the sample holder. After equilibrium is established, the pressure is noted. Additional pressure readings are taken after successively filling or emptying each burette bulb to the appropriate etch mark. Dead space is determined from the equation

$$p(V + V_1 + V_2) = k \quad (17)$$

where V is the sum of the volumes of the burette bulbs which are not filled with mercury at pressure p , V_2 is the dead space and k is a constant.

After the dead space determination, the constant temperature jacket surrounding the sample bulb is removed. Helium is then pumped out of the system, stopcock S_1 is closed and the constant temperature jacket replaced. The mercury level is brought to the lowest etch mark in the gas burette. After admitting a quantity of the adsorbate, stopcock S_3 is closed and gas pressure is measured. The gas is then brought into contact with the sample by opening stopcock S_1 . When equilibrium is attained, pressure is noted.

As discussed earlier, approach to true equilibrium during adsorption on coals at lower temperatures is very slow (due to activated diffusion). Therefore, the so-called 'equilibrium' pressure is noted after an arbitrary fixed time. The amount of gas adsorbed is calculated from the pressure and volume values before and after the occurrence of adsorption. Additional points on the isotherm (up to a maximum of five points) can be obtained by raising the mercury level in the gas burette to the successively higher etch marks. More data points, if needed, can be obtained by introducing more adsorbate gas to the system.

The volumetric apparatus described above can be used for adsorbates for which a relative pressure of 0.35 (which represents the upper limit of relative pressure up to which the BET equation is usually applicable) represents an absolute pressure less than 1 atm. If, however, the absolute pressure is greater than 1 atm, a high pressure adsorption system must be used. A high pressure volumetric apparatus has been used by Nandi and Walker (1970, 1975).

b. Gravimetric Method. This method involves measurements of weight changes during adsorption as a function of the adsorbate pressure. The method is useful when the adsorbate has a low saturation vapor pressure, such as water and many organics, and when adsorption measurements are made near room temperature. Perusal of the literature shows that not much work has been reported on determining surface areas of coals from adsorption of water or organics. There are several reasons for this. First, adsorbates with polar groups, such as water and methanol, interact chemically with the oxygen functional groups present on carbon surfaces (Puri, 1970). Secondly, coals behave as molecular sieve materials (Walker et al., 1966). As a result, surface area is a function of the molecular size of the adsorbate. Thirdly, coals swell on adsorption of organics. Therefore, unless the adsorbate

molecules are excluded from some of the ultrafine pores due to molecular sieving, the areas obtained will be higher than the true areas of coals.

Since water adsorption on coals can be useful in elaborating certain aspects of coal structure (Mahajan and Walker, 1971), we will describe the gravimetric technique for measuring water adsorption isotherms. However, this technique can be used in the case of organics as well. Mahajan and Walker measured the extent of water adsorption with a helical quartz spring having a capacity of 500 mg. The spring was calibrated by adding increasing amounts of weights to a bucket suspended from the spring and measuring the spring extension with a cathetometer. About 0.25 gm coal was held in a quartz bucket (an aluminum bucket can also be used). The bucket was suspended from a 15 cm long Pyrex hook, which in turn was suspended from the quartz spring hook. Before making an adsorption run, the coal sample was outgassed to 10^{-6} torr at 110°C for 8 hr. The sample was then surrounded by a jacket through which water at the desired adsorption temperature was continuously circulated. The desired vapor pressure of water was generated by immersing a bulb of water in a Forma temperature bath containing a water-antifreeze mixture. The bath temperature could be controlled to $\pm 0.1^{\circ}\text{C}$. Since the Forma unit did not cool down -20°C , lower temperatures down to -40°C were obtained by using suitable mixtures of ethanol and water, cooled by liquid N_2 . An arbitrary adsorption time of 90 min was allowed for each point on the isotherm.

