PREPARATION AND PROPERTIES OF ACTIVATED CARBONS PREPARED FROM NITRIC ACID TREATMENT OF BITUMINOUS COAL

by

E. S. TOMEZKO
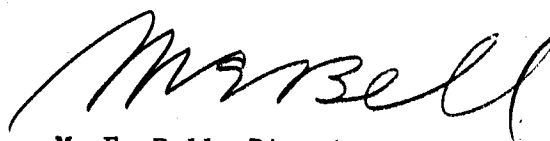
and

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STATEMENT OF TRANSMITTAL

Special Report SR-28 transmitted herewith has been prepared by the Coal Research Section of the Mineral Industries Experiment Station. Each of the Special Reports presents the results of a phase of one of the research projects supported by the Pennsylvania Coal Research Board or a technical discussion of related research. It is intended to present all of the important results of the Coal Board research in Special Reports, although some of the results may already have been presented in progress reports. The following is a list of Special Research Reports issued previously.

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SR-17	The Combustion of Dust Clouds: A Survey of the Literature	November 30, 1959
SR-18	The Ignitibility of Bituminous Coal	June 15, 1960
SR-19	Changes in Coal Sulfur During Carbonization	August 1, 1960
SR-20	The Radiation Chemistry of Coal in Various Atmospheres	September 12, 1960
SR-21	Reaction of Bituminous Coal with Concentrated Sulfuric Acid	October 1, 1960
SR-22	The Nature and Occurrence of Ash Forming Minerals in Anthracite	December 30, 1960

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SUMMATION OF RESULTS

The preparation and properties of low ash activated carbons from a Pennsylvania high volatile bituminous coal have been investigated. The conversion of raw coal to such carbon was carried out in three steps. These are (1) the oxidation of the raw coal to humic acids by air and nitric acid followed by separation of the mineral matter with solvent extraction of the acids, (2) the pyrolysis of the acids to chars at 230°C and 1 and 135 atmospheres nitrogen pressure, and (3) the steam activation of the chars at temperatures from 750° to 900°C.

In the preparation of the chars, the humic acids exhibited a marked exothermic decomposition phenomenon at about 230°C. Esterification of the hydroxyl groups and reduction of the nitro groups decreased this decomposition considerably, suggesting that nitro groups are chiefly responsible for this phenomenon with the possibility that the hydroxyl groups enhance the reaction.

The chars were in an expanded friable form, appearing porous and consisting of a mixture of agglomerated and non-agglomerated particles. Separation of the mixture by hand gave hard silvery-grey particles resembling a coke and soft friable particles with an apparent glazed surface. The yield of char was approximately 50% of the raw coal of which about 60% was in the agglomerated form. Increase of pyrolysis pressure from 1 to 135 nitrogen atmospheres increased both the yield of char and the agglomerated fraction, indicating that internal gas pressure is important in the formation of this fraction.

Steam treatment of the chars gave activated carbons with yields

ranging from approximately 20 to 30% for the agglomerated fraction and from 11 to 16% for the non-agglomerated fraction based on the raw coal. Evaluation of the properties of these carbons for surface area, bulk density, pore volume, mercury density, and iodine and methylene blue adsorption has shown that the carbons have an essentially micropore structure. Based on their data, the properties of these carbons compare favorably for the most part with those of the commercial carbons examined in this investigation.

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I. Introduction and Statement of the Problem:

Activated carbons are of tremendous commercial importance because of their wide applicability in industrial processes. Active carbons are used for the purification of gases, decolorization of carbonated beverages, sugars, foodstuffs, chemicals, and pharmaceuticals.

Hassler (21) lists thirty-three starting materials from which an activated carbon can be produced; these range from bagasse to wood. There are many patents registered for the preparation of activated carbons; but, for the most part, the patents are slight modifications or refinements of already existing processes. The initial step in the production of an activated carbon is the carbonization of the raw material. The carbonization is carried out usually between the temperatures 700° to 1000°C. The carbonized char is then activated by a variety of chemical treatments carried out at elevated temperatures, 750° to 1050°C.

The carbonization process produces various changes which are characteristic of the starting material. Cocoanut shells remain rigid and retain some semblance of the original platn structure. On the other hand, molasses forms a plastic mass that swells due to the evolution of gases and the char product resembles a solid foam. It is the escaping gases which aid in the development of the porosity in the carbonaceous structure.

The general characteristics of carbons may be classified according to their physical structure, particle size, hardness, mechanical strength, and adsorptive properties. Each carbon possesses specifi-

city either for use in water treatment, color removal, metal ion re-
moval, toxin removal or gas adsorption, etc. Carbons used for water
treatment, color removal, medicinal purification and metal ion removal
are generally used only once because of the revivification problem.
No carbon is universally applicable to all processes. For example,
a gas adsorbent carbon must be hard, relatively dense and highly
active while a carbon used for liquid adsorption must be soft, finely
pulverized and highly porous for maximum adsorption.

The two physical features of an activated carbon which best deter-
mine the commercial value of the carbon are surface area and pore
structure. The surface areas of various carbons range from about 2
to 2000 square meters per gram of carbon. This property is not evi-
dent to the microscopic examination of the carbon, but it is easily
determined by indirect methods, such as the BET surface area. It is
important to recognize the fact that the total surface area may not
be the determining factor in the adsorption process. Many substances
when adsorbed only occupy a small fraction of the surface. That is,
adsorption takes place at the less saturated atoms and amounts to less
than the surface area determined experimentally. This concept may
account quantitatively for the difference, but it fails in the differ-
ences in the adsorption specificity of the carbons. The problem may
be compensated for, however, through a consideration of the other
physical characteristic, pore structure. These different adsorptive
properties may be related to the differences in the sizes of pores
which cause molecular screening. It may explain the concept of

limiting adsorptive capacity to molecules whose dimensions are compatable with the pore size.

There is a third feature of the carbon which plays a less significant role in the adsorption process than surface area and pore structure, and this is the chemical nature of the surface. It is generally known that "like dissolves like"; and this may be considered to be analogous to adsorption processes wherein polar surfaces prefer polar adsorbates. A pure carbon surface is considered to be non-polar while a carbon-oxygen complex confers surface polarity. The carbon-oxygen is deemed to form an active center where adsorption is enhanced.

As previously mentioned, many source materials for the manufacture of activated carbons are used. Among these, bituminous coal has been processed directly to activated carbons. Such carbons contain the mineral matter associated with coal. The presence of excessive amounts of mineral matter might be a deterrant which limits the applicability of the carbon especially in liquid phase processes wherein mineral matter would interfere with attaining the purity desired. The removal of mineral matter from coal can be effected by the oxidation of the coal sufficiently to permit the extraction of the organic matter devoid of mineral matter. In order to achieve this extraction, the coal is converted by oxidation to the so-called humic acids. These acids are similar to natural humic acids in certain chemical and physical properties, and their condensed aromatic nuclear structure probably closely resembles the structure of coal itself.

No investigations, however, have been carried out on the prepa-

ration of an activated carbon from the oxidation products of bituminous coal such as humic acids. It is the purpose of this research to investigate the carbonization product of humic acids, or char, its subsequent conversion to activated carbon and the evaluation of the carbon for certain adsorptive properties. The characteristics under consideration will be the surface area, porosity, density and other physical features which may show the active carbon developed in this research to be of some commercial value.

II.   Historical Review:

During the eighteenth century, the investigations on the uses of activated carbons started.   The first description of the adsorptive properties of carbons was that given by Scheele in 1773.   In 1811, Figuier examined the decolorization of sugar solutions by the activity of bone char.   Dietz (11) gives an excellent description of the early history of the activated carbon field and its development.

In 1900, Ostrejko (36) opened the way for activating agents used for the preparation of activated carbons.   He described the techniques for the use of metallic chlorides and carbon dioxide as the activating agents.

Prior to World War I, only the powdered carbons were known in the industry.   The use of poisonous gases during the war provided the necessary impetus for the development of the granular, gas-adsorbing carbon.   After the war, research was projected into the other uses of activated carbons (28) so that today carbons are used for just about every type of recovery, purification and reformation process.

Theories of Adsorption:

1.   Gas Phase Adsorption:

The understanding of the nature of adsorption by carbon received its greatest aid from the pioneering work of Langmuir, Freundlich, and Polanyi, whose theories will be considered briefly.

Langmuir (30) postulated a dynamic equilibrium in which the rate of adsorption k_1 equals the rate of desorption k_2.

$$k_1 = \alpha \nu' (1 - \theta)$$

$$k_2 = \nu (\theta)$$

α is the fraction of inelastic collisions with the surface by the adsorbate molecule, ν and ν' are the rates of condensation and evaporation respectively, and θ is the fraction of the surface covered. At equilibrium, the resulting expression is

$$\frac{v}{v_n} = \frac{kp}{1 + kp}$$

Freundlich [15] developed an empirical relationship given by the expression

$$v = kp^{1/n}$$

in which v is the volume adsorbed, p is the adsorbate gas pressure at equilibrium, k is a constant, and n is a constant greater than unity. The relationship is valid for intermediate pressures; and it has been shown [20] that if the Langmuir equation is applied to a series of sites with an expotential energy relationship, the Freundlich equation is obtained.

The theory developed by Polanyi [39] has become known as the potential theory. Its purpose was to obtain a quantitative picture of multilayer adsorption and to demonstrate how interaction of physical adsorption falls off as to the number of layers increases. The theory produces "affinity" curves in which ϵ is plotted against the volume adsorbed. ϵ is obtained from the relationship

$$\epsilon = RT \ln p/po$$

in which po is the saturation pressure of the adsorbate gase and p is

the equilibrium pressure. Affinity curves at differenct temperature and pressure are parallel and almost coincident. Coincidence of the curves indicates a negligible temperature coefficient of expansion.

The investigation of the adsorption phenomenon turned next to the adsorption isotherm, which is a relationship between volume adsorbed and the pressure of the adsorbate gas, and the analysis of such an isotherm. A typical example of such an isotherm is given in Figure 1 for the sample 1a.

The monolayer region is considered to be the point at which a deviation occurs from the straight line portion of the isotherm and corresponds to the "B" point of Brunauer and Emmett (14).

The contour of the isotherm depends on the adsorbate, the extent and nature of the adsorbing surface, and the pore structure of the solid. Physical adsorption isotherms may be limited to five types (8). These five isotherms are given in Figure 2.

Brunauer, Emmett, and Teller (4) extended the Langmuir theory (30) to cover the multilayer phenomena; this theory has become known as the BET theory. The assumptions of Langmuir are carried over into the BET theory so that a summation of each adsorbed layer is performed. The heat of adsorption of second to the infinity later is considered to be the heat of liquifaction of the adsorbated. The van der Waal's forces are transmitted only to the first layer of the adsorbed gas. Expressions are obtained for a free and restricted surface. If it is assumed that for a free surface an infinite number of layers can be adsorbed, then the BET equation reduces to

$$p/v(p_o - p) = 1/cv_m + (c + 1)p/v_m p_o c$$

in which v is the volume adsorbed, p is the equilibrium pressure, v_m is the monolayer volume, and p_o is the saturation pressure. c is a constant related exponentially to the difference between the heat of adsorption and the heat of liquifaction by the relation

$$c = \exp[-(H_a - H_l)/RT].$$

For a restricted surface, i.e., structures having very small diameters, the BET theory yields

$$v[v_m cx/(1 - x)] = \frac{1 - (n + 1)x^n + nx^{(n + 1)}}{1 + (c - 1)x - cx^{(n + 1)}}$$

in which x is the relative pressure p/p_o, and n is the number of layers. The remaining symbols have the same meaning as before. When n equals one, the equation reduces to the Langmuir expression; and when n equals infinity, the BET equation is obtained.

2. Liquid Phase Adsorption:

Adsorption from solution is rather readily observed, but it is somewhat more difficult to determine quantitatively than it is in the case of gas adsorption. When an aqueous solution of a dye is shaken with charcoal, the color intensity of the solution is lowered; and the dye can be subsequently removed from the charcoal by extraction, indicating that the dye is merely adsorbed.

