Some Properties of Coke.¹

By Prof. J. W. COBB.

COKE is formed when coal, heated out of contact with open air, softens and is blown into a porous mass by its own gaseous products of decomposition. The structure of the coke is determined by a number of circumstances, but the relation between the softening and the evolution of gaseous products of decomposition is all-important.

In the structure of charcoal the original structure of the wood carbonised is, to a considerable extent, retained in the resulting charcoal. The annual rings, marked by a difference in size in the cells, are to be seen quite plainly. In a coke made from a bituminous coal, the original solid structure has disappeared, and has been replaced by a porous honeycombed mass.

It is not every coal which undergoes coking. Anthracite, for example, does not soften or coke. The coking property has been associated chemically with the existence in the coal of substances which can be extracted from it by suitable treatment with solvents, but the interpretation of the results is controversial.

If the various factors are considered, it is not strange to find that the characteristics of a coke made from the same coal under different conditions are themselves very different. This consideration has even greater weight if one visualises the further complication of coke formation as it exists on the large scale, say, in a continuous vertical gas retort. The upper part of such a retort may be quite cool, gases escaping at, say, a temperature of about 100° C. Such an apparatus necessarily acts, to some extent, as a reflux condenser; some of the tarry products of decomposition from the lower and hotter parts of the retort will be recondensed around the cooler particles near the top, so that the descending coal charge is moistened by this film of condensate. If the film evaporates without decomposition a little lower in the retort, it will have produced a caking effect while it was wet and sticky but will have no ultimate coking effect. If it decomposes leaving a cementing residue, the coke will be the stronger for it. At high temperatures such a cementing action can also be exercised by the decomposition of such a gas as methane. Similar considerations apply to the coke oven.

It is for reasons such as these that the type of large scale apparatus used in carbonisation, its method of use, and the preparation of the coal as affecting the penetration of heat to the charge, and the facility of escape of products of carbonisation, become of nearly the same importance as the original character of the coal in determining the character of the coke made from it.

WATER-GAS.

One of the most important properties of coke industrially is its interaction with steam, producing

water-gas—a mixture of carbon monoxide, hydrogen, carbon dioxide, with some undecomposed steam. This is made not only in the water-gas process proper, where coke is blown alternately with a current of air and with steam, but also in the gasification of coal in a gas producer which is blown with a mixture of air and steam, and again to some extent in the making of town gas, when some steam is blown into the bottom of the retort—the so-called steaming process.

ASH CONSTITUENTS.

It was suggested by Haber many years ago in his "Technical Gas Reactions" (1903) that a constituent of the ash of the coke used in the water-gas process might stimulate reaction. We have gone further into this matter, being led to do so partly from a desire to obtain specific and quantitative information on that subject, and partly because we were specially interested in the behaviour of the nitrogen and sulphur compounds in coke where the ash constituents were known in some cases to exercise an important influence. For this purpose we prepared special cokes at 500° and 800° C. from coal with which had been incorporated 5 per cent. of such oxides as silica, alumina, lime, and ferric oxide, or equivalent quantities of other compounds, such as sodium carbonate. Since the original coal had been carefully chosen as containing only 1 per cent. ash, it would be reasonably hoped in this way to obtain an idea of the influence of each of the common ash constituents of coal in turn.

That the ash constituents were going to exercise some influence was obvious from the first trials of these mixtures made in an ordinary crucible test. The original coal when so heated gave coke buttons swollen and honeycombed. The iron oxide and sodium carbonate cokes were close-grained and uniformly porous, while the sodium hydrate mixture gave a barely coherent powder. Dr. Lessing, who had worked previously on the influence of catalysts on the carbonisation of coal, had claimed an influence on the character and yield of coke from this cause.

When we came to examine cokes prepared at 500° and 800° C., the results were suggestive. Considering the cokes prepared at 500° C., the presence of iron oxide and sodium carbonate altered the proportion of residual volatile matter. These cokes also differed in structure from the pure coke, being of a much closer and more evenly porous texture. This result would suggest that, whatever the ultimate explanation may be, the action of oxide of iron is to delay or modify the decomposition below 500° C., lessening the evolution of volatile matter from the softened coal and the consequent puffing-up of the mass. At a later stage, below 800° C. apparently, this volatile matter was evolved, but it was presumably then without effect on the structure because solidification had by that time occurred.

¹ Substance of two lectures delivered at the Royal Institution on Mar. 29 and April 5.

SPECIAL COKES IN STEAM.