c. Thermal Conductivity Method. This method, developed by Nelson and Eggertsen (1958), involves measurement of changes in thermal conductivity of a He-N_2 mixture due to adsorption or desorption. The main advantages of this method over the conventional volumetric and gravimetric methods are speed and simplicity and avoidance of a high vacuum system. The sample is taken in a U-tube. It is first degassed by heating in a flowing stream

of helium and is then cooled to room temperature. A mixture of known composition of helium and N_2 is passed through the 'reference' arm of the thermal conductivity cell. The mixture is then passed through the sample and subsequently through the 'measuring' arm of the thermal conductivity cell. When a steady state condition is attained, that is when the gas composition is the same throughout the system (as indicated by a constant base line on the strip chart), the sample tube is surrounded by a liquid N_2 bath. Adsorption occurs and as a result the composition and, hence, the thermal conductivity of the gaseous mixture changes. Adsorption is indicated on a strip chart by a peak. The recorder pen returns to the baseline when steady state condition is again established. The liquid N_2 bath is then removed. As the sample tube warms up, desorption of N_2 occurs and a peak equal in area but on the opposite side to the adsorption peak is obtained. Either the adsorption or desorption peak may be used to calculate the amount of N_2 adsorbed.[†] Calibration of the system, that is of peak area, is carried out by injecting a known amount of N_2 to the He- N_2 mixture or by comparing the peak area obtained with a sample of known surface area.

Nelsen and Eggertsen (1958) measured N_2 adsorption in the partial pressure range of 0.05-0.3. The adsorbents investigated by them had surface areas in the range 3-500 m^2/gm . The areas obtained by the thermal conductivity method agreed within a few percent with those calculated from the isotherms obtained volumetrically. Haley (1963), who measured surface areas

[†]Nelsen and Eggertsen (1958) preferred to use the desorption peaks because they were relatively free of 'tailing' effects. Unless the areas of the adsorption and desorption peaks are equal, Kantro et al. (1967) caution that the use of the desorption peak may lead to incorrect results due to occurrence of hysteresis in the BET range.

by the thermal conductivity method, found a variation of about $\pm 2.5\%$ in the surface area range of 40-1250 m²/gm.

Commercial versions of the thermal conductivity apparatus have been produced. Although the method has been used for measurement of N₂ areas (-196°C), other adsorbate-diluent mixtures and adsorption temperatures may also be used. For instance, Thomas et al. (1966) have measured surface areas of coals from the adsorption of CO₂ at -78°C from a He-CO₂ mixture.

Cahen and Marechal (1963) have drawn attention to the fact that when the apparatus is connected to the gas reservoir by polyvinyl or rubber tubing, water present in the atmosphere diffuses through these tubes into the gas stream. As a result, when the sample is cooled following the degassing step, water is readsorbed on the adsorbent surface. Therefore, Cahen and Marechal have suggested the use of the copper tubing.

IV. PORE SIZE DISTRIBUTION

A. Mercury Porosimetry

In principle, pore size distributions can be determined by forcing mercury into coals and chars at increasing pressures and measuring the volume of mercury penetration as a function of applied pressure p . The value of radius, r , of the pore is calculated from equation (3). The pore volume-distribution curve is obtained by plotting the incremental volume over the incremental diameter ($\Delta V/\Delta d$) against $\bar{d}$, the average diameter.

Commercial mercury porosimeters capable of operation up to 60,000 psi are available. At this pressure, pores of 18A radius should be filled with mercury. However, pore size distributions calculated from mercury porosimetry data obtained at higher pressures may be faulty because of the possibility of particle breakdown and/or the opening up of closed pores. Whether these

possibilities occur can be ascertained by making successive mercury penetration measurements on the sample and/or measuring helium density on the sample before and after the mercury penetration measurement. After a mercury penetration measurement, all mercury should be removed from the sample by distillation under reduced pressure.

It should be emphasized that the physical significance of mercury porosimetry data needs some clarification. For calculating r from equation (3), it is tacitly assumed that the pores are cylindrically shaped. However, coals and chars are aperture-cavity type materials (Walker et al., 1966). When mercury is forced into such pores, the effective pressure p and the pore radius r for each stage of mercury penetration are determined by the aperture size, whereas the volume of mercury forced in the pores is determined by the volume of the cavity.

Other uncertainties in this method are the values of surface tension and angle of contact of mercury in small pores. Guggenheim (1940) has reported that surface tension becomes independent of pore capillary radius only when the latter exceeds 500A. Scholten (1967) has suggested that for carbons small amounts of adsorbed water or other contaminants may influence the value of contact angle considerably. He has recommended a thorough degassing of samples at temperatures of 100°C and above.