Experimentally, the measurement is conducted colorimetrically. The concentrations are measured before and after adsorption with the difference being the apparent adsorption. In the adsorption process involving adsorption from aqueous solution, there is competition

Relative Pressure P/P$_o$
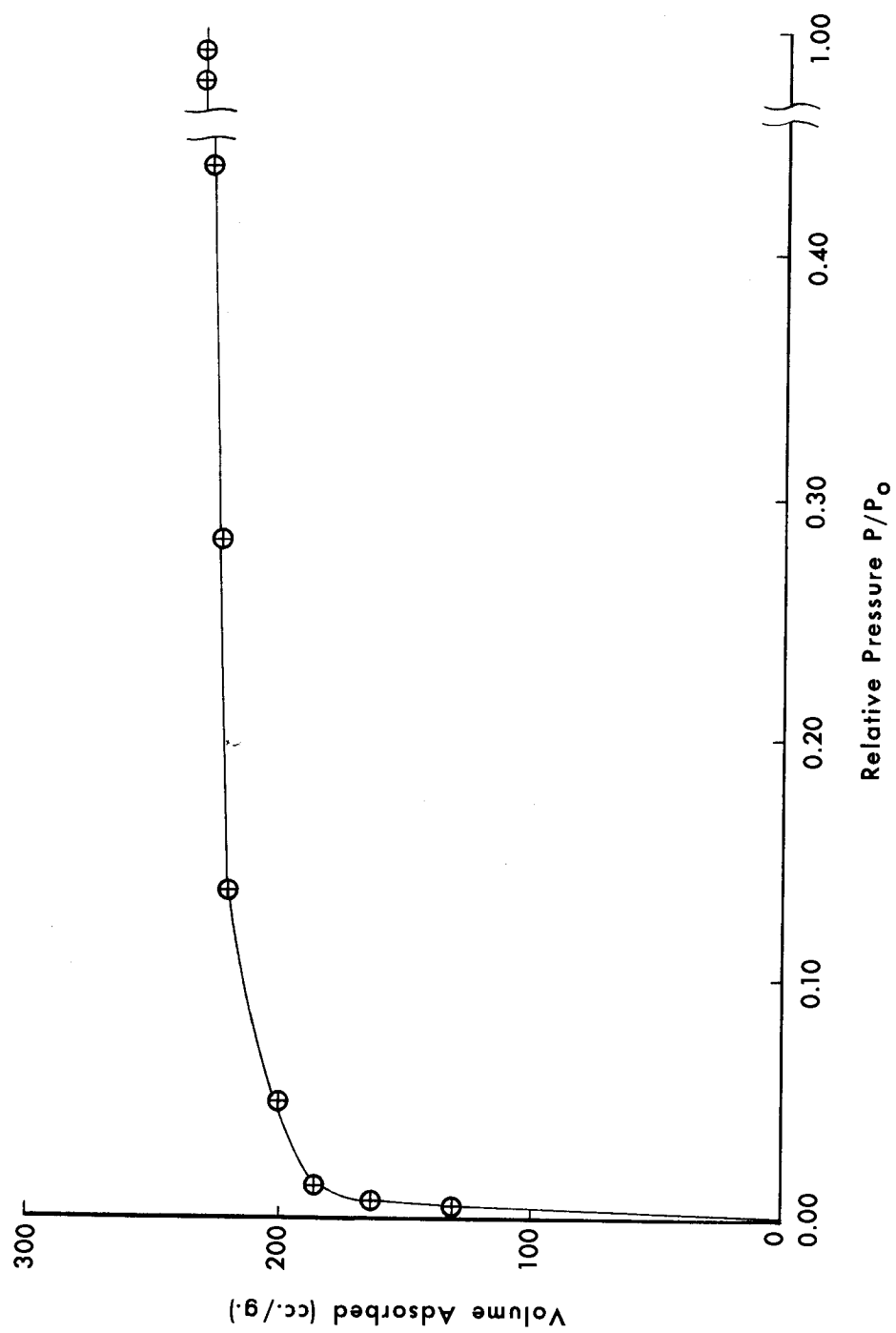
NITROGEN ADSORPTION ON SAMPLE 1-a

Figure 1

Volume Adsorbed (cc./g.)
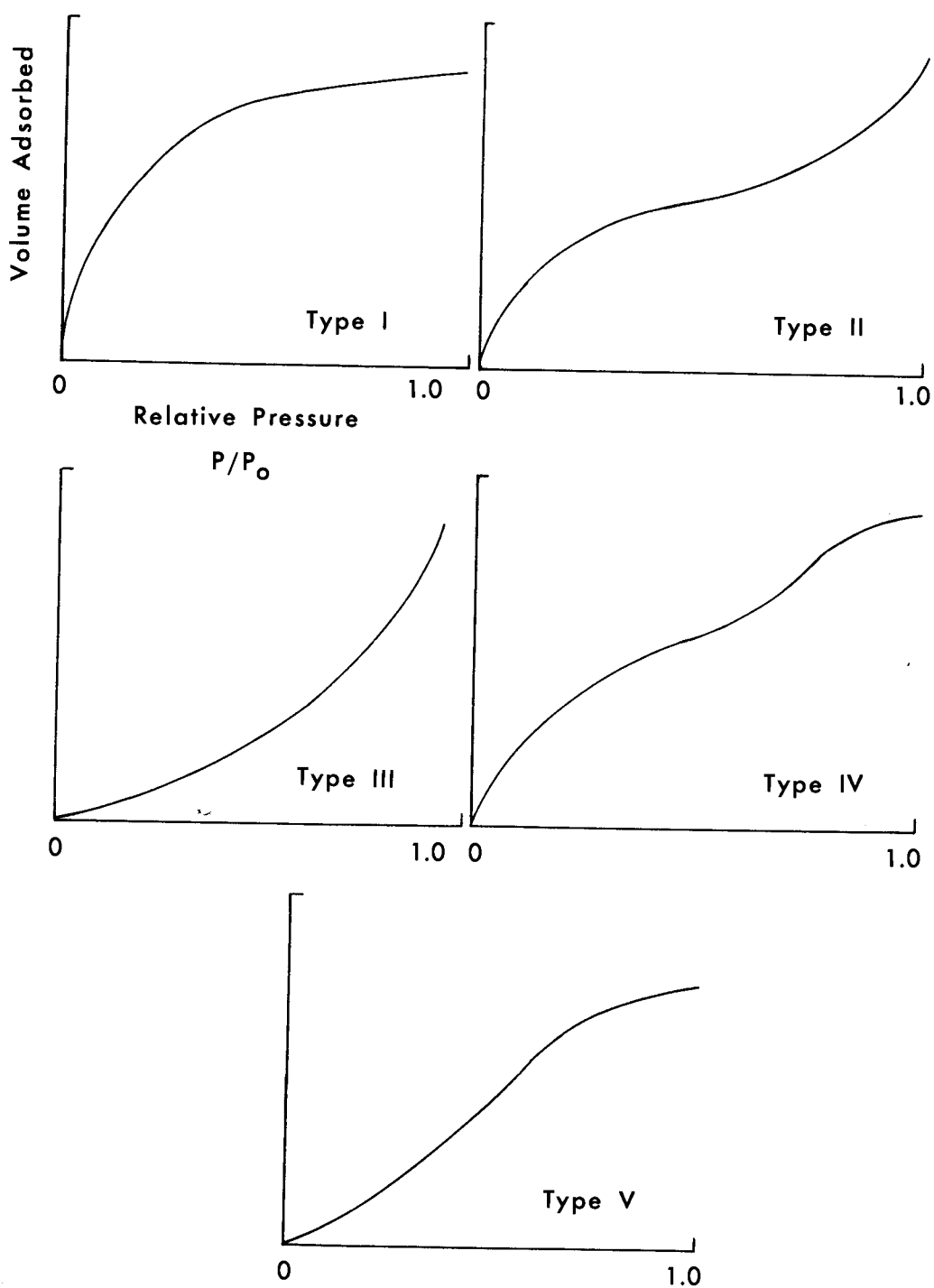
FIVE TYPES OF ADSORPTION ISOTHERMS

Figure 2

between the adsorbate molecule and the solvent molecule for the adsorption site. Figure 3 may illustrate the possible difference between real and apparent adsorption (12).

All types of carbons or charcoals adsorb uncharged molecules. The sorption of electrolytes greatly depends on the composition and the pretreatment of the adsorbent. When the carbon contains a significant amount of ash, ion exchange takes place. When the ash content is so small as to be negligible, hydrolytic or electrochemical adsorption takes place. In the latter case, the net result of the hydrolytic adsorption depends on the amount and the function of oxygen and hydrogen in the carbon adsorbents.

Commercial carbon blacks, after drying in a vacuum at 110°C, may contain from 1 to 12% by weight of oxygen (49). When activated at 1000°C., such a carbon adsorbs inorganic acids but no alkali from solution. This adsorbent behaves as if it contained a basic oxide or it is positively charged by the chemisorbed oxygen. If the basic hydroxide is represented by C-OH, a solution containing hydrochloric acid would yield C-Cl and water. On mixing a neutral salt solute with carbon, the liquid becomes alkaline. If the carbon is slightly platinized to intensify the adsorption of hydrogen, the carbon does not take up hydrogen chloride from aqueous solution; but it does take up molecular hydrogen chloride from dioxane (29).

Considerable difficulty is encountered in the correlation of liquid phase adsorption obtained from different sources. The qualitative differences of carbon used by different workers becomes impor-

Curve 1

Curve 2

Acetic Acid Adsorbed

Final Concentration Acetic Acid
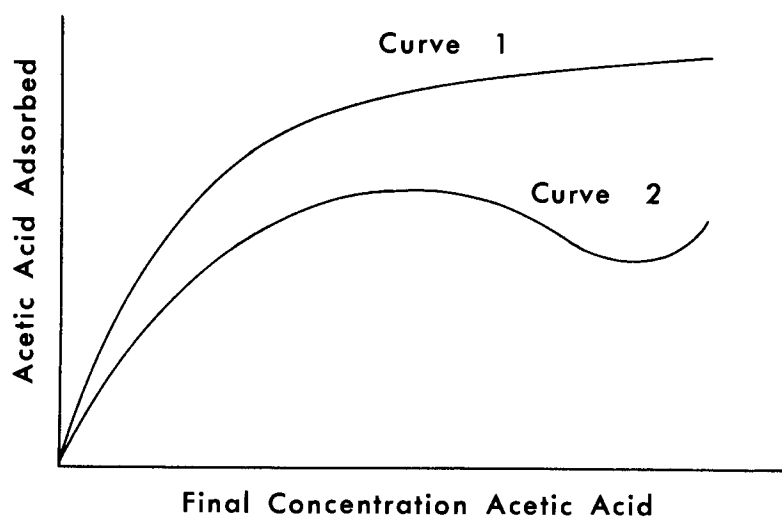
Curve 1   Charcoal with 22% Moisture.
Curve 2   Charcoal with 0.0% Moisture.

POSSIBLE DIFFERENCE BETWEEN REAL AND APPARENT ADSORPTION

Figure   3

tant because of the wide variation of the conditions used for the adsorption investigations. Hassler (22) devotes a chapter to the properties of adsorbable compounds in which the characteristics of the compounds and the effect of various structures within the adsorbate are listed.

Preparation of the Activated Carbon:

For the most part, active carbons are termed amorphous carbons. Investigations of Riley (41, 42, 43, 44) have shown the amorphous carbon to be composed, in fact, of many crystallites. The size of the crystallite is influenced by the temperature of carbonization and probably the structure of the starting material. There are many postulated mechanisms for the growth or formation of the crystallites (16, 17, 43, 44). The carbonization of a substance may cause a regrouping of the fragments which are split off by the carbonization into thermally stable aromatic nuclei. The regrouping is incomplete; and there usually remains a number of hydrocarbon chains and rings, the extent depending on the temperature of carbonization.

It was originally thought that the oxidizing gases used in the activation process attacked these hydrocarbon groups remaining on the rearranged structure. Accordingly then, the surface of the carbon was free to attract and to adsorb other materials. This may be a part of the activation process, but it fails to show the differences in adsorptive capacity that carbons exhibit which are prepared from different substances but activated in the same way (22).

A large part of the commercial activated carbons are prepared by the action of oxidizing gases on the carbonized material. Carbon dioxide and steam are the principle oxidizing gases used for the activation process. The gases are passed through the bed of carbon at temperatures ranging from 800° to 1000°C. Below 800°C., the reaction is slow with the oxidizing gases while above 1000°C. the adsorptive properties are lessened (2, 33). The rate of activation is a function of both temperature and the flow of the oxidizing gases through the bed (47). Therefore, it can be concluded that the consistancy of activation depends on how well the conditions of activation are maintained from run to run.

The reaction between steam and carbon is endothermic. When the reaction starts, there is quite a bit of cooling due to poor thermal conductivity of the carbon particle. This cooling is usually overcome by admitting a slight amount of air to the steam atmosphere.

The amount of steam to be passed over the carbon varies with the application to which the carbon will be put. As the activation process proceeds, the carbon particles decrease in density which may be correlated with the measurement of activity.

Production of Activated Carbons from Coal:

Kuo Ping (39) made an extensive study of the activated carbons produced from bituminous coals of Pennsylvania. He concluded that all possible Pennsylvania coals may be used as a starting material for a commercial activated carbon. He used the steam activation technique

in a static bed in which the pellets were supported on a screen so that the steam could pass through the bed as well as over and under the pellets.

South Arcot lignite was investigated by Madhavan-Nair et al (31). The lignite was activated by metallic salt activating agents. The carbons produced were judged superior to commercial carbons as determined by adsorption of oxalic acid, methylene blue, and malachite green as well as by the decolorization of sugar solutions.

