A STUDY OF THE FINE STRUCTURE OF CARBONACEOUS SOLIDS BY MEASUREMENTS OF TRUE AND APPARENT DENSITIES

PART II.—CARBONIZED COALS

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Measurements of the true and apparent densities and adsorptive properties of coals carbonized at 600-1,650° C have been used to study the variation of the colloidal structure with the temperature of carbonization. It is shown that the true density increases with increasing carbonization temperature, reaching about 2·1 g./cm.^{3} at 1,100-1,200° C.

The porosity of particles small enough to pass a 240 B.S. sieve is large (from 7 % to 23 %) and increases with increasing carbonization temperature in the range 600° to 1,000° C. The specific surface increases with increasing carbonization temperature between 600° and 800° C. The accessibility of the pores and inner surfaces to liquids and gases decreases with increasing carbonization temperature in the range 600° to 1,600° C and is governed by the width of fine constriction in the pore system rather than by the mean diameter of pores which are uniform along their length. As a result of this pore structure, the solids function as molecular sieves, the width of the constrictions in the pore system being of the same order as the diameters of the simple molecules used for the density

measurements (i.e. 2 to 6 Å). This molecular sieve structure must be of importance in determining both the chemical behaviour of the solid and the composition of the gas evolved during carbonization.

The industrial behaviour of coke prepared from any given coal is highly dependent on the maximum carbonization temperature. In particular, there is loss of reactivity when the temperature of carbonization rises above 650° C (the exact temperature varies from coal to coal), and the change is reflected in many of the physical and chemical properties of the material. For example, the adsorption of carbon dioxide, the reactivity to sulphuric acid, the dispersibility in sulphuric acid, the ignition temperature and the " combustibility " of a number of carbonized coals all decrease rapidly with increasing carbonization temperature above 700° C.[1] In an attempt to investigate the underlying structural changes, Cannon, Griffith and Hirst[2] made an extensive survey of the internal surface areas of carbonized coals, as measured by their heat of wetting in methanol. They found that there was apparently marked loss of inner surface above 550°-650° C. This change in structure was further investigated by Maggs,[3] who studied the adsorption of methyl, ethyl and propyl alcohol vapours and showed that the apparent decrease in surface area resulted from a decrease in the accessibility of the inner surfaces. This is in accord with the earlier work of Macpherson, Slater and Sinnatt,[4] who found that the moisture content of laboratory-carbonized coals after exposure to the atmosphere for 48 hr. was greatest for samples carbonized at about 700° C and that the rate of adsorption and desorption of moisture decreased rapidly with further increase in carbonization temperature.

The measurements of the true and apparent densities of carbonized coals given in this paper make clearer the nature of the structural changes which occur between 600° and 1,000° C and which result in the changes in properties mentioned above. In particular, it will be shown that carbonized coals contain a large volume of very fine pores and a large internal surface area, even after heating to temperatures above 1,000° C. The porosity of the solid, due to these fine pores alone, increases with increasing carbonization temperature at least up to 1,000° C. The loss of reactivity and the apparent decrease in porosity and in internal surface area arise from the diminished accessibility of the pores.

The fine-structure porosity of a carbonized coal may be as high as 20%. It must be emphasized, however, that it is in no way related to the bubble-structure developed by coking coals in what is called the " plastic " range. It is, in fact, much smaller in the products obtained from good coking coals than in those from anthracite and low-rank, weakly-caking coals which give no bubble-structure. Moreover, the greater part of the porosity is developed at temperatures above the plastic range, when the carbonized coal has already acquired a rigid structure and no further bubble-formation can occur.

A considerable number of measurements of the apparent densities of carbonized coals have been previously reported.[5] Although the influence both of carbonization temperature and method of density measurement has in no case systematically investigated, the results all appear to be

South Metropolitan Gas Co., *The Solid Products of Carbonisation of Coal* (London, 1934).

Cannon, Griffith and Hirst, *Proc. Conf. on Ultra-fine Structure of Coals and Cokes* (B.C.U.R.A., 1944), p. 131.   [3] Maggs, *ibid.*, p. 147.

Macpherson, Slater and Sinnatt, *Fuel*, 1928, **7**, 444.

Rose, *Ind. Eng. Chem.*, 1922, **14**, 1047; Drakeley and Wilkins, *J. Soc. Chem. Ind.*, 1931, **50**, 331T; Hiles and Mott, *Fuel*, 1937, **16**, 64; Smith and Howard, *Ind. Eng. Chem.*, 1942, **34**, 43; Milner, Spivey and Coff, *J. Chem. Soc.*,

consistent with those of the present work. This suggests that structural changes similar to those described below occur during the carbonization of all coals, and are not peculiar to the specimens studied here.

Experimental

Materials.—CARBONIZED COALS. Samples were prepared from the following four coals.

ANTHRACITE C :   S. Wales anthracite, Group A1, 94·2 % carbon (dry, mineral-free).

COAL F :   S. Wales coking coal, Meta-bituminous, 89·7 % carbon (dry, mineral-free).

COAL H :   Yorkshire caking coal, Meta-lignitous, 83·5 % carbon (dry, mineral-free).

COAL K :   Northumberland weakly caking coal, Meta-lignitous, 82·4 % (dry, mineral-free).

For carbonization at temperatures up to 1020° C samples ground to pass a 72 B.S. sieve were heated in nitrogen in Nichrome-wound furnaces at 5° C/min. and held for 2 hr. at the maximum temperature.

For carbonization at temperatures higher than 1020° C a molybdenum-wound tube furnace was used. The sample was first carbonized at 1000° C as above, and, if coherent, re-ground to pass a 72 B.S. sieve. It was then packed into a ½ in.-bore carbon tube through which nitrogen was passed. The molybdenum furnace was brought to the desired maximum temperature, and the tube containing the sample was then advanced through the furnace in steps so that each part of the sample remained for 2 hr. in the zone of maximum temperature. During the initial stages, and again at the completion of the process, the closed end of a carbon sighting-tube was situated in the zone of maximum temperature, and the temperature was measured with an optical pyrometer.

