[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, PENNSYLVANIA STATE COLLEGE]

Ozonization Studies of Coal Constitution

BY C. R. KINNEY AND L. D. FRIEDMAN

The reaction of ozone on coal and a number of related substances has been studied. Contrary to results with other oxidants, moist ozone converts a significant fraction of the carbon of coal, carbon black and lampblack *directly* to water-soluble products without intermediate formation of humic acids. The results of ozonization of aqueous, alkaline "solutions" of humic acids depend on the source of the acid and the temperature of preparation of the solution. These facts are believed to be in accord with the view that coals and derived humic acids contain, as a part of their structure, "stacked planes" similar to those which X-ray studies have shown to be present in carbon black.

Although the constitution of coal has been studied with a large variety of oxidizing reagents, the use of ozone has been almost entirely neglected. About 30 years ago Franz Fischer and co-workers[1,2] found that as much as 92% of a coal was rendered water soluble by the prolonged action of ozone, but nothing further was done until recently when Ahmed and Kinney[3] ozonized the humic acid-like oxidation products from a bituminous coal. They showed that the main products were carbonic, oxalic and water-soluble acids apparently similar to the benzenecarboxylic acids obtained by the action of other oxidizing reagents.[4] The appearance of oxalic acid and benzenecarboxylic acids can be explained on the basis of an essentially benzenoid structure,[5] but such a structure is not entirely harmonious with certain of the chemical and physical properties of these humic acids which, in many respects, are more like those of "amorphous" carbon than an aromatic compound with a molecular weight of about 300.[6,7,8] Although it has not been found possible to differentiate between polynculear aromatic structures and "amorphous" carbon by means of distinctive ozonization products, it has been found that both coal and "amorphous" carbon are rapidly attacked by ozone and that similar products are obtained.

The coal (see Table I for the source and analysis of the samples ozonized) was first ozonized in an alkaline suspension because the humic acids were readily attacked under these conditions, but in 48 hours only 16.5% was converted to products, Table III. In the absence of alkali, Table II, the dry coal gave 15% of products in 24 hours, while the air-dried coal containing 4.7% moisture gave over 20% and with moist ozone nearly 50%. By decreasing the particle size from −60 to −325 mesh, an additional 6% reacted and, by ozonizing the −60 mesh coal for a total of 72 hours with the products extracted at 24-hour intervals, it was almost completely ozonized.

TABLE I

ANALYSES

Samples	Source	Analyses, %[a] C	H	O + N + S[b]
Coal, Pittsburgh seam	Allegheny Co., Pa.	86.9	5.2	7.9
Carbon black, Carbolac 1	Godfrey L. Cabot Co.	89.1	0.5	10.4
Lampblack, Martin	Speer Carbon Company	95.5	.7	3.8
Graphite, spectroscopic grade	National Carbon Company	99.5	.2	0.3
Pyrene, 95% purity	Frankel & Landau, Berlin, Germany			
Humic acids	HNO_3-oxid. bit. coal	62.4	3.2	34.4
Humic acids	Air-oxid. bit. coal	58.8	3.5	37.7
Humic acids	Ozonized bit. coal	56.4	3.3	40.3
Humic acids	Ozonized carbon black	54.0	2.6	43.6
Humic acids	Ozonized lampblack	46.1	3.5	50.4
H_2O-soluble acids	Ozonized bit. coal	44.1	3.5	52.4
Alkali insolubles	Ozonized bit. coal	87.3	5.5	7.2
Alkali insolubles	Ozonized carbon black	57.6	1.7	40.7
Alkali insolubles	Ozonized lampblack	75.1	0.8	24.1

[a] Moisture- and Mineral Matter-Free Basis. [b] O + N + S by difference.

In all of these experiments the maximum yield of humic acid-like product amounted to only 4.5% of the original carbon in the sample. This appeared to be highly significant because humic acids have long been thought to be intermediate oxidation products in the oxidation of bituminous coals.[4] For example, boiling 1 *N* nitric acid converted 67.5% of the carbon of a Pittsburgh seam coal to humic acids, 14.4% to carbon dioxide, and 9.2% to water-soluble acids.[6] On reozonizing the humic acids isolated from the ozonized coal, Table II, it will be seen that only about 30% reacted in 24 hours and that a sample of humic acids obtained from the coal by air-oxidation at 200°[9] was even more resistant. Considering the fairly slow rate of ozonization of the humic acids and the fact that 58.2% of the carbon of the coal appeared as water-soluble

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(1) F. Fischer, *Ges. Abhandl. Kenntnis Kohle*, **1**, 26 (1915).