Some Indian coals and lignites were activated by steam (10), but no data were reported on their adsorption characteristics. Weclewska (51) activated twenty bituminous coals and compared them for adsorptive properties. The tests determined that the adsorption of basic dyes decrease with increasing carbon content and that the adsorptive properties depend on the basic groups attached to the carbon structure.

Kitazaki and Araki (25) investigated the different rank coals for adsorptive properties. After being heat treated at various temperatures up to 1000°C., they showed either no change in the adsorption of iodine or a maximum at 600°C. independent of the degree of coalification. It was concluded that iodine adsorption indicated chemical reaction rather than physical adsorption.

Grosskinsky (19) described the activation of various coals by air and steam. The coals were briquetted with pitch prior to carbonization. No data on the adsorptive properties were given.

Dubinin (13) described the sorption and structure of activated carbons from cokes produced from birch tar. The coke and activated

carbon from it adsorbed more acetic acid than higher acids, provided that the weight loss from the activation was small.

The preparation and the adsorption characteristics of carbons produced from peat were investigated by Grohma (18). The carbons were activated by various techniques thereby producing different types of carbons. Acid washing of the carbons did little to the activity. The carbons were compared by means of the Freundlich "k". The greater the carbon content, the higher "k" became in its value.

Carbons were prepared from the woody structure of lignite by Asaoka et al (3). The carbons were activated in a steam atmosphere at various temperatures, and it was concluded that these carbons were better in their adsorptive characteristics than commercial carbons produced from lignite coals.

In this review, it was desired to show some of the work which has been carried out in the investigations of activated carbons. The problem which exists in the activated carbon field can be seen to lie in the correlation of various data obtained in these investigations. It seems that there is no fundamental basis on which the carbons can be compared; and for the most part, the carbons are developed for specific uses. Various activating agents are employed to increase the activity for the specific uses to which the carbons will be put. Also, it can be seen that most authors concluded that the carbons were only better than another carbon, but the authors were not definite in saying that the carbons will adsorb a definite quantity of the ad-sorbate more than the carbon to which it was compared.

III. Experimental Techniques

  1. Preparation of Humic Acids

     The humic acids were prepared from Pittsburgh Seam bituminous
coal of High Volatile A rank. The coal was oxidized in two stages:
first, it was air oxidized at 150°C.; and second, the air-oxidized
coal was treated with concentrated nitric acid at 100°C. Details
of the method are given in Appendix I. Figure 4 shows a flow dia-
gram of the process from the raw coal to the activated carbon.
Table 1 gives nomenclature for chars and activated carbons. Table 2
gives the proximate analyses of the coal and its oxidized products
as designated in Figure 4 for each step in the preparation of humic
acids. Also included in Table 2 are the analyses of the combined
char samples 1 + 2 and 3 + 4. Table 9 gives the ultimate analysis
of the humic acids.

  2. Pyrolysis of the Humic Acids

     The humic acids were pyrolyzed at 230°C. at which temperature
the humic acids underwent a spontaneous exothermic decomposition.
The conditions for this decomposition of the humic acids were altered
in three ways:

     1. Static bed pyrolysis under one atmosphere nitrogen pressure

     2. Static bed pyrolysis under 135 atmospheres nitrogen pressure

     3. Static bed pyrolysis of pelletized humic acids under 135
         atmospheres nitrogen pressure

Conditions for pyrolyses 1 and 2 differed by a change in pressure from

RAW COAL 100g.

AIR OXIDIZED COAL 105g.

NITRIC ACID TREATED COAL 120g.

HUMIC ACIDS 96g.

Char, 1 atm. Nitrogen

Char, 135 atm. Nitrogen

Char from Pellets 135 atm. N$_2$

Non-agglomerated Char 23.0g.

Agglomerated Char 34.6g.

Agglomerated Char 49.1g.

Non-agglomerated Char 21.0g.

2a*   2b   2c   1a   1b   1c   3a   3b   3c   4a   4b   4c   5a   5b   5c
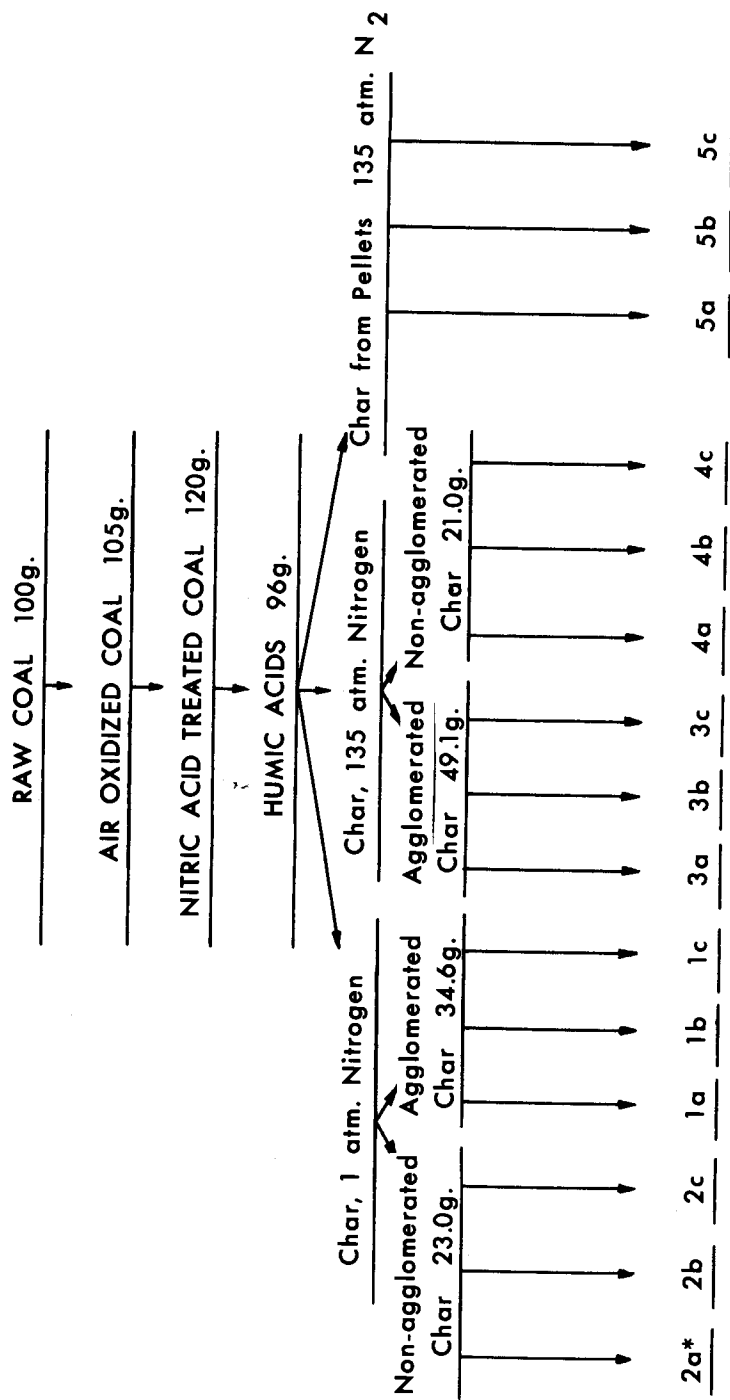
* Yields determined by percent burnoff given in Table 4

FLOW DIAGRAM FOR PROCESSING BITUMINOUS COAL TO AN ACTIVATED CARBON

Figure 4

Table 1

Nomenclature and Description of Products from Humic Acid
Carbonization and Commercial Carbons

Designation	Process	Type Char	Activation Temperature, °C
1*	Static Bed	Agglomerated, Hard	----
1a	"	"	750
1b	"	"	850
1c	"	"	900
2**	Static Bed	Non-agglomerated, Soft	----
2a	"	"	750
2b	"	"	850
2c	"	"	900
3*	Pressure bomb	Agglomerated, Hard	----
3a	"	"	750
3b	"	"	850
3c	"	"	900
4**	Pressure bomb	Non-agglomerated, Soft	----
4a	"	"	750
4b	"	"	850
4c	"	"	900

Table 1 cont.

Designation	Process	Type Char	Activation Temperature, °C.
5**	Pellet; Pres-sure bomb	Pellet; Expanded, Soft	----
5a	"	"	750
5b	"	"	850
5c	"	"	900
6	Commercial Carbon	Hard, gran-ular	----
7	"	"	----
8	"	"	----
9	"	"	----

* Particle size was US sieve 6 x 9 which is the usual size of carbon particle for gas purification carbons.

** Particle size was US sieve 42 x 65 which is the usual size for commercial liquid-decolorizing carbons.

Table 2

Proximate Analysis of Coal and Oxidized Intermediates
Percent, Air-dry

Product	H_2O	V.M.	Ash	F.C.
Raw Coal	1.9	38.4	7.9	51.8
Air-oxidized Coal	2.2	34.2	8.1	55.5
Nitric acid treated coal	7.9	43.2	4.6	44.3
Humic Acids	4.9	46.7	0.6	47.8
(1 + 2)*	---	26.2	0.7	73.1
(3 + 4)*	---	19.9	0.9	79.2

* Combined sample 50% agglomerated and 50% non-agglomerated char.

one atmosphere to 135 atmospheres. In pyrolysis 3 the particle size

of the humic acids was changed from 42 x 65 US Sieve mesh to cylindri-

cally shaped pellets 1/2 inch in diameter and 1/2 inch in length.

Also, in pyrolysis 3, 135 atmospheres pressure was maintained. Fur-

ther details will be explained in section 6.

3. Nature of the Decomposition Behavior of Humic Acids

A. Static Bed Pyrolysis at 1 Atmosphere Nitrogen Pressure

When heated to approximately 230°C., humic acids were known to

undergo an exothermic decomposition which can best be described as

a sudden and vigorous gas release (38). This decomposition produces

a carbonaceous material of a porous nature which can be used as a

starting material for the preparation of an activated carbon.

Ahmed (1), using humic acids prepared by Charmbury et al. (9),

found that at approximately 230°C. the humic acids liberate a large

amount of gas. Ahmed concluded that the humic acids behave similarly

to coal in the release of gaseous products on pyrolysis. At low

temperatures, the gases evolved were due to the decomposition of

peripheral groups which were significantly greater in number in

the humic acids than in coal.

Kaufmann (24) in subsequent investigations showed a net tempera-

ture increase of 60°C. when a 6.5 gram sample of humic acids was

heated to 230°C. and the exothermic decomposition took place.

Kaufmann succeeded in controlling the vigorous gas release by

heating the sample from 190° to 240°C. at a rate of 1°C./min. and

soaking the humic acids at 240°C. for one hour. With this technique,

he was able to pass through the temperature range without expulsion

of the sample from the reaction boat. Kaufmann concluded that the

humic acids were unstable at 230°C. under his experimental conditions;

and he speculated further that nitro, nitroso, and/or isonitroso

groups may be responsible for this behavior.

1. Preliminary Experiments

A series of exploratory experiments were carried out to investi-

gate the exothermic decomposition which Polansky and Nelson first

noted (38) and the functional groups involved in the decomposition.

A 3 gram sample of humic acids was placed in a 50 ml. round-

bottom flask which was equipped with a glass tube for flushing the

system with commercial grade nitrogen. The flask was placed in an

oil bath preheated to 200°C. The oil bath was heated at a rate of

6°C./min. until the decomposition took place. The temperature at

which the decomposition started, i.e., a sudden and vigorous gas

release, was taken as the bath temperature. The decomposition of

the humic acids took place between 230 and 235°C.

The chars obtained from these experiments were found to be

expanded three to four times the particle size of the humic acids.

The chars were black as compared to the dark brown of the humic acids.

Also, they were friable and had a glazed surface. The yield of the

char was 67% of the humic acids or 54% of the raw coal.

In order to learn more of the nature of the decomposition

which humic acids undergo, infrared analysis of the humic acids and

the chars was made. Humic acids show large absorption peaks at 3410,

1530 and 1700 cm.$^{-1}$. These absorption peaks may be interpreted as a hydroxyl stretching peak at 3410 cm.$^{-1}$, a conjugated nitro group at 1530 cm.$^{-1}$ and the carbonyl structure in the carboxyl group at 1700 cm.$^{-1}$. The spectrograms of the chars showed that all of these peaks were essentially absent, and thus the groups were absent in the char.

Experiments were devised to determine the activity of these functional groups in the decomposition behavior of the humic acids. It was planned to chemically remove these groups from reaction and then pyrolyze the product.

