CXX.—*Studies in the Composition of Coal. The Soluble Constituents of Coal and their Degree of Coalification.*

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FISCHER, BROCHE, and STRAUCH (*Brennstoff-Chem.*, 1924, **5**, 299; 1925, **6**, 33), from a study of a series of German coals, have drawn attention to a relationship they had observed between the "rank" (degree of coalification) of the coals and the character of the materials extractable from them by benzene under pressure. The materials so extracted (at 288°) were fractionated by pouring the extracts into light petroleum. Solids separated, to which the name "Festbitumen" was given and, on evaporation of the light petroleum, viscous oils were obtained, termed by them "Ölbitumen." These authors observed that, in their series of German coals, the ratio of "Ölbitumen" to "Festbitumen" increased with increasing rank of the coal.

In a previous communication (J., 1927, 700), we remarked on the importance of this observation, as possibly throwing light on the character of the coalification process, and stated our intention of making a similar examination of series of coals. Through the courtesy of Dr. David White, of the United States Geological Survey, we have been able to examine a number of samples of the Pittsburgh seam, ranging in carbon content from 80·5 to 89·0%; and we are indebted to the South Yorkshire Survey Committee of the Fuel Research Board for samples of the Barnsley seam of carbon content between 80·6 and 84·5%. The advantage of carrying out a study of this kind on coals from the same seam lies in the elimination of possible complications due to wide differences in character of the vegetation from which the coals were formed.

Method of Examination.—For the resolution of coals by means of solvents, we prefer the use of pyridine and chloroform at their normal boiling points to that of benzene under pressure as originally employed by Fischer and Gluud (*Ges. Abh. Kennt. Kohle*, 1916, **1**, 54) and adopted by Fischer, Broche, and Strauch (*loc. cit.*), Bone, Pearson, and Quarendon (*Proc. Roy. Soc.*, 1924, *A*, **105**, 608), Davis and Reynolds (*Ind. Eng. Chem.*, 1926, **18**, 858; 1929, **21**, 1295), and Hoffman (*Glückauf*, 1928, **64**, 1237). At the high temperature (288°) employed for the pressure-extraction by benzene, part of the resins in most coals is liable partially to decompose, whilst with coals of low carbon content there may be extensive decomposition of the ulmins, with the production of phenolic and acidic oils, for the active decomposition point of a coal is lower the lower its carbon content (see Holroyd and Wheeler, J., 1928, 3197). For example, whereas the active decomposition point of Two Foot Nine (Ferndale No. 7) coal, a semi-bituminous coal of 89·8% carbon content, is 360°, that of Seven Foot (Kingsbury), a bituminous coal of 77% carbon content, is 290°. With lignites and brown coals, the carbon contents of which may be as low as 66%, the active decomposition point is well below 288°. False deductions may, in consequence, be drawn from changes in the character of the material extractable at 288° from a series of coals of different carbon contents.

Our method of analysis of coal by means of solvents was described in some detail in our previous paper. Briefly, it involves an initial partial dispersion of the colloidal mass of coal with pyridine, followed by extraction with chloroform, whereby the α-, β-, and γ-fractions (see Stopes and Wheeler, "The Constitution of Coal," London, 1918) are obtained. The γ-fraction is then resolved by successive extractions with light petroleum and ethyl ether, giving fractions γ_1, soluble in light petroleum, γ_2, soluble in ethyl ether, and γ_3, insoluble. (Originally, there was a subsequent treatment with acetone, but this can be omitted.) The γ_1-fraction consists mainly of hydrocarbons, the γ_2 of resins (resinols, resines, and resenes), and the γ_3 of compounds akin to the resins.

From a comparison between our method of analysis and that of Fischer, Broche, and Strauch, we identify (for coals that are not decomposed at 288°) their "Ölbitumen" with our γ_1-fraction, and their "Festbitumen" with our combined γ_2- and γ_3-fractions.