Analyses.—Proximate and ultimate analyses of the carbonized samples are given in Tables I to IV.

TABLE I.—ANALYSIS OF CARBONIZED COAL C

Carboniza-tion Temp., ° C	Proximate Analysis					Ultimate Analysis (Parr's basis)			
	Moisture	Volatile less Moisture	Fixed Carbon	Ash	Volatile Matter (dry, ash-free)	Carbon	Hydro-gen	Nitrogen	Oxygen + Errors
—	2·6	4·7	90·6	2·1	4·9	94·2	2·9	1·2	1·7
305	1·6	4·9	91·4	2·1	5·1	94·1	2·8	1·0	2·1
410	2·0	4·5	91·2	2·3	4·7	94·6	2·7	0·9	1·8
510	2·2	4·3	91·3	2·2	4·5	94·7	2·6	0·9	1·8
605	2·9	3·9	91·1	2·1	4·1	94·7	2·4	0·8	2·1
700	4·4	3·0	90·5	2·1	3·2	95·5	1·7	0·9	1·9
805	5·0	2·5	90·5	2·0	2·7	96·3	1·0	0·8	1·9
910	4·9	1·5	91·5	2·1	1·6	96·9	0·6	0·6	1·9
1,015	0·1	0·3	97·3	2·3	0·3	98·6	0·5	0·6	0·3

Liquids.—METHANOL, BENZENE, ACETONE, ETHER, CHLOROFORM, CARBON TETRACHLORIDE : Analar reagents were used.

n-HEXANE boiling at 67–69° was supplied by B.D.H.

CARBON DISULPHIDE was purified by treatment with potassium permanganate, mercury and mercuric sulphate according to the method of Hammick and Howard[6] and was subsequently dried and distilled.

Gases.—HYDROGEN was prepared by electrolysis of 10 % caustic potash solution saturated with baryta, and was purified by diffusion through a palladium tube.

OXYGEN, METHANE.—Cylinder gases were used without purification.

[6] Hammick and Howard, *J. Chem. Soc.*, 1932, 2915.

TABLE II.—ANALYSIS OF CARBONIZED COAL F

Carboniza-tion Temp., °C	Proximate Analysis					Ultimate Analysis (Parr's basis)			
	Moisture	Volatile less Moisture	Fixed Carbon	Ash	Volatile Matter (dry, ash-free)	Carbon	Hydro-gen	Nitrogen	Oxygen + Errors
	0·8	24·0	71·1	4·1	25·2	89·7	5·0	1·8	3·5
405	0·6	19·6	73·3	4·5	20·7	89·7	4·7	1·8	3·8
510	1·2	12·0	81·7	5·1	12·8	91·2	3·2	1·8	3·8
605	3·0	6·0	85·2	5·3	6·6	93·9	2·4	1·8	1·9
700	3·4	4·0	87·1	5·5	4·4	95·3	1·7	1·9	1·1
915	0·7	1·9	91·1	6·3	2·0	97·5	0·6	1·6	0·3

TABLE III.—ANALYSIS OF CARBONIZED COAL H

Carboniza-tion Temp., °C	Proximate Analysis					Ultimate Analysis (Parr's basis)			
	Moisture	Volatile less Moisture	Fixed Carbon	Ash	Volatile Matter (dry, ash-free)	Carbon	Hydro-gen	Nitrogen	Oxygen + Errors
	5·9	34·9	57·3	1·9	37·9	83·5	5·4	2·2	8·9
300	1·6	34·0	62·5	1·9	35·3	87·8	5·1	1·9	10·2
400	1·3	21·9	74·5	2·3	22·7	84·8	4·5	2·3	8·4
500	2·4	11·3	83·3	3·0	11·9	88·9	3·1	2·2	5·8
605	3·3	—	—	2·2	—	90·7	2·2	—	—
710	5·6	4·2	87·6	2·6	4·6	93·6	1·5	2·0	2·9
760	6·1	2·8	88·6	2·5	3·1	94·7	1·2	2·0	2·1
800	6·2	—	—	3·0	—	95·5	0·8	—	—
855	6·0	—	—	2·9	—	96·5	0·8	—	—
905	2·8	—	—	2·9	—	96·8	0·6	1·1	1·5
950	2·2	—	—	3·4	—	96·7	0·7	—	—
1,000	1·3	0·9	9[?]·4	3·4	0·9	96·7	0·4	1·5	0·4

TABLE IV.—ANALYSIS OF CARBONIZED COAL K

Carboniza-tion Temp., °C	Proximate Analysis					Ultimate Analysis (Parr's basis)			
	Moisture	Volatile less Moisture	Fixed Carbon	Ash	Volatile Matter (dry, ash-free)	Carbon	Hydro-gen	Nitrogen	Oxygen + Errors
	10·5	33·8	54·7	1·0	38·2	82·4	5·1	1·9	10·6
300	2·0	33·5	63·4	1·1	34·6	82·2	5·1	2·0	10·7
400	2·2	24·9	72·0	0·9	26·0	83·2	4·5	2·2	10·1
505	1·9	13·7	83·0	1·4	14·2	88·4	3·3	2·3	6·0
550	3·6	8·9	86·0	1·5	9·4	90·7	2·9	2·4	4·0
620	2·6	7·2	88·3	1·9	7·5	92·1	2·5	2·3	3·1
680	—	—	—	1·9	—	92·1	2·2	—	—
720	5·4	5·6	87·3	1·7	6·0	95·3	1·6	2·0	1·1
820	6·2	4·1	88·0	1·7	4·5	97·1	0·7	1·5	0·7
915	6·7	2·1	89·0	2·2	2·3	97·5	0·4	1·8	0·3

Measurement of Density.—The apparatus and methods used for the measurements of densities in helium and in liquids have been described in a preceding paper.[7]

Density " Drift ".—The " density drift," or increase of apparent density with time, was investigated by making measurements 2 hr. and 24 hr. after immersing the solid in the liquid. In helium, measurements were normally continued until no further drift occurred in 24 hr. ; in a few cases the density drift in helium continued for many days and was not followed to completion.