The hydroxyl groups were esterified to change their behavior as a hydroxyl group on pyrolysis. A 5 gram sample of humic acids was dissolved in 50 ml. pyridine and a 10% excess of benzoyl chloride added to the solution. Analysis* for functional groups in the humic acids showed that the acids contained 7.87% hydroxyl groups. The amount of benzoyl chloride used for the esterification was calculated from this analysis. The solution was refluxed overnight at 110°C., cooled and filtered. A black residue remained which was washed with pyridine and dried. The yield of the residue was 133% of the humic acids. Evaporation of the pyridine filtrate yielded a dark brown product. The weight of this residue which was the unreacted or partially reacted humic acids was less than 100 milligrams.

The esterified humic acids, i.e., the black insoluble residue,

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*Functional group analysis performed by Schwarzkofp Microanalytical Laboratories, New York, New York. Method of analysis not supplied when requested.

were then pyrolysed under the same conditions as the humic acids.
There was no sudden evolution of gases up to 300°C. The yield on
heating to 300°C. was 87% of the esterified humic acids.

Infrared analysis of the esterified humic acids and of the
char was made and compared. The peak at 3410 cm.$^{-1}$, indicating an
hydroxyl group, was less pronounced in the esterified humic acids
than in the humic acids. The peak at 1700 cm.$^{-1}$ which is char-
acteristic of the carbonyl structure in the carboxyl group was
increased in intensity. These peaks were evident in the esterified
humic acids but were absent in the spectrum of the char.

Next, an investigation into the role of the nitro group in the
decomposition of the humic acids was undertaken. Using the technique
of Blanksma (5), nitro groups which are ortho to an alkoxy or
hydroxy group are presumed to be reduced. By use of this method,
it was believed that a part of the nitro groups would still be
present. However, in the removal of some of the nitro groups,
assuming these were an integral part of the exothermic decomposition,
this reaction should be less violent in comparison to the original
humic acids. Appendix II gives a description of the method.

The reduced product was a dark brown slurry which, upon filtering
and washing, yielded a black residue. The residue was assumed to be
the reduced humic acids and amounted to 48% of the humic acids. The
filtrate was evaporated but remained a paste which could not be
dried at 110°C. The filtrate undoubtedly contained some reduced humic
acids because amino groups are known to hydrate more readily than

nitro groups. The difficulty entailed in the recovery of the acids in the filtrate made it impossible to determine the behavior on pyrolysis at 230°C.

The black residue obtained by the reduction was pyrolyzed under the same conditions as the humic acids. Again, there was no sudden gas release when the sample was heated to 300°C. The yield was 93% of the residue.

Infrared analysis of the residue and the char from that residue showed the absorption peak at 1530 cm.$^{-1}$ was absent in both cases.

2. Large-Scale Pyrolysis of Humic Acids

In order to have sufficient sample of activated carbon for a detailed investigation of its properties, 200 grams of humic acids were pyrolyzed at atmospheric pressure and in an atmosphere of nitrogen gas. The pyrolysis was carried out in a standard design hydrogenation bomb (4-3/8 inch O.D.) manufactured by the American Instrument Company.

The humic acids were placed into a Pyrex liner which was made to fit into the bomb. The bomb was closed and evacuated. Nitrogen was admitted through a bleeder line into the bomb until the pressure was slightly greater than one atmosphere. The bleeder line was closed and the temperature raised to 200°C. at 2°C./min. At 200°C., the pressure was brought back to one atmosphere. The release valve was so constructed that it could be left open, but no air could seep back into the reaction chamber. Also, as the heating continued, there was

a positive flow of the gas through the bleeder valve assuring that no air could enter into the reaction chamber. The heating rate between 200° and 240°C. was 3°C./min., and the soak time at 240°C. was one hour. The yield of char was 60% of the humic acids charged.

The resulting char appeared to be a coherent mass, slightly expanded with a dull black surface. The cylindrical char mass was broken into two pieces for further investigation. It was immediately evident that there were two forms of the char. In the center, the pyrolyzed humic acids had definitely undergone agglomeration. The surface of this material appeared silvery-grey, somewhat resembling a coke. The agglomerated mass, after the removal of the outer crust, produced particles which were quite hard and resisted attrition.

The outer crust appeared to be similar to the carbons obtained in the preliminary experiments, but the particles were not quite as expanded. However, they were roughly twice the size of the humic acid particles. Also, they were soft, friable, and with a glazed surface.

The yield of the two forms of the char was estimated to be about 60% in the agglomerated form and 40% in the non-agglomerated form. Table 3 gives the ultimate analysis of these components.

The agglomeration of the humic acids on pyrolysis led to the investigation of the effect that high pressure would have on the type of carbon produced by the spontaneous exothermic reaction. It was also desired to know whether pressure would increase the yield of the agglomerated form. It is well known that bituminous coking coals

possess agglomerating properties. Oxidation reduces and ultimately

eliminates the agglomerating tendencies. Kattwinkel (23) showed that

treating coking coals in a steam drying oven completely destroyed the

agglomerating tendency. Some coals on very mild oxidation show an

increase in coke strength (27, 44). However, in general any oxidation

of a coking coal decreases or destroys the agglomerating properties

depending on the extent of the oxidation.

In the carbonization of coals, the heating rate influences the

coke strength (34). The coke strength is more adversely affected by

slow than fast heating. This effect is explained on the basis that a

greater internal gas pressure is produced whereby it is believed that

the coal mass becomes sufficiently fluid under these conditions, thus

accounting for the stronger cokes produced.

It was assumed then that the agglomeration of humic acids during

pyrolysis at 230°C. occurred because of the increase in pressure within

the particles. This increase was due to the sudden gas release,

probably causing fluid flow properties. In addition, the compression

effect of the charge which prevented free expansion of the particles

within the bomb and/or the rapid heating rate within the sample after

the exothermic reaction commenced could have been contributing factors

causing the agglomeration of the humic acids.

B. Determination of the Rate of Temperature Rise During the
Exothermic Decomposition

As mentioned in the preceeding section, one of the causes of the

agglomeration of the humic acids could have been the rapid heating of the sample by the exothermic reaction itself. An experiment was devised to determine the rate of temperature rise when the reaction commenced. A thermocouple was placed in a 3.0 gram sample of the humic acids. The humic acids were pyrolyzed, as in the preliminary experiments, in a 59 ml. round-bottom flask. The experimental conditions were exactly the same as those described in section 3-A-1, except that a thermocouple was positioned in the center of the charge.

When the reaction started, the temperature increase was 6-8°C/sec. The reaction started at approximately 235°C. and lasted about 30 seconds. The final temperature of the charge was approximately 450°C.

Under normal laboratory conditions, it would be difficult to reproduce this heating rate.

In another experiment, a roll of Pyrex glass wool was placed on the central axis of a glass liner. About 150 grams of the humic acids were placed around the glass wool in the liner and the pyrolysis carried out as described in section 3-A-2. After the pyrolysis, the glass wool was found to be fused together in some places indicating a temperature of at least 600°C. being reached during the exothermic decomposition of the humic acids. The maximum temperature which the bomb reached was 240°C.

C. Static Bed Pyrolysis at 135 Atmospheres Nitrogen Pressure

The apparent large amount of gas released during the decomposition reaction and the possible effect of high pressure on the nature

of the char produced led to the idea that the exothermic reaction could quite possibly be influenced by increasing the pressure in the reaction chamber.

1. Preliminary Experiments

In a series of experiments at 135 atmospheres nitrogen pressure, small charges of humic acids were pyrolyzed to determine the effect of the increased pressure on the characteristics of the char. A 3 gram sample of humic acids was put into the liner, the liner put into the hydrogenation bomb, and the bomb sealed and evacuated. The bomb temperature was raised to 200°C., and nitrogen was admitted to the system at 135 atmospheres. A heating rate of 3°C./min. was used to raise the temperature from 200° to 240°C. The sample was soaked at 240°C. for one hour.

The char particles obtained from these preliminary experiments were individual, hard, and shiny. There was essentially no expansion of the particles of the humic acids during the pyrolysis while those at one atmosphere pressure experiments were expanded three to four times. The yield of the high pressure char was 73% as compared to 67% for the char produced at one atmosphere pressure.

2. Large-Scale Pyrolysis of Humic Acids

In order to make a detailed study of the char produced at high pressure, a 200 gram sample of the humic acids was pyrolyzed using exactly the same procedure as described in the preceeding paragraph.

The char appeared to consist of two forms: an agglomerated and

a non-agglomerated form. The yields of the two components were esti-
mated to be 70% of the former and 30% of the latter, the total yield
being 73% of humic acids charged.

The agglomerated char appeared to be similar to the agglomerated
char produced by pyrolysis at one atmosphere pressure. The char was
silver-grey, hard and homogeneous in appearance.

The non-agglomerated portion of the char was similar to the char
particles produced in the preliminary experiments at high pressure,
i.e., hard, shiny and not expanded. Unlike the non-agglomerated par-
ticles formed at one atmosphere pressure which were soft and friable,
these particles were quite hard. An ultimate analysis of the two
forms of char is given in Table 3.

D. Static Bed Pyrolysis of Pelletized Humic Acids at 135
Atmospheres Nitrogen Pressure

The conditions used previously for the low temperature pyrolysis
of humic acids consisted only of varying the pressure in the system.
In the first case, the pressure was one atmosphere while in the
second case the pressure was 135 atmospheres. In order to determine
the possible effect of particle size of the humic acids on the nature
of the char, pellets were made and pyrolyzed. By increasing the
particle size together with the influence of high pressures, it was
thought that it may be possible to produce a completely agglomerated
char.

Pellets were formed in a cylindrical press by exerting a pres-
sure of 1500 psig. on the humic acids for five minutes. The press

Table 3

Chemical Analysis of Char from Humic Acids
Percent, Dry, Ash-Free

Sample	C	H	N	S	O*	Yield**
1	75.7	3.18	4.75	.28	16.1	34.6%
2	73.2	3.36	5.93	.99	16.6	23.0%
3	80.3	2.88	4.96	.77	11.0	49.1%
4	80.2	3.09	5.13	1.43	10.2	21.0%
5	74.6	4.01	4.71	----	16.7	78.6%

Note:

 * By difference

** Based on original coal

consisted of a steel sleeve with a 1/2-inch diameter bore and two
steel pistons. One of the pistons was 1/2 inch long and served as a
support for the humic acids. The other piston was 2 inches long and
served as the ram. One gram of the humic acids was placed into the
bore on top of the support piston. The ram piston was put in place,
and the pressure was maintained on the ram by means of a hydraulic
automobile jack. No binder was used in the humic acid sample. The
pellets obtained from this apparatus were 1/2-inch in diameter and
1/2-inch in length.

1. Pyrolysis of the Pelletized Humic Acids at 135 Atmospheres
   Nitrogen Pressure

Humic acid pellets amounting to 25.0 grams were pyrolyzed under
the same conditions and procedure as described in section 3-C. The
resultant chars retained their pellet form. However, they were
slightly expanded, and some fractures were evident. The fractures
were probably caused by gas release during the pyrolysis. The yield
of the char was 80% of the humic acids.

The char pellets were easily crushed and ground to the 42 x 65
mesh size of the humic acids used to make the pellets. The 42 x 65
mesh char particles were quite resistant to further grinding. They
appeared to be similar to the chars obtained in the preliminary high
pressure experiments. The particles were hard and shiny. It was
apparent that only one type of char, the non-agglomerated type, was
present from this pyrolysis. Table 3 gives an ultimate analysis of

the pyrolyzed pellets.

E.   Preparation of the Chars for Steam Activation

The chars produced at the conditions giving the exothermic de-
composition were classified into five groups. Table 1 gives the
nomenclature used to designate the sample of char and the activated
carbons.

The agglomerated carbons were ground to 6 x 9 US sieve mesh and
the non-agglomerated carbons to 42 x 65 US mesh size. These sizes
were chosen so that a comparison could be made with commercial
activated carbons as to physical properties and adsorptive character-
istics.

Because the agglomerated chars were reasonably hard, it was
also interesting to know the behavior of a large char particle
during the activation process. Information on the effect of a high
activation temperature on the particle size would also be of some
value toward the future development of the carbons. Because it is
true that the higher the temperature, the faster the volatiles are
released, it would be safe to assume that the carbons could be
readily regenerated after use if the particles did not fracture at
these high activation temperatures.

The non-agglomerated chars were soft and friable, and thus it
was obvious that regeneration would be difficult. These particles
were ground to 42 x 65 mesh, and no attempt was made to determine
particle size decrease during the activation process.

F. Steam Activation of the Chars

The usual methods of steam activation involve temperatures between 750° and 1000°C. At 750°, the activation process is slow while at 1000° the reaction between steam and the carbon becomes appreciable so that considerable loss of carbon may result.

Activation temperatures of 750°, 850°, and 900°C. were selected for these studies. According to Walker (50), the logarithm of the equilibrium constant is -0.36 for the reaction at 900°C. The reaction is

$$C + 2H_2O \longrightarrow CO_2 + 2H_2.$$
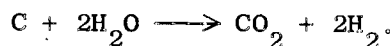
At this temperature the loss of carbon becomes appreciable, and the loss of surface area would become evident at any higher temperature.