We passed on to an examination of the comparative behaviour of these cokes when treated with steam at 1000° C. Marked differences between the cokes now appeared. The lime coke was plainly much more reactive than the pure coke, the iron oxide coke more reactive again, while the rate of steaming with sodium carbonate coke had to be pushed very high before there was any appreciable falling away from complete decomposition. Moreover, the composition of the gas attained was different. At a rate of 10 litres an hour, taking extremes, with the pure coke 61 per cent. of the steam was decomposed, and the water-gas contained 9.2 per cent. carbon dioxide, while the sodium carbonate coke had decomposed 98 per cent. of the steam, giving a water-gas containing only 0.4 per cent. carbon dioxide. It was interesting to speculate whether this difference in behaviour was a specific chemical effect due to the presence of these special constituents in the coke, or whether it was due mainly to the difference in physical structure which we knew had been brought about in the cokes during the preliminary process of carbonisation.

The tendency of opinion for some time has been to attach primary importance to the physical structure of coke as influencing its reactivity, and there seems to be no doubt that it is an important factor. It has, however, been demonstrated by impregnating the 'pure' coke with sodium carbonate (soaking in a solution and drying), that practically the same enhanced reactivity can be brought about in that way as by mixing with sodium carbonate before carbonisation, which eliminates the altered physical structure as playing the principal part in the enhancement of reactivity in this case. The results at lower temperatures were equally striking, a very noticeable feature being the low carbon dioxide content of the gas made by steaming sodium carbonate coke at 800° C.

REACTIVITY IN CARBON DIOXIDE AND AIR.

Reactivity to carbon dioxide is probably most important of all and was next examined. The formation of carbon monoxide from carbon dioxide is at the root of the manufacture of producer gas by blowing air through a deep column of coal or coke, is all-important to the working of the blast furnace, and plays its part in every coal or coke fire.

Lower temperatures were used than with steam, because of the higher reactivities. 1 per cent. of oxide of iron was found to give more than half the enhanced effect which came from 5 per cent. An impregnated sodium carbonate coke was proved to be almost as active as one prepared by adding the sodium carbonate before carbonisation. With some of the special cokes, and more particularly the sodium carbonate coke, there was a falling off in reactivity as an experiment proceeded. An interesting observation made on the oxide of iron coke, which is likely to be of theoretical importance,

suggests that reduced iron may be present and taking part in the cycle of reactions.

It is difficult to test for differences between cokes as to their reactivity with air at temperatures above the ignition point. This is largely owing to the experiment getting out of hand on account of rise in temperature when air or oxygen is used. We have made some attempts by limiting the heating effect in two ways, by using air diluted with nitrogen until it only contained 2 per cent. to 3 per cent. oxygen, and by leading it over a small flat surface of coke with a limited surface of 1 cm. square. Measurement showed that by this method it was possible to obtain combustion without accumulation of heat or rise in temperature.

In these experiments the behaviour of all the cokes was practically the same above 700° C., but at lower temperatures—400° to 600° C.—wide differences appeared. The opinion previously put forward is thus confirmed that at high temperatures the reactivity of cokes in general is so high in air that differences in behaviour depend upon the rate of supply of air to the coke particles rather than on the reactivity of the cokes. One remarkable feature noticed in these experiments was the apparent slowness with which the highly reactive sodium carbonate coke began to react with oxygen. The same phenomenon had been noticed in experiments on the temperature of ignition of the special cokes.

HEATING OF COKE IN AIR.

When air is passed through hot cokes differing in their degree of reactivity, the result obtained appears, at first sight, somewhat anomalous. In each case there is an effect due to the burning of coke to carbon dioxide on first contact, and while the air is in excess. Heat is generated, and if the air supply is the same for each of two cokes, the same heat will be generated by this primary reaction in each case. There follows, however, the further interaction between carbon dioxide and carbon, reducing some of the carbon dioxide to carbon monoxide, and the degree to which this action is carried on is greater the more reactive the coke. It is with respect to this second reaction that cokes differ so much.

Now one characteristic of the conversion of carbon dioxide to carbon monoxide by carbon is that it absorbs heat. The net result is that the difference between the two cokes shows itself in the difference of the cooling effect, and it is with the more reactive coke that the cooling effect is more pronounced. Hence, in blowing air into hot cokes, it is the less reactive coke which generates heat most quickly in the mass.

A comparison of this property has been effected on the laboratory scale. 10 gm. of coke was placed in a vertical, electrically heated furnace. A thermocouple was inserted from the bottom end of the furnace tube in such a way that the junction was 2 cm. distant from the upper surface of the coke. The furnace was then heated up to 700° C. and maintained at that temperature for one hour, after which the heating current passing through

the furnace was left unchanged throughout the remainder of the experiment, and air was passed down the coke column at the rate of 50 litres an hour. The results obtained for three cokes named in the order of their reactivity to carbon dioxide—sodium carbonate coke, 'pure' coke, and beehive oven coke—indicate that the highest temperature effect in the interior of the mass has been attained with the least reactive coke for the reason explained, doubtless an important point in high-temperature melting by coke.