(2) F. Fischer and H. Tropsch, *ibid.*, **2**, 160 (1917).

(3) M. Ahmed and C. R. Kinney, THIS JOURNAL, **72**, 559 (1950).

(4) H. C. Howard, "Chemistry of Coal Utilization," H. H. Lowry Editor, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 357.

(5) W. A. Bone, L. G. B. Parsons, R. N. Sapiro and C. M. Groocock, *Proc. Roy. Soc.* (*London*), **A148**, 492 (1935).

(6) B. Juettner, R. C. Smith and H. C. Howard, THIS JOURNAL, **57**, 2322 (1935).

(7) S. A. Herbert, H. B. Charmbury and C. R. Kinney, *Fuel*, **27**, 168 (1948).

(8) R. Belcher, *J. Soc. Chem. Ind.*, **67**, 213 (1948).

(9) L. D. Friedman and C. R. Kinney, *Ind. Eng. Chem.*, **42**, 2525 (1950).

TABLE II

OZONIZATION OF SOLID SAMPLES

	Time, hours	Carbon of sample converted to products,[a,b] % Alkali insolubles	Humic acids	Carbon dioxide	Acetic acid	Balance H_2O-sol. acids
Coal, oven-dried, −60 mesh, dry ozone	24	85.0	0.5	1.2	4.8	8.5
air-dried, −60 mesh, dry ozone	24	76.8	2.6	5.5	0.9	14.2
air-dried, −60 mesh, moist ozone	24	51.3	2.4	10.5	1.9	33.9
air-dried, −325 mesh, moist ozone	24	45.1	2.1	12.9	2.4	37.5
air-dried, −60 mesh, moist ozone	72	40.5	1.3	20.1	1.0	37.1
air-dried, −60 mesh, moist ozone	72[c]	6.2	4.5	28.2	2.9	58.2
Humic acids, from ozon. coal, moist ozone	24	...	69.8	6.5	...	23.7
from air-oxid. coal, moist ozone	24	1.6	79.9	7.2	1.9	9.4
Carbon black, oven-dried, dry ozone	4.5	Exploded	..	11.5	...	..
as recd., moist ozone	12	...[d]	0.9	33.5	0.9	..[e]
as recd., moist ozone	24	14.3	5.9	45.4	.8	33.6
Lampblack, as recd., moist ozone	24	70.7	..	6.9	.6	21.8
as recd., moist ozone, 99°	24	34.9	3.2	36.6	.8	24.5
as recd., moist ozone, 99°	40	...	10.1	..	...	..
Graphite, as recd., moist ozone	48	100.0	..	..	...	..
Pyrene, −200 mesh, moist ozone	24	68.9	..	5.8	.4	24.9
Oxalic acid·$2H_2O$, moist ozone	8	...	..	13.2	...	..
Phthalic acid, moist ozone	8	...	..	0.0	...	..

[a] Moisture- and mineral matter-free basis. [b] Traces of oxalic acid were found in all experiments <0.1%. [c] Interrupted at 24, 48 and 72 hours and the products extracted with alkali; percentages cumulative. [d] Residue not analyzed, wt.-% yield was 77.6%. [e] Found 0.3% oxalic acid in this experiment.

