

## ELECTRICAL RESISTIVITY OF POWDERED WOOD CHARCOAL

A. SATTAR SYED, M.A. HOSSAIN and M. MOSLEM

*East Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Dacca*

(Received March 27, 1967)

Electrical resistivity of powdered wood charcoal of different grain sizes thermally activated at 350°, 500°, 600°, 700°, 800° and 1000°C was determined upto an applied pressure of 1931 lb/in<sup>2</sup>. The results show that the resistivity decreases with increasing applied pressure and becomes almost steady beyond 1725 lb/in<sup>2</sup>. No meaningful dependence on particle size was observed. The resistivity decreases with increasing carbonisation temperature and most of the decrease takes place under 700°C; between temperatures of 350° and 700°C the resistivity changes from 0.35 ohm c.m. to 0.05 ohm cm, and from 700° to 1000°C the resistivity decreases only to 0.03 ohm cm. Analyses of the volatile matter evolved from the wood chars show appreciable increase in the amount of hydrogen at carbonisation temperatures above 700°C.

### Introduction

Compared with other solid fuels, charcoal prepared from wood received relatively little study of its physical properties. It was formerly believed that coke consists largely of amorphous carbon which was considered to be a separate allotrope. X-ray analysis does not indicate an amorphous allotrope but all forms of carbon examined so far show interference figures similar to those of graphite.<sup>1</sup> Cathode ray diffraction, chemical tests and observation with electron microscopy indicate that coke consists of minute graphite crystallites surrounded by high molecular weight organic compounds.

In this paper we attempt to throw some light on the physical structure of wood charcoal by studying the electrical resistivity of thermally activated charcoal of various grain sizes under different pressures and densities, and the analysis of volatile matter. The charcoal was obtained from 'goran' (*Cariops candolleara*) heart wood chips by destructive distillation<sup>2</sup> at 350°C.

### Experimental

(a) *Preparation of Samples.*—About 2.5 kg charcoal was washed in running water and dried at 105–110°C for 2 hr and then powdered in a grinding machine. About 0.5 kg of the powdered charcoal was then loosely packed in a porcelain dish (diameter 15 cm) which was covered with another dish (diameter 15.5 cm) and heated in a muffle furnace at 800°C for 8 hr after which the contents were allowed to cool. The top mass which turned into ash was meticulously scraped off and the contents of the dish were sieved in a machine. Different samples of grains between 37 and 300 $\mu$  were thus separated. In a similar manner charcoal samples were prepared at 500°, 600°, 700° and 1000°C.

(b) *Measurements.*—A 2-in mild steel pipe of 1.06 in i.d. and a wall thickness of 0.125 in, was

lined inside with asbestos (high pressure steam joint type) for electrical insulation. A stopper of the same material was made to fit the bottom. 3 g of the sample was filled in the above hollow cylinder and force was exerted with the help of a mild steel piston of length 2.56 in and diameter 0.86 in; the length of the piston is graduated in 1/8 in. The force was applied from a Universal Press, the smallest scale reading in gauge of which was 11.2 lb weight.

The length of piston penetrating the pipe was used to derive the volume of the pressed sample which helped to calculate the apparent density. The apparent density—that is, the density of the carbon including the pores or voids—may be considered as a characteristic of the mechanical structure.

A Pye Portable Wheatstone Bridge was used for resistance measurements. A low resistance potentiometer was used to extend the range down to  $1 \times 10^{-6}$  ohm and an external galvanometer (Model Pye Scalamp 7902) was used for greater sensitivity. All the metallic surfaces coming in electrical contact with the sample were nickel plated.

Contact effects were tested first by the following experiment. The overall resistance between the nickel plated leads (the char being held under a fixed pressure with the help of a vise) was measured as a function of current density in both directions. The current was measured by a Taylor Model 38B multirange meter in the range 0 to 100mA, having an accuracy of 2%. A potentiometer (Pye 7569/P) was used to measure the potential drop in the sample. No dependence on current direction was noted and also, no appreciable change of the resistance was observed within the measured range. The constant resistance of charcoal over the value of the current used shows that the sample was free from injected carriers.

(c) *Volatile Matter.*—The volatile matter ob-



tained from wood charcoal at 500°, 700° and 800°C were analysed with the help of an Orsat gas analyser. About 20 g of granular charcoal was taken in a silica tube. Both ends were closed by rubber stoppers through which ran gas exit pipe and Pt-PtRh thermocouple junction for temperature measurement. Before heating, the tube was flushed with nitrogen.

In order to protect the rubber stoppers from heat, wet asbestos cloth was wrapped at the tube ends. The temperature was maintained until gas evolution almost ceased. The silica tube used stood a maximum of 800°C and only a single run was made.

### Results and Discussion

Figure 1 shows a typical curve for the variation of resistivity and apparent density with applied force for the char activated at 1000°C. A number of observations with separate samples were made and the root mean square error was found to be less than  $\pm 0.0006$  ohm-cm. Limitations in the determination of the mass of the sample and length of penetration of the piston placed the reliance on the measured density to be within 7%. The curves show that the resistivity of charcoal decreases with increasing applied force (and thus also with increase in apparent density, and as a result the resistivity increases with the increase of porosity, cf. Mantell<sup>3</sup>).