A fluidized bed was designed for the steam activation of the chars. Figure 5 is a diagrammatic sketch of the apparatus. The steam was generated in a three-neck round-bottom flask, C, and carried into the preheating system, F and G, by a stream of helium from tank A. The preheaters were set at 250°C. for F and 700°C. for G. The preheaters were wound with high resistance nichrome wire (B.S. #16), and current was supplied by two 115 v. Variacs. A split tube furnace, H, was operated at 750°C. by a Variac setting of 90v., at 850°C. by 98 v., and at 900°C. by 108 v.

The reaction tube, I, was a quartz tube, 1-1/4 inch in diameter and 14 inches long. The quartz tube was connected to the system by two 28/42 standard taper ground joints.

The steam temperature was measured as it entered the reaction

A Helium Tank
B Flow Meter
C Steam Generator
D Thermometer
E Bubbling Tip
F Pre-Heater
G Pre-Heater
H Split Tube Furnace
I Reaction Tube
K Thermocouple
L Thermocouple
M Support Disc
N Sample
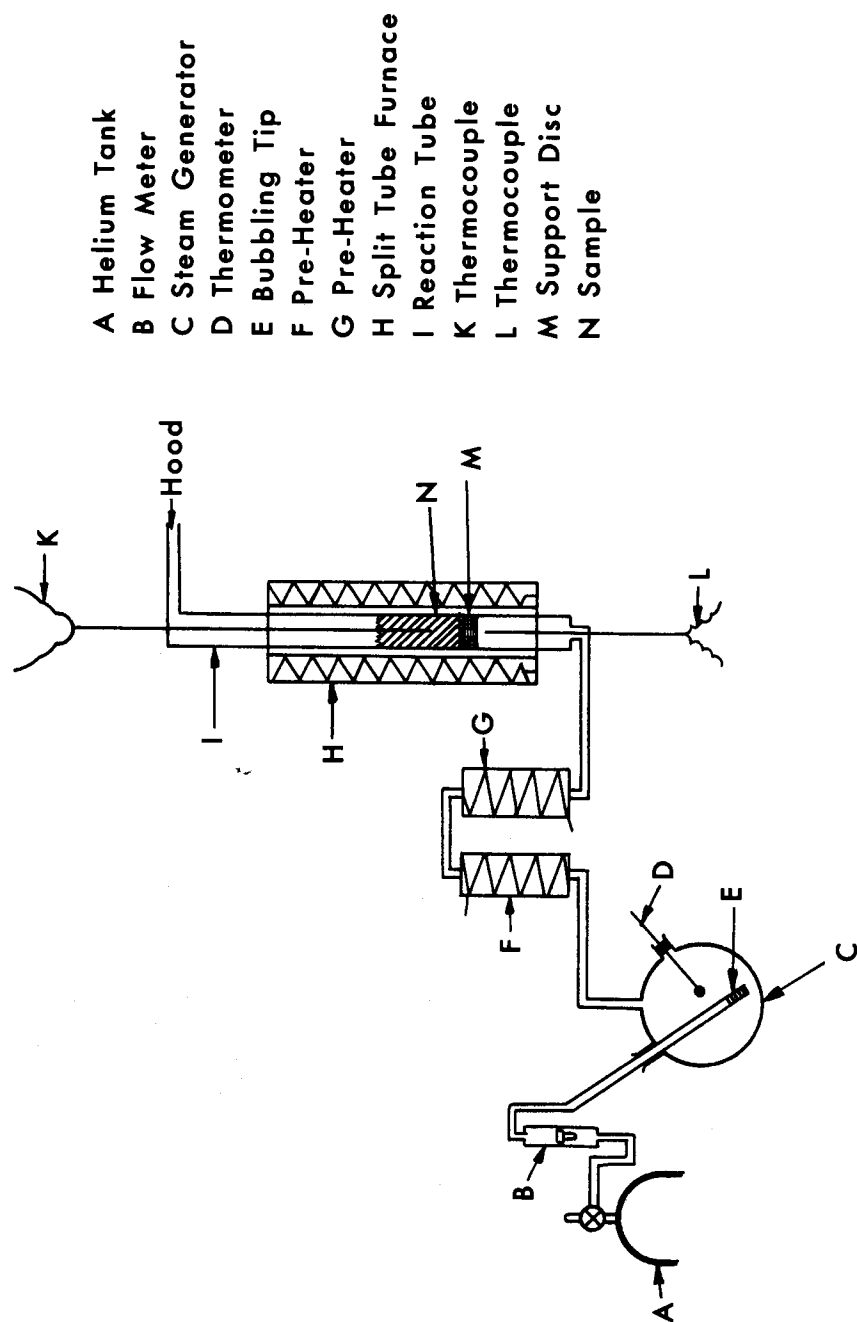
SCHEMATIC DIAGRAM FOR STEAM ACTIVATING APPARATUS

Figure 5

chamber by a chromel-alumel thermocouple, L, positioned just below measured by another thermocouple, K, located in the center of the sample, N. The temperatures measured by thermocouples L and K varied from one to the other a maximum of 20° at 900°C.

To eliminate sample loss during activation, it was determined that the maximum helium flow rate for a 5 gram sample was 2.4 l./min. for the 6 x 9 mesh sample and 1.0 l./min. for the 42 x 65 mesh sample.

The amount of steam generated by this system was determined by the use of the procedure presented in an Indian patent by the Council of Scientific and Industrial Research (10). This procedure suggested that one pound of steam per hour per pound of coal be used for coals with a volatile matter content ranging from 25 - 50%. At a flow rate of 2.4 l./min., 25 grams of steam were generated per hour. With a 5 gram sample of the char in the reaction chamber at 750°C., approx- imately 18-20 grams of steam per hour were condensed at this gas flow. Under these conditions, about 5 - 7 grams of steam reacted with 5.0 grams of carbon per hour.

Through the use of a helium flow rate of 1.0 l./min., 10 grams of steam were generated per hour. With a 5 gram sample of 42 x 65 mesh char in the reaction chamber at 750°C. and at this helium flow rate, 5 grams of water were condensed. This indicated that 5 grams of steam reacted with 5.0 grams of the char per hour.

Using these criteria established by experiment, the chars were activated at 750°, 850°, and 900°C. for one hour each. An indication

of the similarity of conditions exists in a comparison of the various

percent burn-off for each char sample. The values which are reason-

ably consistent ranged between 55% and 73%. Table 4 gives the data

in percent burn-off for the various samples.

G. Methods for the Evaluation of the Activated Carbons

1. Surface Area

Nitrogen surface areas of the chars and activated carbons were

determined by the volumetric technique of Brunauer, Emmett, and

Teller (6). The nitrogen gas was adsorbed at 77.3°K. and isotherms

constructed. Equilibrium times were 40 minutes per nitrogen slug.

The surface areas were determined by estimation of the "B" point,

from the BET equation and the Langmuir equation. Table 5 gives a

comparison of the surface areas obtained.

2. Iodine Adsorption.

The iodine adsorptions were carried out according to the sug-

gestions of Koide (26). Koide suggested that the following condi-

tions be kept constant.

1) Pretreatment of the sample

2) Amount of the sample

3) Initial concentration of the iodine solution

4) Quantity of solution for adsorptions

5) Ratio of KI to I_2 in the iodine solution $(I:I::KI:I_2)$

6) Time of adsorption

7) Temperature

Carbon samples 1a and 2a were used to determine the time neces-
sary for equilibrium to set in for the adsorption of iodine on the
carbon. A 0.5 gram sample of the carbon was shaken in a 250 ml.
Erlenmeyer flask with 20.0 ml. of 0.1 N. iodine solution. The flask
was agitated for one minute every fifteen minutes. These trials
were done in triplicate. Every hour a 1 ml. aliquot was withdrawn
from each of the flasks and titrated with standard thiosulfate and
starch indicator. Equilibrium was reached after three hours.

In constructing the isotherms for iodine adsorption, 0.5 gram
of each of the activated carbons was swirled in 20.0 ml. of six dif-
ferent concentrations of standard iodine solution. The concentrations
of the iodine solutions were 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 N.
After three hours, a 5.0 ml. aliquot was withdrawn and titrated as
before. The temperature was 24 - 25°C. The iodine number was deter-
mined by estimating the "B" point on the isotherms. Table 6 gives
the iodine numbers for the activated carbons.

3. Methylene Blue Adsorption

Through the application of Koide's (26) suggestions to methy-
lene blue adsorption, values were obtained for the activated carbons
by again estimating the "B" point.

Adsorption equilibrium was established after two hours. A
correction must be applied for the amount of methylene blue adsorbed
by the glass. This amount is simply subtracted from the amount
adsorbed as determined from the isotherms. The isotherms were

Table 4

Weight Loss of Carbon During Activation Process

Sample	% Loss
1a	62.5
1b	69.0
1c	73.0
2a	64.2
2b	69.0
2c	64.0
3a	67.0
3b	58.1
3c	73.2
4a	55.5
4b	63.3
4c	54.8
5a	63.3
5b	65.6
5c	67.0

Table 5

Surface Areas in Square Meters Per Gram of Activated Carbons
as Determined by BET, "B" Point and Langmuir Methods

Sample	BET	"B" Point	Langmuir
1	38.4	33.2	24.2
1a	920.0	960.0	1103.0
1b	1570.0	1920.0	1855.0
1c	1375.0	1780.0	1670.0
2	113.0	138.0	138.0
2a	312.0	242.0	281.0
2b	574.0	609.0	619.0
2c	417.0	514.0	369.0
3	23.7	27.7	25.3
3a	930.0	1125.0	1109.0
3b	1580.0	2090.0	1863.0
3c	1228.0	1421.0	1362.0
4	.9	1.2	1.3
4a	402.0	523.0	519.0
4b	682.0	779.0	793.0
4c	525.0	588.0	596.0

Table 5 cont.

Sample	BET	"B" Point	Langmuir
5	1.0	2.3	2.5
5a	382.0	431.0	449.0
5b	451.0	501.0	518.0
5c	749.0	802.0	823.0
6*	950		
7*	1050		
8*	1000		
9*	1000		

* Commercial specification

obtained from the data obtained by swirling six different aqueous

methylene blue concentrations with the activated carbon. The solu-

tions were filtered, a correction was made for adsorption by the

filter paper, and the resulting methylene blue concentration was

determined colorimetrically using the absorption peat at 3000 $\overset{o}{A}$.

4. Mercury Pore-size Distribution

The pore-size distribution in the activated carbons within the

range 214 to 10^6 $\overset{o}{A}$. diameter was determined by the technique of

Raats (40). The technique involves essentially forcing mercury into

the pores of the sample by applying an external pressure to the mer-

cury column and measuring the decrease in the column height. This

volume of mercury forced into the pores is the pore volume of the

sample within the pore diameter corresponding to the applied pressure.

The pressure is related to the pore radius by means of the Kelvin

equation,

$$r = -\frac{2\sigma}{P} \cos\theta.$$

Table 7 gives the pore volume with a diameter greater than 214 $\overset{o}{A}$.

The reproducability of these data is about 10%. Appendix III gives

porisimeter plots.

5. Mercury Density

Mercury density was determined by the volume of mercury displaced

by the carbon. The mercury height was measured in the sample holder

filled with mercury and again filled with mercury and the activated

carbons. These measurements were taken at 1 atmosphere pressure, the

Table 6

Adsorption of Iodine and Methylene Blue by Activated Carbons

Sample	Iodine No. Milligrams Adsorbed Per Gram Carbon	Methylene Blue No. Milligrams Adsorbed Per Gram Carbon
1a	584	122
1b	1015	111
1c	1154	161
2a	323	84
2b	583	129
2c	837	129
3a	501	109
3b	571	133
3c	850	101
4a	444	96
4b	475	133
4c	850	168
5a	824	105
5b	875	126
5c	1256	94
6*	900	---**
7*	1125	---**

Table 6 cont.

Sample No.	Iodine No.	Methylene Blue No.
8*	1000	----**
9*	1000	----**

*   Specifications for commercial carbons

** Not available

Table 7

Bulk Density, Mercury Density and Pore Volume > 214 Å

Sample	Bulk Density	Mercury Density	Pore Volume
1	0.22*	----**	----***
1a	0.202	0.486	1.5
1b	0.133	0.398	2.3
1c	0.126	0.330	2.5
2	0.39	-----	-----
2a	0.313	0.398	1.4
2b	0.303	0.355	1.4
2c	0.299	0.311	1.4
3	0.13	-----	-----
3a	0.112	0.374	2.8
3b	0.109	0.316	2.7
3c	0.088	0.239	3.7
4	0.31	-----	-----
4a	0.278	0.395	3.0
4b	0.251	0.310	2.2
4c	0.205	0.298	1.7

Table 7 cont.