B. Capillary Condensation of Nitrogen

Gan et al. (1972) found that up to a relative pressure of 0.93, N_2 adsorption isotherms on coals varying in rank from anthracite to lignite were of type II or IV, according to the classification of Brunauer et al. (1940). Such curves are amenable to the calculation of pore size distributions. The value of radius r corresponding to a given point on the isotherm,

that is a given value of relative pressure, can be calculated from the Kelvin equation:

$$\ln \left(\frac{p}{p_0} \right) = - \frac{2V \gamma \cos \theta}{rRT} \quad (18)$$

where p_0 is the saturation vapor pressure, γ is the surface tension, p is the equilibrium pressure, V is the molar volume of the liquid adsorbate and θ is the contact angle between the liquid and the pore wall. It is generally assumed that θ is zero, that is, the liquid wets the pore walls.

Before capillary condensation occurs in a given pore, one or more adsorbed layers are formed on the pore walls. The thickness of this layer is taken into account in the calculation of pore size distribution. The Kelvin radius of capillary condensation is assumed to be the pore radius minus the thickness of the adsorbed film. The thickness of the adsorbed film is evaluated from the adsorption isotherm of N_2 on a non-porous adsorbent. It is assumed that at a given relative pressure thickness of the multilayer formed on the non-porous solid is the same as that on the walls of the porous solid. Monolayer capacity, V_m , for the non-porous solid is calculated from the BET equation. The extent of adsorption V at any relative pressure is converted into thickness of the film (t) by the relationship $t = (V/V_m)\sigma$ or $t = n\sigma$, where σ is the average thickness of a single layer of adsorbed molecules and n is the number of molecular layers formed; σ is usually taken as 3.5Å (Gregg and Sing, 1967). Knowing the value of t , the volume of pores and surface area of the pore walls can be evaluated for radii between r and $r + \Delta r$.

There is a controversy regarding the use of the adsorption or desorption branch of the N_2 isotherms for calculating pore size distribution. Most workers have used the desorption branch for their analyses. A good agreement between the calculated cumulative pore wall area and the BET area and also

between the calculated and experimental cumulative pore volume should be the deciding factor in choosing the adsorption or desorption branch. Cranston and Inkley (1957) analyzed both the adsorption and desorption branches for a wide variety of materials. In the majority of cases, they found good agreement when using the adsorption branch. Gan et al. (1972) calculated pore size distributions of coals in the diameter range 12-300A from the adsorption branch using the Cranston and Inkley method.

Cranston and Inkley (1957) derived the following equation for calculating pore size distribution:

$$v_r \delta r = \frac{(r - t_r)^2}{r^2} V_r \delta r + \delta t \int_{r + \delta r}^{\infty} \frac{(r - t_r)}{r} \frac{2V_r}{r} dr \quad (19)$$

where $v_r \delta r$ is the total volume of nitrogen adsorbed (as liquid) and $V_r \delta r$ is the total volume of pores in the range δr considered. The first term on the right-hand side represents the volume of nitrogen which has filled the pores whose critical pressures have been reached, while the second term represents the volume which has contributed to the increasing thickness of the adsorbed layer on the walls of larger pores.

Integrating equation (19) with limits r_1 and r_2 (corresponding to p_1 and p_2 , respectively) and solving for V_{12} assuming V_r to be constant over the range r_1 and r_2 the working equation becomes

$$V_{12} = R_{12} \left(v_{12} - k_{12} \int_{r_2}^{\infty} \frac{r - t_{12}}{2r^2} V_r dr \right) \quad (20)$$

where V_{12} = volume of pores having radii between r_1 and r_2 .

v_{12} = total volume of nitrogen adsorbed during this step

$$R_{12} = \frac{r_2 - r_1}{\int_{r_1}^{r_2} \left[(r - t_1)^2 / r^2 \right] dr}$$

$$k_{12} = 4 (t_2 - t_1)$$

$$t_{12} = \frac{1}{2} (t_1 + t_2)$$

For computational purposes, the integral term is replaced by a summation term for all increments of diameters instead of radii. Thus, equation (20) becomes

$$V_{12} = R_{12} \left(v_{12} - k_{12} \sum_{d_2}^{d_{\max}} \frac{d - 2t_{12}}{d^2} V_d \Delta d \right) \quad (21)$$

where Δd is an increment of pore diameter, $V_d \Delta d$ represents the volume of pores having diameters between $(d - 1/2\Delta d)$ and $(d + 1/2\Delta d)$, and $d_{\max}$ is the diameter of the largest pore. The established values for R_{12} , k_{12} and the function $(d - 2t)/d^2$ in each standard increment of the pore diameter are reported elsewhere (Cranston and Inkley, 1957).

