CCCLII.—*Studies in the Composition of Coal. Oil-yielding Constituents.*

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BITUMINOUS coal being a conglomerate of different types of compounds which decompose at different temperatures, yielding characteristic liquid and gaseous products, it is reasonable to suppose that by the slow destructive distillation of the coal as a whole the contributions of each type of compound to the distillates might be recognised. In particular, it would seem probable that those constituents of the coal which, when separated therefrom by means of solvents, are found to melt below 100° (see Cockram and Wheeler, J., 1927, 700) should become liquid and flow from the coal at quite low temperatures. The work of Burgess and Wheeler (J., 1914,

105, 131) and, more recently, of King and Willgress (Fuel Research Board Tech. Paper No. 16, 1927) is significant in this connexion.

We have carried out slow destructive distillations, in a vacuum, of a number of bituminous coals, using varieties which had already been studied by solvent analysis and other means, so that their general character was known. We record in detail in this paper the results obtained with one coal, bright coal (mixed vitrain and clarain) from the Wigan Six Foot seam.

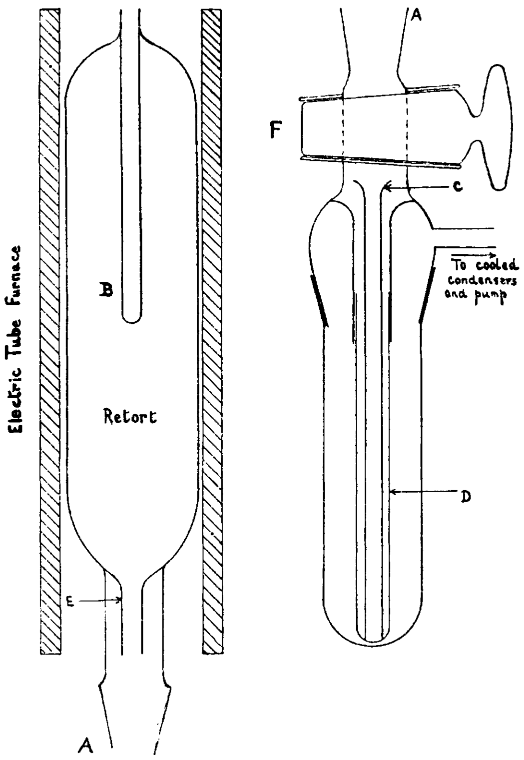
The main conclusions to be drawn from the results (which experiments with other coals amply confirm) are : (1) That the hydrocarbons and resins, extractable from the coal by organic solvents, yield a high proportion of the oils obtained on distillation, the former being distilled unchanged, quantitatively, and the latter partly distilled and partly decomposed. (2) That the coal has a definite decomposition point, which is not appreciably affected by changes in the experimental conditions. With the Wigan Six Foot coal the decomposition point occurs at 318°. Characteristic products of this decomposition, which is of the ulmin constituents of the coal, are water and phenolic compounds. As soon as the decomposition point of the coal has been passed, its character, as evinced by its behaviour towards solvents, its caking-power, and its reactivity in general, undergoes a sudden and marked change.

EXPERIMENTAL.

The method of experiment was similar to that used by Burgess and Wheeler (*loc. cit.*). A charge of 250 g. of the undried coal, ground to pass a 20-mesh and remain on a 50-mesh sieve (I.M.M. standard), filled a cylindrical retort of Jena glass, fixed vertically with its mouth downwards. The retort (see Fig. 1), which was heated electrically in a tube furnace specially designed to secure a uniform temperature throughout its length, was connected by a ground glass joint, A, through a series of three condensers, to an automatic mercury Sprengel pump. A glass tube, B, reaching to the centre of the charge of coal, was fused into the head of the retort for the reception of a thermo-couple. A second thermocouple was lashed to the outer wall of the retort. The required temperature was regulated by means of the outside thermo-couple. About 12 hours elapsed before the inside thermo-couple recorded the same temperature as the outside, but thereafter both records remained constant and identical.

