

whether the swelling is of the predicted order of magnitude.

No satisfactory explanation of the hollow-tube appearance of chrysotile fibers when viewed in the electron microscope^{7-9,19} can be offered other than to suggest the obvious: the sample viewed in the electron microscope no longer bears a one to one relationship with the native fiber. Whether this is the result of the treatment the fibers have received

(19) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955, p. 208.

during the preparation or of the exposure to the electron beam in a high vacuum remains to be determined.

Acknowledgment.—The successful execution of this work is due in large part to Mr. George Reim-schussel who made many of the density measurements reported here. Mr. Marion Badollet and Mr. William Streib made available certain excellent specimens of chrysotile which were measured in the course of this investigation.

CHANGES IN PHYSICAL PROPERTIES OF GRAPHITIZED CARBON RODS UPON GASIFICATION WITH CARBON DIOXIDE^{1,2}

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Changes in the physical properties of graphitized carbon rods after gasification to different burn-offs at 1000° and to 11% burn-off at temperatures between 970 and 1372° have been determined. The physical properties investigated were surface area, total and incremental pore volume, average pore radius, macropore surface area and specific reaction rate. The results can be explained if the carbon rods are considered to be composed of relatively homogeneous, non-porous particles of petroleum coke bound together by a thin shell of coal tar pitch coke, which essentially consists of a condensed "bubble type" structure.

Introduction

The widespread importance of the heterogeneous gasification reactions of carbons in present-day industry necessitates a complete understanding of the mechanism of these reactions. On the one hand, the primary interest in gasification is related to the conversion of carbonaceous materials to either gaseous fuels or synthesis gas. Here of primary concern is the attainment of high gasification rates. On the other hand, the primary interest is connected with the lack of gasification of carbons and graphites when used as electrodes, structural carbons or moderators in atomic reactors. In either case, a basic understanding of the relationship between reactivity of carbon to gases and the physical properties of the carbons is essential.

In the present work, the reactivity of a highly graphitized carbon with carbon dioxide, as a function of burn-off and temperature, has been compared with changes in the physical structure of the carbon. This work is an extension of the finding of Walker and Rusinko,³ who investigated the reactivities of six different carbons.

Experimental

Carbon.—The samples used were National Carbon Company AGKSP special graphite spectroscopic electrodes containing an ash content less than 0.01%. They were 5 cm. long by 1.3 cm. in diameter. A more detailed description of the manufacture of graphitized carbon can be found elsewhere.⁴

(1) Based on a Ph.D. thesis submitted by Emile Raats to the Graduate School of The Pennsylvania State University, June, 1955.

(2) This paper presents the results of one phase of research carried out under Contract No. AT(30-1)-1710, sponsored by the Atomic Energy Commission.

(3) P. L. Walker, Jr., and F. Rusinko, Jr., *THIS JOURNAL*, **59**, 241 (1955).

(4) H. W. Abbott, "Encyclopedia of Chemical Technology," Vol. 3, The Interscience Encyclopedia Inc., New York, N. Y., 1949, pp. 1-23.

Reaction Rate Apparatus.—The reactor was the same as that described in a recent gasification study.⁵ Two methods were used to suspend the samples in the reactor. For reaction studies to 1 g. weight loss (11% burn-off) at different temperatures, a hole 1/8-inch in diameter and 1/8-inch deep was drilled into the top of the sample. Into this hole was cemented a 1/8-inch diameter ceramic rod which connected to the balance. In studies to carbon burn-offs greater than 1 g., it was found that reaction weakened the bond between the rod and sample sufficiently to result in the inability of the rod to support the sample during weighing. For this work, a 1/8-inch hole was drilled through the center of the samples. The ceramic support in this case consisted of a base plate 1/2-inch in diameter connected directly to the 1/8-inch rod. The carbon sample was placed over the 1/8-inch rod and sat on the base plate with no cement being used.

Mercury Porosimeter.—A description of the design and operation of the mercury porosimeter used has been given recently.⁶

Low Temperature Gas Adsorption Apparatus.—A standard gas adsorption apparatus was employed and has been described recently.⁵ Surface areas and micropore volume distributions were determined from the adsorption and capillary condensation of nitrogen using the BET equation⁷ and Pierce technique,⁸ respectively.