V. SELECTED EXPERIMENTAL RESULTS

A. Helium and Mercury Densities of Coals

Gan et al. (1972) measured helium and mercury densities of coals (40 x 70 mesh) varying in rank from anthracite to lignite. The variation of helium density (dmmf) with carbon content (daf) is shown in Figure 5. The curve has a shallow minimum at about 81% carbon and rises sharply as 90% carbon is approached. Franklin (1949) and Fujii and Tsuboi (1967) observed similar trends for British and Japanese coals, respectively, although the minimum in each case occurred at somewhat higher carbon contents than that observed for American coals.

Figure 5

VARIATION OF HELIUM DENSITY OF COALS WITH CARBON CONTENT
From Gan et al. (1972)

A plot of the variation of mercury density with carbon content of coals has a shape similar to that for helium density (Gan et al., 1972).

B. Surface Areas of Coals

1. N₂ and CO₂ Areas

Gan et al. (1972) determined N₂(-196°C) and CO₂ (25°C) areas of 40 x 70 mesh fractions of a number of coals of different rank. A plot of these areas, expressed on a dry-mineral-matter-containing basis, against carbon content (daf) is given in Figure 6. Also included in this plot are the N₂ areas of four samples taken from the data of Nandi and Walker (1971). In general, coals with N₂ areas greater than 10 m²/gm fall in the carbon content range of about 76 to 82%. In this range, also, fall some coals (two out of a total of fourteen) with negligible N₂ area (< 1 m²/gm). Surface areas of most coals on both sides of this carbon content range, that is 76-82%, are less than 1 m²/gm, exceptions being the anthracites which have surface areas of 5 to 8 m²/gm.

The CO₂ areas of the anthracites are high. There is a general decrease in area with decrease in carbon content to about 83%. The area remains more or less constant down to about 76% carbon and increases thereafter. The CO₂ areas fall within a band rather than on a line; the differences in the areas of coals with essentially the same carbon content being as great as 80 m²/gm. In general, coals with higher N₂ areas have lower CO₂ areas.

Surface areas of lignites may be in significant error. Gan et al. (1972) heated the samples under vacuum at about 130°C prior to surface area measurements. It has been reported that lignites once dried very thoroughly do not adsorb as much water as freshly mined samples (Gauger, 1945). The gel-like structure of lignites may be irreversibly altered upon drying; and as a result, the area is expected to change.

Figure 6

VARIATION OF N₂ AND CO₂ SURFACE AREAS OF COALS WITH CARBON CONTENT

From Gan et al. (1972)

○ N₂ ■ CO₂ • N₂ (From Nandi and Walker, 1971)

Nitrogen surface areas of mineral matter obtained from the low temperature ashing of coals can be as high as $10 \text{ m}^2/\text{gm}$ (O'Gorman, 1971). Since surface area of whole coals in some cases is less than $1 \text{ m}^2/\text{gm}$, it has been suggested (Gan et al., 1972) that the finely divided mineral particles distributed in the coal organic matrix are not accessible to N_2 at -196°C . Clearly the reported CO_2 areas would not be too much affected by the surface area contributed by mineral matter, since total area in each case is greater than $100 \text{ m}^2/\text{gm}$ (Figure 6).

2. Surface Area from Water Adsorption Isotherms

Mahajan and Walker (1971) determined surface areas of six 200 x 325 mesh coals (varying in carbon contents (daf) from 72.7 to 95.2%) from water adsorption isotherms measured at 20°C . It was found that in each case the water area was lower than the CO_2 area. The disparity in the areas was attributed to the difference in the nature of adsorptive forces involved during adsorption of water and CO_2 molecules. A carbon surface devoid of volatile matter and inorganic impurities is essentially hydrophobic in nature (Walker and Janov, 1968), indicating that the role of dispersive forces involved in the adsorption of water molecules is minimal. Therefore, the magnitude of the carbon surface plays a secondary role in water adsorption. However, adsorption of CO_2 on a clear carbon surface is determined by dispersive forces alone.

