

LIX.—*The Constitution of Coal.*

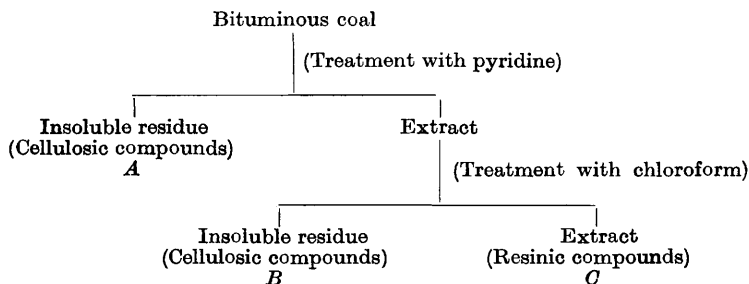
By DAVID TREVOR JONES and RICHARD VERNON WHEELER.

A DETAILED discussion of the various views held as to the probable origin of "coal," the material from which it is derived, and the manner of its formation is outside the scope of this paper. The general trend of opinion is that the material from which coal has been formed has been essentially vegetable. There is no consensus of opinion as to the manner of formation of coal, probably because attempts have been made to assign a common rationale to all the varieties, whereas there seems to be no adequate reason why different varieties, or, indeed, different accumulations of similar varieties, should not have been produced in different manners. The agencies that have produced coal from the original (vegetable) substances are generally supposed to be, in the first instance, decay through the agency of bacteria, followed by pressure, heat, and time.

The present research is an attempt to determine the chemical character of the main components of "coal," which, accepting the usual view as to its vegetable origin, we regard as essentially a conglomerate of cellulosic and resinic compounds.

It has been shown (T., 1913, **103**, 1706) that these two main constituents of bituminous coals (with which our experiments have mainly dealt) can be separated by means of solvents. Extraction of the dried coal with pure, dry pyridine brings about a partial separation, there being an insoluble residue consisting mainly of the cellulosic constituents. Further extraction of the soluble portion after it has been freed from pyridine, using chloroform or benzene, effects a further resolution, there being a soluble portion containing the resinic compounds and an insoluble residue

consisting of cellulosic compounds resembling in every respect those separated directly from the coal by means of pyridine. The scheme of separation is as follows:



That the residue *B*, insoluble in chloroform, is to be regarded as composed of cellulosic compounds in the coal conglomerate that possess (or acquire during extraction) the property of solubility in pyridine, rather than as resinic compounds that have lost the property of solubility in chloroform, is apparent from the following facts:

(1) *A* and *B* are infusible; *C* softens at about 100°. (2) *C* on exposure to air undergoes some form of oxidation, exhibited also by resins, which exerts photochemical action on a sensitised plate. *A* and *B* under similar conditions have no such action (*loc. cit.*, p. 1713).

(3) On distillation in a vacuum at a given temperature *A* and *B* yield gaseous mixtures which closely resemble one another both in quantity and composition, and differ markedly in both respects from the gaseous mixtures obtained by distilling *C* under like conditions (*loc. cit.*, p. 1710).

(4) The liquid distillates from *A* closely resemble those from *B* both in quantity and kind, and bear no resemblance to those obtained from *C*. The liquid distillates from *A* and *B* represent but a small percentage of their weights, and in both cases consist almost entirely of phenols. *C* loses half its weight at 450° as liquid distillates, which contain all the components of tar obtained by the low-temperature carbonisation of coal, with the exception of phenols which are absent.

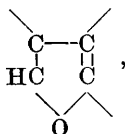
The Character and Composition of the Cellulosic Compounds.

Boudouard's work (*Compt. rend.*, 1909, **148**, 348) has shown that unchanged celluloses, if present at all in bituminous coals, can only be present in minute quantities. The cellulosic compounds are degradation products of the original plant celluloses,

the extent to which change has taken place being indicated by comparison of the ultimate analysis of cellulose with that of either portion *A* or portion *B* of a bituminous coal.

