

GASIFICATION OF CARBON RODS WITH CARBON DIOXIDE^{1,2}

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The possible relation between the properties of six commercial carbons and their gasification rates with carbon dioxide at a series of temperatures between 900 and 1300° has been investigated. The following properties of the carbons have been determined: quantitative and qualitative ash analyses, hydrogen content, interlayer spacing, average crystallite size, true and apparent density, porosity, surface area and effective diffusion coefficients of hydrogen through the carbons. No general correlation between these properties and the carbon gasification rates was found.

Introduction

The heterogeneous gasification reactions of carbon are of considerable theoretical and industrial interest and have been the subject of extensive research in recent years. Although a number of comprehensive kinetic studies have been reported, where equations of the Langmuir type have been found to describe the rate data, little attention has been given toward explaining these rates in conjunction with properties of the given carbon. The authors feel that the final test toward the understanding of gas-solid reactions (be it carbon or not) is to amass sufficient data about a solid to be able to predict its relative reactivity.

A long-range program, on this basis, has been set up in this Laboratory with the present investigation serving as an exploratory look into the success of relating what are commonly considered important properties of a carbon to its gasification rate.

Experimental

Samples.—Six different commercial carbons were studied. The samples were in the form of carbon rods 2 in. long by 1/2 in. in diameter, weighing approximately 10 g. All samples were extruded, using coal tar pitch as the binder. Four of the six samples used petroleum coke flour as the filler—lampblack and carbon "D" being the exception. Carbon "D" used a mixture of 13% graphitized carbon "A" and 87% carbon "C" as filler material. Graphitized carbons "A" and "B" were heated to approximately 2500 and 3000°, respectively. The lampblack and carbon samples were gas baked at approximately 1000°. A more detailed description of the manufacture of these carbon samples can be found elsewhere.³

Reaction Rate Apparatus.—The reactor was the same as that described in a recent gasification study.⁴ Briefly, a porcelain "top plate" and "bottom cone" were cemented to the top and bottom, respectively, of the carbon rod to restrict reaction to its sides. The sample was suspended from a balance into a vertical porcelain reactor tube and the gasification rate determined by frequent weight readings. A platinum-platinum-10% rhodium thermocouple, with hot junction located at a point level with the top of the sample, indicated reaction temperature, which could be maintained within 2° of the desired value. The carbon dioxide flow rate through the reactor was maintained constant within ±1%.

X-Ray Diffraction Apparatus.—A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, with copper radiation was used to determine interlayer spacings and average crystallite sizes of the carbons. Standard X-ray procedures

and subsequent calculations, discussed in detail in recent papers,^{5,6} have been used in the present investigation.

Gas Adsorption Apparatus.—A standard gas adsorption apparatus was employed and has been recently described.⁴ Carbon dioxide (99.95% pure and bone dry) was used as the adsorbate with adsorption occurring in a bath consisting of a 50-50 mixture of carbon tetrachloride and chloroform in Dry Ice. Results⁴ indicated that although the B.E.T. areas determined from carbon dioxide adsorption on carbon rods were up to 20% smaller than areas determined from nitrogen adsorption, the trends of the results were similar. In the present case, relative differences and changes in surface areas were of primary importance.

Diffusion Apparatus.—The gas-flow apparatus described by Weisz and Prater⁷ was used to determine effective diffusion coefficients of hydrogen through the carbon rods. (The authors are indebted to Dr. P. B. Weisz of the Socony-Vacuum Laboratories who determined experimentally the diffusion data.) Briefly, the experimental setup consisted of heating a 1/8-in. long by 1/8-in. diameter carbon rod and forcing it into a piece of Tygon tubing, which fused around the sample's periphery. The Tygon tubing was mounted in the diffusion apparatus, and equal pressures of nitrogen and hydrogen applied at the adjacent ends of the rod in the form of a high-velocity gas stream. The diffusion rate of hydrogen through the carbon rod was determined by analyzing the percentage of hydrogen in the nitrogen stream, as a function of time, with a thermal conductivity cell. Effective diffusion coefficients for hydrogen were based on the geometrical dimensions of the carbon rod.

