X-Ray Diffraction Studies on Carbon Gasification

P. L. WALKER, Jr and F. RUSINKO, Jr

Three different carbons have been gasified with carbon dioxide to various weight losses and the structure of the residual carbons has been investigated by X-ray diffraction techniques. The spacing between layer planes of the residual carbon was found to decrease for one of the carbons and to remain constant, within experimental accuracy, for the other two carbons upon gasification. The average crystallite size of the residual carbon, on gasification, is found to change for one carbon, remains essentially constant for a second, and is too large to determine accurately for a third. These results indicate that the change in lattice parameter and average crystallite size of the residual carbon on gasification is dependent on the starting material.

P. L. WALKER, H. A. MCKINSTRY and J. V. PUSTINGER[1] have shown, on gasification of cylindrical samples of a graphitized carbon with carbon dioxide at 1100°C, that the interlayer spacing of the residual carbon decreases, the average crystallite size increases and the ratio of intensities of the (002) to the (100) x-ray diffraction peak increases. Recent bulk density profile studies by E. E. PETERSEN and C. C. WRIGHT[2], with the same graphitized carbon, have shown that the gasification of the cylindrical samples at 1100°C was not uniform, the reaction rate being greatest on the periphery of the sample. On the other hand, these authors found that, if the gasification was carried out at temperatures around 900°C, the reaction was quite uniform throughout the rod. Therefore, it was thought desirable in the present work, where the gasification results of the graphitized carbon were to be compared with those of a more highly graphitized spectroscopic graphite and a gas baked petroleum coke, to gasify all the samples at a sufficiently low temperature so that the reaction would be uniform throughout the rod. This work again consisted in the examination of the residual carbons, after gasification, by x-ray diffraction techniques to determine significant differences, if any, in the carbon from the original material, for the purpose of expanding and possibly generalizing on the findings of the earlier investigation.

EXPERIMENTAL

Gasification apparatus—The gasification apparatus used has previously been described in detail[3]. Briefly, the technique consisted in suspending a carbon rod inside a *Globar* furnace by a ceramic rod, 18 in. long, and determining weight loss of the carbon with time by a Roller-Smith balance attached to the upper end of the ceramic rod. The carbon samples employed in the present work were 0·5 in. long and of 0·5 in. diameter. In each case, the samples were cut from rods originally 13 in. long, so that one rod of each carbon supplied all the samples required for the investigation. A hole, diameter 0·125 in., was drilled through the centre of the samples, allowing the carbon to slide over the ceramic support rod and rest on a ceramic

platform of 0·5 in. diameter, which was connected to the end of the 18 in. rod. The underside of the ceramic platform was made conical in shape so as to fit into the top of the support tube previously described[3]. The carbon samples were lowered into the furnace at reaction temperature and pre-heated in helium for 1 hour prior to initiating the reaction with carbon dioxide. To ensure uniform reaction of the three carbons investigated, the weight loss of carbon was not allowed to exceed 0·01 g/h. The reaction temperatures employed to satisfy this condition were 900°C for the graphitized carbon, 970°C for the spectroscopic graphite and 770°C for the gas baked petroleum coke. After reacting the carbons to pre-determined weight losses, the furnace was flushed with helium and the sample slowly removed from the reaction chamber in such a manner as to permit it to cool approximately to room temperature before coming in contact with air.

Sample preparation for X-ray investigation—The carbon specimen was removed from the ceramic support rod, the entire sample ground in an agate mortar and pestle to pass through a 200 mesh screen (U.S. sieve series), and thoroughly mixed before sampling. A sample of the carbon was then intimately combined with $18 \pm 0{\cdot}1$ per cent by weight of high purity (− 200 mesh) sodium chloride. A $30{\cdot}5 \pm 0{\cdot}3$ mg portion of the mixture was weighed on glass slides to give three slides of each sample. Subsequently, the mixture was dispersed in collodion and amyl acetate over an area of 0·375 in.^{2} of the slide and allowed to dry. The samples were then ready for the X-ray analysis.