TABLE III

OZONIZATION IN ALKALINE MEDIUM

Sample and conditions	Time, hours	Carbon of sample converted to products,[a] % Alkali insol.	Humic acids	Carbon dioxide	Oxalic acid	Acetic acid	Balance H_2O-sol. acids
Coal, −60 mesh, suspended	48	83.5	0.4	..	2.9	5.0	..
Humic acids, from HNO_3-oxid. coal,	8	0.1	5.8	26.6	0.4	1.5	65.6
dissolved at room temperature	16	1.0	2.0	29.4	0.5	1.3	65.8
	16[b]	1.1	0.1	31.7	1.9	3.3	61.9
	24	0.1	.0	32.9	11.8	2.4	52.8
	50	0.4	.0	42.3	19.7	3.2	34.4
Humic acids, from air-oxid. coal, dis-	0	3.0	97.0				
solved in boiling alkali	2	3.4	1.7	14.4	2.1	0.4	78.0
	8	4.9	0.1	36.4	18.3	1.5	38.8
	16	4.6	.0	36.9	22.4	1.8	34.3
	24	4.7	.0	38.3	22.9	1.9	32.2
	40	2.9	.0	40.7	31.2	2.9	22.3
	96	1.9	.0	46.1	35.0	3.7	13.3
Humic acids, from air-oxid. coal, dis-	0	24.2	75.8				
solved at 60°	8	17.3	55.3	20.1	2.8	0.7	3.8
	16	9.2	50.1	23.1	8.4	1.5	7.7
	24	6.8	36.0	27.5	17.2	2.0	10.5
	72	5.2	4.0	45.1	26.5	2.6	16.6
	96	0.0	0.0	53.4	44.0	2.8	None
Humic acids, from ozon. carbon black	40	0.0	.0	79.8	21.0	3.9	None
Pyrene, −200 mesh, suspended	24	77.0	.0	0.6	0.1	2.4	19.9
Phthalic acid	3.5[c]	..	..	10.0	0.1	1.0	88.9
	14[d]	..	..	24.0	21.6	2.2	52.2
	24[e]	..	..	34.0	28.0	3.1	34.9
Oxalic acid	3.5	..	..	..	99.3	...	..
	11	..	..	..	91.9	...	..
	24	..	..	..	89.9	...	..
	32.5	..	..	..	81.8	...	..

[a] Moisture- and mineral matter-free basis. [b] Check run. [c] Solution amber colored. [d] Color began to lighten. [e] Solution colorless.

acids, it seems that the coal molecules were transformed for the most part directly into water-soluble acids. Belcher[10] also found that water-soluble acids appeared to be formed directly during anodic oxidations which were unfavorable to the oxidation of humic acids to water-soluble acids.

The water-soluble acids contained small amounts of acetic acid but only traces of oxalic acid. They were almost black in color and carbonized with

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[10] R. Belcher, *J. Soc. Chem., Ind.*, **67**, 217 (1948).

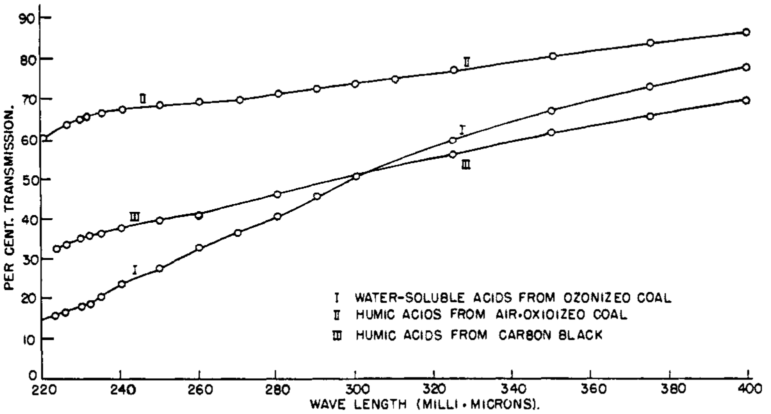

Fig. 1.—Ultraviolet absorption of humic acids: concentration, 0.01 g./100 ml. 0.1 *N* sodium hydroxide; slit widths of 0.2 to 1.9 mm.; fused silica absorption cell of 1 cm. width.

little apparent fusion or sublimation. In these respects, they showed a close relationship with the humic acids. On the other hand, a small quantity of terephthalic acid was identified and, on decarboxylation, benzene was formed which further demonstrated that they contained benzene carboxylic acids. Therefore, these acids are unquestionably a broad mixture of products and additional work must be done to establish the identity of individual components. However, the assumption that coal molecules are essentially large polynuclear aromatic structures[5] does not appear likely because ozone would hardly be expected to reduce the size sufficiently under the conditions used to form water-soluble acids. For this reason, it appears that the molecular units in coal must be relatively small in size. This is also borne out by the ease of converting coal to humic acids which have an apparent molecular weight in catechol of only about 300.