The 1/8-in. long by 1/8-in. diameter samples used were cut on a lathe from rods, similar to those used in the reaction rate studies. Effective diffusion coefficients were determined on six separate samples of each carbon with the average value being reported. Results on a given carbon were duplicated within ±5%.

Results

Carbon Gasification Rates.—Table I presents the gasification rates of the carbons investigated

TABLE I
REACTION RATES OF CARBONS AT VARIOUS TEMPERATURES (G./HR.)

	Reaction temp., °C.				
	900	1000	1100	1200	1300
Graphitized carbon "A"	0.04	0.40	1.83	6.00	12.00
Graphitized carbon "B"	.24	1.15	3.40	7.10	12.30
Carbon "C"	.19	1.13	3.98	8.88	13.95
Carbon "D"	.23	0.98	4.04	8.55	13.20
Carbon "E" ^a	.20	0.44	1.71	5.50	12.72
Lampblack	.21	0.95	3.00	6.84	10.32

^a Reaction rates taken after 1 g. weight loss.

at a series of temperatures. The rate curves were similar to those previously discussed,⁴ with the rate increasing sharply at the start of the run and then remaining constant over a considerable period

(5) P. L. Walker, Jr., H. A. McKinstry and J. V. Pustinger, *ibid.*, **46**, 1651 (1954).

(6) P. L. Walker, Jr., and F. Rusinko, Jr., submitted to *Fuel*.

(7) Paper #48 presented before the Division of Physical and Inorganic Chemistry at the 125th Meeting of the American Chemical Society in Kansas City, Mo., March 23–April 1, 1954.

(1) Based on an M.S. thesis submitted by F. Rusinko, Jr., to the Graduate School of The Pennsylvania State University.

(2) Presented before the Division of Gas and Fuel Chemistry at the 126th meeting of the American Chemical Society in New York, N. Y., September 12–17, 1954.

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

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

of time. The rates reported are those over the constant rate portion of the curve with the exception of carbon "E." The rates could be duplicated within $\pm 2.5\%$.

The gasification rate of carbon "E" failed to reach a constant value; instead it continued to increase with reaction time. This can probably be explained by the fact⁴ that carbon "E" also failed to attain an essentially constant surface area upon reaction, although data on this point and the explanation as to why its area development should be different from the other carbons are not yet forthcoming.

At the lowest reaction temperature of 900° , where the chemical reactivity of the carbon should play its most important part in determining the gasification rate,⁸ it is seen that rates of five of the carbons are very similar and considerably higher than that of graphitized carbon "A." It is noteworthy that the reaction rate of graphitized carbon "B" at 900° is slightly higher than the rates for the four ungraphitized carbons.

Over-all activation energies for the gasification of the carbons have been determined over the lower temperature range (900 to 1000°), using the Arrhenius equation.⁴ They range from 43 kcal./mole for carbon "C" to 68 kcal./mole for graphitized carbon "A."

TABLE II
ANALYSES OF CARBON SAMPLES

	C	Analyses, %		H ₂ O	O + N
		H	Ash		
Graphitized carbon "A"	99.77	0.08	0.07	0.02	0.06
Graphitized carbon "B"	99.37	.06	.06	.01	0.50
Carbon "C"	97.37	.28	.24	.58	1.53
Carbon "D"	97.61	.13	.58	.05	1.63
Carbon "E"	98.32	.07	.32	.00	1.29
Lampblack	98.93	.09	.22	.05	0.71

TABLE III

SPECTROGRAPHIC ANALYSES OF CARBONS^c, IN %

Carbon	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	CaO	MnO	CuO	V ₂ O ₅	PbO
Graphitized carbon "A"	0.028	0.017 ^a	0.009 ^a	0.001	0.004		0.003	0.028	^b
Graphitized carbon "B"	.023	.017 ^a	.015 ^a	.001	.005	^b	.003	.029	^b
Carbon "C"	.032	.054	.068	.008	.009	.005	.004	.038	0.04 ^a
Carbon "D"	.088	.124	.068	.007	.006	.005	.004	.055	.04 ^a
Carbon "E"	.051	.052	.053	.007	.009	.005	.005	.038	.04 ^a
Lampblack	.044	.066	.039	.003	.006	.005	.004	.030	^b

^a Maximum values. ^b Not detected. ^c Ni, all samples 0.00X % except Carbon "D" which had 0.029%; Sn, present in trace amounts in graphitized carbon "B," not detected in others; Cd, may be present in trace amounts in Carbon "C," not detected in others; Cr, Na, Ti, present in all samples in trace amounts; Ag, As, B, Be, Bi, Co, Ga, Ge, Mo and Zn, sought but not detected.