X-Ray procedure—A 164° (2θ) General Electric X-ray diffraction unit, XRD-3, with copper radiation was used. Throughout the investigation an X-ray slit width of 1° and a detector slit width of 0·1° were employed. The intensities at selected angles were determined by a Geiger counter connected to an electric timer which allowed a pre-selected number of counts as well as the time to be recorded. The Geiger counter was mounted on a goniometer so that patterns could also be plotted over a desired range of angles on a recording Leeds and Northrup potentiometer.

A detailed description of the X-ray procedure has already been published[1]. Briefly, the lattice constant of the sodium chloride, used as an internal standard, was accurately determined in a powder camera. The sodium chloride spacings determined on the X-ray unit were then used each time to correct the carbon peak angles also determined on this unit to absolute values, which in turn gave absolute values of carbon interlayer spacing. Furthermore, the line broadening of the sodium chloride was taken as that produced by the inherent machine factors and from this the line broadening due to the crystallite size of the carbons was determined.

The sharpness and high intensity of the (004) diffraction peak of the graphitized carbon and spectroscopic graphite made possible a high degree of precision in the determination of interlayer spacing, and justified the use of the longer and more accurate Geiger counter and timer technique to evaluate X-ray intensities. On the other hand, the diffraction peaks of the petroleum coke carbon were rather diffuse and did not warrant the use of the counting technique due to subsequent corrections required to be made on the original data. The data, in this case, were taken from a

recorder trace. In order to obtain from the diffuse experimental intensity curve of the petroleum coke carbon the true position of the diffraction maximum and, hence, the true interlayer spacing of the carbon, it was necessary to transform it into a true structure factor curve, as discussed by R. E. FRANKLIN[4] and W. R. RUSTON[5].

This was done in the present case by first drawing a smooth curve through the background profile of the peak in question and then subtracting the background from the peak at close intervals to obtain the peak intensity as a function of angle. The resulting intensities were divided by the product of the trigonometrical factor[6] $(1+\cos^2 2\theta)/\sin^2\theta\cos\theta$, the absorptivity factor[7] $1-\exp(-2\mu t/\sin\theta)$—where μ is the mass absorption coefficient of the specimen and t the thickness of the sample on the slide—and the atomic scattering factor for carbon[8]. This produced a true structure factor curve from which the peak angle used to calculate interlayer spacing could be derived.

Carbons used in the investigation—The graphitized carbon and gas baked petroleum coke carbon were supplied by the Speer Carbon Company. The spectroscopic graphite was supplied by the National Carbon Company. The graphitized carbon has previously been described in detail[3,9,10]. Briefly it was produced from a mixture of petroleum coke flour and coal tar pitch by high temperature treatment at about 2500°C. The spectroscopic graphite was produced from similar raw materials but was heated at 3000°C. The gas baked petroleum coke was produced from a mixture of petroleum coke flour and coal tar pitch, heated at approximately 1000°C for several weeks. The petroleum coke flour had previously been calcined at about 1200°C.

RESULTS AND DISCUSSION

Variation of interlayer spacing of the carbons on gasification—The data for the variation of interlayer spacing of the carbons on gasification are given in *Table 1*. All the spacings are reported at 15°C by using the coefficient of expansion ($28{\cdot}6 \times 10^{-6}$) of the graphitized carbon previously reported by P. L. WALKER, H. A. MCKINSTRY and C. C. WRIGHT[9]. As stated earlier, spacings on three samples of each carbon were determined, and the plus or minus variation of each set is listed in *Table 1*.

The overall trend of the values of the interlayer spacings for the graphitized carbon is similar to that found previously when the carbon was gasified with carbon dioxide at 1100°C. It is seen that the average spacing after 5 per cent gasification is lower than that after 10 or 20 per cent gasification. It is possible that this is not a true difference, considering the plus or minus variation of the data; however, the same trend was found for the spectroscopic graphite rods. One sample of graphitized carbon was reacted to 50 per cent weight loss at 1100°C to compare the interlayer spacing of the residual carbon with that resulting from the same weight loss at 900°C. As can be seen, the resulting spacings are very similar. The spacing obtained in the present case (3·3582Å) also agrees well with the value (3·3581Å) previously reported[1] for 45 per cent weight loss at 1100°C.