A sample of dry carbon black was also treated with dry ozone in an attempt to differentiate between coal and "amorphous" carbon,[3,11] Table II. Carbon dioxide was evolved in large amounts, but after 4.5 hours a mild explosion occurred and the experiment was stopped. With undried carbon black and moist ozone 33.5% of the carbon was converted to carbon dioxide in only 12 hours. In 24 hours over 85% of the sample had reacted; 45.4% was converted to carbon dioxide, 33.6% to water-soluble acids, and 5.9% to humic acids similar in properties to those obtained from coal. An ultraviolet spectrogram of the latter acids is compared in Fig. 1 with similar spectra obtained from air-oxidized coal humic acids and water-soluble acids from ozonized coal. The spectrum of the humic acids from ozonized carbon shows a greater similarity with that from air-oxidized coal humic acids, but no fine structure appears in any of the spectra.

The isolation of humic acids from the ozonization products of carbon black was particularly significant because it implies that the nuclei of these humic acids are composed of carbon atoms arranged in the manner characteristic of carbon black. That the formation of humic acids was not peculiar to carbon black was shown by obtaining similar acids from lampblack, Table II. The best yield from this source was 10.1% of the carbon (21.0% by weight) obtained at 99°. Graphite *failed* to react with ozone at room temperature at all. The similarities in the properties of the humic acids obtained from the carbon samples and those obtained from coal suggest that carbons and coal have, to a limited degree, common structures. It also seems likely that the proportion of carbon structures in a coal similar to that in "amorphous" carbon is related to its rank which would account for many of the properties of coals in relation to their rank.

In addition to the ozonizations in the solid state, several humic acid preparations obtained from coal and carbon were ozonized in the presence of alkali, Table III. With the nitric acid-oxidized coal humic acids dissolved in alkali at room temperature and the air-oxidized coal humic acids dissolved in boiling alkali, the primary products were carbon dioxide and "water-soluble" acids. On continuing the ozonization, the "water-soluble" acids were converted to additional carbon dioxide and oxalic acid. Since phthalic acid was found to be transformed into these same products at about the same rate and in about the same proportion, it appears likely that the carbon dioxide and oxalic acid derived from the "water-soluble" acids resulted from the ozonization of aromatic structures. This was further borne out by the isolation and identification of terephthalic acid from the "water-soluble" acids. Therefore it may be assumed that the transformation of the humic acids involves the oxidation of the "amorphous" carbon structures down to the point where the carbon planes are no longer held together and consequently become free to shift into the single plane, aromatic structure.

The air-oxidized coal humic acids were also ozonized when poorly dispersed in alkali at 60° and the results were so striking that they have also been included in Table III. Under these conditions the acids were but slowly attacked by ozone. The maximum conversion to "water-soluble" acids amounted to only 16.6% and occurred at 72 hours instead of at 2 hours of ozonization. In spite of this difference, the humic acids were completely converted to carbon dioxide and oxalic acid plus the usual small quantity of acetic acid in 96 hours. This difference in behavior appears to be due entirely to the difference in the degree of dispersion of the humic acids and it may be assumed that the poorly dissociated acids were attacked by the ozone largely on the surface of the particles, apparently with the result that oxidation frequently proceeded beyond the point where aromatic acids could be formed from the carbon planes before dissociation occurred. The humic acids obtained from carbon black behaved in a similar manner, although they appeared to be more readily dispersed in alkali. The similarity of the air-oxidized coal humic acids

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(11) B. Bruns, E. Kozlova and M. Maksimova, *J. Phys. Chem.* (*U. S. S. R.*)., **6**, 997 (1935); *C. A.*, **30**, 2073^4 (1935).

and the ozonized carbon black humic acids is further shown in the figure in which the ultraviolet absorption curves are compared together with the "water-soluble" acids from ozonized coal.

Experimental

Samples used for ozonization are listed in Table I, together with their source and analysis. The nitric acid-oxidized bituminous coal humic acids were a part of a preparation used previously[3,7] as were the air-oxidized bituminous coal humic acids.[9] The remainder of the samples were prepared during the present investigation.