Sample	Bulk Density	Mercury Density	Pore Volume
5	0.74	-----	-----
5a	0.615	0.877	0.3
5b	0.588	0.743	0.4
5c	0.518	0.565	0.4
6	0.48	0.75	0.85
7	0.50	0.80	0.80
8	0.44	0.78	0.81
9	0.44	0.70	0.94

Note"

* Unit of bulk density is grams per cubic centimeter

** Unit of mercury density is grams per cubic centimeter, mercury displacement.

*** Unit of pore volume is cubic centimeters per gram of carbon.

difference in to two values being the volume of mercury displaced.

Table 7 gives the data for the chars and activated carbons.

6. Helium Density

The helium densities of the chars and activated carbons were

measured by helium displacement. No accurate data were obtained for

the activated carbons. It was apparent that adsorption of helium

was taking place as evidenced by a slow decrease in the helium

pressure in the system. The helium densities for samples 1, 1a, 1b,

and 1c are given in the following table as an illustration.

Sample	Helium Density, g/cc	BET Surface Area m^2/g
1	0.94	38.4
1a	1.86	920
1b	3.09	1570
1c	2.80	1375

It seems from these values that the adsorption of the helium in the

activated carbon depends on the surface area of the sample. Greyson

(17) measured helium adsorption at low temperatures on graphitized

carbon black, the value being approximately 2.00 cc./gram at 20°K.

Tuck (48) reports "appreciable" adsorption of helium and neon on

charcoal at 30°C. There are a multitude of data which report

helium densities which are within the accepted values for density.

No attempt was made to measure an isotherm and to determine

the quantity of helium adsorbed. An approximation from the measured

densities and the graphite density indicate that about 0.3 to 0.5

cc./gram of carbon of helium is adsorbed.

7. Bulk Density

The bulk density of the carbon sample was determined by placing
an analytical sample of 42 x 65 mesh size of each carbon in a gradu-
ate cylinder. The graduate was vibrated until there was no further
decrease in the volume. These data were reproduced within 10% in
three determinations. Table 7 gives the bulk densities for the char
and the activated carbons.

8. X-ray Diffraction Data

X-ray data on the activated carbons were obtained with a Norelco
Diffraction unit using Cu K_α radiation. By the technique of Biscoe
and Warren (4), it is possible to calculate crystallite dimensions
for activated carbons. $\overline{L}_a$, the average crystallite diameter, is
determined from the (100) peak; and $\overline{L}_c$, the average crystallite
height, was determined from the (002) peak. The expressions for the
crystallite height and dimaeter were taken as:

$$\overline{L}_c = \frac{0.89 \, \lambda}{\beta \, \cos \, \theta}$$

$$\overline{L}_c = \frac{1.84 \, \lambda}{\beta \, \cos \, \theta}$$

in which λ is the wavelength of incident radiation, θ is the angle of
diffraction and β is the half peak width in radians.

The d-spacing for the activated carbons was obtained by use of
the Bragg equation $n \lambda = 2d \sin \theta$

Extremely diffuse (002) peaks were obtained for all samples, and

no (100) peaks were obtained for the samples. The interpretation of the data is doubtful as may be observed in Table 8.

9. Chemical Analysis

Chemical analysis of the activated carbons was performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. Table 9 gives the chemical analysis of the carbons.

Table 8

X-Ray Diffraction Data for Activated Carbons

Spacings in Angstrom Units

Sample	$\overline{L}_a$	$\overline{L}_c$	d
1a	---	7.69	3.89
1b	---	7.89	4.00
1c	---	7.82	3.98
2a	---	7.68	4.05
2b	---	7.78	3.90
2c	---	7.24	4.08
3a	---	---	---
3b	---	---	---
3c	---	---	---
4a	---	---	---
4b	---	---	---
4c	---	---	---
5a	---	10.78	3.89
5b	---	10.45	3.90
5c	---	9.60	3.93

Table 9

Chemical Analysis and Yield of Activated Carbons
Percent, Dry, Ash Free

Sample	C	H	N	S	O*	Yield**
Humic Acids	60.10	3.47	5.18	0.34	30.91	96.0
1a	78.50	2.82	0.82	0.32	17.55	21.6
1b	94.15	1.40	1.49	0.92	2.04	23.9
1c	93.75	1.36	1.62	0.65	2.62	25.3
2a	78.30	2.54	4.53	0.47	14.16	14.7
2b	87.00	1.75	3.12	1.41	6.72	15.9
2c	88.25	2.13	3.05	2.15	4.42	14.7
3a	88.96	1.83	1.93	0.59	6.75	33.0
3b	98.62	1.97	0.67	0.80	6.93	28.6
3c	94.10	1.65	0.65	1.13	2.47	36.0
4a	88.55	2.10	3.79	0.78	4.79	11.7
4b	92.60	3.24	3.96	1.00	0.20	13.3
4c	94.00	1.98	1.89	2.23	0.00	11.5
5a	84.75	2.13	4.62	0.00	8.50	20.5
5b	88.75	0.89	4.43	0.00	5.93	18.7
5c	86.75	0.95	3.42	0.00	9.88	17.6

Note:

  * Oxygen determined by difference

** Yield determined from percent burnoff given in Table 4

IV. Summary and Discussion of Results

  1. Nature of the Exothermic Decomposition

     Previous investigators (1, 24, 38) have speculated that the exo-
thermic decomposition of humic acids prepared by nitric acid oxida-
tion when heated to approximately 230°C. was due to the interaction
or decomposition of peripheral groups on the humic acid molecules.
Also it was shown that careful control of the heating rate diminished
the violence of the decomposition. While the principal aims of this
research were to investigate the char produced by low temperature
pyrolysis and activated carbons prepared from this char, it was
also deemed important to investigate the nature of the decomposition
in order to try to improve the properties of activated carbons pro-
duced in this way.

     Infrared analysis of the humic acids showed that the carbonyl
structure was present in a carboxyl group, hydroxy and nitro groups
were present on the periphery of the humic acid molecules. It is
well known that nitro groups and hydroxy groups are extremely reac-
tive. Also, nitro groups are a fundamental constituent of explo-
sives. It has been shown that there is an increase in detonation
velocity when a nitroaromatic has a hydroxy group or an alkoxy
group added to the molecule (32).

     Chemical treatment of the hydroxy and/or the nitro group that
would change their chemical identity would permit some understanding
of the role these groups play during the decomposition. In this
research the hydroxy groups were esterified and the nitro groups

reduced.

The hydroxy groups were reacted with benzoyl chloride to produce a black insoluble substance which was assumed to be esterified humic acids. Infrared spectrum showed that there was a decrease in the absorption peak for the hydroxyl groups and an increase in the absorption peak for the carbonyl structure. The nitro groups were reduced by sodium sulfide-sulfur. In the original paper this reduction technique was stated to affect only nitro groups ortho to hydroxy or alkoxy structures. It was assumed that this technique would reduce only a fraction of the nitro groups in the humic acid molecule. The spectrum showed the absorption peak for the nitro groups to be absent; and, unfortunately, no evidence was apparent for an absorption peak for an amino group. Thus, it was assumed that reduction did take place; and it was likely that some groups remained in an intermediate state.

The pyrolytic behavior of the esterified or reduced humic acids was quite different from that of the humic acids. The sudden gas release at 230°C. characterizing the untreated humic acids did not occur in the treated humic acids. With the esterified humic acids, the amount of volatile matter produced at 300°C. was 13%, from the reduced humic acids 7%, while the original humic acids produced 33% of volatile matter at 235°C. Thus, the volatile release decreased by more than half upon chemical treatment.

These differences in volatility between the treated humic acids and the original humic acids indicate that the exothermic decompo-

sition depends on presence of the nitro group with the hydroxyl group enhancing the decomposition. If the volatility is considered 7% for the reduced humic acids and 13% for the esterified humic acids, when compared to 33% in original humic acids, the nitro group seemed to have greater influence on this decomposition. By removing some of the nitro groups by reduction, the volatile matter decreased by 80% from that of the original humic acids against 60% for the esterified humic acids. This was quite a significant decrease and pointed toward the greater influence of the nitro group in the reaction.

2. Effect of Pressure and Pelletization on the Formation of an Agglomerated Char

The production of an agglomerated char from the exothermic decomposition of humic acids at 230°C. was an interesting phenomenon considering what is known about the effect of oxidation of the coal on its agglomerating tendency. Normally, any oxidation of the coal decreases and eventually destroys the agglomerating properties of the coal (23). At the same time, it was known that increasing the heating rate increases the coke strength for weakly coking coals (34).

The high rate of temperature rise, 6-8°C./sec., measured during the decomposition was quite a bit faster than heating rates employed during normal coking operations. It would seem reasonable then that this sudden heat release accompanied by large amounts of volatile matter must have played an important part in this agglomeration

phenomenon. Under these conditions, it was assumed that a fluid

phase develops as the decomposition proceeds and forms a coherent mass

of decreased bulk density.

If the assumption that a fluid phase exists is correct, the ag-

glomerated portions of the chars should be identical, independent of

starting conditions in this system, i.e., pressure. Examination of

the surface areas of the activated carbons from the agglomerated chars

in Table 5 shows an excellent agreement. This would indicate that

the chars behave similarly during activation. In the same way, dif-

ferent values for the surface areas of the non-agglomerated chars and

the pelletized char suggest a different behavior of these products

during activation.

The influence of pressure is most evident on the non-agglomer-

ated form of the char. As stated previously, pyrolysis at one at-

mosphere pressure yielded an expanded non-agglomerated particle

while increasing the pressure gave an essentially unexpanded particle.

The high pressure non-agglomerated char sample has quite a bit of

internal pore surface which is opened by activation. Consider the

non-activated chars in Table 5. Sample 2 has an area of 113 m^2/gram

while sample 4 has only 0.9 m^2/gram surface. It seemed then that

pressure during pyrolysis causes a slower release of gas and there-

by exposes very little of the internal pore structure which on act-

ivation is opened.

The influence of pressure on volatile matter release can be cited

as another piece of evidence to show a slower decomposition. At 135

atmospheres, 27% of volatiles is released as contrasted with 40% at one atmosphere pressure. The proximate analysis shows that humic acids have a volatile matter content of 46%. It may be considered that the increased pressure only slows down the start of the decomposition or the gas release during the first few seconds. But, once the heat release becomes great, the decomposition becomes uncontrolled; and the retarding action of the pressure is overcome by the rapidly increasing temperature.

Another contributing factor to the agglomeration of the decomposing humic acids is probably the restricted expansion of the acids by the glass liner and possibly the piling up of humic acids in the liner. As described in the sections on preliminary experiments, such small charges were used that the humic acid particles were never more than a few layer's high. The chars produced in these cases were still composed of individual particles even though the atmospheric pressure chars were expanded and those at 135 atmospheres were not. In the char from the pyrolysis of 200 grams of humic acids in a Pyrex liner, only the particles at the top were exactly similar to the chars from the preliminary experiments while the center of the char was agglomerated.

The pyrolysis of the pelletized humic acids showed very little of the agglomerating phenomenon. The high pressure seemed to slow down the decomposition. The amount of volatile matter released from the pellets was 20% while it was 27% from the 42 x 65 mesh material.

Comparison of the surface areas of the activated char pellets in

Table 5 shows one interesting fact. The surface areas increase with increasing activation temperature. For the other chars, a maximum is reached at 850°C. This steady increase indicates a more uniform char in which the internal surface is exposed only by the reaction of the steam with the carbon to react away the carbon structure of the char and open the pores. The effect of increasing the activation temperatures causes a decrease in the surface area above 850°C. The pore walls are reacted away by the reaction

$$C + 2H_2O \longrightarrow CO_2 + 2H_2.$$
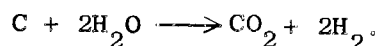
This is the case only for char samples 1, 2, 3, and 4. It is apparent then that for these samples volatile matter release opens some of the internal pore structure while more is made available through the oxidation by steam.

The only reasonable X-ray data were obtained on the char and activated carbons from the pelletized humic acids. As shown in Table 8, the crystallite height decreases with increasing activation temperature, indicating that the crystallites were being somewhat ordered by the carbon-steam reaction. The equilibrium constant for the reaction determined by Walker (50) showed that at 900°C. the reaction proceeds left to right with an equilibrium constant of approximately 0.6.

Under the conditions imposed by the violence of the decomposition and the experimental conditions used in the research, the causal influence for the agglomeration of the humic acids probably is the large amount of heat released and the restricted expansion of the

humic acids. The large heat released undoubtedly caused an abnormally high heating rate within the charge; and the restricted expansion concentrated or localized the heat. The influence of pressure, if there was any effect, seems to be the delay of the initial decomposition. It may be assumed that the reaction started at the external surface of the humic acid column, then proceeded inward to the middle of the charge since the agglomerated portion of the char was found at the middle of the charge.