Mahajan and Walker (1971) suggested that besides adsorption on inorganic impurities, sorption of water on coals, which always contain different amounts and types of oxygen functional groups (van Krevelen, 1961), involves adsorption at the 'primary' specific oxygen sites. Adsorbed water molecules then act as 'secondary' sites for the adsorption of additional water, thus leading to cluster formation, the growth of clusters increasing with

increasing surface coverage. Iyenger and Lahiri (1957) have suggested that the application of the BET equation to moisture sorption isotherms on coals gives a measure of specific adsorption sites on the coal surface, as determined by oxygen functional groups, rather than the amount of the adsorbate needed for monolayer formation.

C. Distribution of Total Open Pore Volume in Coals

Gan et al. (1972) estimated the pore volumes contained in the following pore diameter ranges for a number of coals (40 x 70 mesh) varying widely in rank:

(i) total open pore volume V_T for pores accessible to helium, as estimated from the helium and mercury densities.

(ii) pore volume V_1 contained in pores greater than 300A in diameter, as estimated from mercury porosimetry.

(iii) pore volume V_2 contained in pores in the diameter range 12-300A, as estimated from the adsorption branch of the N_2 isotherms.

(iv) pore volume V_3 contained in pores smaller in diameter than 12A, as estimated from $V_3 = V_T - (V_1 + V_2)$.

The pore volumes in different diameter ranges for the various coals are given in Table III. The proportion of V_3 is significant for all coals. Its value is a maximum for the anthracite sample (PSOC-80) and is a minimum for the lignite sample (PSOC-89). These results show that essentially all coals, irrespective of their rank, show molecular sieve properties. From the results given in Table III, it may be concluded that: (i) in coals with carbon contents less than about 75%, porosity is primarily due to the presence of macropores, (ii) in coals with carbon contents in the range 75-84%, porosity is predominantly due to the presence of macro and transitional pores, and (iii) in coals varying in carbon content from 85 to 91%, microporosity predominates.

TABLE III

Gross Open Pore Distributions in Coals (from Gan et al., 1972)

Sample	Rank	C, %(daf)	V _T (cm ³ /gm)	V ₁ (cm ³ /gm)	V ₂ (cm ³ /gm)	V ₃ (cm ³ /gm)	V ₃ (%)	V ₂ (%)	V ₁ (%)
PSOC-80	Anthracite	90.8	0.076	0.009	0.010	0.057	75.0	13.1	11.9
PSOC-127	LV Bit.	89.5	0.052	0.014	0.000	0.038	73.0	nil	27.0
PSOC-135	MV Bit.	88.3	0.042	0.016	0.000	0.026	61.9	nil	38.1
PSOC-4	HVA Bit.	83.8	0.033	0.017	0.000	0.016	48.5	nil	51.5
PSOC-105A	HVB Bit.	81.3	0.144	0.036	0.065	0.043	29.9	45.1	25.0
Rand	HVC Bit.	79.9	0.083	0.017	0.027	0.039	47.0	32.5	20.5
PSOC-26	HVC Bit.	77.2	0.158	0.031	0.061	0.066	41.8	38.6	19.6
PSOC-197	HVB Bit.	76.5	0.105	0.022	0.013	0.070	66.7	12.4	20.9
PSOC-190	HVC Bit.	75.5	0.232	0.040	0.122	0.070	30.2	52.6	17.2
PSOC-141	Lignite	71.7	0.114	0.088	0.004	0.022	19.3	3.5	77.2
PSOC-87	Lignite	71.2	0.105	0.062	0.000	0.043	40.9	nil	59.1
PSOC-89	Lignite	63.3	0.073	0.064	0.000	0.009	12.3	nil	87.7

D. Effect of Heat Treatment of Coal on Properties

When coals are thermally heated, volatile matter is released from the coal skeleton framework creating additional porosity and surface area. Some of the additional porosity is due to the opening up of previously closed porosity and the remainder is due to the enlargement of pores which were previously open. Concurrent with the loss of volatile matter, some crosslinks are broken which permit the aromatic regions to better align and result in a loss of open porosity and surface area. At lower temperatures, the loss of volatile matter predominates. As a result, there is an overall opening up of the structure. But as the temperature is further raised and volatile release becomes small, breakage of crosslinks and crystallite alignment become significant. Thus, it is to be expected that over a certain temperature range the surface area and open pore volume will go through a maximum.