Correction for Mineral Matter.—The density values recorded have in all cases been corrected for the mineral content of the samples by use of the correction formula of Wandless and Macrae.[8] Although the mineral content of carbonized coals is somewhat greater than that of raw coals, the uncertainty in the density correction is less since the composition of the mineral matter differs less from that of the ash whose density was determined. The correction did not exceed 3 % for any of the carbonized coals used.

Results

APPARENT DENSITIES OF COALS CARBONIZED AT TEMPERATURES UP TO 1650° C.—Measurements of the densities of coals C, F, H and K carbonized at temperatures from 300-1650° C were made with helium, methanol, water and n-hexane. With coal H, carbon disulphide was also used and with coal K,
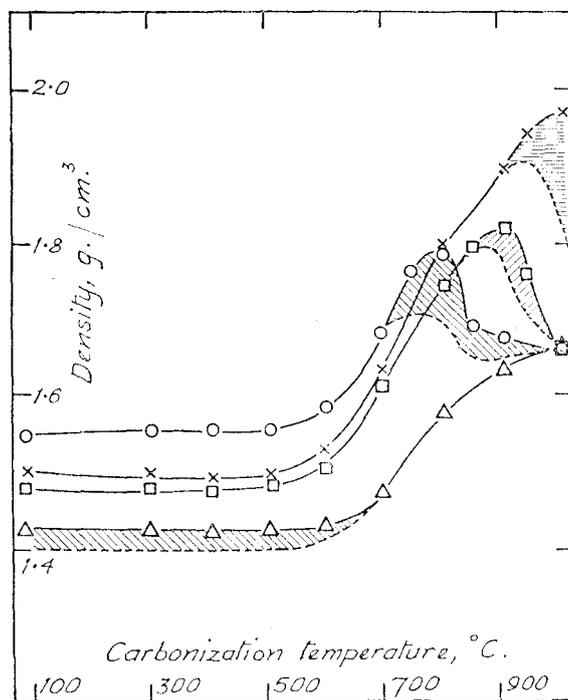

FIG. 1.—Anthracite c.

× Helium.   ○ Methanol.   ☐ Water.   △ n-Hexane.

benzene. In Fig. 1 to 4, densities are plotted against carbonization temperature for temperatures up to 1020° C. The full-line curves in the Figures represent density values after 24 hr. immersion in the liquids and the final values obtained with helium, and the broken line curves represent apparent densities

[7] Franklin, *Trans Faraday Soc.*, 1949, **45**, 274.
[8] Wandless and Macrae, *Fuel*, 1934, **13**, 4.
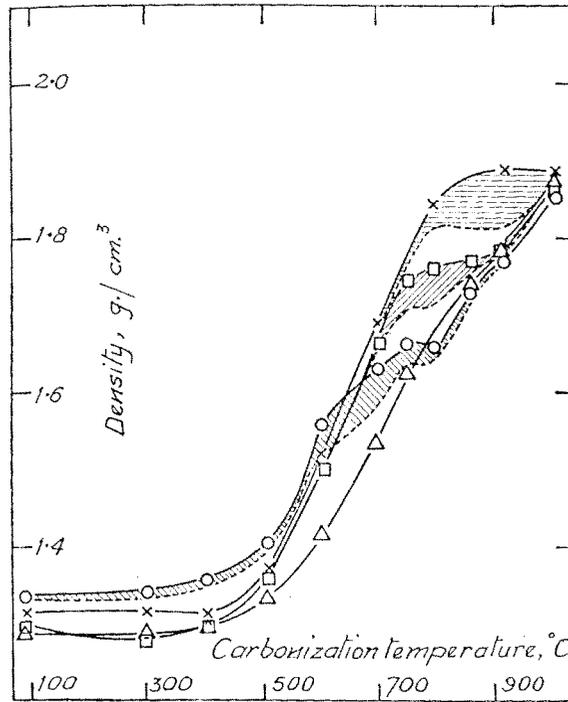
FIG. 2.—Coal F.

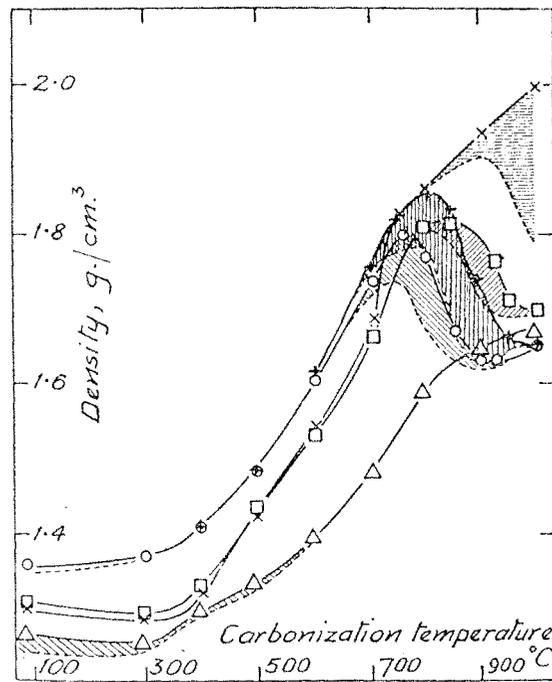Helium.　　○ Methanol.　　□ Water.　　△ n-Hexane.

FIG. 3.—Coal H.