3. Adsorption Characteristics of the Activated Carbons Compared
    to Commercial Carbons

From the data presented in Tables 5, 6, and 7, it is obvious that these carbons produced from humic acids are the equivalent of the commercial carbons. The variation of the conditions for the pyrolysis seemed to cause very little effect on the adsorptive characteristics. Very little can be derived from the adsorption data without a more extensive investigation of the liquid phase adsoprtion properties of the carbons.

The rate of adsorption from solutions is analogous to that from gases. The process at the interface usually is rapid and its rate can be measured for specific experiments. The rate in granular adsorbents is determined either by the rate of delivery of material to the grains from the bulk of the solution or by the rate of transportation of this material from the grain surface to the adsorption sites within the particle. The first process includes diffusion and con-

vection; therefore, it is accelerated by agitation. Inside the particle, convection is negligible and material transport is not influenced by agitation.

If the area of an iodine molecule is taken as 17 $\overset{\circ}{A}^2$, an iodine number of 1000 corresponds to a surface area of approximately 100 m^2/gram carbon. In no case in this research does the iodine surface area correspond to the nitrogen surface area. Apparently then, the iodine numbers are too low because of the mass transport of the iodine molecules into the bulk of the particles. This transport effect is probably related to the pore sites within the particles.

4. Physical Properties of the Activated Carbons Compared to Commercial Carbons

The physical properties of bulk density, mercury density, and pore volume of the activated chars from humic acids decomposition are favorable when compared to commercial carbons. The densities are less than the commercial products by an appreciable amount except for the pelletized humic acids char. The pelletized chars are approximately of the same densities as the commercial carbons. The densities of the carbons are roughly one half as much as the commercial material.

The surface areas of these carbons are equal to the commercial carbons. The agglomerated carbons have a surface area one and one-half times as large. No commercial literature was obtained for a comparison between the non-agglomerated carbons and liquid adsorbing

commercial carbons.

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V. Conclusions

From the experimental data, the following conclusions may be drawn:

1- The exothermic decomposition of the humic acids is primarily due to the reaction of the nitro group which is enhanced by the presence of hydroxyl groups on the periphery of the humic acid molecule.

2- While no exact explanation can be drawn due to limited experimental conditions, the agglomeration phenomenon would seem to be caused by an interdependence of two effects: first, the large heat release causing an abnormally high rate of heating within the sample; second, restricted expansion of the humic acids by the liner walls.

3- The activated carbons produced in this research are equivalent to the four commercial carbons used for comparison. An important feature is the very high surface area in the carbons produced from humic acids.

4- The best activated carbon is produced by steam activation of the agglomerated form of the char at 850°C. At this temperature, maximum surface area is obtained. The influence of the high pressure is negligible on the characteristics of the activated carbon produced from the agglomerated portion of the char.

It is obvious that these experiments have not exposed all of the possibilities of producing an activated carbon from exothermic

decomposition of humic acids at 230°C. It would be interesting to know the pyrolytic behavior of humic acids packed into a column and completely restrained from expanding by steel walls and top. This would probably cause more agglomeration and probably show that it would be unnecessary to separate the two forms of the char to produce a commercially attractive carbons.

Other techniques of activation would most likely give different adsorptive characteristics and make a wide range of application for these carbons.

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APPENDIX I:

The humic acids used for these experiments were prepared from Hi-Volatile A bituminous coal from the Pittsburgh seam by means of the technique developed by Kaufmann (24). The coal was first air oxidized at 150°C. for 48 hours; second, refluxed for one hour in a 3:1 HNO_3 - air oxidized coal slurry at 100°C. The nitric acid treated coal was then filtered and washed until the NO_3^- ion could be no longer detected by the usual methods. The following is the preparation of humic acids in explicit detail.

The bituminous coal was ground to -200 mesh (US Sieve) and dried in a vacuum oven for 24 hours at 80°C. A sample of the dried coal, 200 grams, was placed in a vertical glass column which had a glass wool plug on top of a rubber stopper for support of the coal. The glass column was arranged so that dry air could be passed into the bottom of the tube and at a rate sufficient to fluidize the coal. The fluidized bed column was 36 inches long and consisted of two concentric glass tubes. The inner tube was 1 1/4 inches in diameter, and 30 inches of the tube was wound with #20 (B and S) nichrome heating wire. When the inner tube was wound with the heater, the inner tube was put inside the second tube. This outer tube was 2 inches in diameter and acted as an air jacket. A consistant temperature could easily be maintained in this arrangement. The temperature was measured at two positions within the bed by means of a chromel-alumel thermocouple. One position was 12 inches from the top, the other 12 inches from the bottom of the tube. Optimum fluidization of the bed

was attained with an air rate of 2.50 cu. ft./hr. measured by a wet-test meter at 25°C. A Variac supplied the potential, and for 150°C. 84.0 volts were used.

The coal was added to the column at room temperature. The air was slowly started into the bed to avoid losses by bumping, and the flow rate was slowly increased to 2.50 cu. ft./hr. Then the Variac was set to 84 volts and turned on. The temperature of 150°C. was attained within one hour and maintained for the air-oxidation time of 48 hours.

This air oxidized coal was then treated with HNO_3 at 100°C. A 1.0 liter three-necked round bottom flask was fitted with a stirrer, condenser and funnel. 300 grams of the air-oxidized coal was put into the flask. The stirrer, condenser and funnel were put into place. Maximum yield of humic acids was obtained by using a 3:1 ratio HNO_3 to coal. For 300 grams of air-oxidized coal, 634 ml. of concentrated HNO_3 were slowly admitted to the coal. The flask was submerged in an ice bath to prevent excessive foaming of the slurry. When all of the HNO_3 was in the flask and the coal slurried, the ice bath was removed and a Glas-col heating mantle put on the flask. The funnel was now replaced with a thermometer. The temperature was raised to 100°C., and the slurry was refluxed for one hour.

After the HNO_3 treatment, the slurry was mixed with one liter of water in a 2 liter beaker. This solution was filtered and continually wasted until the NO_3^- could not be detected.

The HNO_3 treated coal was then put into a 2 liter Erlenmeyer

flask. 1.5 liters of 90% acetone-water solvent was mixed with the coal and stirred for two hours. The solution was centrifuged to remove all the insolubles, and the humic acid was recovered from the acetone-water solvent by vacuum distillation of the solvent at 80°C.

The dried humic acids were stored in stoppered bottles in a desiccator until used for pyrolysis.
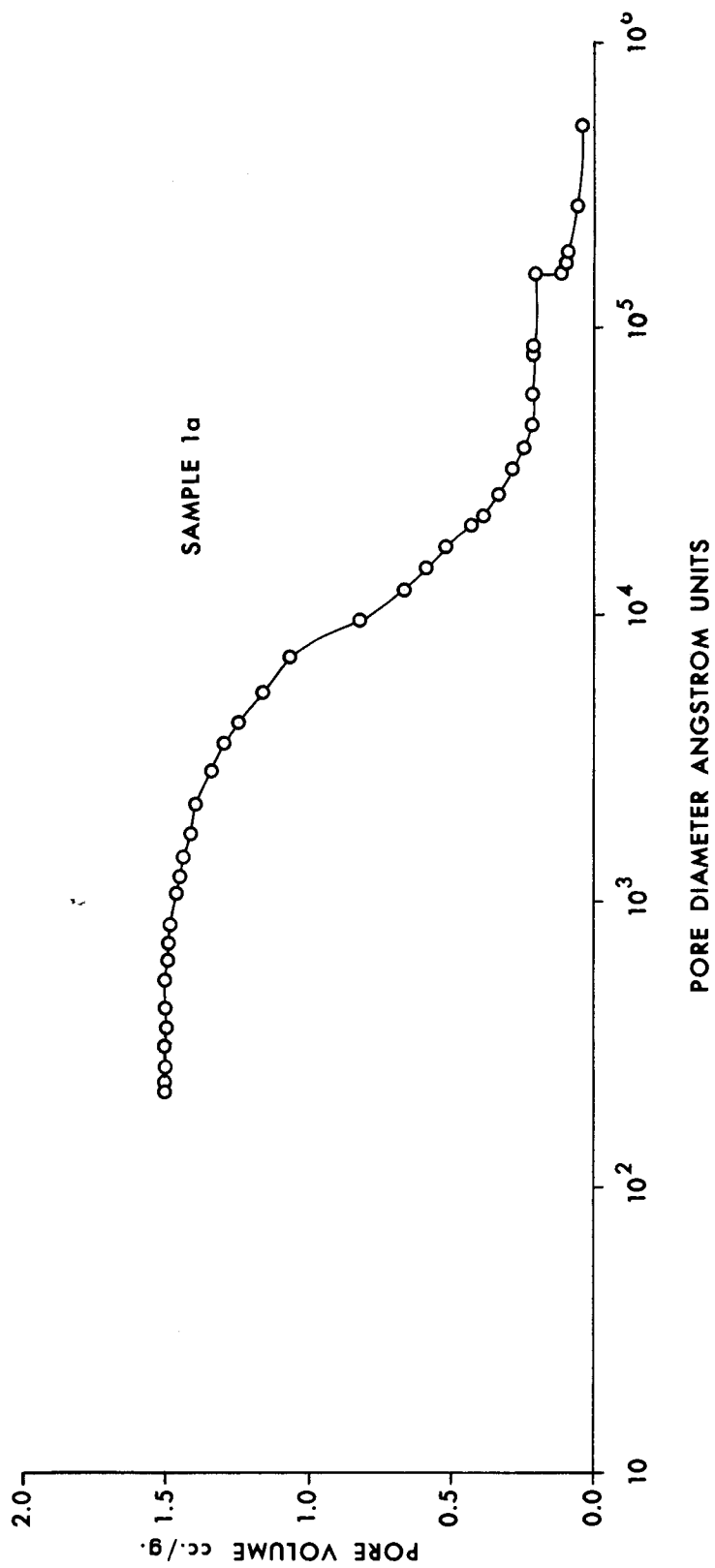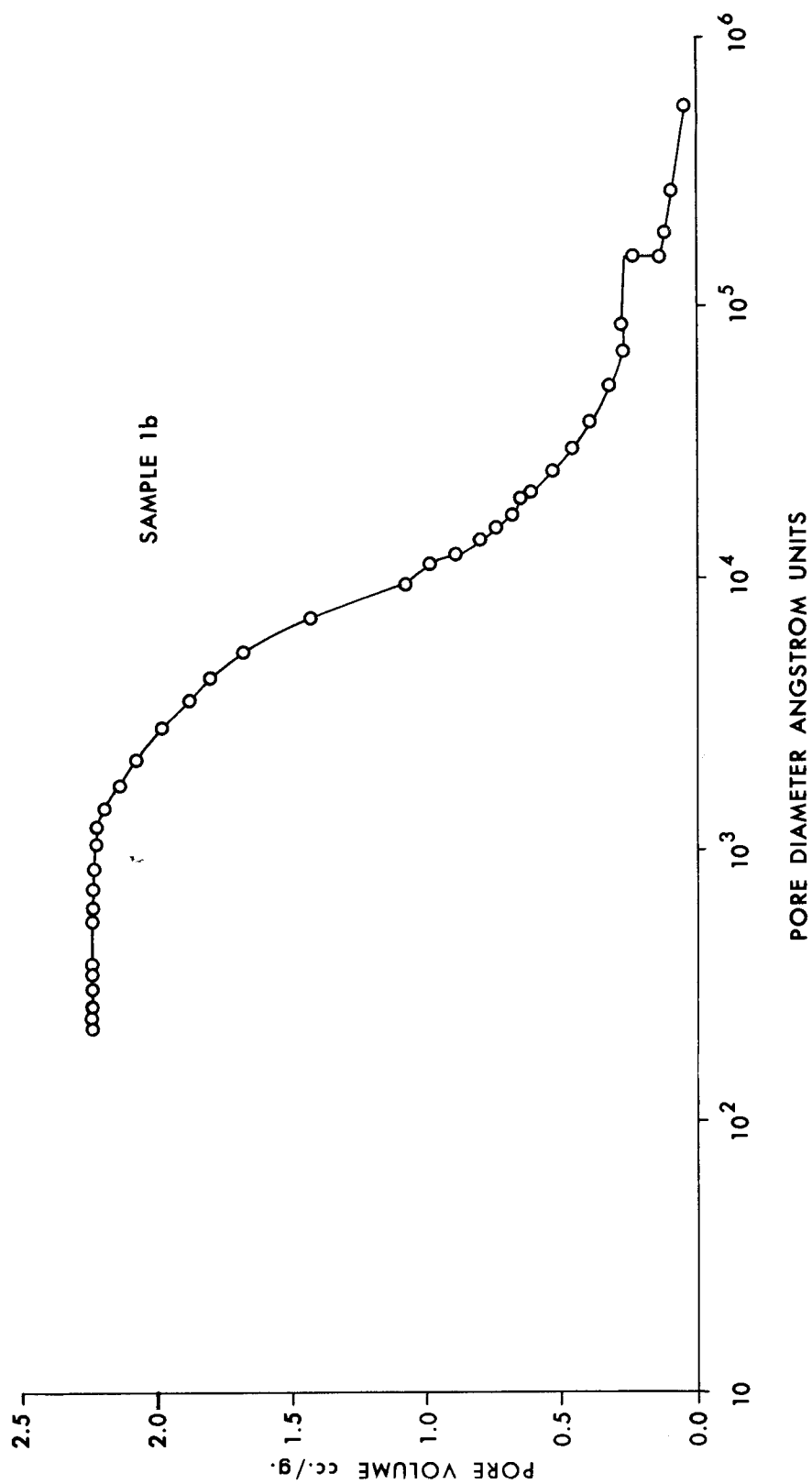
APPENDIX II:

The humic acids were reduced following the technique of Blanksma (5). Nitro groups which are ortho to alkoxy structures are reduced by means of Na_2S in aqueous solution. Using the mole ratios for reactions given (5), 1.75 gm. of humic acids was dissolved in 250 ml. of 10% acetone-water solution. 3.80 gm. of Na_2S and 0.6 gm. of S were added and the solution refluxed in a 1 liter three necked round bottom flask for 0.5 hours at 70°C.