The nature of variations obtained for charcoal powder prepared at 350°, 500°, 700°, 800°, and 1000°C was similar. For a particular carbonisation temperature the resistivity attains an almost steady value beyond 1000 lb wt (1725 lb in<sup>2</sup>). In Fig. 2, we have plotted the resistivity at 1931 lb/in<sup>2</sup> for the charcoal (particle size 3600-4900 mesh per cm<sup>2</sup>) at different activation temperatures. It shows that the resistivity decreases at increasing activation temperature upto 700°C. For higher temperatures of activation the resistivity decreases only slightly. No significant increase of apparent density with increasing activation temperature was observed.

The role of particle size was investigated by plotting the resistivity for the different particle sizes under an initial applied force of 224 lb wt (386 lb in<sup>2</sup>) of the charcoal activated at the above temperatures. No meaningful dependence was observed. Calculations at the above pressure also showed no significant dependence of the apparent density on the particle size.

Amongst the carbons formed as solid residues of carbonisation in the condensed phase (i.e., ex-

cluding the carbon blacks) measurements of electrical conductivity have been reported only for coke.<sup>4,5</sup> These reports indicate that coke only begins to have an appreciable electrical conductivity in the neighbourhood of 700°C. On the other hand, in the case of wood char we find that the greatest decrease in resistivity is observed for carbonising temperatures below 700°C (Fig. 2). Between carbonising temperatures of 500° and 700°C the resistivity changes from 0.30 ohm cm to 0.05 ohm cm and from carbonising temperatures of 700° to 1000°C the resistivity decreases only to 0.03 ohm cm. Recent work<sup>6</sup> on the change of resistivity of solid wood char with the change of temperature of burning also supports our findings in a general way. They also state that the maximum decrease in resistivity was observed from 600° to 700°C (from 10<sup>4</sup> to 10 ohm cm) and from 700° to 1000°C the resistivity decreases to 0.1 ohm cm.

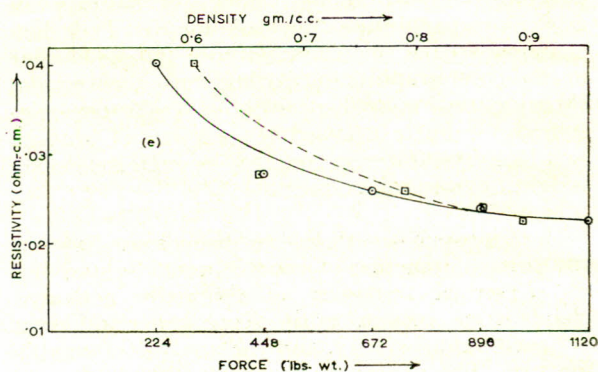


Fig. 1.—Variation of resistivity with applied force (circles) and with apparent density (squares) for grain sizes 3600-4900 mesh/cm<sup>2</sup>.

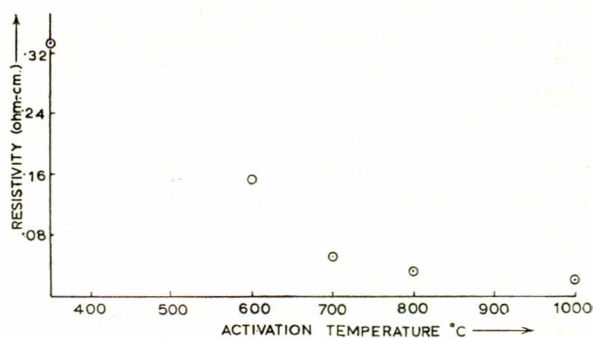


Fig. 2.—Resistivity at 1931 lb/in<sup>2</sup> pressure for the charcoal (grain size 3600-4900 mesh/cm<sup>2</sup>) at different temperatures of activation.



These studies thus reveal another striking difference between the two groups of carbons, that is, cokes and chars. Carbonised solid fuels are divided according to their type of physical structure into the two groups of cokes and chars. A coke is considered to be a carbonised solid residue which shows evidence of fusion and possesses a typical bubble structure. A char, on the other hand, possesses a capillary structure and retains, in considerable detail, the structural features of the original, uncarbonised, parent substance.

It is interesting to note that the quantitative X-ray analysis of crystallite growth in graphitizing and non-graphitizing carbons conducted by Franklin<sup>7</sup> show that non-graphitizing carbons are formed from low rank coals, sugar char and Saran [polyvinylidene chloride ( $C_2H_2Cl_2$ ) $n$ ], while graphitizing carbons are prepared from pitch coke, petroleum coke, coking coals and PVC [polyvinyl chloride ( $C_2H_3Cl$ ) $n$ ]. She concludes that the non-graphitizing carbons are formed, in general, from substances containing little hydrogen or much oxygen (which would thus put wood char in the non-graphitizing type) and graphitizing carbons are prepared, in general, from substances containing much hydrogen.