The Pittsburgh Seam.—The Pittsburgh seam extends over wide areas in Pennsylvania, Ohio, West Virginia, and Maryland, and the coal varies in carbon content from 78% at its westernmost limit, where it is a sub-bituminous coal (Seyler's ortho-perlignitous), to 90% in the Georges Creek region of Maryland, where it is a semi-anthracite (Seyler's sub-meta-bituminous). When the coal measures of the Allegheny formation were deposited, there existed over these areas a vast coastal plane, or an area of subsidence, upon which a series of almost continuous stretches of vegetation accumulated, each in turn to be gradually covered by detrital matter carried by the encroachment of water (see White, Bull. 38, U.S. Bureau of Mines, 1913). The Pittsburgh seam, which lies above the coals of the Allegheny formation, was formed under similar conditions. The variations in composition of the seam would appear to be due mainly to changes in pressure and temperature caused by earth movements during the coalification process, the changes in rank throughout the deposit having been correlated with changes in the thrust pressure of the superincumbent strata.

The samples, 17 in number, examined by us were collected by Dr. David White personally at collieries situated along the route of the Baltimore and Ohio railway, the distance covered from west to east being about 100 miles. Towards the east, in the region of the Allegheny mountains, the land rises steeply and the character of the coal changes from bituminous to semi-bituminous. All the samples were of bright macroscopic appearance, there being a complete absence of durain bands. Microscopic examination of thin sections, perpendicular to the bedding plane, confirmed the absence of durain, the sections being uniformly translucent and containing but few microspore and sometimes no megaspore exines.

As the carbon content of the coal increased, the colour of the sections became darker and resin inclusions, which were numerous and well defined in the western samples, became more difficult to distinguish. Analytical data regarding the samples, arranged in order of their occurrence west to east of the coal-field, are given in Tables I and II. The names of the samples are those of the collieries at which they were collected.

TABLE I.

Ultimate Analyses. Pittsburgh Seam.

(% on an ash-free dry basis.)

Sample.		C.	H.	N.	S.
Bailey's Mills (Barnsville, Ohio)	(*a*) top bench	78·2	5·9	1·3	4·5
	(*b*) upper bench	79·6	5·7	1·3	3·5
	(*c*) bottom bench	78·9	5·8	1·3	4·4
Elm Grove (Wheeling, W. Virginia)	(*a*) top	77·9	5·4	1·6	7·2
	(*b*) upper	81·1	5·3	1·6	3·2
	(*c*) bottom	80·4	5·6	1·6	3·2
Monongah (Marion County, W. Virginia)	(*a*) top	83·3	5·6	1·9	0·6
	(*b*) above double band	84·1	5·4	1·9	0·7
	(*c*) bottom	82·2	5·4	1·8	1·3
Hustead (W. Virginia), bottom		84·9	5·9	*ca.* 1·5	1·5
Scotch Hill (Newburg, W. Virginia)		85·2	5·2	1·3	1·0
Revere (Uniontown, Pennsylvania), bottom		86·1	5·4	1·8	0·7
Jamison (Pleasant Unity, Pennsylvania), bottom		86·5	5·6	*ca.* 1·5	0·8
Vogele (Ligonier, Pennsylvania), bottom		87·4	5·4	1·9	1·8
Ocean Mine (Allegheny County, Maryland)	(*a*) top	89·0	4·7	1·9	0·9
	(*b*) upper	88·8	4·4	2·1	0·8
	(*c*) bottom	88·4	4·7	1·9	1·4

At Scotch Hill, the Pittsburgh seam is not worked, but it occurs, under shallow cover, in a syncline passing through Newburg.

All the samples, with the exception of the Ocean Mine coal, yielded highly swollen residues on carbonisation at 600° in the Gray-King assay, those of low carbon content passing through a semi-fluid plastic stage. In this and other respects, *e.g.*, their volatile matter contents, they differ from British coals of like carbon contents. For example, the Bailey's Mills samples, C 80—81%,

TABLE II.

Proximate Analyses. Pittsburgh Seam.