The most striking point of resemblance between the "cellulosic compounds," *A* or *B*, separated from coal, and cellulose is that both yield phenol or phenols on destructive distillation. Wichelhaus (*Ber.*, 1910, **43**, 2922) found that cellulose yielded phenol, but homologues of phenol were not obtained. In the case of the cellulosic compounds in coal, analyses of the phenols obtained on distillation show a composition ranging between that of the cresols and the xylenols.

The production of phenols on destructive distillation is occasioned by the presence of the furan grouping,



in the substance distilled. This grouping is stable, and it can readily be understood that it should survive the degradation changes to which the cellulose molecule has been subjected. These changes would, most naturally, be such as would bring about the elimination of hydroxyl groups and hydrogen, with the consequent formation of oxide or ether groupings of the structure $\text{>C}\cdot\text{O}\cdot\text{C}<$, and possibly of peroxide groupings, $\text{>C}\cdot\text{O}\cdot\text{O}\cdot\text{C}<$. The furan grouping would remain unchanged.

There is thus reason to believe that the compounds that constitute the cellulosic constituents of coal may not comprise many types. This suggestion is borne out by the fact that *A* and *B* classes of cellulosic compounds yield on distillation below 450° gaseous and liquid products almost identical in composition. The readily decomposable portions of the cellulosic compounds *A* and *B* thus closely resemble one another in constitution, and the same may be true of the more stable portions.

The question arises whether in some of the cellulosic derivatives the characteristics of the cellulose grouping may not have disappeared entirely and molecules approximating in structure to that of carbon have resulted.

The Presence of "Free" Carbon in Coal.

The idea seems to be widespread that most coals contain a certain proportion of free carbon, and the difference between one

class of coal and another, between bituminous and anthracitic coals, for example, has been ascribed to a difference in the proportion of free carbon present. This view appears to be maintained largely on account of the colour and general appearance *en masse* of coal, which become more carbon-like the older the coal measure, and from the knowledge that the parent substance of coal has been subjected to various degrees of molecular attrition, involving the loss of hydrogen and oxygen, which, it is supposed, may have been sufficient in the case of some components to have effected complete carbonisation.

The argument respecting the colour of coal may be answered by pointing out that the portions of coal insoluble in pyridine and chloroform are indistinguishable in appearance from Cross and Bevan's dehydrated cellulose ("pseudo-carbon"), a carbon-like substance which contains no free carbon (*Phil. Mag.*, 1882, [v], **13**, 325).

The agencies that have in the course of time produced coal, presumably from vegetable matter, are bacterial decay, heat, and pressure. Excluding as highly improbable the possibility of micro-organisms having effected a segregation of free carbon, there remain for consideration the influence of heat and pressure.

It is doubtful whether any coal-seam has, in the normal course of events, attained a temperature as high as 300°. Below this temperature every variety of distillate ordinarily found in coal-tar begins to make its appearance, and these compounds in an uncombined state are not normally present in coal. There are isolated instances of the occurrence of paraffin waxes oozing from coal-seams, usually in the neighbourhood of a fault (for example, Cohen and Finn, *J. Soc. Chem. Ind.*, 1912, **31**, 12), which are accounted for by local heating, due probably to earth movement, at some period in the history of the seam, just as there are instances of complete carbonisation (coking) of part of a coal-seam by volcanic intrusion. It seems impossible, however, that coals in general can ever have approached during their formation a temperature of 300°, and such a temperature is too low to effect complete carbonisation.

The effect of pressure is adverse to molecular disintegration, as the polymerisation of hydrocarbons under pressure instances. It is noteworthy that hydrogen is found in but small quantity when it results from decompositions carried out under high pressures. For example, Ipatiev (*Ber.*, 1911, **44**, 2978), in the course of experiments in thermal decomposition, observed that with increasing pressure the gases became richer in paraffins and poorer in carbon monoxide and hydrogen.

There seems, in fact, no reason to believe that any of the factors, singly or combined, involved in the formation of coal can have brought about the complete carbonisation of any portion of the mother substance of coal. On the other hand, the existence in coal of substances the molecules of which are similar in type to the carbon molecule must be presumed. Dimroth and Kerkovius (*Annalen*, 1913, **399**, 120) have shown that the carbon molecule contains the fluorene grouping, whilst Pictet and Ramseier (*Ber.*, 1911, **44**, 2486) have extracted hexahydrofluorene from Montrambert coal. Moreover, both carbon and coal yield benzenehexacarboxylic acid (mellitic acid) on oxidation, showing that in both cases there are molecules present the structure of which involves a six-carbon ring, each carbon atom being attached to another carbon atom.