Results

Effect of Gasification of Carbon Rods to Different Burn-Offs at 1000° on their Physical Properties.—In studying the effect of gasification of carbon rods to different burn-offs on their physical properties, it was desirable to work at a sufficiently low temperature so that the gasification process proceeded uniformly through the sample. It was found from the uniformity of the bulk density profile data, a technique previously described,⁸ that a gasification temperature of 1000° fulfilled this requirement.

The reaction rate curves for four carbon rods

(5) P. L. Walker, Jr., R. J. Foresti, Jr., and C. C. Wright, *Ind. Eng. Chem.*, **45**, 1703 (1953).

(6) P. L. Walker, Jr., F. Rusinko, Jr., and E. Raats, *THIS JOURNAL*, **59**, 245 (1955).

(7) P. H. Emmett, *A.S.T.M. Tech. Publ.*, **51**, 95 (1941).

(8) C. Pierce, *THIS JOURNAL*, **57**, 129 (1953).

gasified at 1000° with carbon dioxide to 11.5, 23.0, 34.5 and 46.0% burn-off are shown in Fig. 1. It is seen that the gasification rate increases gradually to a maximum at ca. 2-g. weight loss (23.0% burn-off) and then decreases upon further gasification. The extended period of constant reaction rate characteristic of some other carbons investigated^{3,5} is not found in this case.

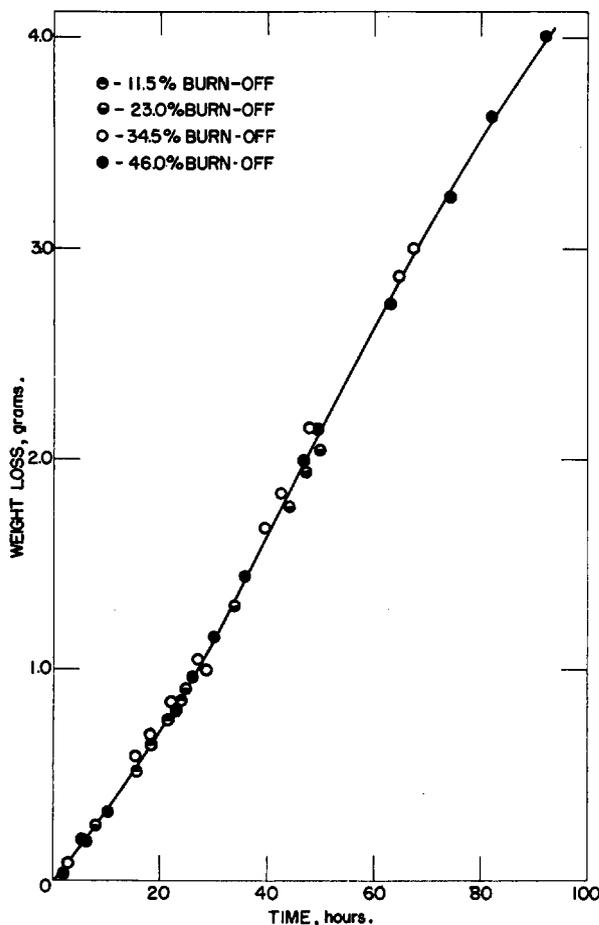


Fig. 1.—Reaction rate curves for graphite rods at 1000°.

Figure 2 shows the sorption isotherm of nitrogen on the unreacted sample from which its surface area and micropore volume distribution were determined. This type II isotherm is quite typical of those found for all the carbon samples gasified.

Table I summarizes the data on surface area, apparent density and average pore radius of the carbon rods before and after the different degrees of gasification. It is seen that there is a marked increase in both specific and total surface area of the carbon rods up to approximately 23.0% burn-off. Further gasification, at least up to 46.0% burn-off, produces a decrease in both surface areas.

The apparent densities, determined by a weighing technique using a specific gravity bottle and mercury as displacement fluid, naturally decrease with gasification. Pore volumes, calculated from the difference of the reciprocals of apparent and true density⁹ increase with burn-off.

(9) The true density is 2.269 g./cc., as calculated from X-ray diffraction values of 3.357 Å. for the interlayer spacing and 1.416 Å. for the C-C bond distance in the layer plane.