The solution was filtered and washed with 0.1 N HCl until no $S^=$ ion could be detected. A dark brown residue was left. This residue was washed with 90% acetone-water to remove all unreacted humic acids, and a black residue remained. This black residue was assumed to be the reduced humic acids.
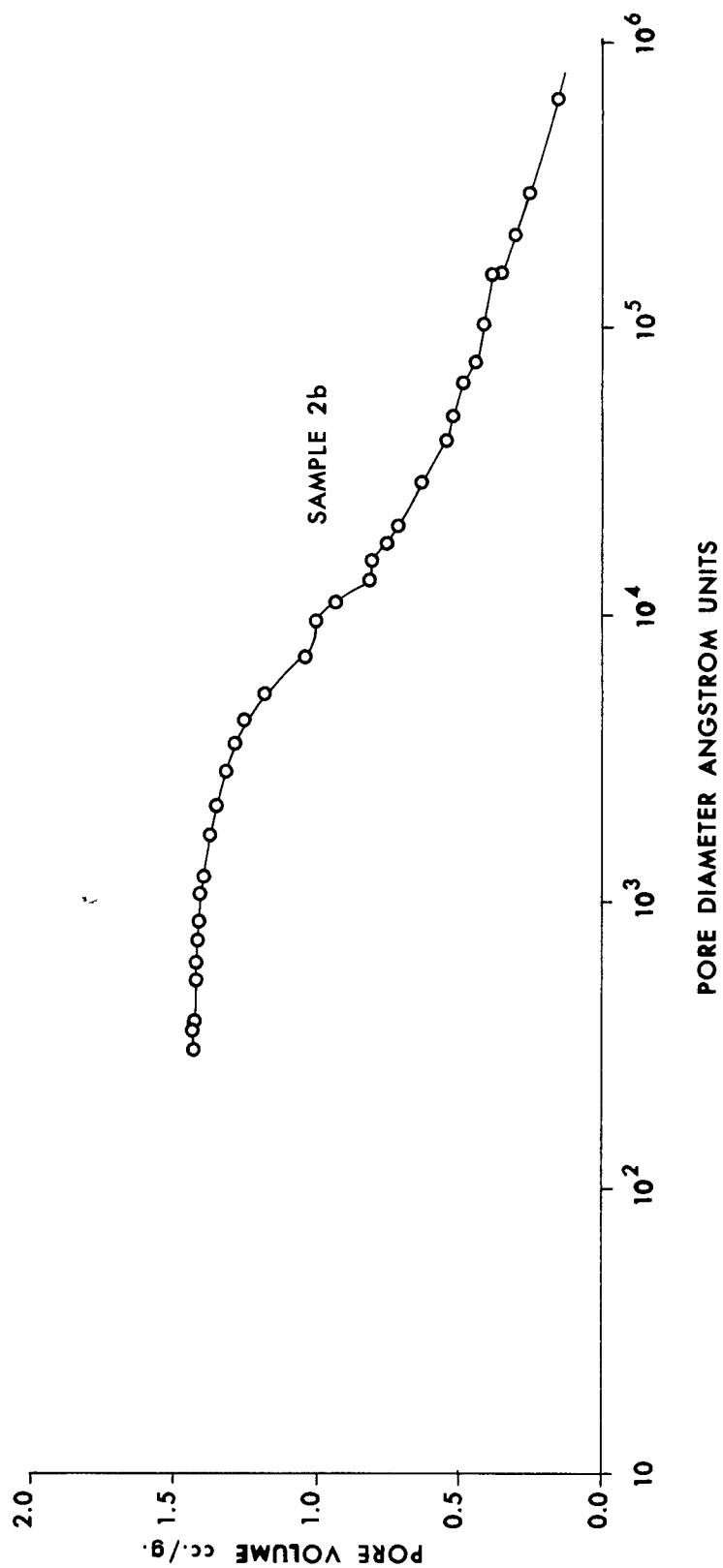
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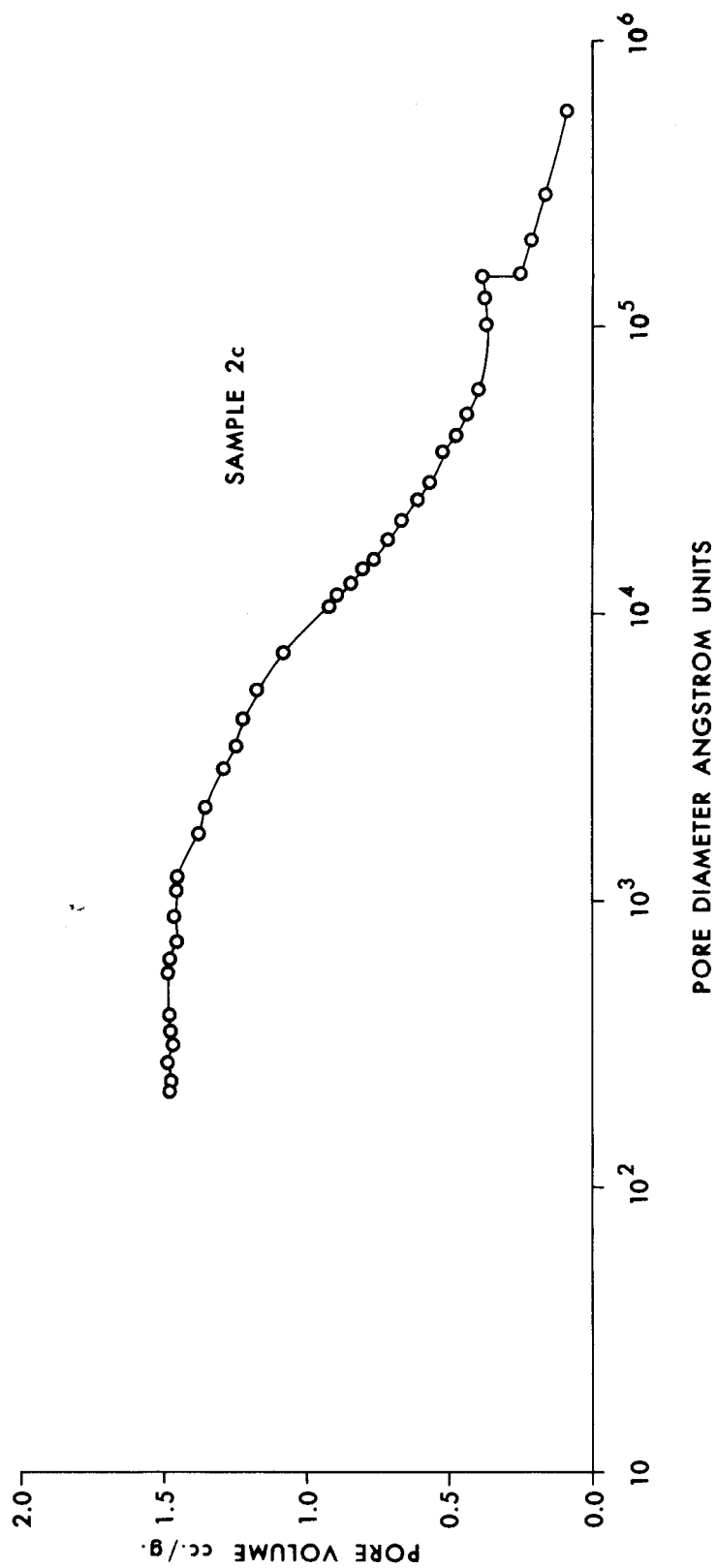

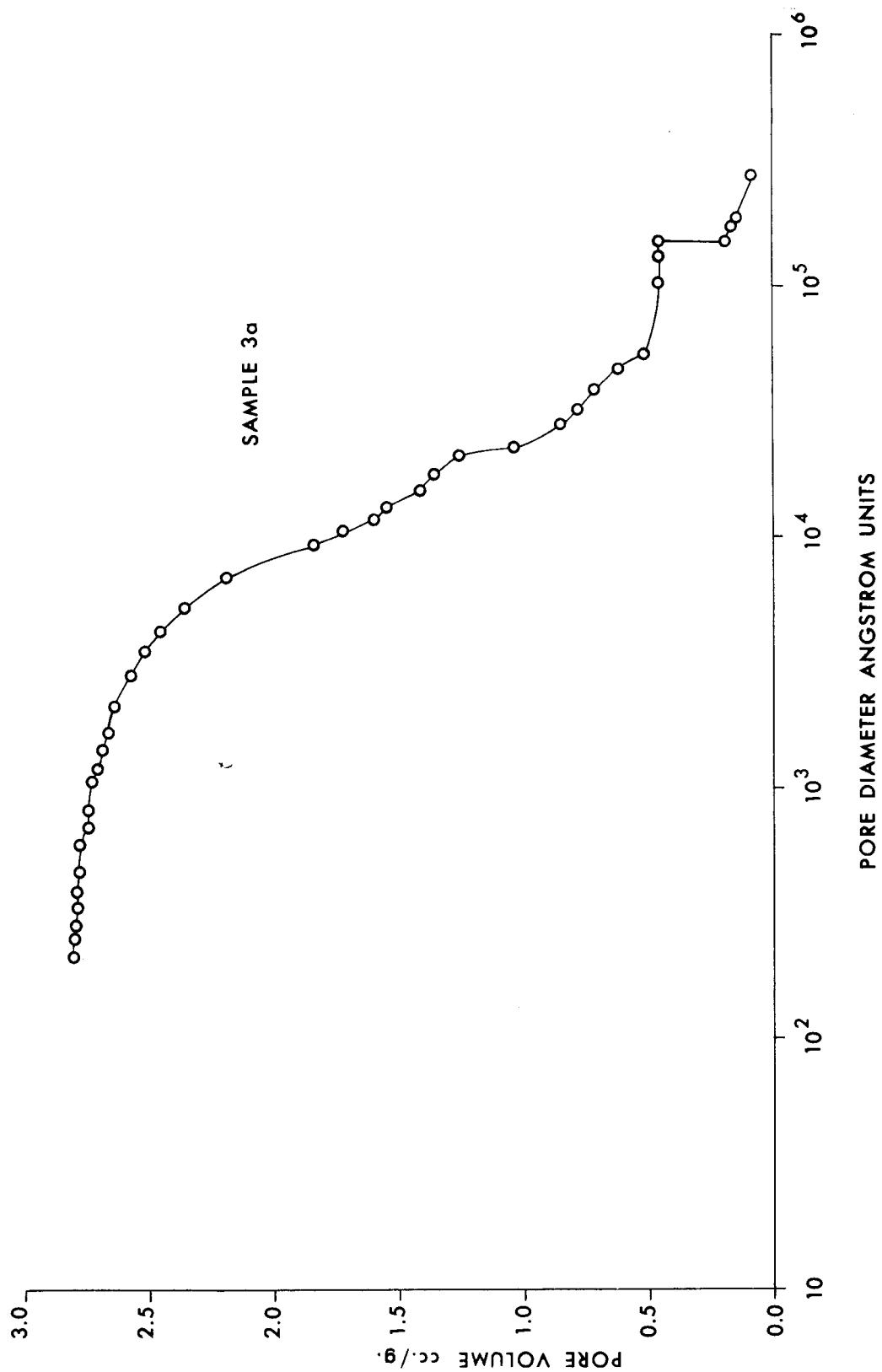Porisimiter Plots for

Activated Carbons

SAMPLE 1a

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 1b

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 1c

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 2a

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 2b

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 2c

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 3a

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 3b

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 3c

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 4a

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 4b

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 4c

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 5a

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 5b

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.

SAMPLE 5c

PORE DIAMETER ANGSTROM UNITS

PORE VOLUME cc./g.