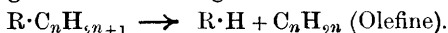
The Resinic Compounds.

The "resinic" compounds in coal are more diversified than the "cellulosic," and are presumably derived from the numerous substances, such as gums, resins, starches, sugars, etc., in the original plants. They comprise compounds containing residual alkyl, naphthene, and unsaturated hydroaromatic groupings linked to larger and more complex groupings, the latter being the polymerisation and degradation products of the gums, resins, etc., and, it may be, to some extent of the celluloses. It is probable that the original unsaturated hydrocarbons present have, under the influence of pressure, either become polymerised or concerted into compounds containing the naphthene grouping.

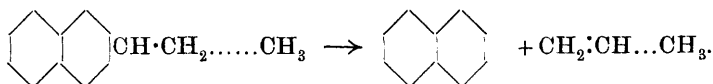
It has been shown in previous papers that all the compounds obtained as low-temperature distillates from coal (with the exception of small quantities of paraffins) are decomposition products and are not present in a free state in the coal. In order to account for their appearance in coal distillates at low temperatures, under conditions which preclude the possibility of their pyrogenic synthesis, we have advanced an hypothesis of "bound" molecules (T., 1914, **105**, 141) which satisfactorily accounts for the production of olefines, paraffins, and naphthenes. The distillation of aromatic compounds at temperatures below 350° requires further explanation. The aromatic compounds distilled from bituminous coals at a temperature of 300—350° form picrates the characteristic stability of which in water shows them to be homologues of naphthalene, and give analyses corresponding with that of dimethylnaphthalene.*

* Acenaphthene, the picrate of which is also stable in water, has a much higher boiling point than the aromatic compounds distilled from coal.

Brooks and Humphrey (*J. Amer. Chem. Soc.*, 1916, **38**, 393), as a result of experiments on the thermal decomposition at temperatures below 420° of a synthetic mixture having the average composition of tetracosylbenzene, $C_6H_5 \cdot C_{24}H_{49}$, from which they obtained benzene and toluene, have suggested the possibility of such a change as the following:

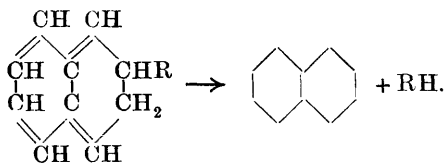


For example:



Naphthalene and its homologues are, however, neither frequent nor plentiful constituents of plant life, and cannot be the direct source of more than traces in coal of compounds containing aromatic (as distinct from hydroaromatic) and naphthalene groupings in either the free or the "bound" condition; and it is unlikely that during the formation of coal, under the influence of pressure, hydrogen should be eliminated from such hydroaromatic compounds as may originally have been present. Nor can the aromatic compounds found in coal distillates be formed from "bound" hydroaromatic compounds by elimination of hydrogen during distillation, for they appear at a lower temperature than that at which hydrogen is eliminated from dihydronaphthalene (T., 1915, **107**, 1582).

The mechanism of decomposition of santanous acid, $C_{15}H_{10}O_3$, between 300° and 350° , which does not involve the elimination of hydrogen, suggests that the mode of formation of naphthalene derivatives from hydrogenated nuclei in coal may be according to the following scheme:



As regards the nature of the oxygenated compounds present in the resinic constituents of coal, the chemical indifference of the bulk of the coal towards saponifying and hydrolysing reagents generally makes it difficult to believe that much of the oxygen can be present in any reactive group, such as the hydroxylic or carboxylic. It is possible that the chemical indifference of coal is due to the oxygen being present in the groupings $C \cdot O \cdot C \cdot O \cdot C$, $C \cdot O \cdot C$, and $C \cdot O \cdot O \cdot C$ as a constituent of cyclic and, to a less extent, of open-chain oxides. Such a condition would account

also for the occurrence of water in the distillates from dried coal (often considered as necessarily implying the presence of hydroxyl groups), for Senderens (*Compt. rend.*, 1908, **146**, 1311) has shown that ethyl ether, for example, $\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$, decomposes readily in contact with dehydrated alumina, the mechanism of decomposition involving the elimination of water and the formation of ethylene. It should be noted, however, that Benedict and Bamberger (*Monatsh.*, 1890, **11**, 262) have shown that the methoxyl grouping, present in woods and lignites, is absent from bituminous coals (and cellulose).