In contrast, the spectroscopic graphite rods do not show a significant decrease in interlayer spacing with gasification, with the possible exception

of the 5 per cent reacted sample. It will be recalled[1] that the decrease in interlayer spacing of the graphitized carbon was attributed to the preferential elimination, during reaction, of the less graphitic bonding phase. In order to determine whether the elimination during reaction of the graphitized bonding phase of the spectroscopic graphite rods could be expected to have a significant effect on residual interlayer spacing, the interlayer

Table 1. Variation of interlayer spacing of carbons on gasification

Description of carbon	*Spacing (15°C)* Å
Graphitized carbon rods	
Unreacted	3·3596 ± 0·0003
5% *reacted*	3·3588 ± 0·0002
10	3·3592 ± 0·0004
20	3·3591 ± 0·0001
30	3·3586 ± 0·0003
50	3·3585 ± 0·0001
50% *reacted at* 1100°C	3·3582 ± 0·0002
Spectroscopic graphite rods	
Unreacted	3·3576 ± 0·0004
5% *reacted*	3·3569 ± 0·0004
10	3·3572 ± 0·0005
30	3·3574 ± 0·0001
50	3·3573 ± 0·0003
Powder	3·3574 ± 0·0002
Petroleum coke rods	
Unreacted	3·461 ± 0·009
10% *reacted*	3·457 ± 0·004
30	3·459 ± 0·005
50	3·460 ± 0·004

spacing of spectroscopic graphite powder (no bonding phase present) was evaluated. It is seen from *Table 1* that the spacing of the spectroscopic powder and that of the unreacted spectroscopic rod are almost identical, and this fact possibly accounts for the constancy of the spacing on gasification.

L. GREEN[11] examined a 0·1 μ section of a spectroscopic graphite rod under the electron microscope and reported that no bonding phase was visible—the particles appeared to have been joined by a sintering process. If the original premise regarding the decrease in interlayer spacing of the graphitized carbon was correct, it would seem that between 2500° and 3000°C the bonding phase of carbon rods becomes an integral part of the particle system, both in location and character.

The absolute spacing of the artificial spectroscopic graphite rods is of interest with regard to the correlation between interlayer spacing and the graphitic character of the carbon, as proposed[4] by Franklin. Its interlayer spacing (3·3576Å) is significantly greater than that found for Ceylon graphite[1] (3·3546Å) and, according to Franklin's correlation (assuming Ceylon graphite as 100 per cent graphitic), the spectroscopic graphite is approximately 13 per cent non-graphitic in character. The fact that the spectroscopic graphite still is less graphitic than natural Ceylon graphite, even though in quality it equals the best artificial graphites available today, is perhaps due to the average diameter of the crystallites. M. BRADBURN, C. A. COULSON and G. S. RUSHBROOKE[12] established theoretically that the interplanar binding

ability is greater, the larger the hexagonal layer plane. Even though the $\overline{L}_a$ (the average diameter of the crystallites) dimension of the spectroscopic graphite and that of the Ceylon graphite are too large to be measured by X-ray diffraction line broadening, it is thought that the long flat particles of Ceylon graphite are probably characteristic of the long flat crystallites composing the particles and that this suggests their $\overline{L}_a$ dimension to be larger than that of the spectroscopic graphite. It is of considerable experimental and theoretical interest to determine whether it will be possible to subject artificial graphites to sufficiently severe heat treatment so as to equal or surpass the graphitic character of Ceylon graphite, as defined by interlayer spacing.