Analyses of Carbons.—Table II shows the over-all analyses of the carbons with oxygen and nitrogen reported as the difference. Table III shows detailed spectrographic analyses of the carbons.

Interlayer Spacing and Average Crystallite Size of Carbons.—Table IV presents data for the interlayer spacing and average crystallite size of the carbons. Since carbon "D" was a mixture of graphitized carbon "A" and carbon "C," its X-ray diffraction peaks were all unsymmetrical in shape,⁵ consisting of the superposition of the broader and weaker peak of carbon "C" onto the sharper peak

of graphitized carbon "A." Its average interlayer spacing and crystallite size can be considered as being intermediate between graphitized carbon "A" and carbon "C."

In agreement with Biscoe and Warren,⁹ among others, the carbon-carbon bond distance within the carbon plane was found to be constant for all carbons, having a value of 1.42 Å.

Using the Franklin correlation,¹⁰ the carbon interlayer spacings have been related to the percentage of graphitic structure in the carbon, as seen in Table IV.

Densities and Porosities of Carbons before and after Gasification.—Table V presents data for the densities and porosities of carbons before and after the gasification. Samples gasified at 900 and 1100° reacted to one and two grams weight loss, respectively. These weight losses were selected since it placed the reaction in all cases, except carbon "E," on the constant rate portion of the reaction curve. Due to the different weight losses employed at the two gasification temperatures, unfortunately interpretation of the data for each carbon at the two temperatures is impossible. However, comparison and interpretation of the data at a particular gasification temperature for all carbons are fruitful. (Work is now in progress where carbon rods are gasified to different weight losses at a constant temperature and their change in properties investigated.)

The true densities have been calculated from the unit cell parameters of the different carbons, as determined by X-ray diffraction. Apparent densities were determined by mercury displacement at atmospheric pressure in a pycnometer. Pore volumes were calculated as the difference in the reciprocals of the apparent and true densities times the weight of carbon remaining in the rod.

TABLE IV

AVERAGE INTERLAYER SPACING AND CRYSTALLITE SIZE OF CARBONS

	d Spacing, Å.	\bar{L}_c , Å.	\bar{L}_a , Å.	Graphitic carbon content, %
	Graphitized carbon "A"	3.360	900	1100
Graphitized carbon "B"	3.357	1200	∞	89
Carbon "C"	3.456	33	55	0
Carbon "D"	10
Carbon "E"	3.450	41	62	0
Lampblack	3.484	28	59	0

(8) A. Wheeler, "Advances in Catalysis," Vol. 3, Academic Press Inc., New York, N. Y., 1951, p. 286.

(9) J. Biscoe and B. E. Warren, *J. App. Phys.*, **13**, 364 (1942).

(10) Rosalind E. Franklin, *Acta Cryst.*, **4**, 253 (1951).

TABLE V
DENSITIES AND POROSITIES OF CARBONS BEFORE AND AFTER
GASIFICATION

Reaction conditions	True density, g./cc.	Apparent density, g./cc.	Porosity, %	Total pore vol., cc.
Graphitized carbon "A"				
Unreacted	2.248	1.549	31.1	1.889
900°		1.390	38.2	2.364
1100°		1.189	47.1	2.897
Graphitized carbon "B"				
Unreacted	2.250	1.561	30.6	1.937
900°		1.418	37.0	2.243
1100°		1.280	43.1	2.498
Carbon "C"				
Unreacted	2.186	1.579	27.8	1.664
900°		1.438	34.2	2.070
1100°		1.390	36.4	1.854
Carbon "D"				
Unreacted	2.194	1.512	31.1	1.916
900°		1.440	34.4	1.957
1100°		1.312	40.2	2.150
Carbon "E"				
Unreacted	2.192	1.584	27.8	1.734
900°		1.447	34.0	2.162
1100°		1.362	37.9	2.257
Lampblack				
Unreacted	2.168	1.361	37.2	2.311
900°		1.224	43.6	2.761
1100°		1.074	50.5	2.983