A difficulty encountered with regard to the collection of the less fluid oils distilled from the coal, which it was desired to separate at intermediate stages of the heating, arose through their condensation at the neck of the retort, whence they could be removed only after dismantling the apparatus. To obviate this difficulty, the arrangement shown in Fig. 1 was devised. A glass tube, C, bearing a small cylinder of soft iron at its lower end, was placed within a test-tube, D, and the two were inserted within the first of the series of three condensers connected to the retort. When the apparatus was assembled for an experiment, the whole being thoroughly evacuated, the tube C was raised by means of a solenoid, so that its upper end fitted closely over the mouth of the retort at E. It was then gripped in position by slightly turning the wide-bore tap, F. At any stage in the distillation of the coal the tube C could be withdrawn below the tap F (which could then be closed) and the oils that had condensed within it examined.

FIG. 1.



Method of Carrying out a Distillation.—After evacuation of the apparatus, the temperature of the charge of coal was slowly raised to 100° and maintained continuously during 120 hours. Any liquid and gaseous products evolved were collected, the former in the condensers, the second and third of which were cooled by immersion in solid carbon dioxide dissolved in ethyl ether, and the latter over mercury at the Sprengel pump. The temperature was now raised over the second desired range, 48 hours being taken in doing so, and maintained at the higher value during 120 hours, the liquids and gases evolved being collected as before. And so for each temperature range. The pressure within the apparatus, even at periods of maximum gas-evolution, never exceeded 3 and was usually less than 1 mm.

Examination of Liquid Products.—The liquid products were collected in two portions over each temperature range: (1) Water and " light oils " condensing at −80° in the two cooled receivers; and (2) " heavy oils " condensing at atmospheric temperature in the first receiver. The " light oils," consisting mainly of light petroleum, were weighed but not closely examined. The " heavy oils " were analysed in the following manner. A chloroform solution of them was washed successively with dilute solutions of sodium carbonate, potassium hydroxide, and sulphuric acid, from which solutions acidic, phenolic, and basic oil fractions were recovered. The residual neutral oil was extracted in a Soxhlet apparatus successively with light petroleum, ethyl ether, and chloroform. The extract by light petroleum, consisting mainly of hydrocarbons, was treated with concentrated sulphuric acid, thereby making a separation of saturated from unsaturated compounds, and in some experiments the saturated compounds were treated with fuming sulphuric acid and nitration mixtures for the removal of aromatic compounds.

Distillation of Wigan Six Foot Coal.—The sample of coal used for these experiments was the bright portion of the seam, a clarain with numerous streaks of vitrain. It contained 2·7% of ash and the ultimate analysis, on the ash-free dry coal, was: C, 81·8; H, 5·5; O, 9·24; N, 1·52; S, 1·94. Solvent analysis (see Cockram and Wheeler, *loc. cit.*) by pyridine and chloroform gave: Insoluble in pyridine (α), 81·54; soluble in pyridine but insoluble in chloroform (β), 12·34; soluble in both pyridine and chloroform (γ), 6·12. The γ-compounds contained: Soluble in light petroleum (γ_1), 1·53; soluble in ethyl ether (γ_2), 1·46; residue (γ_3 and γ_4), 3·14 (all expressed as percentages on the ash-free dry coal).

Table I records the production of gaseous and liquid distillates by successive stages up to 550°.

The gases evolved up to 100° were mainly the higher paraffins. No marked increase in the rate of evolution of gases occurred up to 300°, but the proportion of paraffins decreased and that of oxides of carbon increased. Hydrogen was first noticed in the gases evolved over the range 300—320°, but even at 350° the gases contained no more than 1% of hydrogen, the fraction collected over the range 320—350° consisting mainly of the paraffins (ratio C/A on explosion analysis, 1·50), with about 10% of higher olefines. At 300°, hydrogen sulphide first made its appearance, a mobile oil, condensed at −80°, with a pungent garlic-like odour being evolved simultaneously.