Toda (1973) had studied changes in the helium, methanol and n-hexane densities of twelve coals (28 x 60 mesh) upon heat treatment (HT) to a series of temperatures up to 1200°C. The coals investigated had carbon contents (daf) in the 77.8-89.7% range. The densities were found to change slightly upon HT up to 350°C. Toda concluded that apart from dehydration no significant structural changes occurred up to 350°C. The densities increased sharply for coals heated above 350°C indicating opening up of porosity. For the lower rank coals, the helium and methanol densities showed maxima at about 800 and 900°C, respectively. No such maxima were observed for the higher rank coals, that is, for such coals the helium and methanol densities continued to increase up to the maximum HTT of 1200°C. These results reflect differences in the thermal stability of open porosity in coals of different rank when they are heated to higher temperatures because a decrease

in density can be taken to indicate the conversion of open porosity to closed porosity.

Toda also found that for all the coals heated up to about 700-800°C, the densities varied in the order: methanol > helium > n-hexane. The difference between methanol and n-hexane densities invariably showed a maximum corresponding to a HTT of about 600°C. The difference between the two densities became essentially zero for all the coals heat treated up to 1200°C. Since the apparent density of a microporous solid in a given fluid is dependent upon the accessibility of the fluid to the internal pore structure, the results of Toda (1973) show that coals can be converted into molecular sieve materials by heat treatment, the character and extent of molecular sieving depending upon the rank of the starting coal and its HTT.

Changes in surface areas of coals occurring during heat treatment have been studied extensively. In general, surface area increases with increasing HTT, passes through a maximum and decreases thereafter. The temperature at which the maximum occurs depends upon the nature of the starting coal. For instance, the N_2 and CO_2 areas of anthracites reach maxima at about 700°C and decrease sharply at 900°C (Nandi et al., 1964). For an HVA bituminous coal, the N_2 area remains essentially constant ($< 1 \text{ m}^2/\text{gm}$) up to 900°C, whereas the CO_2 area reaches a maximum at about 600°C (Jenkins et al., 1973). The N_2 surface areas of HVB bituminous and lignite coals increase by factors of about 15 and 30, respectively, upon HT to 600°C; at higher temperatures the N_2 areas decrease sharply (Jenkins et al., 1973). In both cases, the CO_2 areas increase by a factor of about three upon heating to 600°C before starting to decrease, although the areas for the 900°C heat treated samples in each case are almost twice the areas of the starting coals. For brown coals carbonized up to 400°C, surface area accessible to

N_2 is negligible (Siemieniewska, 1968). Above 500°C and especially in the $700\text{--}900^\circ\text{C}$ range, the CO_2 and N_2 areas are almost equal.

E. Effect of Oxidation and Carbon Deposition on Properties of Chars

In addition to open porosity, chars also contain some closed porosity, that is, some of the pores are inaccessible to helium. Upon gasification, two important phenomenon occur: (i) enlarging of pores that were open in the unreacted char, and (ii) opening of closed porosity. Since the total number of pores is increased as well as their average radius, specific pore volume and specific surface area increase with increase in the extent of gasification. However, at some point, depending upon the pore structure of the char, walls between existing pores are gasified away. As a result, the total number of open pores commences to decrease. This leads to a continuous increase in specific pore volume, whereas specific surface goes through a maximum as gasification proceeds.

Recently, Kamishita et al. (1977) have shown that the process opposite to gasification, that is carbon deposition (CD), decreases the specific surface area and specific pore volume of a char (Table IV). CD was carried out by cracking of methane at 855°C on two char samples prepared by the heat treatment of N_2 of a lignite coal (40 x 100 mesh) at 855 and 1000°C . The results listed in Table IV show unmistakably that the chars are aperture-cavity type materials. It is seen that deposition of 2.6%, by weight, carbon leads to a reduction in open porosity from 35.6 to 23.8%. It is obvious that some apertures are being reduced in size by CD to the extent that helium no longer can pass through at room temperature. Thus, the accessibility of helium to the larger cavities existing behind the apertures has been removed. This leads to a reduction in porosity considerably in excess of the total volume of carbon which has been deposited, if it is assumed that deposited carbon has the same density as the char itself.