Hydrocarbons in Coal.

The presence of traces of free hydrocarbons in different coals has been proved by Pictet and Ramseyer (*loc. cit.*), who isolated hexahydrofluorene, and by Pictet and Bouvier (*Ber.*, 1915, **48**, 930), who distilled a solid naphthene (melene, $\text{C}_{30}\text{H}_{60}$, m. p. 62—63°) from Pictet and Ramseyer's extract of a Montrambert coal. We have obtained solid paraffins corresponding with heptacosane, $\text{C}_{27}\text{H}_{56}$, from several British coals by extraction with pentane. The presence of complex unsaturated (olefinic) hydrocarbons is difficult of proof, but, since such hydrocarbons are important constituents of plants, can be assumed.

Apart from these traces of free hydrocarbons, the occurrence of which we have shown to be, in a sense, accidental, coal must contain hydrocarbons in a "bound" condition, which on distillation are set free in the manner already described. The "bound" paraffin hydrocarbons no doubt owe their origin to long-chain esters and acids, such as oleic, palmitic, and linolic acids, present in the original plants, although the manner of disappearance of the alcoholic and carboxylic groupings is, as in the parallel case of the formation of petroleum, largely a matter of conjecture.

The resemblance between low-temperature distillates from coal and certain varieties of petroleum is such as to have suggested a common origin, and Pictet and Bouvier (*loc. cit.*) have identified various naphthenes derived from coal with naphthenes derived from Galician and Canadian petroleum. We do not consider, however, that these similarities can be regarded as pointing to more than a partial identity of the parent substances of coal and petroleum, to the presence in both parent substances of compounds, such as aliphatic esters, which are common to both vegetable and animal remains.

The outstanding difference between the "petroleum" distilled from coal and the natural oils is the presence in the former of phenols. The difference is explicable when the conglomerate

character of coal is borne in mind and when it is remembered that phenols are distilled only from the cellulosic portions. The absence of phenols from petroleum suggests that its parent substance contained no material of cellulosic structure, for phenols are highly stable compounds and would withstand the temperature of the oil springs. The possibility of celluloses having been present originally and of their having undergone transformation with entire loss of structure must be admitted, but on the whole the absence of phenols from petroleum must be regarded as evidence in favour of their non-vegetable origin.

Summary.

Coal is considered to have been formed from decayed vegetable matter by the action of pressure and temperature. The temperature cannot have approached 300°.

The coal conglomerate can be resolved by means of solvents into cellulosic and resinic portions.

The cellulosic derivatives contain compounds the molecules of which possess the furan structure and yield phenols when destructively distilled. There are also compounds present the molecules of which have structures resembling that of the carbon molecule, but it is unlikely that "free" carbon is present in coal. The cellulosic derivatives are probably few in type.

The resinic derivatives contain compounds in which alkyl, naphthene, and unsaturated hydroaromatic radicles are attached to larger and more complex groupings. It is doubtful whether aromatic groupings are present. Under the influence of pressure the bulk of the resinic derivatives have become highly polymerised. The oxygenated resinic derivatives are chiefly oxides, probably cyclic oxides; esters, lactones, anhydrides, acids, and ketones are absent or present only in small quantity.

Hydrocarbons exist in the resinic portion of coal; saturated hydrocarbons (paraffins) are, however, present in small quantity only.

The main distinction between low-temperature distillates from coal and petroleum is the absence of phenols in the latter. This is held to be corroborative evidence of the non-cellulosic origin of petroleum.

ESKMEALS,
CUMBERLAND.

[Received, June 9th, 1916.]