Helium.　○ Methanol.　□ Water.　△ n-Hexane.　+ Carbon disulphide.

after 2-hr. immersion in liquids and the first recorded values in helium. The height of the shaded areas is a measure of the density drifts. (The initial values recorded here and elsewhere for samples which show a large drift in helium refer to measurements made as quickly as possible after admitting the gas to the sample ; they have only qualitative significance.*)
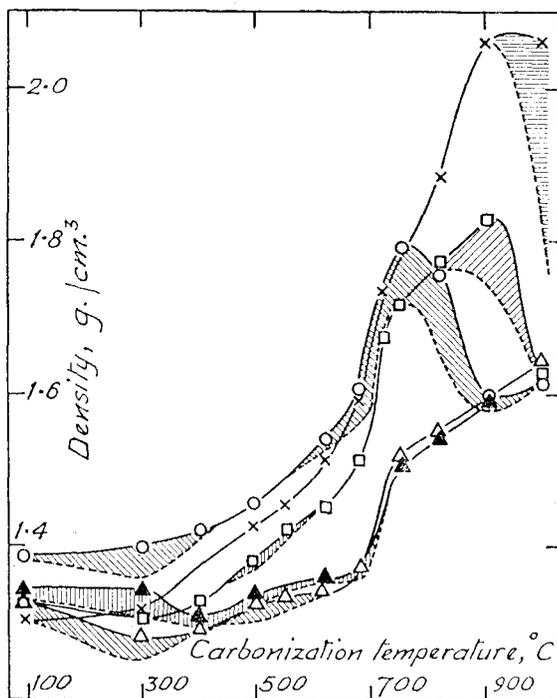

FIG 4 —Coal K

X Helium.   ○ Methanol.   □ Water   △ n-Hexane.   ▲ Benzene.

TEMPERATURES BELOW 500° C.—Below 500° C the variation of apparent density with carbonization temperature is different for each of the four coals investigated. For the anthracite c there is no appreciable change. The apparent densities of coal F in water, of coal H in water, n-hexane and helium, and of coal K in water and in n-hexane are slightly *decreased* by heating to 300° C, and apparent densities in methanol in all cases increase continuously with increasing carbonization temperature.

TEMPERATURE RANGE 500° C TO 600° C.—Between 500° C and 600° C an increase in the apparent densities of the anthracite c sets in and the densities of the other coals all increase.

TEMPERATURE RANGE 600° C TO 1020° C.

(i) *Coals* c, H *and* K.—Fig. 1 to 4 show clearly that large and significant structural changes occur in all four coals between 600° C and 1000° C. The results for coals c, H and K may be summarized as follows.

n-Hexane gives a low density value which increases continuously with increasing carbonization temperature and shows no appreciable drift. The results obtained with benzene for coal K are similar. Helium gives a density which is from 7 % to 23 % in excess of the n-hexane value and which increases more rapidly with increasing carbonization temperature. When the temperature of treatment rises above about 900° C the density in helium begins to show some drift, and at 1000° C the drift is large and the initial density is only slightly in excess of the density in n-hexane.

* In all cases sufficient time elapsed to ensure that thermal equilibrium between the sample and the thermostat was established before the helium was admitted.

The density in methanol exceeds that in helium for all carbonization temperatures up to 700° C. Between 600° C and 750° C a density drift in methanol begins to appear and increases with increasing carbonization temperature. At about 800° C the density in methanol (measured after 24-hr. immersion) passes through a maximum, and between 800° and 900° C it decreases sharply to a value approximately equal to the n-hexane value. At 1,000° C the densities in methanol and in n-hexane are equal and show no drift.

The variation of the apparent density in water is similar to that observed with methanol, except that the corresponding changes occur about 100° C higher. Up to 800° C the density in water shows no drift and is only slightly less than that in helium. Between 800° and 900° C a density drift develops, and the density after 24-hr. immersion is at a maximum at about 900° C. After carbonization at 1,000° C the densities of the coals c and k in water are equal to the low, n-hexane values and show no drift, while with coal h the density is only slightly higher than the n-hexane value and the drift is small.

Carbon disulphide gives apparent densities for the carbonized coal h which are identical with the methanol values for carbonization temperatures up to 600° C. Between 600° and 900° C the apparent densities in carbon disulphide are rather higher than in methanol, although a density drift is observed in approximately the same temperature range for the two liquids. After carbonization at 1,000° C the apparent density in carbon disulphide is equal to the low, n-hexane value and shows no drift.

(ii) *Coal* F.—The density changes which occur in the coal F in the temperature range 600-1,000° C are fundamentally similar to those described above for coals c, h, and k, but differ significantly in two respects.

Firstly, the density of this coal in n-hexane increases more rapidly with carbonization temperature, and the difference between the densities in helium and n-hexane for any one carbonization temperature is less ; in methanol and water the maxima which appear in the curves for the other three coals are flattened into strong inflexions. Secondly, all the changes occur about 100° C lower for the coal F than for the coals c, h and k. The drift in density in methanol sets in below 600° C and at 800° C the density in methanol has fallen to the n-hexane value. At 900° C the density in water is equal to that in n-hexane. A density drift in helium begins below 800° C and at 1,000° C the density in helium too has fallen to the n-hexane level and shows no drift.

The results described above show clearly that after heating to 600° there is, in all four coals, a large pore volume which is accessible to helium but inaccessible
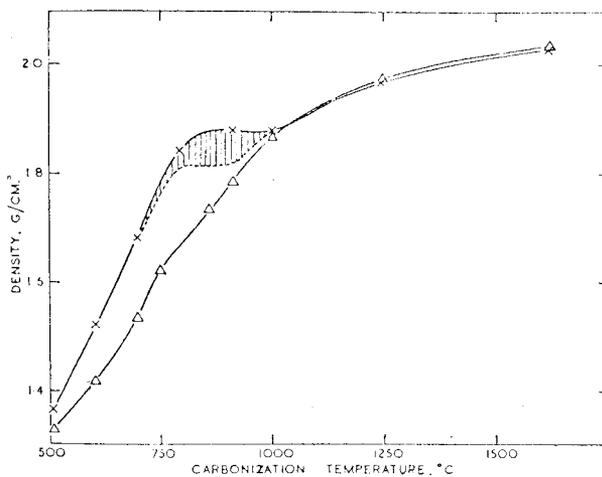

FIG. 5.—Coal F.