INDUSTRIAL AND DOMESTIC APPLICATIONS.

I should like now to say a few words on the influence of some properties of coke (particularly reactivity) when used for various purposes. The simplest case is perhaps that of the gas producer, in which coal is gasified by blowing with air or a mixture of air and steam. There is a first conversion of carbon to carbon dioxide by air quite near the grate of the producer at the bottom, but after that the gasification of the descending carbon is the result of the conversion of carbon dioxide to carbon monoxide by the reaction $C + CO_2 = 2CO$. The efficiency and rapid working of the producer depends upon this reaction, so that the coke which is more reactive to carbon dioxide is, other things being equal, the best for the process. This is a reproduction on the large scale of the laboratory experiment last described.

Another interesting example is the domestic fire, where so much depends on the relative ease of ignition and the rapid spreading of heat through the body of the fire. With a hard and unreactive coke it is difficult to carry the heat forward from piece to piece. If there is a little volatile matter left in the coke which comes away in flames, the heat transference is much more rapid. Or, if the coke for any reason is more reactive, the same advantages obtain. There are, however, limitations to the advantages obtainable in either of these ways. If the amount of volatile matter is too great, or if too much carbon monoxide is produced by excessive reactivity of the coke, there may be a twofold loss. In the first place, these gases may screen the solid coke from oxygen and so prevent that rise of temperature on the surface which is all important if a cheerful fire is to be obtained, or if the fire is to have a high radiant

efficiency. The other detrimental effect is more important and depends upon the following phenomenon.

A bunsen flame burning in the open radiates only about 10 per cent. to 15 per cent. of its total heat of combustion, or rather more if the flame is luminous. If, however, the flame is used as in a modern gas-fire, to heat a solid radiating surface, the proportion radiated comes up to somewhere about 50 per cent. Consequently, in a coke fire, that portion of the combustion which is raising the temperature of the solid coke surface is being very much more efficiently utilised than in combustion of flames from the top of the fire burning in the open. Thus one may take it that if the amount of gas evolved is relatively small, so that it can burn in the fire, raising the temperature of the radiating surface of coke, it is very effective. But larger quantities of gas burning from the top of the fire are comparatively inefficient.

In experiments made at Leeds on the same fire, burning different solid fuels, this phenomenon was much in evidence on measuring the radiant efficiencies obtained from the fires. The experiments require extension, but I may say that the results were in accordance with the foregoing considerations, and agreed substantially with those of Dr. Margaret Fishenden of the Fuel Research Board, in that coke was found to give a higher radiant efficiency than coal. One striking result obtained, however, pointed to the necessity of not having present in the coal, ash of such a quantity and kind as to form a coherent coating during the burning, which thus formed a screen around the burning material and lowered its radiant efficiency.

Another very interesting point was the behaviour of a coke soaked in sodium carbonate solution, and therefore very reactive. It burned very freely, with visible flames a foot long. In appearance it was attractive. As a matter of fact, its radiant efficiency was not so high as that of the medium temperature coke, and that for the reason that I have explained. It reacted freely, generated carbon monoxide in quantity, the carbon monoxide burned with long flames at the top of the fire, and its radiant efficiency was correspondingly low—a defect due to the high reactivity of the coke.

Obituary.

PROF. A. A. LAWSON.

IT is little more than a month since the formal opening of the new Botanical Department in the University of Sydney was described in *NATURE*, with an illustration given of the building itself (April 2, p. 509). Before those who read it were able to formulate, much less to convey to Prof. Lawson their congratulations on this tangible mark of his successful tenure of his chair, he was in his grave, in the South Head Cemetery that looks out seawards over the entrance to Sydney Harbour. His death, following closely on a serious operation from the effects of which he never rallied, took place on Mar. 26 at Sydney.

Abercrombie Anstruther Lawson was born in Fife, and entered the University of Glasgow as a medical student. After passing through the course in elementary botany, where his artistic skill had already attracted attention, for reasons of health he went to California, and entered the University of Berkeley, coming under the influence of such teachers as Setchell and Osterhout. Graduating as Master of Science in 1898, he became instructor in botany, having already entered on a career of research. He also studied later in Chicago and at Bonn, with published results which led to his appointment as lecturer in his old University of Glasgow in 1907. Having held this position for