An ozonizer similar to that described by Smith[12] was used. With an oxygen flow rate of 12 liters per hour and 13,000 volts in the secondary circuit, a quite constant yield of 5.9–6.0% ozone by volume was produced. Spherical ground glass joints were used for most of the connections, but it was found that Tygon tubing could be used without affecting the results. Oxygen flow rates were measured during experiments by means of a capillary flow meter. Absolute flow rates were obtained, before the ozonizer was turned on, with a calibrated wet test meter placed at the end of the train. During the runs the wet test meter was disconnected and the rate of flow shown on the capillary flowmeter maintained by adjusting the oxygen supply valve. The oxygen stream was dried by passing it through two towers filled with activated alumina, followed by another filled with glass wool to remove dust.

Ozonizations of solids were carried out in 250-ml. standard taper erlenmeyer flasks. Two-gram samples were spread out in a thin layer over the bottom of the flask. The ozone inlet came to within 1 to 2 cm. of the samples. A carbon dioxide-absorbing train followed the sample flask and was composed of three 250-ml. standard taper flasks containing standard barium hydroxide. In certain experiments the ozone stream was moistened by bubbling through a water trap before being admitted to the sample. This did not affect the yield of ozone by a detectable amount.

At the end of the ozonization period, yields of alkali-insoluble products, carbon dioxide, oxalic acid, steam-volatile acids, and the balance, the water-soluble acids, were determined by the following methods. Yields were calculated on the basis of the carbon in the original sample converted to products and appear in Table II.

Alkali-insoluble residues were determined by repeatedly extracting the ozonized samples with boiling 5% sodium hydroxide until the extract was no longer colored. Usually two or three extractions were sufficient. The insoluble matter was centrifuged each time and the solution decanted through a tared fritted glass filter or filter paper. The residue was finally washed onto the filter, dried at 105°, and weighed. Residues from the ozonized air-oxidized coal humic acids and from ozonized carbon black had a very strong tendency to disperse colloidally when washed with water. The dispersed solids could be thrown down by recentrifuging at 2100 r.p.m. for 30 minutes or by boiling for 10–15 minutes, but the best way to handle these residues was to transfer them to an evaporating dish and evaporate them to dryness on the steam-bath, after which washing could be accomplished without dispersion. Analyses of certain of these residues appear in Table I.

Yields of humic acids were obtained on the alkaline filtrate and washings from the alkali insolubles. These solutions were diluted to a known volume and aliquots were removed for the determinations. Humic acids were precipitated by acidifying with dilute sulfuric acid. They were coagulated by boiling for 10–15 minutes, filtered through a tared fritted glass filter or filter paper, and washed free from sulfates. After drying at 105°, the acids were weighed and in certain instances analyzed (Table I).

Volatile acids were determined on another aliquot. The alkali was just neutralized with sulfuric acid and made slightly acid with sodium acid sulfate.[13] The volatile acids were then distilled into standard base as long as acids distilled, constantly adding fresh carbon dioxide-free water to replace that distilled. The excess standard base was titrated with standard acid using phenolphthalein indicator. The acids were calculated as acetic since Duclaux constants indicated that this was the major acid present. Acetic acid was also identified as the *p*-phenylphenacyl ester in several cases.

Oxalic acid was usually determined on fresh aliquots but may be determined on the residue from the acetic acid determination. Any humic acids present were precipitated and removed as described above. The filtrate was neutralized with dilute sodium hydroxide and made acid to litmus with dilute sulfuric acid. Calcium oxalate together with calcium sulfate was then precipitated with excess calcium acetate. Oxalate was determined on the precipitate by oxidation with acid permanganate.

Yields of carbon dioxide were determined by titrating the excess barium hydroxide remaining in the absorption train with standard hydrochloric acid using phenolphthalein as the indicator.

Water-soluble acids reported in Table II were calculated as the balance between the sum of the percentages of the other constituents and 100%. For purposes of study, however, these acids were either extracted directly by water from the ozonized sample or were extracted by methanol from the residue obtained by evaporating the filtrate from the humic acids precipitated with hydrochloric acid.