× Helium   △ n-Hexane

to n-hexane. As the carbonization temperature is increased above 600° this pore volume is increased ; at the same time, however, it becomes less accessible to fluids. Methanol, carbon disulphide and water are successively excluded, and after carbonization at 1,000°, helium too is excluded from the pores of coal F and penetrates only slowly in the other coals.

The low values obtained with n-hexane for the coals carbonized above 600° are sharply defined and the apparent density in this liquid appears to represent a real characteristic of the solid material. There is no appreciable drift, and when apparent densities in water, methanol and carbon disulphide fall to the n-hexane level, these too show no drift. On the other hand, apparent densities intermediate between the *n*-hexane and helium values are associated with large drifts, showing that penetration of the pores by the liquids is slow and incomplete.

RANGE 1,000° C to 1,650° C.—The general pattern of the results outlined above is further clarified by measurements made on samples carbonized at temperatures above 1,000° C. Results for coals F and H are shown in Fig. 5 and 6. For each of the three coals C, F and H carbonized at 1,000°, the densities
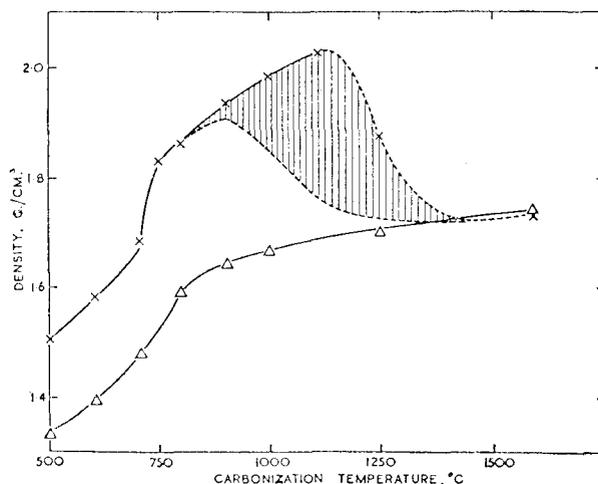
FIG 6.—Coal H.

× Helium.   △ *n*-Hexane.

given by methanol, water and *n*-hexane are equal and show no drift, and this is true also of higher carbonization temperatures. For the coal F, the density in helium, too, continues equal to the value obtained with the liquids. With increasing carbonization temperature from 1,000° C to 1,650° C the apparent density of the carbonized coal F in helium and in liquids increases from 1·87 g./cm.³ to 2·04 g./cm.³.

The density of the carbonized coal H, measured in methanol, water or *n*-hexane, increases only slowly above 1,000°, reaching 1·75 g./cm.³ at 1,600° C The density in helium at first increases, and then decreases to the low value given by the liquids.* The highest densities in helium are associated with large and prolonged drifts. The maximum value recorded was 2·03 g./cm.³ for a carbonization temperature of 1,100-1,130° but since the drift was not followed to completion, this figure is lower than the true density of the sample ; a higher value was obtained when the sample was more finely ground (see below).

The Influence of Particle Size on Apparent Density.—All the results described above were obtained with samples ground to pass a 72 B.S. sieve. Measurements were also made on samples of coal H carbonized at temperatures above 600° C and ground to pass a 240 B.S. sieve. The results are shown in Table V. The density in methanol of the sample carbonized at 805° C and the densities in helium of those carbonized at 1,100° and 1,250° C were considerably

* The density in helium of the anthracite C carbonized at 1,450° C shows no drift and is equal to the *n*-hexane value (obtained by interpolation) for coal H carbonized at the same temperature. Since the apparent densities of the anthracite C and of the coal H carbonized between 700° and 1,000° C and measured in helium, water and *n*-hexane are almost identical (see Fig. 1 and 3), it is probable that the density of coal H in helium after carbonization at 1,450° C would be equal to the low *n*-hexane value and would have no drift. This result was taken into account in drawing the broken part of the helium curve in Fig 6.

increased by reducing the particle size. On the other hand, the results obtained with *n*-hexane for samples carbonized above 800° C and with helium for those prepared below 1,000° C were not altered. Thus, where no density drift was observed the density was not increased by grinding to the lower size limit. The density drift in helium of the sample carbonized at 1,000° C was completed in considerably less than 24 hr., and in this case, too, the density measured after 24 hr. was independent of the particle size. For samples which showed large and prolonged density drifts, the apparent density after a given time was highly dependent on the particle size of the material.

TABLE V.—INFLUENCE OF PARTICLE SIZE ON APPARENT DENSITY OF CARBONIZED COAL H

Carbonization Temp., ° C	Size	Helium			Methanol			*n*-Hexane	
		Density after 24 hr., g./cm.³	Final Density, g./cm.³	Drift, %	Density after 24 hr., g./cm.³	Drift, % (2 hr. to 24 hr.)	Drift, % (2 hr. to 72 hr.)	Density after 24 hr., g./cm.³	Drift, % (2 hr. to 24 hr.)
600	72 B.S.	1·542	1·542	0·0	1·600	0·2	——	1·364	0·3
	240 B.S.	1·543	1·543	0·0	—	——	——	1·384	0·6
805	72 B.S.	1·848	1·848	0·0	1·761	7·9	10·4	1·558	0·0
	240 B.S.	1·861	1·861	0·0	1·816	7·4	9·0	1·558	0·1
1,000	72 B.S.	2·001	2·001	10·7	1·655	0·0	——	1·663	0·0
	240 B.S.	2·005	2·005	7·6	——	——	——	1·665	0·0
1,100-1,130	72 B.S.	1·982	2·029	13·4	—	—	——	·—	·—
	240 B.S.	2·028	2·087	15·8	—	—	——	——	——
1,245-1,250	72 B.S.	1·875	—	8·0 (to 24 hr.)	1·723	0·0	——	1·724	0·0
	240 B.S.	1·979	2·056	11·9	——	——	—	——	—

The maximum density value recorded was 2·09 g./cm.³ for coal H carbonized at 1,100° C. The true density of the material exceeds this value, since a slight drift was still observable after 9 days.