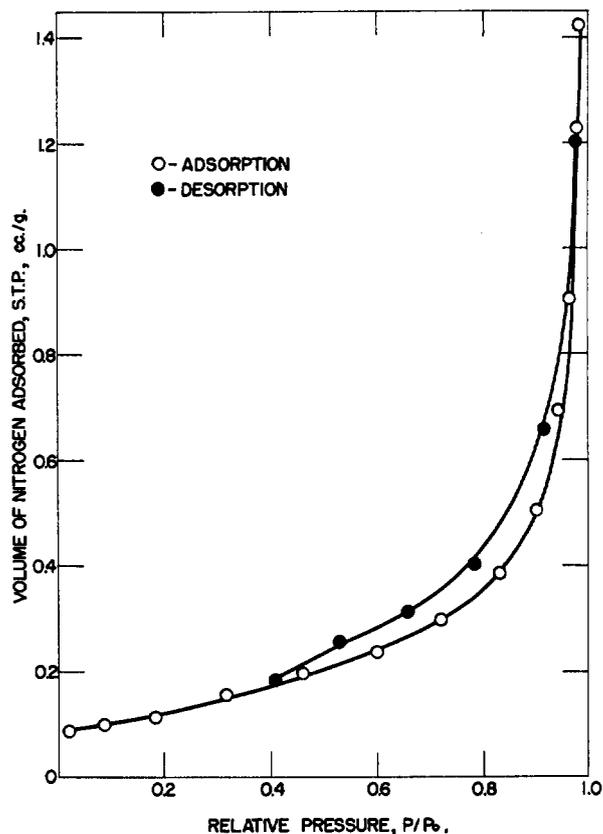


Fig. 2.—Adsorption isotherm for nitrogen at 77.2°K. on unreacted graphite rod.

Average pore radii are calculated using the relationship for cylindrical pores,¹⁰ $\bar{r} = 2V/A$, where V is the total pore volume and A the total surface area. It is seen that upon gasification to only 11.5% burn-off there is a marked decrease in average pore radius over the unreacted sample. This is followed by a further, minor decrease in radius up to 23.0% burn-off and then an increase in radius with further gasification.

TABLE I
SURFACE AREA, DENSITY AND POROSITY DATA FOR GRAPHITE RODS AFTER VARIOUS BURN-OFFS AT 1000°

Burn-off, %	Surface area, m. ² /g.	Total surface area, m. ²	Apparent density, g./cc.	Pore vol., cc./g.	Av. pore radius, Å.
Unreacted	0.41	3.54	1.562	0.199	10,140
11.5	1.61	12.15	1.378	.285	3,520
23.0	2.02	13.55	1.255	.355	3,480
34.5	2.03	11.31	1.154	.426	4,120
46.0	1.72	8.23	1.076	.488	5,530

It is of interest to examine the relationship between reaction rate, surface area and total pore volume as a function of burn-off. Table II presents these data. It is seen that the specific reaction rate expressed per unit of total surface area continually increases with burn-off—a particularly large increase being observed after 34.5% burn-off. On the other hand, the specific reaction rate expressed per unit of total pore volume reaches a maximum at approximately 23.0% burn-off and then decreases.

(10) P. H. Emmett and Thomas W. DeWitt, *J. Am. Chem. Soc.*, **65**, 1253 (1943).

TABLE II
CORRELATION OF AVERAGE INSTANTANEOUS REACTION RATE
WITH SURFACE AREA AND PORE VOLUME AT VARIOUS
BURN-OFFS

Burn-off, %	Av. reaction rate, g./hr.	Specific reaction rate, g./m. ² hr. × 10 ³	Specific reaction rate, g./cc. hr. × 10 ³
11.5	0.040	3.29	1.87
23.0	.052	3.84	2.20
34.5	.045	3.98	1.93
46.0	.040	4.86	1.76

Table III presents detailed data on the distribution of micropore volume in pore radius increments covering the range 14.7 to 400 Å. for the unreacted and gasified samples. It is seen that in all radius increments the total micropore volume reaches a maximum at 23.0 or 34.5% burn-off. For the specific micropore volume, there are two exceptions to the above maxima; the volume in pores from 14.6 to 20 Å. and 50 to 75 Å. continue to increase over the entire burn-off range.