The coal, which had previously been exhausted at room temperature during 4 days, lost 5% by weight of moisture up to 100°. This is not recorded as a product of distillation in Table I. Very little water was evolved between 100° and 300°. The " light oils "

TABLE I.

Distillation Products of Wigan Six Foot Coal.

(Liquid products expressed as per cent. by weight on ash-free dry coal.)

Temp. up to	100°	200°	250°	300°	320°	350°	400°	550°
Total gas (c.c. per 100 g. of coal)	40	127	150	178	602	1772	(not measured)	
Water	—	0·12	0·16	0·29	0·79	2·09	4·09	5·39
Light oils	Nil	0·04	0·10	0·35	0·57	1·30	2·31	2·70
Heavy oils	,,	Nil	0·23	1·33	3·24	8·79	10·90	10·99
Fractionation of heavy oils.								
Sat. hydrocarbons	—	—	0·19	0·70	0·99	1·75	2·06	2·06
Unsat. hydrocarbons	—	—	0·04	0·46	1·50	3·35	3·72	3·80
Phenolic and acidic oils	—	—	—	—	0·37	1·72	1·94	1·94
Ether-sol. oils	—	—	—	0·07	0·09	0·85	1·24	1·24
Chloroform-sol. oils	—	—	—	0·06	0·08	0·26	0·35	0·35
Bases	—	—	—	—	Trace	0·12	0·55	0·55
Loss during fractionation	—	—	—	0·04	0·21	0·74	1·04	—

were noticed first at 150° and the "heavy oils," condensing at atmospheric temperature, at 225°. The first runnings of heavy oils were mobile and of a red colour. They continued to be of this character up to 300°, very little gas being evolved meanwhile. At 318°, there was a sudden acceleration in the production of gases, water, and oils. At this temperature, phenolic and acidic compounds were noticed in the oils for the first time, but the bulk consisted of unsaturated hydrocarbons. At 330°, oils of another type were distilled simultaneously with the hydrocarbons. These were viscous and insoluble in light petroleum but soluble for the most part in ethyl ether. The production of heavy oils ceased at about 390°, the greater proportion being distilled over the range 300—375°. Light oils continued to be evolved in small quantities above 400° and water up to 550°, the highest temperature employed. Analyses of different fractions of the heavy oils are given in Table II, comparison being made with the γ_1 and γ_2 extracts of the original coal.

TABLE II.

Analyses of Oil Fractions.

Material.	Per cent. on ash-free dry coal.	Carbon %.	Hydrogen %.
Total heavy oils up to 300°	1·33	87·3	9·25
γ_1 extract from the coal freed from resins	1·20	86·5	9·10
Sat. hydrocarbon oils up to 300°	0·70	86·8	10·10
Sat. hydrocarbon oils from γ_1 extract	0·76	86·4	10·50
Ether-soluble portion of oil first evolved at 330°	1·24	81·8	7·02
γ_2 extract from the coal	1·46	81·6	6·40

The amount of γ_1-extract from the coal was 1·53%. The removal of resinous compounds by Robinson's method (J., 1925, **127**, 768) left 1·20% of a hydrocarbon oil. Both in quantity and in composition this oil corresponded closely with the " heavy oil " distilled from the coal up to 300°. Moreover, both the distilled oil and that removed from the coal by solvents lost 40% by weight on treatment with concentrated sulphuric acid, and from the saturated hydrocarbons remaining, of both oils (see Table II), a white solid hydrocarbon, m. p. 56—58°, was obtained by precipitation on cooling from boiling acetone. This close similarity (and the fact that very little gas accompanied the oils distilled from the coal) suggests that the primary oil obtained below 300° was yielded, without decomposition, by the γ_1-fraction. With all the coals we have examined in this manner there is close correspondence, both in quantity and in composition, between the hydrocarbon oils distilled from the coals below 300° and the γ_1-extracts (freed from resinous compounds).