The water-soluble acids extracted directly from ozonized coal were prepared from 7.0 g. of a −200 mesh sample. After ozonizing 24 hours, the water-soluble acids were extracted and the process repeated for a total of four times, leaving very little coal. The combined extracts were evaporated to dryness in a vacuum of about 20 mm. The residue was finally dried at 80° for two days and no further loss was observed on additional drying. The yield was 4.0 g. or 57% by weight. An analysis is given in Table I. The acids were black and hygroscopic. A 2-g. sample was dissolved in water and poured into ammonia according to the directions of Juettner,[14] but no ammonium mellitate crystallized out. On the other hand, a positive fluorescein test was obtained.

Soluble acids isolated by the methanol-extraction method were obtained from 10.0 g. of coal which was ozonized continuously for 96 hours. On extracting the ozonized coal with 5% sodium hydroxide, 22% of insoluble residue remained. The humic acids were precipitated with hydrochloric acid and removed. The filtrate was evaporated to dryness on the steam-bath. The dry residue was ground and extracted four times with boiling methanol. The first two extracts were black, but the fourth was light brown and contained a negligible amount of extract. The salt residue was a tan color. After distilling the combined extracts, the residue was dried to a constant weight of 8.0 g. in a vacuum oven at 75°. The product gave positive tests for sodium and chloride ions, and was black and hygroscopic. The product was boiled with 300 ml. of water and 1.4 g. of insoluble acids were recovered. Terephthalic acid was identified in the latter by making the methyl ester which was confirmed by mixed melting point with a known specimen. The insoluble acids also gave a positive fluorescein test but a negative chloranil test for *o*-phthalic acid. The water-soluble portion gave a negative test for mellitic acid with ammonia but gave a positive fluorescein test. On distilling the barium salt with excess barium hydroxide directly into a nitrating mixture, benzene was identified as *m*-dinitrobenzene. Insoluble barium, silver and lead salts gave equivalent weights of 144, 180 and 202, respectively.[15] A suspension of the lead salts, when treated with hydrogen sulfide, yielded grayish crystalline acids melting at 195–228° with decomposition.

Ozonizations of the substances listed in Table III were made in 500-ml. containers. Samples weighing 2 g. were dissolved or suspended in 200 ml. of 5% sodium hydroxide. Solutions which had been heated to aid the solution of the sample were cooled before ozonizing. Analyses for alkali insolubles, humic, acetic, oxalic and water-soluble acids followed the procedures described above. Carbon dioxide was determined on an aliquot part of the alkaline solution following the filtration of the alkali insolubles. The aliquot was placed in a 500-ml. 3-neck flask which had a gas-inlet tube, a dropping funnel and a condenser attached. The sample was acidified by adding dilute sulfuric acid through the dropping funnel. A slow stream of carbon dioxide-free

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(12) L. I. Smith, This Journal, **47**, 1844 (1925).

(13) C. R. Kinney, *ibid.*, **69**, 284 (1947).

(14) B. Juettner, *ibid.*, **59**, 210 (1937).

(15) J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1942.

air was passed over the solution, out through the condenser, and into standard barium hydroxide. By using a fritted glass bubbler it was found possible to use but one trap, however the fritted glass face must be turned downward or the pores soon become clogged. After the air had been turned on, the solution was refluxed gently for 1.5 hours. The reflux condenser efficiently prevented the escape of the volatile acids as was shown by analyzing a test mixture containing known amounts of sodium carbonate, sodium acetate, and oxalic acid.

Ultraviolet absorption spectra of the water-soluble acids from ozonized coal, humic acids from air oxidized coal, and humic acids from carbon black were obtained with a Beckman quartz spectrophotometer. For this purpose, 0.1-g. samples were dissolved in 100 ml. of 0.1 N sodium hydroxide. Fused silica cells and slit widths of 0.2 to 1.9 mm. were used. Spectrograms were constructed as shown in Fig. 1.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, PITTSBURGH COKE AND CHEMICAL COMPANY]

A Comparison of Pore Size Distributions of Activated Carbons Calculated from Nitrogen and Water Desorption Isotherms

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Pore size distribution curves for several activated carbons computed by the Barrett, Joyner, Halenda method from the low temperature nitrogen desorption isotherms were compared with pore size distribution curves computed from water desorption isotherms by the method described by Juhola and Wiig. A semi-quantitative agreement was found between the distribution curves computed by the two methods for pores in the 22 to 300 Å. radius range. Below 22 A. radius the method based on nitrogen absorption is not theoretically applicable. The water adsorption method was found to be theoretically applicable to the complete gamut of pores found in activated carbons and the method yielded distribution curves from which surface areas were computed that were in essential agreement with the Brunauer, Emmett and Teller (BET) areas.