Influence of Molecular Size.—The order in which *n*-hexane, methanol, water and helium are excluded from the pores as the carbonization temperature is raised is the same for each of the four widely different coals C, F, H and K. It is, in fact, the order of decreasing molecular size. Further measurements were made on the carbonized coal H with acetone, ether, chloroform and carbon tetrachloride ; these, together with the results obtained with carbon disulphide for coal H and with benzene for coal K confirm that molecular size is the principal factor determining the power of organic liquids to penetrate into the pores of carbonized coals. The results obtained with 8 liquids and with helium for coal H carbonized at temperatures between 700° and 1,000° C are given in Table VI, together with the molecular volumes of the liquids at 25° C. The 4 liquids which have the largest molecular volumes give apparent densities approximately equal to the low, *n*-hexane values. No apparent densities appreciably lower than the *n*-hexane values have been observed.

Adsorption of Gases on Carbonized Coal.—The density of fine-structured carbonaceous solids cannot be measured in gases other than helium since all other gases are to some extent adsorbed at room temperature. However, since physical adsorption is a very rapid process, measurements of the apparent rate of adsorption may serve to study qualitatively the rate of penetration of gases into the fine pores in carbonized coals. With this object, the room-temperature adsorption of hydrogen, methane and oxygen on coal H carbonized at 600°, 800° and 1,000° C was briefly investigated. The apparatus and method were the same as those used for the measurements of densities with helium. The true volume of the sample was first determined with helium, which was then pumped off, and the measurements repeated with one of the other gases. The difference between the apparent volumes of the sample in this gas and in helium gave the volume of the gas adsorbed.

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TABLE VI

Material	Temp.	700° C	750° C	800° C	950° C	1,005° C	Molecular Volume of Liquid at 25° C cm.³
Helium .	Density, g./cm.³	1·64*	1·831	1·861	1·96*	1·998	—
	Drift, %	—	0·0	0·0	---	10·6	
Water .	Density after 24 hr., g./cm.³	1·62*	1·75*	1·808	1·710	1·695	18
	Drift, % (2 hr. to 24 hr.)	---	—	0·1	2·8	0·9	
Methanol .	Density after 24 hr., g./cm.³	1·70*	1·80*	1·759	1·64*	1·660	41
	Drift, % (2 hr. to 24 hr.)	---	—	7·9	—	0·2	
Carbon di-sulphide .	Density after 24 hr., g./cm.³	1·757	1·828	1·855	1·663	1·656	61
	Drift, % (2 hr. to 24 hr.)	0·7	4·3	4·2	1·4	0·0	
Acetone .	Density after 24 hr., g./cm.³	—	1·810	—	1·629	—	74
	Drift, % (2 hr. to 24 hr.)	—	1·0	—	0·1	—	
Chloroform .	Density after 24 hr., g./cm.³	1·480	---	1·552	---	1·659	81
	Drift, % (2 hr. to 24 hr.)	0·0	---	0·0	---	0·0	
Carbon tetra-chloride .	Density after 24 hr. g./cm.³	---	---	1·560	---	1·660	99
	Drift, % (2 hr. to 24 hr.)	---	---	0·0	—	0·0	
Ether .	Density after 24 hr., g./cm.³	—	1·533	—	---	---	105
	Drift, % (2 hr. to 24 hr.)	—	0·3	---	---	---	
n-Hexane .	Density after 24 hr., g./cm.³	1·47*	1·53*	1·550	1·65*	1·663	128
	Drift, % (2 hr. to 24 hr.)	---	—	0·2	---	0·0	

* Obtained by interpolation.

HYDROGEN : The quantities of hydrogen adsorbed on the three samples are shown graphically in Fig. 7. The heat of adsorption, calculated from measurements made at 15° and 25° C, was about 1,800 cal./g.-mol. Since the isotherms shown in Fig. 7 are approximately linear, and the heat of adsorption is the same for each sample, the slopes of the isotherms give a relative measure of the specific surfaces. Between 600° and 800° C the specific surface increases by about 40 %.

Adsorption equilibrium was established immediately (i.e. in less than $\frac{1}{2}$ min the time required for making the first measurement) on the samples carbon ized at 600° and 800° C. On the 1,000° C sample, a rapid initial adsorption was followed by a large adsorption drift, and equilibrium was established within 24 hr. Between 800° and 1,000° there is a small *decrease* in specific surface and the good agreement between the results obtained with the 72 mesh and the 240 mesh sample suggests that this decrease is real.

METHANE : The results obtained with methane are given in Table VII The heat of adsorption on the sample carbonized at 610°, calculated from measurements made between 12° and 30°, was 5,800 cal./g.-mol.

Much larger quantities of methane were adsorbed than of hydrogen, but the process was considerably slower. With the sample carbonized at 610° C there was a large initial adsorption, 81 % of the total occurring in the first

2 min.; equilibrium was established within 5 hr. On the 810° C sample less than 1 % of the total adsorption occurred in the first 2 min., and 5 days were
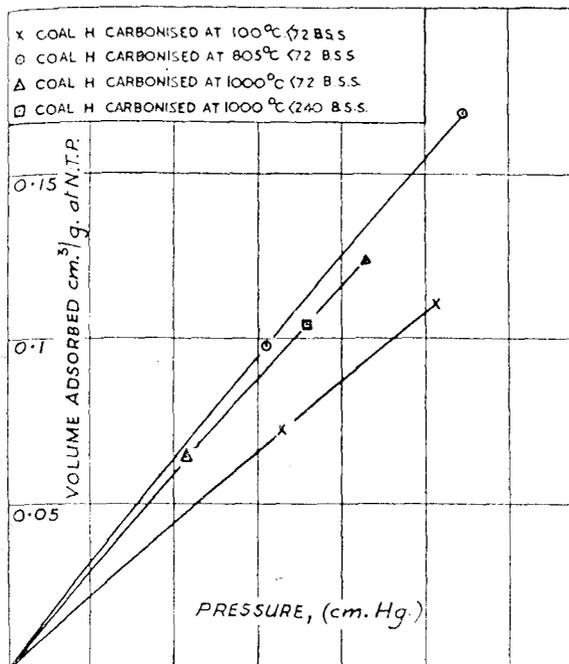

X COAL H CARBONISED AT 100°C (72 BSS
O COAL H CARBONISED AT 805°C (72 BSS
△ COAL H CARBONISED AT 1000°C (72 B S.S.
▢ COAL H CARBONISED AT 1000 °C (240 B.S.S.