The viscous oil that first made its appearance at 330° could be separated from the hydrocarbons by treatment with light petroleum and ethyl ether. On evaporation of the solvent, a red-brown solid was obtained similar in composition and general character to the resinous γ_2-extract from the coal. The quantity of this resinous material distilled from the Wigan Six Foot coal approximated to that of the γ_2-fraction, but with other coals the quantity may be considerably less.

Two fractions of the primary liquid distillation products of bituminous coal can thus be identified with the γ_1 (hydrocarbon) and γ_2 (resinic) constituents that are removed from the coal by solvents, and can be regarded as having been liquated from the coal conglomerate, not produced by decomposition of the coal substance. The thermochemical decomposition point of the coal is marked by a copious evolution of gases and water and by the appearance of phenolic and acidic compounds. With the Wigan Six Foot coal this thermochemical decomposition point was 318°. The work of Jones and Wheeler (J., 1914, **105**, 140) shows that the phenolic compounds are products of decomposition of the ulmin portion of the coal exclusively. They are accompanied by much gas and water.

Examination of Residues from Distillation of Wigan Six Foot Coal.—In view of the close correspondence between the γ_1 (hydrocarbon) and γ_2 (resinic) fractions, extractable from the Wigan Six Foot coal by solvents, and certain portions of the oils obtained on distillation of the coal, it was considered desirable to examine the solid residues remaining after distillation at different temperatures, more particularly as to their contents of substances extractable by solvents.

To this end a series of distillations of different charges of the same coal was carried out, in the manner already described, heating being stopped at 250°, 280°, 300°, 320°, and 350°, respectively. Each residue, after being washed with chloroform in the cold to remove traces of liquid distillates that might be adhering to it, was subjected to " solvent analysis " according to the scheme outlined by Cockram and Wheeler. The results are in Table III.

TABLE III.

Solvent Analysis of Distillation Residues.

(Per cent. on original coal, ash-free dry.)

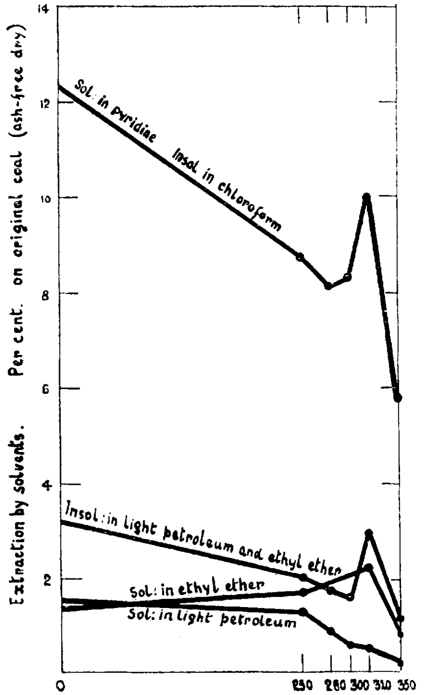
				(Soluble in chloroform.)		
	Insol. in pyridine.	Sol. in pyridine. Insol. in chloroform.	Sol. in chloroform.	Sol. in light petroleum.	Sol. in ethyl ether.	Insol. in light petroleum and ethyl ether.
Original coal ...	81·54 (α)	12·34 (β)	6·12 (γ)	1·53 (γ_1)	1·46 (γ_2)	3·14 ($\gamma_3+\gamma_4$)
Residue at 250°	86·31	8·79	4·90	1·33	1·64	1·93
,, 280°	87·48	8·12	4·40	0·91	1·82	1·67
,, 300°	87·71	8·25	4·04	0·58	1·95	1·51
,, 320°	84·35	10·08	5·57	0·52	2·10	2·95
,, 350°	92·28	5·73	1·99	0·19	0·78	1·02

The general character of the changes that have taken place during the distillations is shown in Fig. 2. The residue after distillation at 300° contained but a small quantity of material extractable by light petroleum after fractionation with pyridine and chloroform (*i.e.*, material corresponding with the γ_1-fraction of the original coal). This, on examination by Robinson's method, was found to be wholly resinic. Corresponding, therefore, with the liquid hydrocarbons collected from the distillation at this temperature, the coal residue is devoid of an equivalent amount of material of like nature which, before the coal was heated, could be extracted from it by solvents. This, coupled with the fact, already recorded, that but little gas is evolved at this temperature, is strong presumptive evidence that the oils distilled were originally present, as such, in the coal. Additional evidence is afforded by the fact that the hydrocarbon oils collected from the distillation of the coal up to 300° can be redistilled unchanged (in a vacuum) over a temperature range but little lower than that at which they were distilled from the coal.