Sample.		Ash, %.	Moisture, %.	Volatile matter, % on ash-free dry basis.	Tar yields, % (Gray-King assay).
Bailey's Mills	(*a*) top	8·5	1·9	48·8	16·8
	(*b*) upper	3·0	2·4	46·5	17·3
	(*c*) bottom	13·2	2·0	50·4	18·0
Elm Grove	(*a*) top	9·6	1·9	43·1	13·5
	(*b*) upper	4·5	2·2	42·3	15·5
	(*c*) bottom	6·2	1·7	44·3	15·5
Monongah	(*a*) top	4·6	1·6	39·8	14·3
	(*b*) above double band	5·1	1·6	39·2	13·1
	(*c*) bottom	10·1	1·7	37·5	9·5
Scotch Hill		3·6	1·2	35·5	10·9
Ocean Mine	(*a*) top	6·3	0·8	18·7	7·5*
	(*b*) upper	5·4	0·7	19·6	6·0*
	(*c*) bottom	10·3	0·8	20·0	7·0*

* Combined tar and liquor.

yielded caked residues comparable with those given by Durham coals having C, 84—86%. It is, indeed, impossible to generalise solely from their ultimate analyses with regard to the properties of coals from widely-separated fields.

Solvent analysis. Solvent analyses were carried out in the manner previously described. The fractions were of similar character and properties to those obtained from British coals. The results are recorded in Table III.

TABLE III.

Solvent Analyses. Pittsburgh Seam.

(% on ash-free dry basis.)

Sample.		Fractions. α.	β.	γ.	Sub-fractions. γ_1.	γ_2.	γ_3.
Bailey's Mills	(*a*) top	66·7	24·3	9·0	3·0	3·2	2·8
	(*b*) upper	68·2	23·0	8·8	2·3	3·5	3·0
	(*c*) bottom	68·5	22·8	8·7	2·35	3·0	3·35
Elm Grove	(*a*) top	66·5	24·1	9·4	2·45	3·5	3·4
	(*b*) upper	68·8	21·6	9·6	2·0	4·4	3·2
	(*c*) bottom	69·1	20·9	10·0	2·5	3·45	4·05
Monongah	(*a*) top	79·4	12·1	8·5	1·95	3·1	3·45
	(*b*) above double band	77·8	13·4	8·8	1·8	2·35	4·65
	(*c*) bottom	78·2	14·0	7·8	1·7	2·15	3·95
Hustead	bottom	71·9	20·0	8·1	1·9	2·15	4·05
Scotch Hill	bottom	78·2	12·9	8·9	0·9	3·45	4·55
Revere	bottom	79·2	12·3	8·5	1·1	2·5	4·9
Jamison	bottom	82·9	10·1	7·0	0·7	2·1	4·2
Vogele		98·8	0·6	0·6	0·25	0·15	0·2
Ocean Mine	(*a*) top	99·2	0·8 (β + γ)				
	(*b*) upper	99·2	0·8 (β + γ)				
	(*c*) bottom	99·2	0·8 (β + γ)				

Considering the three analytical tables together, it is clear that the progressive changes in geological conditions that have caused a gradual increase in the carbon content of the coal have rendered its ulmins gradually more complex, for the proportion of the β-fraction, which measures the ability of the ulmins to disperse in pyridine, gradually decreases. To the east of Jamison, in the region where there is a rapid alteration in the depth of cover, the ulmins have become so condensed as to be almost insoluble in pyridine.

There is no progressive variation in the proportion of the complete γ-fraction, which does not in fact vary much until the most easterly part of the field is reached. The fairly regular decrease in the "volatile matter" content of the coal with increasing carbon content must therefore be due to the increasing complexity of the ulmins, for the γ-fraction yields almost its whole weight as volatile matter.

Most interest attaches to the variations in the proportions of the fractions γ_1 (hydrocarbons) and $\gamma_2 + \gamma_3$ (resinic), corresponding with the "Ölbitumen" and "Festbitumen" of Fischer, Broche, and Strauch. Whereas the results obtained by the German workers suggested a gradual increase in the proportion of free hydrocarbons during the coalification process (see Table VIII of our previous paper), ours for the Pittsburgh seam show a reverse effect, the relationship being too well defined to be accidental.

We can more readily understand a progressive loss of hydrocarbons from the coal as its "rank" increases than we can a gain. There has not necessarily been any marked temperature change, for, as White, when dealing with the progressive regional carbonisation of coal, points out (*J. Amer. Inst. Min. Met. Eng.*, 1925, **71**, 253), "time and temperature may, within limits, each be substituted for the other . . . and pressure is partially interchangeable with both," but the gradual distillation of free hydrocarbons from the coal under slight elevation of temperature seems to us more likely than their gradual formation from some other constituents. Simultaneously, as an effect of temperature and pressure, we might expect a gradual elimination of the resinic compounds. This is not apparent from our results, but a gradual change in their character took place as the "rank" of the coal increased, as is shown by their ultimate analyses, recorded in Table IV.