TABLE IV

Area, Density and Porosity Data for Various Char Samples Following Carbon Deposition

(from Kamishita *et al.*, 1977)

Sample	Surface Area		Helium Density gm/cm ³ (daf)	Mercury Density gm/cm ³ (daf)	Open Pore Volume cm ³ /gm(daf)	Open Porosity (%)	
	$\frac{\text{m}^2/\text{gm}(\text{daf})}{\text{N}_2}$	CO_2					
	CD %(daf)						
855°C Char	0	241	960	2.05	1.32	0.270	35.6
	1.7	76	771	1.94	1.37	0.214	29.3
	2.6	33	249	1.80	1.37	0.174	23.8
1000°C Char	0	130	681	2.06	1.36	0.250	34.0
	3.6	31	457	1.98	1.35	0.236	31.9

REFERENCES

- Ahuja, L.D., Nandi, S.P., Kini, K.A., and Lahiri, A. (1961). J. Sci. Ind. Research (India) 20B, 295-296.
- Anderson, R.B., Bayer, J., and Hofer, L.J.E. (1965). Fuel 44, 443-452.
- Bond, R.L., and Spencer, D.H.T. (1957). Conf. on Industrial Carbon and Graphite, Soc. Chem. Ind. London, pp. 231-251.
- Brunauer, S., Deming, L.S., Deming, W.E., and Teller, E. (1940). J. Am. Chem. Soc. 62, 1723-1732.
- _____, Emmett, P.H., and Teller, E. (1938). J. Am. Chem. Soc. 60, 309-319.
- Cahen, R.M., and Marechal, J. (1962). Anal. Chem. 35, 259-260.
- Cranston, R.W., and Inkley, F.A. (1957). In "Adances in Catalysis," vol. IX, pp. 143-154, Academic Press, New York.
- Deitz, V.R., Carpenter, F.G., and Arnold, R.B. (1964). Carbon 1, 245-254.
- Dubin, M.M. (1966). In "Chemistry and Physics of Carbon" (P.L. Walker, Jr., ed.), vol. II, pp. 51-120, Marcel Dekker, New York.
- Emmett, P.H. (1941). ASTM Symp. on New Methods for Particle Size Determination in the Subsieve Range, pp. 95-105.
- _____, and Brunauer, S. (1937). J. Am. Chem. Soc. 59, 1553-1564.
- Ergun, S. (1951). Anal. Chem. 23, 151-156.
- _____, and Orning, A.A. (1949). Ind. Eng. Chem. 41, 1179-1184.
- Ettinger, I.L., and Zhupakhina, E.S. (1960). Fuel 39, 387-392.
- Franklin, R.E. (1949). Trans. Faraday Soc. 45, 274-286.
- Fujii, S., and Tsuboi, H. (1967). Fuel 46, 361-366.
- Gan, H., Nandi, S.P., and Walker, P.L., Jr. (1972). Fuel 51, 272-277.
- Gauger, A.W. (1945). In "Chemistry of Coal Utilization" (H.H. Lowry, ed.), vol. I, pp. 600-626, John Wiley, New York, and Chapman and Hall, London.
- Greenhalgh, E., Miles, B.J., Redman, E., and Sharman, S.A. (1966). Second Conf. on Industrial Carbon and Graphite, Soc. Chem. Ind. London, pp. 405-417.
- Gregg, S.J., and Pope, M.I. (1959). Fuel 38, 501-505.