In a recent publication Barrett, Joyner and Halenda[1] described a method for computing the pore size distributions of various types of porous adsorbents from nitrogen adsorption data determined at liquid nitrogen temperature. This technique was developed to deal with relatively coarsely porous adsorbents, such as some clay cracking catalysts, bone chars and silica gel. In their computations, it was assumed that equilibrium between the gas phase and the adsorbed phase (liquid state) during desorption was determined by two mechanisms: (1) physical adsorption in multi-layers on the pore walls, and (2) condensation in capillaries. The pore radius corresponding to a specified relative vapor pressure on the desorption isotherm was the thickness, t, of the physically adsorbed layer plus the meniscus radius, r_K, of the condensed phase in the inner capillary. To get the relationship between t and P/P_0, they used the experimental data of Shull,[2] determined on a non-porous crystalline material, assuming that the same relationship applied to porous materials. The capillary radius, as a function of P/P_0, was expressed by the classical Kelvin equation

$$r_K = \frac{2\sigma \; V \cos \theta}{RT \ln P_0/P}$$

Here σ is the surface tension and V the molar volume of the liquid adsorbate, θ, the contact angle, which is assumed to be zero for nitrogen, and P/P_0 the relative vapor pressure.

In an earlier publication, Juhola and Wiig[3] described a method for computing the pore size distributions of activated carbons from the desorption side of the water adsorption isotherms determined at room temperature. In this case the pore radius corresponding to any P/P_0 was given directly by the Kelvin equation, since it was believed that the formation of any physically adsorbed layer on the pore walls was negligible. This method is limited because it is applicable only to activated carbons which do not possess hydrophilic groups on the surface.

In this paper a comparison is made between these two methods of computing pore size distributions as applied to activated carbons. Since both methods (although based on considerably different adsorption theories) should give the same pore size distribution for a given carbon, the agreement or disagreement serves to confirm the validity, and/or to indicate the weaknesses of the methods.

Experimental

The nitrogen adsorption–desorption isotherms were determined at liquid nitrogen temperature in a conventional volumetric apparatus of the type used by Brunauer and Emmett.[4]

The apparatus and procedure used in determining the water adsorption–desorption isotherms, except for small modifications, were described in the paper by Juhola and Wiig.[3] The weight of water adsorbed on the carbon was determined gravimetrically following each adsorption or desorption, after allowing a suitable length of time (1 to 2 hours) for the system to attain equilibrium. These measurements were made at 25°.

According to previous water adsorption studies on activated carbons,[3] $\cos \theta$ (in the Kelvin equation) was found to be 0.49 giving a contact angle of 60.6°. The molar volume, V, of the adsorbed water was in part a function of P/P_0. The best average V for several carbons investigated was 20 cc. This value was used in the Kelvin equation and in converting weight of adsorbed water to pore volume.

The carbon samples were evacuated at about 400° for 1 to 2 hours prior to the adsorption experiments. For each carbon the same sample was used in each gas adsorption measurement.

Results and Discussion

The experimental results on four activated carbons, representing rather widely differing types of pore structures, are presented in these comparisons. Some physical data which are intended

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[1] Elliott P. Barrett, Leslie G. Joyner and Paul P. Halenda, THIS JOURNAL, **73**, 373 (1951).

[2] C. G. Shull, *ibid.*, **70**, 1405 (1948).

[3] A. J. Juhola and E. O. Wiig, *ibid.*, **71**, 2069 (1949).

[4] P. H. Emmett and S. Brunauer, *ibid.*, **59**, 1553 (1937); S. Brunauer and P. H. Emmett, *ibid.*, **59**, 2682 (1937).