Table IV presents detailed data on the distribution of macropore volume in pore radius increments covering the range 400 to 130,000 Å. In contrast to the behavior of the total micropore volumes all going through maxima with increasing burn-off, the total macropore volumes show maximum, increasing, and decreasing values with burn-off depending upon the radius increments. Particularly to be noted are the steady and marked decrease in total pore volume for pore radii from 20,000 to 30,000 Å. and the comparable increase in total pore volume for pore radii from 30,000 to 60,000 Å. The specific macropore volumes go through a maxima with increasing burn-off up to a pore radius of 20,000 Å., the volume in the 20,000 to 30,000 Å. range shows some over-all decrease, and the specific macropore volume in pores from 30,000 to 130,000 shows a continual increase with burn-off.

It is found that the sum of pore volumes calculated from micropore and macropore distributions is from 2.1 to 5.8% less than the total pore volume as calculated from the density data, with no trend apparent with increasing burn-off. In all probability this is due, in part, to the fact that the density calculated from X-ray data does not take inaccessible or "blind pores" into consideration. For example, it was shown by Dresel and Roberts,¹¹ by comparing helium with X-ray densities, that unreacted, synthetic graphite has roughly 6% closed pore volume, which is in qualitative agreement with this work.

The reason that the discrepancy in volumes does not decrease upon gasification in the present case probably can be explained as follows. The slope of the mercury porosimeter curve for the unreacted carbon rod is essentially zero at the upper limit (130,000 Å.), indicating little or no volume above this pore size. This is not the case for the gasified rods, the shape of the curve indicating the existence of a significant volume in pores greater than 130,000 Å. Since the pore volume determined by density measurements is thought to include all

pores up to approximately 200,000 Å.,¹² the two methods will be in disagreement by the magnitude of the pore volume between 130,000 and 200,000 Å. Therefore, possibly the unaccounted-for volume in the gasified samples is predominantly due to volume above the upper limit of porosimeter measurements rather than to "blind pore" volume.

In a manner analogous to that discussed previously,⁶ macropore areas are calculated from porosimeter data and shown in Table V. It is seen that the percentage contribution of the macropore area to the total area decreases markedly upon gasification. Using the total micropore volumes determined by gas adsorption and the total micropore areas determined by difference, an average micropore radius is calculated. It is seen that the unreacted sample has a calculated average pore radius significantly greater than 400 Å. On the other hand, the gasified samples all have average pore radii markedly less than 400 Å.

Effect of Gasification of Carbon Rods to 11% Burn-off at Various Temperatures on their Physical Properties.—Carbon rods were gasified to 1.0 g. (11%) weight loss at a series of temperatures between 970 and 1372°. Table VI presents data on the specific surface area, apparent density, specific pore volume and average pore radius of these samples after gasification. Since the gasified samples all have the same final weight, total surface areas and total pore volumes are not presented in this case. It is seen that the specific surface area increases with increasing gasification temperature up to 1224° and then decreases. This is in qualitative agreement with the findings of Petersen, Walker and Wright,¹³ who in the same apparatus as used in the present work found a maximum area developed at ca. 1180° for a more reactive carbon, which also developed a considerably higher surface area upon gasification.

Developed apparent densities and pore volumes are also found to be affected by gasification temperatures but not in as uniform a manner as surface areas. As in the previous results to different burn-offs, the average pore radius decreases markedly upon gasification temperature up to 1224° and then increases with higher temperatures.

Table VII presents data on the total micropore volumes in pore radius increments. No obvious trend is seen to exist between the incremental pore volumes and gasification temperatures. However, samples gasified at 1200 to 1246° do have maximum incremental volumes for most of the radius ranges listed. This observation parallels the development of maximum surface area at ca. 1224°.

Table VIII presents data on total macropore volumes in pore radius increments. Here again no obvious trend between gasification temperature and incremental pore volume is observed. Figure 3 emphasizes the close similarity of macropore distributions for four of the samples gasified at different temperatures. These are also typical of samples gasified at other temperatures.

(12) J. L. Ritter and L. C. Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782 (1945).

(13) E. E. Petersen, P. L. Walker, Jr., and C. C. Wright, *Ind. Eng. Chem.*, **47**, 1629 (1955).