- Gregg, S.J., and Sing, K.S.W. (1967). "Adsorption, Surface Area and Porosity," Academic Press, London and New York.
- Guggenheim, E.A. (1940). Trans. Faraday Soc. 36, 397-412.
- Haley, A.J. (1963). J. Appl. Chem. 13, 392-399.
- Hirsch, P.B. (1954). Proc. Roy. Soc. (London) A226, 143-169.
- Howard, H.E., and Hulett, G.A. (1924). J. Phy. Chem. 28, 1082-1095.
- Iyenger, M.S., and Lahiri, A. (1957). Fuel 36, 286-297.
- Jenkins, R.G., Nandi, S.P., and Walker, P.L., Jr. (1973). Fuel 52, 288-293.
- Kamishita, M. (1976). M.S. Thesis, The Pennsylvania State University.
- _____, Mahajan, O.P., and Walker, P.L., Jr. (1977). Fuel (in press).
- Kantro, D.L., Brunauer, S., and Copeland, L.E. (1967). In "The Solid-Gas Interface" (E.A. Flood, ed.), vol. I, pp. 413-429, Marcel Dekker, New York.
- Kini, K.A. (1963). Fuel 42, 103-104
- _____ (1964). Fuel 43, 173-180.
- _____, and Stacy, W.O. (1963). Carbon 1, 17-24.
- Kipling, J.J., Sherwood, J.N., Shooter, P.V., Thompson, N.R., and Young, R.N. (1966). Carbon 4, 5-11.
- Kotlensky, W.V., and Walker, P.L., Jr. (1960). Proc. Fourth Carbon Conf., pp. 423-442, Pergamon Press, London.
- Lamond, T.G., and Marsh, H. (1964). Carbon 1, 281-292.
- Maggs, F.A.P., Schwabe, P.H., and Williams, J.H. (1960). Nature, Lond. 186, 956-958.
- Mahajan, O.P., and Walker, P.L., Jr. (1969). J. Colloid Interface Sci. 29, 129-137.
- _____ (1971). Fuel 40, 308-317.
- Malherbe, P. (1951). Fuel 30, 97-109.
- Marsh, H. (1965). Fuel 44, 253-268.
- _____, and Siemieniowska, T. (1965). Fuel 44, 355-367.
- Nandi, S.P., Ramdass, V., and Walker, P.L., Jr. (1964). Carbon 2, 199-210.

Nandi, S.P., and Walker, P.L., Jr. (1970). Fuel 49, 309-323.

_____ (1971). Fuel 50, 345-366.

_____ (1975). Fuel 54, 81-86.

Nelsen, F.M., and Eggertsen, F.T. (1958). Anal. Chem. 30, 1387-1390.

Nelson, J.R. (1977). The Pennsylvania State University, unpublished results.

O'Gorman, J.V. (1971). Ph.D. Thesis, The Pennsylvania State University.

Puri, B.R. (1970). In "Chemistry and Physics of Carbon" (P.L. Walker, Jr, ed.), vol. II, pp. 191-282, Marcel Dekker, New York.

Ramsey, J.W. (1965). Fuel 44, 277-284.

Robert, L., and Brusset, H. (1965). Fuel 44, 309-316.

_____, and Pregermain, S. (1963). Fuel 42, 389-393.

Scholten, J.J.F. (1967). In "Porous Carbon Solids" (R.L. Bond, ed.), pp. 225-249, Academic Press, London and New York.

Siemieniewska, T. (1968). Koks, Smola, Gaz 13, 57-68, 231-237, 309-317.

Spencer, D.H.T. (1967). In "Porous Carbon Solids" (R.L. Bond, ed.), pp. 87-154, Academic Press, London and New York.

_____, and Bond, R.L. (1966). Advanc. Chem. Ser. No. 55, 724-728.

Thomas, T., Jr., Benson, G.S., and Hieftje, G.M. (September 1966). Preprint Div. Fuel Chem., 152 nd Natl. Meet. Amer. Chem. Soc., New York.

Toda, Y. (1972). Fuel 51, 108-112.

_____ (1973). Fuel 52, 99-104.

Tschambler, H., and de Ruiter, E. (1963). In "Chemistry of Coal Utilization" (H.H. Lowry, ed.), Suppl. vol., pp. 35-118, John Wiley, New York.

Vander Sommen, J., Zwietering, P., Eillebricht, B.J.M., and van Krevelen, D.W. (1955). Fuel 34, 444-448.

van Krevelen, D.W. (1961). "Coal," Elsevier, Amsterdam.

Walker, P.L., Jr., Austin, L.G., and Nandi, S.P. (1966). In "Chemistry and Physics of Carbon" (P.L. Walker, Jr., ed.), vol. II, pp. 257-371, Marcel Dekker, New York.

_____, Cariaso, O., and Patel, R.L. (1968). Fuel 47, 322-324.

- Walker, P.L., Jr., and Geller, I. (1956). Nature, Lond. 178, 1001.
- _____, and Janov, J. (1968). J. Colloid Interface Sci. 28, 449-458.
- _____, and Kini, K.A. (1965). Fuel 44, 453-459.
- _____, and Patel, R.L. (1970). Fuel 49, 91-94.
- Washburn, E.W. (1921). Proc. Natl. Acad. Sci. 7, 115-116.
- Youssef, A. (1976). The Pennsylvania State University, unpublished results.