Similar changes in analysis of the γ_2- and γ_3-fractions as the carbon contents of the coals from which they are obtained increase have been observed also with British coals.

The Barnsley Seam.—The Barnsley seam, in the Yorkshire coalfield, although not so extensive as the Pittsburgh, exhibits progressive variations in composition and thus provides another,

TABLE IV.

Ultimate Analyses of Resinic Materials in Pittsburgh Seam.

Sample.		γ_2-Fraction. C, %.	γ_2-Fraction. H, %.	γ_3-Fraction. C, %.	γ_3-Fraction. H, %.
Bailey's Mills	top	81·6	6·7	77·6	6·3
Bailey's Mills	bottom	80·6	6·6	77·8	6·1
Elm Grove	top	83·8	6·7	80·6	5·8
Elm Grove	bottom	82·6	6·7	78·9	6·1
Monongah	top	84·8	6·5	81·6	6·0
Monongah	bottom	84·2	6·5	81·8	6·0
Scotch Hill		86·6	6·5	82·6	6·1

though not so divergent, series of coals of different "rank" formed from the same original accumulation of vegetable débris.

An increase in the carbon content is observed in two directions, from east to west and, less well defined, from north to south. The samples chosen for examination were obtained from collieries situated between two parallel lines, about two miles apart, running from east to west and extending over about 20 miles. The Barnsley seam is composed of three well-defined portions, the "bottom softs" (a clarain) the "hards" (a durain) and the "top softs" (a clarain), some of which thin out in parts of the field. To ensure that the samples should be from the same horizon of the seam, they were all taken from the "Bottom Softs," a bright coal readily identified in all parts of the field by reason of its position in relation to a central band of durain. Analyses of the samples, arranged in order of their occurrence east to west of the field, are recorded in Tables V—VII.

TABLE V.

Ultimate Analyses. Barnsley Seam.

(% on an ash-free dry basis.)

Sample.	C.	H.	N.	S.
Colliery C	80·6	5·4	1·7	1·7
Colliery A	81·9	4·9	1·6	1·7
Colliery E	81·8	5·4	1·6	1·1
Colliery F	84·5	5·5	1·6	0·7
Colliery D	83·5	5·3	1·7	1·9

TABLE VI.

Proximate Analyses. Barnsley Seam.

Sample.	Ash, %.	Moisture, %.	Volatile matter, % on ash-free dry basis.
Colliery C	2·9	5·4	36·2
Colliery A	3·6	7·1	35·2
Colliery E	2·3	6·4	35·4
Colliery F	1·2	3·4	33·9
Colliery D	3·5	2·3	35·8

TABLE VII.

Solvent Analyses. Barnsley Seam.

(% on an ash-free dry basis.)

Sample.	Fractions.			Sub-fractions.		
	α.	β.	γ.	γ_1.	γ_2.	γ_3.
Colliery C	74·2	19·5	6·3	1·25	2·35	2·7
Colliery A	79·2	15·0	5·8	1·0	2·35	2·45
Colliery E	74·0	20·6	5·4	1·2	2·1	2·1
Colliery F	81·0	13·4	5·6	1·15	1·65	2·8
Colliery D	77·8	15·8	6·4	1·35	3·45	1·6

There is no indication of a progressive change in the amount of any constituent, either along the line of the seam from east to west or with increasing "rank" of the coal as judged by its carbon content. This conforms with our experience with regard to a series of British coals of increasing carbon contents, from different coal-fields, as previously recorded (*loc. cit.*, p. 712).

These results emphasise the necessity for caution when attempting to compare coals that may have been formed under widely different conditions. We have seen that, from the results obtained by Fischer, Broche, and Strauch, for a number of varieties of German coals, it has been suggested that the proportion of free hydrocarbons in coal increases as its "rank" increases. The results for the series of American coals, from the same seam, recorded in this paper suggest that the hydrocarbons gradually disappear during the coalification process. With British coals, whether from the same seam or collected from different parts of the country, there is no relationship between their "rank" and their content of free hydrocarbons.

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