(11) E. M. Dresel and L. E. J. Roberts, *Nature*, **171**, 170 (1953).

TABLE III
MICROPORE VOLUMES IN PORE-RADII INCREMENTS AS CALCULATED FROM GAS ADSORPTION DATA

Pore radius range, Å.	Vol. in range indicated after different burn-offs, cc. × 10 ³					Vol. in range indicated after different burn-offs, cc./g. × 10 ⁴				
	Unreacted	11.5%	23.0%	34.5%	46.0%	Unreacted	11.5%	23.0%	34.5%	46.0%
14.7- 20	0.3	2.6	3.0	2.6	2.4	0.3	3.5	4.5	4.7	5.1
20- 36	1.3	3.3	3.6	3.5	2.1	1.5	4.4	5.4	6.3	4.4
36- 50	0.8	1.5	2.1	1.6	1.1	0.9	2.0	3.1	2.9	2.3
50- 75	1.4	2.5	2.8	2.6	2.3	1.6	3.3	4.2	4.7	4.9
75-100	1.3	2.8	2.7	2.8	2.1	1.5	3.7	4.0	5.0	4.4
100-150	2.3	4.7	5.9	4.3	3.4	2.6	6.3	8.8	7.7	7.2
150-200	1.5	4.8	5.8	3.8	2.9	1.7	6.4	8.7	6.8	6.1
200-300	2.7	7.8	9.8	9.7	5.8	3.1	10.4	14.6	17.4	12.2
300-400	3.1	6.9	16.6	8.3	3.7	3.6	9.2	24.8	14.9	7.8

TABLE IV
PORE VOLUMES IN PORE RADII INCREMENTS IN THE MACROPORE RANGE AS DETERMINED BY THE MERCURY POROSIMETER

Pore radius range, Å.	Vol. in range indicated after different burn-offs, cc.					Vol. in range indicated after different burn-offs, cc./g. × 10 ²				
	Unreacted	11.5%	23.0%	34.5%	46.0%	Unreacted	11.5%	23.0%	34.5%	46.0%
400- 1,000	0.04	0.04	0.04	0.03	0.02	0.5	0.5	0.6	0.5	0.4
1,000- 2,000	.04	.06	.07	.03	.02	.5	.8	1.0	0.5	0.4
2,000- 3,000	.02	.05	.08	.04	.03	.2	.7	1.2	0.7	0.6
3,000- 6,000	.05	.05	.10	.12	.08	.6	.7	1.5	2.2	1.7
6,000- 10,000	.02	.12	.11	.14	.10	.2	1.6	1.6	2.5	2.1
10,000- 20,000	.29	.54	.47	.30	.25	3.3	7.2	7.0	5.4	5.3
20,000- 30,000	.97	.70	.72	.55	.37	11.2	9.3	10.8	9.9	7.8
30,000- 40,000	.13	.15	.23	.50	.59	1.5	2.0	3.4	9.0	12.4
40,000- 60,000	.08	.10	.12	.32	.48	0.9	1.3	1.8	5.7	10.1
60,000-130,000	.02	.20	.24	.22	.20	0.2	2.7	3.6	4.0	4.2

TABLE V
DISTRIBUTION OF SURFACE AREA BETWEEN MACROPORES AND MICROPORES AS DETERMINED BY MERCURY POROSIMETER

Burn-off, %	Total surface area, m. ²	Macropore area, m. ²	Micropore area, m. ²	Macropore area, %	Micropore vol., cc.	Av. micropore radius, Å.
Unreacted	3.54	3.47	0.07	98.0	0.015	(4,270)
11.5	12.15	4.33	7.82	35.6	.037	94
23.0	13.55	4.04	9.51	29.8	.052	110
34.5	11.31	3.62	7.69	32.0	.039	102
46.0	8.23	2.84	5.39	34.5	.026	96

TABLE VI
SURFACE AREAS, APPARENT DENSITIES, PORE VOLUMES AND AVERAGE PORE RADII OF GRAPHITE RODS REACTED TO 11% BURN-OFF AT VARIOUS TEMPERATURES