Naturally there was a marked increase in porosity of the samples upon gasification, but differences and similarities in the degree of porosity development for the different samples should be noted. Porosity development of the two graphitized carbons was quite similar, as was the development for the comparable non-graphitized carbons "C" and "E." The unreacted lampblack rod is seen to have had a significantly higher porosity than the other unreacted samples and to have maintained its higher porosity upon gasification over the other gasified carbons.

Total Surface Areas of Carbons before and after Gasification and their Specific Gasification Rates.—Table VI presents data for the total surface area of the unreacted and reacted carbon rods. As much as a 10-fold difference is noted in the surface areas of the unreacted carbon rods. Furthermore, it is seen that there was a marked (but not a uniform) increase in surface area upon gasification. For some reason, the area of graphitized carbon "A" was increased much more markedly upon gasification than that of graphitized carbon "B." The same can be said for carbons "D" and "E," which had essentially the same original area. It is further seen that for five of the carbons the surface area developed after 2 grams weight loss at 1100° was greater than after 1 gram weight loss at 900°. Carbon "C," however, was a notable exception to this fact. Other interesting comparisons in Table VI are possible.

From a knowledge of the surface areas and the reaction rates of the carbons, as presented in Table

TABLE VI
TOTAL SURFACE AREAS OF CARBONS BEFORE AND AFTER
GASIFICATION AND THEIR SPECIFIC REACTION RATES

Reaction conditions	Total surface area, m. ² × 10 ³	Specific rate g./hr. (m. ² of surface) × 10 ³	Reaction conditions	Total surface area, m. ² × 10 ³	Specific rate g./hr. (m. ² of surface) × 10 ³
Graphitized carbon "A"			Carbon "D"		
Unreacted	4.7	Unreacted	5.4
900°	24.7	1.6	900°	10.9	21.1
1100°	49.5	36.9	1100°	26.8	150
Graphitized carbon "B"			Carbon "E"		
Unreacted	3.7	Unreacted	5.0
900°	6.0	342	900°	5.3	37.7 ^a
1100°	9.2	2833	1000°	14.1	180.6 ^a
Carbon "C"			Lampblack		
Unreacted	36.5	Unreacted	27.3
900°	205.6	0.9	900°	63.8	32.9
1100°	116.0	34.3	1100°	111.8	26.8

^a Reaction rates at 1 and 2 grams weight loss, respectively.

I, the specific reaction rates can be calculated and are also shown in Table VI. In the case of carbon "E," which failed to attain a constant rate, the slopes of the tangents to the rate curves at the particular weight losses used were taken as the rates.

Effective Diffusion Coefficients of Hydrogen in Carbon Rods.—Table VII presents data for the effective diffusion coefficients of hydrogen in the carbon rods. These results are discussed in detail in an accompanying publication.¹¹

TABLE VII
EFFECTIVE DIFFUSION COEFFICIENTS OF HYDROGEN IN
CARBON RODS

	Diff., cm. ² /sec. (H ₂ at STP)
Graphitized carbon "A"	0.046
Graphitized carbon "B"	.032
Carbon "C"	.028
Carbon "D"	.035
Carbon "E"	.039
Lampblack	.049

Discussion

Perhaps the best way to analyze the results is to enumerate properties of carbon which are commonly thought to have an effect on its gasification rate and compare the present reaction rates of the carbons with their known properties.

Long and Sykes¹² postulate that the top and bottom edge atoms of a carbon crystallite are most reactive to gasification. From this, the conclusion is drawn that the smaller crystallites, with their higher concentration of edge atoms per unit weight, should be more reactive than the larger crystallites. It is seen from Table I, however, that even though the average crystallite size of graphitized carbon "B" was more than an order of magnitude larger than that of the non-graphitized carbons, its gasification rate at 900 and 1000° was larger than these carbons. On the other hand, graphitized carbon

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

(12) F. J. Long and K. W. Sykes, *Proc. Roy. Soc. (London)*, **A193**, 377 (1948).