VOLUME ADSORBED cm.³/g. at N.T.P.

0·15

0·1

0·05

PRESSURE, (cm. Hg.)

FIG. 7.

required for the establishment of equilibrium. Adsorption on the 1,010° C sample was very slow ; a measurement made immediately after admitting the gas gave an apparent density little different from that in n-hexane.

TABLE VII.—ADSORPTION OF METHANE ON CARBONIZED COAL H

Carbonization Temperature, ° C	Equilibrium Pressure, cm.	Volume Adsorbed cm.³/g. at N.T.P.
610	1·18	0·5
	6·86	2·33
810	2·76	0·39

OXYGEN : Oxygen was adsorbed in larger quantity than methane, and the adsorption proceeded, on the whole, more rapidly. For example, on the sample carbonized at 810° C, 55 % of the gas admitted was adsorbed in the first 2 min., as compared with 1 % for a similar quantity of methane. The rapid adsorption was, however, always followed by a long slow drift which is probably due, at least in part, to slow chemical adsorption. On the sample carbonized at 1,010° C the initial measurement with oxygen gave, as with methane, an apparent density approximately equal to the n-hexane value.
The above results show that the accessibility of the pores of the carbonized coal H to each of the four gases (helium, hydrogen, methane and oxygen) decreases with increasing carbonization temperature, and, as was found with

liquids, the larger the molecule of the gas, the lower the carbonization temperature for which it is first excluded from the pores. The results are summarized in Table VIII.

TABLE VIII

Gas	Molecular Diam.	Coal H Carbonized at		
		600° C	800° C	1,000 ° C
Helium .	1·9	No drift, penetration complete	No drift, penetration complete	Large drift, penetration complete within 24 hr.
Hydrogen	2·4	No drift, penetration complete and adsorption rapid	No drift, penetration complete and adsorption rapid	Large drift, penetration and adsorption complete within 24 hr.
Oxygen .	3·0	Large rapid adsorption followed by long slow drift. 82 % of total adsorption occurred in first 2 min.	As for 600° C but rather slower. 55 % of total adsorption occurred in first 2 min.	Penetration and adsorption very slow
Methane	4·0	Adsorption equilibrium established in 5 hr. 81 % of total adsorption occurred in first 2 min.	Adsorption equilibrium practically established in 5 days. 1 % of total adsorption occurred in first 2 min.	Penetration and adsorption very slow

It may be noted that the ease with which different fluids penetrate into the pores of carbonized coal increases with decreasing molecular size for both liquids and gases taken in a single series. Although strictly comparable values of the molecular diameters of all the fluids are not available, the general relationship is clear, and provides striking confirmation that the penetrating power does in fact depend primarily on molecular diameter and not on any other property of the liquids.

Specific Surface.—The specific surface of carbonized coals and its variation with the temperature of carbonization has been studied for a wide range of coals by Cannon, Griffith and Hirst,[2] who measured the heat of wetting of the materials in methanol. Further measurements on the carbonized coals C, F, H and K have been made by Griffith, and the results are shown in Fig. 8 The curves conform to the types previously described by Cannon, Griffith and Hirst, who have discussed their interpretation. In all cases the heat of wetting decreases with increasing carbonization temperature above 550-650° C. Maggs[3] has shown that this does not necessarily indicate a decrease in the true specific surface, since the accessibility of the pores also decreases—a result which is amply confirmed by the present work. Adsorption of hydrogen has shown that the increase in specific surface which occurs between 450° and 600° C and which is detected by methanol continues, also, at higher temperatures. The heat of wetting in methanol of coal H carbonized at 600° C is 12 cal./g. ; on increasing the carbonization temperature to 800° C the heat of wetting is reduced to 2 cal./g but adsorption of hydrogen is increased by about 40 %.

Cannon, Griffith and Hirst[2] have emphasized that the internal surface of coals is never entirely lost during carbonization and that coals which have large inner surfaces yield, in general, carbonized products with large inner surfaces. The present work provides further evidence that the fine-pore structure of a carbonized coal is directly related to that of the raw coal. Of the four coals investigated, coal K has the greatest porosity[7] and yields the most highly porous carbonized products. The raw coal F has a lower porosity and smaller specific surface than the coals C, H and K, and also a more highly constricted

pore system ;[7] after carbonization, the fine-structure porosity, surface area and accessibility of the pores are all less than for the other coals carbonized at the same temperature.
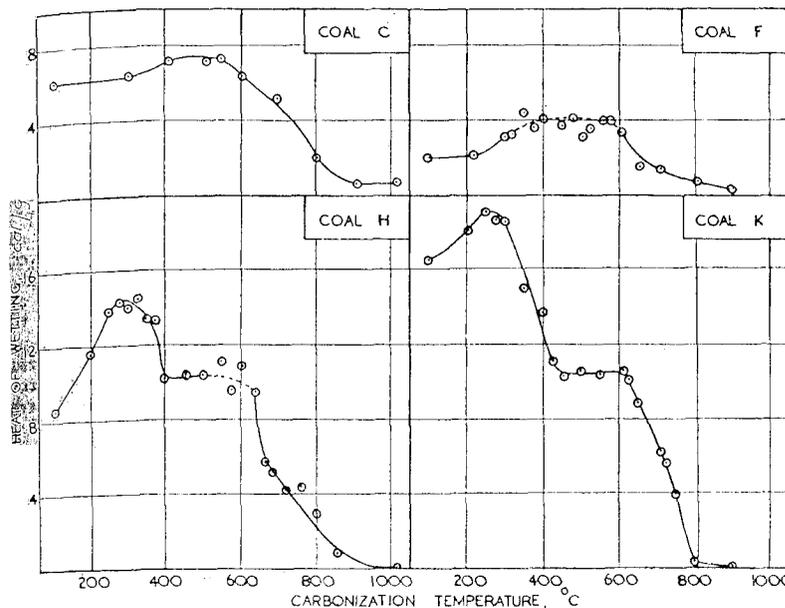

FIG. 8.