Temp., °C.	Surface area, m. ² /g.	Apparent density, g./cc.	Pore vol., cc./g.	Av. pore radius, Å.
Unreacted	0.41	1.562	0.199	10,140
970	1.67	1.402	.273	3,270
1090	2.10	1.448	.250	2,380
1130	2.23	1.437	.255	2,280
1158	2.37	1.422	.262	2,210
1200	2.48	1.419	.264	2,130
1224	2.66	1.415	.266	2,000
1246	2.62	1.372	.288	2,200
1342	2.21	1.459	.245	2,220
1372	2.21	1.426	.260	2,350

It is again found that the sum of pore volumes calculated from micropore and macropore volume distributions is less than that calculated from density data. There is a decrease in the unaccounted-for pore volume upon gasification. In the original sample, it is 5.8%; and in the gasified samples, it ranges from 0.4 to 3.7%. However, there is no systematic variation between the unaccounted-for pore volume and gasification temperature.

It is found that the percentage contribution of the macropore surface areas, as calculated from porosimeter data, to the total surface area (BET)

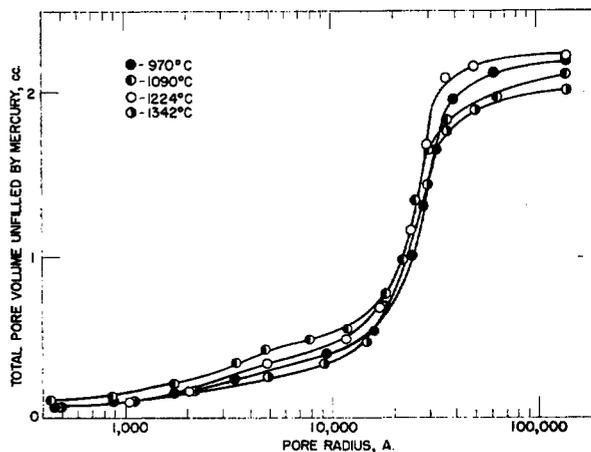


Fig. 3.—Change in macropore volume of graphite rods at various temperatures for 11.0% burn-off.

varies from 20.7 to 31.1%, it reaching the minimum value at 1224°. Furthermore, the average micropore radius, calculated as previously discussed,

TABLE VII

PORE VOLUMES IN PORE-RADII INCREMENTS IN THE MICROPORE RANGE FOR 11% BURN-OFF AT VARIOUS TEMPERATURES, AS CALCULATED FROM GAS ADSORPTION DATA

Pore radius range, Å.	Unreacted	Vol. in range indicated for 11% burn-off at various temp., cc. × 10 ³								
		970°	1090°	1130°	1158°	1200°	1224°	1246°	1342°	1372°
14.7- 20	0.3	1.8	2.8	4.0	2.3	3.1	3.9	3.1	4.0	1.7
20- 36	1.3	3.8	5.2	4.2	4.7	5.1	5.5	5.3	4.2	5.5
36- 50	0.8	2.2	1.9	1.7	1.3	1.9	1.7	2.0	2.5	1.7
50- 75	1.4	2.7	2.8	3.4	2.8	2.7	2.7	3.8	3.4	3.0
75-100	1.3	3.5	3.0	4.0	2.7	5.1	3.0	3.4	3.2	3.4
100-150	2.3	4.9	5.6	5.9	4.5	8.5	6.0	5.8	5.3	6.3
150-200	1.5	3.8	6.1	4.2	4.6	6.0	5.0	6.7	3.3	5.2
200-300	2.7	12.1	12.6	10.2	7.3	8.4	9.3	12.8	7.4	7.4
300-400	3.1	8.0	11.1	10.2	7.3	6.5	7.5	12.9	7.0	6.5

TABLE VIII

PORE VOLUMES IN PORE-RADII INCREMENTS IN THE MACROPORE RANGE FOR 11% BURN-OFF AT VARIOUS TEMPERATURES, AS DETERMINED BY THE MERCURY POROSIMETER