In the case of the petroleum coke carbon rods, there was also no significant change in interlayer spacing on gasification, as shown by *Table 1*. As previously reported by Franklin and Ruston, and confirmed by the present authors, the values of interlayer spacings for a material such as petroleum coke, which produces a diffuse diffraction band, cannot be duplicated better than $\pm 0{\cdot}005$Å, in most cases. This limit of reproducibility of course restricts the precision of the quantitative interpretation of interplanar spacing changes on gasification for the petroleum coke carbon. Franklin has shown[4] that petroleum coke and pitch coke, subjected to heat treatment at the same temperature up to 1480°C, have the same interlayer spacing within experimental accuracy. Therefore, even if preferential reaction of one of the two constituents did occur, this alone would not be expected significantly to change the spacing. Possible decrease in the $\overline{L}_a$ dimension of the crystallites upon gasification, in the light of the previous reasoning, would be expected to increase the interlayer spacing somewhat. However, as results to be presented show, both the $\overline{L}_c$ (height of the average crystallite) and $\overline{L}_a$ dimensions of the petroleum coke carbon rods failed to change significantly on gasification.

Variation of average crystallite size of carbons on gasification—The average crystallite size of the carbons before and after the different increments of gasification were determined by the usual equation, $L = K\lambda/\beta\cos\theta$, where K is a constant, λ the wavelength of the copper radiation, θ the Bragg angle at which the peak occurs and β the diffraction line width at half peak intensity. For the $\overline{L}_c$ dimension, K is taken equal to 0·89 and for the $\overline{L}_a$ dimension, in the case of the two-dimensional lattice reflections for petroleum coke, K is taken equal to 1·84[13]. The data are given in *Table 2*. Again three determinations for each sample of carbon were made and the plus or minus variations for each set of data listed.

The overall change in the $\overline{L}_c$ dimension of the graphitized carbon on gasification at 900°C to 50 per cent weight loss was from 570 to 660Å, which agrees relatively well with the change from 507 to 706Å on gasification of the same carbon to 45 per cent weight loss at 1100°C, as previously reported[1]. Furthermore, the change of the average crystallite size on reaction follows that previously predicted[1]. It was stated that, for an increase in average crystallite size, gasification must be continued until at least some of the smaller crystallites have been eliminated. Apparently

for 5 and 10 per cent gasification the elimination of the smaller crystallites had not yet occurred and the average crystallite size decreased due to reaction. On partial elimination of the smaller crystallites, with more complete gasification, the average crystallite size should increase, reaching a maximum when they are completely eliminated. A similar change of the L_a dimension with gasification would be expected from the above reasoning, and the previous data[1] obtained at 1100°C suggested that this is the case. However, corresponding data have not been determined in the present case.

The $\overline{L}_c$ dimension of the unreacted and reacted samples of the spectroscopic graphite was found to range between 2500 and 4000Å. However, since the line width of the graphite peaks so closely approached that of the standard sodium chloride, slight errors in determining line widths of either material produced differences in the calculated crystallite size of a given sample which were greater than differences between samples. Consequently, the quantitative trend of the crystallite size of the spectroscopic graphite on reaction cannot be given. However, in essence it may be said that, on reaction to even 50 per cent weight loss, the average crystallite size was still in the range of 2500 to 4000Å with no significant trend; $\overline{L}_a$ was greater than 4000Å but could also not be determined quantitatively.

Table 2 shows that, on gasification of the petroleum coke carbon rods, the change in $\overline{L}_c$ is small and the change in $\overline{L}_a$ is insignificant. Unlike the graphitized carbon where the bonding phase was thought to have a crystallite size appreciably smaller than the particle system, Franklin has shown that up to 1480°C the crystallite size of pitch coke (the bonding phase) is essentially the same as the crystallite size of the petroleum coke (the particle system) for similar heat treatment. Therefore, the $\overline{L}_c$ and $\overline{L}_a$ dimensions of the unreacted crystallites probably represent closely the size of both