Fine-Structure Porosity of Coals Carbonized above 600° C.—It appears, from the results described above that the low apparent density obtained for carbonized coals with n-hexane or with other liquids of large molecular size is substantially independent of the experimental conditions, and is a well-defined and significant property of the solids. There is considerable evidence that it is approximately equal to the lump density of the individual particles. Not only is it constant for a wide range of liquids, but it was also unchanged when samples of coal H pre-heated to 600° and 800° were exposed to dry air at room temperature for 1 hr. after evacuation and before admitting the liquid. The presence of air would obviously impede the diffusion of a liquid into fine pores, and the same treatment did, in fact, reduce considerably the apparent density of the same samples in methanol. Moreover, Maggs has measured the adsorption of n-hexane on coal K carbonized at 600°. The amount adsorbed at saturation pressure at 25° C corresponds approximately to that required to form a monolayer on the external surface of the powder.

Helium may be considered to measure the true density of carbonized coals when the carbonization temperature is not so high that the gas is excluded from the whole or a part of the pore space. This condition is fulfilled for coals C, H and K carbonized at temperatures up to 900° C and for coal F at temperatures up to 790° C. It follows that the fine-structure porosity of these materials is given by

$$P = (d_{He} - d_{hex})/d_{He},$$

where d_{He} and d_{hex} are the densities in helium and n-hexane respectively.

In Fig. 9, P is plotted against carbonization temperature. It is seen that throughout the range of carbonization temperature for which the true density is measurable (by helium) the fine-structure porosity increases with increasing temperature for all four coals.

Thus, the fine-structure porosity *increases* while the accessibility of the pores *decreases*. This leads to the conclusion that the accessibility of the pores is governed by the size and frequency of fine constrictions or " bottle-necks " in the pore system, and not by the mean diameter of pores which are uniform along their length. The alternative assumption of uniform pores would require that, with increasing temperature, the diameter of the pores steadily decreased

while their number increased rapidly, new pores formed at any one temperature being narrower than those formed at a lower temperature. In such a system the increase in porosity would be accompanied by a still larger increase in specific surface. It has been shown, however, that between 800° and 1,000° C the specific surface *decreases* while the porosity increases.

The structural changes which accompany increasing carbonization temperature between 600° and 1,000° are associated with the loss of volatile decomposition products from a rigid solid. The existence of the decomposition products (mainly CO, CH_4 and H_2) implies that there is a re-arrangement of surface atoms or small groups 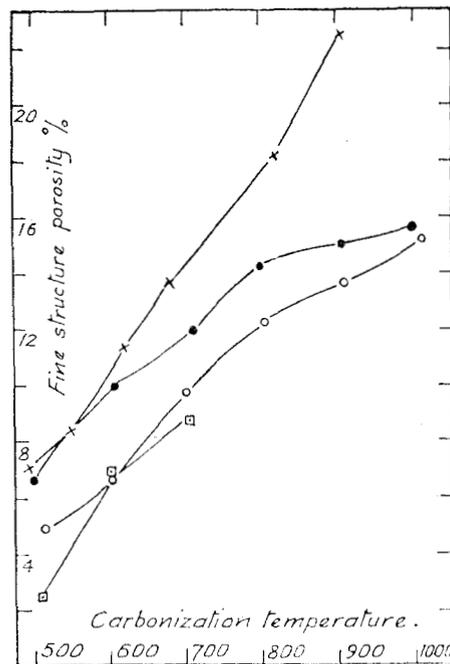of atoms within the solid. This may be sufficient to account for the creation of a more highly constricted pore system resulting from increased intermicellar contacts. A similar effect may perhaps account for the slight decrease in surface area between 800° and 1,000° by elimination of surface roughness. The increase in fine-structure porosity, on the other hand, shows that the rigidity of the structure is too great (or the carbonization temperature too low) to permit such large-scale re-arrangement as would be necessary to compensate for the loss of volatile matter and the increase in true density.

Molecular Sieve Properties of Carbonized Coals.—The volume of fine pores in coals carbonized at 1,000° C or at higher temperatures may amount to more than 20 % of the volume of the solid. For carbonization temperatures between 600° and 1,000° C the solids behave as molecular sieves; in any given sample all molecules larger than a certain size are completely excluded from the pores. Carbonized coals may be compared in this respect with the zeolites studied by Barrer,[9] although their adsorption capacity is much less. The sieve " mesh " depends both on the starting material and on the temperature of carbonization, and in the materials studied here it is never large enough to permit appreciable penetration of liquids with molecules as large as those of *n*-hexane and benzene.

Fig. 9.

○ Coal c.   ⊡ Coal f.   ◉ Coal h.   × Coal k.

The molecular sieve properties of carbonized coals must obviously be of considerable importance in determining the chemical behaviour of the materials, and probably also in determining the course of the later stages of the carbonization process. The principal volatile products of carbonization above 600° C are methane, hydrogen and carbon monoxide, and, above 700° C, hydrogen and methane, the proportion of hydrogen increasing with increasing temperature. It has been shown that methane penetrates the pore structure only slowly after carbonization at 600° C and still more slowly after carbonization at higher temperatures, whereas hydrogen penetrates freely after carbonization at 600° and 800° C. The very different rates of diffusion of the gaseous products may well have an important influence on the final composition of the gas evolved.

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[9] Barrer, *Diffusion in and through Solids* (C.U.P., 1941).