Pore radius range, Å.	Unreacted	Vol. in range indicated for 11% burn-off at various temp., cc.								
		970°	1090°	1130°	1158°	1200°	1224°	1246°	1342°	1372°
400- 1,000	0.04	0.04	0.04	0.03	0.04	0.03	0.03	0.03	0.03	0.03
1,000- 2,000	.04	.08	.08	.06	.08	.06	.06	.10	.06	.06
2,000- 3,000	.02	.09	.08	.06	.10	.09	.07	.03	.05	.05
3,000- 6,000	.05	.15	.13	.12	.14	.22	.12	.10	.07	.09
6,000- 10,000	.02	.08	.08	.08	.09	.13	.09	.11	.09	.07
10,000- 20,000	.31	.35	.29	.32	.34	.30	.37	.65	.39	.35
20,000- 30,000	1.04	.75	.87	.69	.84	.78	.95	.69	.73	.78
30,000- 40,000	0.14	.21	.19	.60	.20	.26	.31	.19	.33	.38
40,000- 60,000	.09	.11	.13	.17	.11	.14	.07	.18	.13	.14
60,000-130,000	.02	.14	.10	.10	.14	.08	.04	.16	.07	.10

ranges from 105 to 59 Å. for the reacted samples, reaching a minimum also at 1224°.

Discussion

Before analyzing the results of this work, it is desirable to describe as clearly as possible the nature of the carbon rods. The original raw materials used for the production of these rods consisted of *ca.* 25% coal tar pitch and 75% calcined petroleum coke. According to Abbott,¹⁴ for rods of the size used in this work all of the coke is less than 60 mesh (250 μ), with *ca.* 60% by weight passing 200 mesh (74 μ). Upon mixing and extruding of the green rods, the coke particles are coated with a layer of pitch to a thickness amounting to *ca.* 7% of the particle diameter.¹⁵ Baking of the green rods to *ca.* 1000° is primarily a destructive distillation process whereby the lighter fractions of the pitch (approximately 40% by weight) are volatilized away leaving behind a binder coke structure resembling a collection of condensed bubbles. The loss in weight also results in some shrinkage of the binder and in the formation of cracks in part of the bubble structure. The rods are then graphitized to 3000°, resulting in a product in which each particle can be visualized as consisting of a highly graphitic, homogeneous inner core (filler carbon) surrounded by a "slightly less" graphitic outer shell (binder carbon).¹⁶

(14) Private communication from H. W. Abbott, 1952.

(15) S. Mrozowski, "Physical Properties of Carbons and the Formulation of the Green Mix," paper presented before the 2nd Carbon Conference at Buffalo, N. Y., June 9, 1955.

(16) The degree of difference in the graphitic character of the filler and binder carbon is, of course, primarily determined by the nature of the starting raw materials. Abbott¹⁴ suggests that the binder carbon

Results on the unreacted carbon rod lead to the following conclusions, if the above picture is kept in mind.

1. The original surface area of 0.41 m.²/g. indicates that there is relatively little available internal particle porosity. That is, Petersen,¹⁸ using the microscope sizing technique developed by Petersen, Walker and Wright¹⁹ on a typical sample of petroleum coke, calculated an area of 0.11 m.²/g. assuming no particle porosity.

2. A rod porosity of 31% suggests that the particles are packed in essentially a rhombohedral array, which has an ideal porosity of 25.95%.²⁰ The difference, *ca.* 5%, agrees well with the unaccounted-for pore volume, 5.8%, which is thought to be primarily located in completely closed bubbles of binder carbon.

3. A calculated micropore surface area (Pierce technique) of 0.54 m.²/g., which is greater than the total surface area, suggests the presence of some micropore constrictions. These constrictions are possibly cracks leading into larger diameter bubbles of binder carbon.

4. Likewise, as previously reasoned, the calculated macropore surface area from porosimeter data is too high. This suggests again the presence of

is only slightly graphitic, whereas, X-ray diffraction results¹⁷ on the residual carbon structure upon gasification of these rods indicates a similar interlayer spacing in the two carbons.

(17) P. L. Walker, Jr., and F. Rusinko, Jr., *Fuel*, **34**, 822 (1955).

(18) E. E. Petersen, Ph.D. Thesis, The Pennsylvania State University, 1953.

(19) E. E. Petersen, P. L. Walker, Jr., and C. C. Wright, *A.S.T.M. Bulletin*, **183**, 70 (July 1952).