Heating at each stage up to 320° caused in the residues an increase in the amounts of extracts corresponding with the γ_2-fraction of the original coal. This was probably derived from the resin-like constituents originally soluble only in chloroform or acetone (the γ_3- and γ_4-fractions), since the effect of moderate heat on them is to render them in part soluble in ethyl ether, when they are recognisable as resins.

The residue after heating at 350° had lost most of the original ether-soluble material (γ_2-fraction), and, as already recorded, an identical material first appeared in the liquid distillation products just below this temperature (at 330°) and could be separated from them as a red-brown solid. The source of this solid is thus the extractable resins of the coal, but complete distillation of the resins, unchanged, from the coal cannot be presumed (as it can with the hydrocarbons), for with the majority of coals less is obtained by distillation than by extraction. Moreover, this resinous distillate from the coal cannot be redistilled unchanged. On distillation at 400° in a vacuum, for example, the distillate amounts to about 70% of the original, is more fluid and is soluble (60%) in light petroleum, and the undistilled residue is soluble in chloroform.

FIG. 2.



Temperature at which coal was distilled, °C.

Two observations suggest the manner in which this resinous distillate is yielded by the coal. When the duration of heating was much prolonged, the temperature at each stage being maintained during 720 instead of the usual 120 hours, a quantity of the ether-soluble resin was present in the distillate at a rather lower temperature than before (at 310°), and some could be washed out of the residual coal charge with cold chloroform, suggesting that the first action of heat on the resinic constituents of the coal was to liquate them to the surface of the coal particles. Further, when a number of coals are examined in the manner described in this paper, it is found that the relationship between the quantity of resins extractable from the coal by solvents and obtained from them by distillation is dependent on the amount of hydrocarbon oil that accompanies them. The greater the quantity of hydrocarbon oil distilled from the coal, the nearer does the quantity of resins distilled correspond with the quantity extractable from the original coal by solvents. The suggestion is that, during the heating of the coal, the resins are first melted and then in part carried away by the hydrocarbon oil vapours that are being distilled at the same time. No doubt such of the resins as are not vapour-distilled in this manner are later decomposed or modified by the heating in much the same manner as they are found to be on redistillation, becoming mobile and for the most part soluble in light petroleum.

The thermochemical decomposition point of the coal is sharply defined and is unaltered by changes in the experimental conditions. With the Wigan Six Foot coal the decomposition point is 318° whether the distillation is effected in a vacuum or at atmospheric pressure. Heating during one month at 310° causes no appreciable decomposition.

Marked by a copious evolution of gases, water, and oils, the decomposition point of a coal is the beginning of the breakdown of the ulmin constituents (the major part of the coal), and thereafter the effect of heat is to produce profound changes in the coal substance. These changes, apparent on examination of the solid distillation residues, affect not only the behaviour of the coal towards solvents (see Fig. 2) but its reactivity in general (with oxygen, for example) and its caking power. A further communication, in which the decomposition points of a number of coals are compared, will deal with this subject more fully.

Whilst the characteristic liquid products of destructive distillation of the ulmin portion of the coal are phenolic and acidic compounds, hydrocarbon oils are also produced and contribute to the yield of such oils obtained on heating the coal above its decomposition point. For the most part, however, the hydrocarbon oils obtained over the higher temperature ranges are derived from the organised plant entities (mainly spore exines and cuticular tissues) preserved in the coal. Details of the researches on which this conclusion is founded will be given later.

The work described in this paper forms part of a research on the constitution of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

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