"A," which also had a much larger average crystallite size than the non-graphitic carbons, did have significantly smaller reaction rates at 900 and 1000°.

Franklin¹³ raised the question as to whether non-graphitic carbons with their larger interlayer spacings would be substantially more available to attack by gases than graphitized carbons. Data in Table I indicate that this apparently was not a major factor in determining gasification rates. Graphitized carbon "B," with a smaller spacing than the non-graphitic carbons, had a higher gasification rate. Furthermore, lampblack which possessed a significantly higher spacing than either carbon "C" or "E" had a smaller gasification rate.

Long and Sykes¹⁴ and Gulbransen and Andrew¹⁵ have shown the marked effect which inorganic and metallic impurities have on the chemical reactivity of carbon toward gases. Comparison of Table II with reaction rate data shows, however, that the carbon with the highest ash content, carbon "D," was not the most reactive at either 900 or 1000°. Again graphitized carbon "B," with its very low ash content, gave anomalously high reaction rate results. As a matter of fact, no single constituent of the analyses listed in Table II can be correlated with the carbon reactivity.

It is generally conceded that the analysis of the ash, as well as its magnitude, is of importance in affecting chemical reactivity of carbons. However, the spectrographic analyses presented in Table III fail to indicate, among other things, why the gasification rate of graphitized carbon "B" was comparatively high. For all elements determined, their concentration level was less in this carbon than in any of the non-graphitized samples. Unfortunately the state (free metal, oxide, carbide, etc.) and location of the impurities in the carbon matrix cannot be determined and this could well be of importance in determining reaction rates.

Individual carbon particles are known to be composed of a large number of crystallites.¹⁶ In line with previous reasoning, it would be expected that the larger the average crystallite forming the parti-

cle the fewer the number of top and bottom edge carbon atoms in the surface of the particle. If as previously reasoned, these atoms have a greater chemical reactivity for gasification than other atoms, the specific reaction rate of a carbon should decrease with increase in average crystallite size. Table VI, however, showed that such was not the case at either 900 or 1100°, with the specific reaction rates of graphitized carbon "B" having been greater in all cases and the rates of graphitized carbon "A" having been greater in three instances than those of the non-graphitized carbons. Furthermore, even though lampblack and carbon "C" had very similar crystallite sizes, the specific reaction rate of carbon "C" at 900° was markedly less than that of the lampblack. It is further difficult to explain why carbon "D," which was a mixture of 87% carbon "C" and 13% graphitized carbon "A," had considerably higher specific reaction rates than either of the original materials.

It might be thought, in light of the inability of the carbon properties which should affect chemical reactivity to satisfactorily explain differences in reaction rate, that the factor which controlled the gasification rates, even at 900°, was the resistance to mass transport of the carbon dioxide to the internal active carbon sites. However, this is not substantiated by fact if the relatively high reaction rate of graphitized carbon "B" is explained as being due to a relatively high diffusion rate of gas through its porous network. The effective diffusion coefficient of hydrogen in this carbon was lower than three of the non-graphitized carbons. Furthermore, the effective diffusion coefficient of hydrogen in lampblack was the highest of any carbon and yet it did not have the highest gasification rate. Another case was the graphitized carbon "A," through which hydrogen had the second highest diffusion rate and yet a gasification rate at 900° appreciably smaller than the other carbons.

In conclusion, it is obvious that no property or properties of the carbons investigated has satisfactorily explained differences in reaction rates. It is felt that the behavior of graphitized carbon "B" toward gasification where all of its presently discussed properties predict that it should have a relatively low reaction rate and yet it has the opposite, points most strikingly to the necessity of a more complete understanding of how the characteristics of a carbon affect its gasification rate.

(13) Rosalind Franklin, *J. chim. phys.*, **47**, 573 (1950).

(14) F. J. Long and K. W. Sykes, *ibid.*, 361 (1950).

(15) E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, **44**, 1048 (1952).

(16) W. D. Schaeffer, W. R. Smith and M. H. Polley, Paper #11 presented before the Division of Gas and Fuel Chemistry at the 124th meeting of the American Chemical Society in Chicago, Ill., Sept. 6-11, 1953.