(20) J. M. Dallavalle, "Micromeritics," Pitman Publ. Corp., New York, N. Y., 1948, p. 128.

pore constrictions in the form of cracks in the binder carbon.⁶

Results on the carbon rods reacted to different burn-offs at 1000° lead to the following conclusions.

1. The relatively large increase in specific surface area for 11.5% burn-off, followed by a much smaller increase for further, comparable weight losses, suggests that the majority of the early activation is obtained by opening up area which was originally closed. It is visualized that this consists of selectively breaking through relatively thin walls of binder carbon leaving the exposed area of the inner bubble walls. On the other hand, the homogeneous and rather non-porous graphitized petroleum coke particles develop little porosity upon gasification, in line with the findings of Schaeffer, Smith and Polley,²¹ who oxidized graphitized carbon black particles. Gasification beyond 11.5% burn-off results in some surface area increase mainly because of the reacting through of thicker bubble walls of binder carbon surrounding the larger filler particles. Finally upon opening up of all available binder carbon area (between 23.0 and 34.5% burn-off), the specific area commences to decrease because of the higher efficiency of destroying area per unit weight of binder carbon reacted. The specific reaction rate (per unit surface area) markedly increases after 34.5% burn-off, however, since the specific rate of the filler carbon is higher than that of the binder carbon.

2. The increase in total micropore volume in all radius increments up to 23.0% burn-off should be due primarily to the opening of the bubble structure of the binder carbon. The particularly large increase in volume for pores from 14.7 to 36 Å. for 11.5% burn-off coincides with the initial, high increase in surface area.

3. The substantial decrease in macropore volume in the range 20,000 to 30,000 Å. upon 11.5% burn-off, accompanied by the large increase in volume for pores from 60,000 to 130,000 Å. suggests that the majority of macropore constrictions in the original sample was of the former size.

4. The large increase in pore volume in the range 10,000 to 20,000 Å. upon 11.5% burn-off indicates the opening up of previously closed-off pore volume in this range. Subsequent decrease in pore volume for pores between 10,000 and 30,000 Å. with gasification and increase in pore volume from 30,000 to 60,000 Å. suggests the complete destruction of some pore walls in the binder carbon, leaving larger bubbles.

(21) W. D. Schaeffer, W. R. Smith and M. H. Polley, "Surfaces of Heat Treated Carbon Blacks," paper presented before the 2nd Carbon Conference at Buffalo, N. Y., June 9, 1955.

5. For the reacted samples, the calculated micropore surface areas are all less than the total surface area. This indicates that the micropore constrictions were significantly opened up by gasification.

6. Likewise, the calculated macropore surface areas of the reacted samples give reasonable figures for the average micropore radii, indicating opening up of macropore constrictions. Furthermore, the relative constancy of average pore radius with increasing burn-off past 11.5% suggests that the removal of the pore constrictions was accomplished prior to this burn-off.

Results on the carbon rods reacted to 1 g. weight loss at a series of temperatures lead to the following conclusions.

1. The increase in surface area with gasification temperature up to 1224° can be explained by the higher efficiency of surface area development in the binder carbon as compared to the filler carbon. The lower the reaction temperature the more uniform will be the gasification of carbon through the rod⁶ and, likewise, through individual particles composing the rod. This means that since the percentage of filler carbon reacted per unit weight loss is at a maximum at the lowest temperature, the over-all resulting surface area development will be at a minimum. As the gasification temperature is increased, non-uniformity of reaction will be the greater within particles (filler plus binder) than radially across the rod. This is because of the much larger pore size available for transport of gas between particles than within particles. This will result in decreasing the percentage of filler carbon reacted per unit weight loss and, hence, increasing the surface area development. However, as temperature is further increased, diffusion of the reactant gas between particles will not be sufficiently rapid to supply gas to the interior of the sample.²² Finally, even though the fraction of the sample being reacted has a greater percentage of binder carbon activated and, hence, a greater surface area per unit weight, the resulting surface area for the entire sample will decrease because of the unreacted portion. In the limit, at sufficiently high temperatures, reaction will be found to occur solely on the surface of the rod with little area increase.

2. The reasoning for the other data follows in line with point 1 and the discussion under different degrees of burn-off at 1000°.

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(22) P. L. Walker, Jr., and E. Raats, *THIS JOURNAL*, **60**, 370 (1956).