The mechanism of the carbonisation process of coke has been pictured by Hofmann<sup>8</sup> as follows. In the initial stages of the pyrolysis of an organic compound, highly condensed aromatic molecules are formed which arrange themselves in a graphite-like layered structure. As the temperature rises, graphite nuclei are formed surrounded by chemically bound complex hydrocarbon rings and chains. These can neither be extracted by solvent nor removed in high vacuum at 500°C, and it is therefore, inferred that they are chemically bound round the borders of the hexagon planes of the graphite nuclei. As coking proceeds, they decompose, some of the carbon atoms being lost in the form of volatile compounds, the remainder attaching themselves to the edges of the hexagon planes, so causing the lateral growth of the graphite crystallites. In the 400°C coke there are sufficient disordered carbon, hydrogen and oxygen atoms fully to satisfy the valency requirements of the border carbon atoms and to bring about rapid lateral growth of the plane by a condensation process as the temperature rises.

In the 700°C coke plane it is only possible to satisfy the valency requirements of the unsaturated border atoms by assuming a large and improbable number of triple bonds. The possibility of chemical linkage between separate crystallites is neglected. It, therefore, appears probable that in this coke an appreciable number of border

carbon atoms must be unattached to extraneous atoms with their valency requirements unsatisfied. The amount of disordered organic matter is so small that any pronounced growth by aromatic condensation is no longer possible. At 1300°C most of the border carbon atoms are unattached to extraneous atoms. Little volatile matter then remains in the carbon, and it is therefore highly probable that this process of growth, due to aromatic condensation, is practically complete at this temperature. Further pronounced growth can only occur by thermal recrystallisation, which only takes place at much higher temperature.

Riley<sup>9</sup> offered an explanation of the sudden development of electrical conductivity of coke at the carbonisation temperature of 700°C by a theory which involves the bonding of disordered hydrogen atoms between the hexagon layer planes of the graphite crystallites. Riley states that the character of the volatile matter evolved during carbonisation changes abruptly at about 700°C and above this temperature is principally hydrogen. He suggests that the rapid increase of the electrical conductivity with increasing carbonisation temperature in the region of 700°C means that the electrons which were employed in bonding the disordered hydrogen atoms at the borders of the hexagon planes became free and confers upon carbon its metallic conductivity.

Riley also points out that the yield of mellitic acid obtained from various carbons by controlled oxidation with nitric acid followed by alkaline permanganate, increases rapidly with carbonisation temperature upto 700°C and thereafter only slightly, indicating that aromatization is nearly complete at 700°C. Riley concludes that the much slower oxidation velocities of carbons prepared at lower temperatures and also the fact that the carbonisation temperature at which the carbons of minimum reactivity in a solution of chromic acid in syrupy phosphoric acid coincides with that at which the carbon commences to have an appreciable electrical conductivity, indicate that the penetration of the reagent between the hexagon layer planes is retarded by the presence of hydrogen associated with the graphite crystallites of the sample.

In the case of volatile matter we notice similarity between wood char and coke. Our studies of the character of volatile matter evolved from wood char (Table 1) also show appreciable increase in the amount of hydrogen as the temperature is raised beyond 700°C. Further investigations of X-ray diffraction, Hall coefficient, adsorptive capacity, and yield of mellitic acid may throw light on the electronic structure in wood chars.



TABLE I.—PERCENTAGE COMPOSITION OF VOLATILE MATTERS OBTAINED AT DIFFERENT TEMPERATURES.

Temp °C	CO <sub>2</sub>	CO	O <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub> and hydrocarbons
500	47.4	23.0	1.4	4.2	24.6
700	5.0	2.3	1.0	12.4	79.3
800	1.4	4.3	2.8	57.3	34.2

**Acknowledgements.**—The authors wish to thank Dr. N.A. Khan, Director, East Regional Laboratories, for his encouragement during the progress of the work. They are most grateful to Dr. Salimuzzaman Siddiqui, F.R.S., Dr. S.A. Samad and Mr. Mokbular Rahman for their kind assistance and many helpful discussions. They express sincerest appreciation to Dr. M.B. Das for guidance during the initial stages of the work, to the Central Testing Laboratories, Dacca for

the use of the Universal Press and to Mr. M. Raquib-ud-Dowla and the Workshop for assistance.

### References

1. H.L. Riley, *Quarterly Rev. Chem. Soc. Lond.*, **1**, 59(1947).
2. M. Qudrat-i-Khuda, S.A. Samad, M. Rahmatullah and A. Rahman, *Scientific Researches*, **1**, 24(1964).
3. C.L. Mantell, *Industrial Carbon* (Van Nostrend, New York, 1946), 2nd edition.
4. E. Sinkinson, *J. Chem. Soc.*, **127**, 839 (1920).
5. *Solid Products of the Carbonisation of Coal* (South Metropolitan Gas Company, Gt. Britain, 1934).
6. I.I. Agranovskii and L.I. Gailevskii, *Khim. Volokna*, 38(1961).
7. Rosalind Franklin, *Proc. Roy. Soc. Lond.*, **A209**, 196(1951).
8. U. Hoffmann, *Chem. Ber.*, **B65**, 1821(1932).
9. H.L. Riley, *Trans. Farad. Soc.*, **34**, 1011 (1938).