Table 2. Variation of average crystallite size of carbons on gasification

Description of carbon	$\overline{L}_c$, Å	$\overline{L}_a$, Å
Graphitized carbon rods		
Unreacted	570 ± 40	
5% *reacted*	485 ± 7	
10	510 ± 7	
20	550 ± 7	
30	700 ± 30	
50	660 ± 30	
Petroleum coke rods		
Unreacted	25·7 ± 0·5	49·0 ± 1·9
10% *reacted*	24·0 ± 0·3	48·0 ± 1·6
30	24·0 ± 0·3	49·5 ± 2·5
50	23·8 ± 0·6	48·5 ± 1·0

the pitch coke and the petroleum coke. Consequently, unlike the graphitized carbon, complete elimination of the bonding phase surrounding the petroleum coke particles would not be expected to affect the residual crystallite size significantly. It is of course realized that, if the weight loss of a rod could be attributed to a proportional weight loss in each crystallite, the crystallite size of the residual carbon would have to decrease. For

example, if all reaction was assumed to occur along $\overline{L}_a$, for simplicity, and all the unreacted crystallites were 48Å in size, it is calculated that a weight loss of 50 per cent distributed over all crystallites would result in a decrease in their $\overline{L}_a$ size to about 34Å. Such a change would be easily detectable by x-ray diffraction. The fact that no detectable change in $\overline{L}_a$ occurred on 50 per cent gasification indicates that in the present case a relatively small fraction of the total number of crystallites within the carbon rod was undergoing significant reaction at any one time. This is to be compared with the fact that the reaction of the particle system itself is thought to be quite uniform at the low gasification temperatures employed. Thus, it seems that, in the case of the gas baked petroleum coke rods, reaction occurred predominantly on the surface of the particle system with little or no gas penetrating beneath the particle surface to react with crystallites.

Division of Fuel Technology,
The Pennsylvania State University,
State College, Pennsylvania

(Received August 1954)

REFERENCES

[1] WALKER, P. L., Jr, MCKINSTRY, H. A. and PUSTINGER, J. V. *Industr. Engng Chem.* 46 (1954) 1651

[2] PETERSEN, E. E. and WRIGHT, C. C. to be published

[3] WALKER, P. L., Jr, FORESTI, R. J., Jr, and WRIGHT, C. C. *Industr. Engng Chem.* 45 (1953) 1703

[4] FRANKLIN, R. E. *Acta cryst., Camb.* 4 (1951) 253

[5] RUSTON, W. R. *Fuel, Lond.* 32 (1953) 52

[6] HENRY, N. F. M., LIPSON, H. and WOOSTER, W. A. *The Interpretation of X-Ray Diffraction Photographs* p 205 Van Nostrand: New York, 1951

[7] ALEXANDER, L. and KLUG, H. P. *Analyt. Chem.* 20 (1948) 886

[8] *Internationale Tabellen zur Bestimmung von Kristallstrukturen* p 571 Borntraeger: Berlin, 1935

[9] WALKER, P. L., Jr, MCKINSTRY, H. A. and WRIGHT, C. C. *Industr. Engng Chem.* 45 (1953) 1711

[10] — and WRIGHT, C. C. *ibid* 45 (1953) 1715

[11] GREEN, L., Jr *J. appl. Mech.* 20 (1953) 289

[12] BRADBURN, M., COULSON, C. A. and RUSHBROOKE, G. S. *Proc. roy. Soc. Edin.* *A*62 (1946) 336

[13] BISCOE, J. and WARREN, B. E. *J. appl. Phys.* 13 (1942) 364

Reprinted from **FUEL** *a Quarterly Journal of Fuel Science*
VOLUME XXXIV SUPPLEMENT APRIL 1955
Published by BUTTERWORTHS PUBLICATIONS LTD
BELL YARD TEMPLE BAR LONDON
Subscription : UNITED KINGDOM FIVE GUINEAS PER ANNUM
U.S.A. $ 16.00 „ „

WIGHTMAN & CO. LTD., THE LEWES PRESS, Lewes, Sussex