CCCCXXIV.—*Studies in the Composition of Coal. The Active-decomposition Point of Coal.*

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DURING the slow distillation of a bituminous coal in a vacuum, gases and liquids (water and oils) are evolved at quite low temperatures. At 100°, for example, traces of liquid pentane can be detected in the water which, together with " occluded " gases, may

be evolved in considerable quantity from an air-dried coal at that temperature. Such gases and liquids are not products of decomposition of the coal. Even the red oils that first make their appearance at about 225° are not decomposition products, but are liquated from the coal conglomerate, being yielded by free hydrocarbons. The main mass of the coal begins to decompose at a definite temperature which, for a given coal under standard conditions of heating, is constant within $\pm 2°$. Wide variations in the experimental conditions do not markedly affect the result, but this temperature of active decomposition varies for different coals. Representing as it does the beginning of disruption by heat of the ulmin molecules, it would appear to be an important constant characteristic of the type and properties of different coals, and we have therefore determined it for a number of samples.

Before recording the results, we must recount the observations, referred to briefly in our paper on oil-yielding constituents (this vol., p. 2669), which enable this decomposition point to be specified and related to the ulmin constituents of the coal.

The method of experiment involved the heating of 250-g. charges of the finely powdered coals under high vacuum at different temperatures, the standard period of heating at each temperature being 120 hours. Under these conditions, the action of heat on the individual ingredients of the coal could be followed comparatively easily. No marked decomposition occurred with any bituminous coal below about 300° : as recorded in our previous paper, for example, Wigan Six Foot coal first began to decompose rapidly over the range 315—320°.

The characteristic products of this extensive decomposition during its early stages are, with all coals, water, phenolic oils (yielded exclusively by the ulmin constituents of the coals, see J., 1915, **107**, 1318), and gaseous paraffins. Prolonged heating of a coal just below its decomposition point yields only small quantities of these characteristic products, whilst prolonged heating just above it yields greatly enhanced quantities. This is well illustrated by the results recorded in Table I. With the Wigan Six Foot coal, parallel distillations were carried out at 300° and 320° during 120 hours (the " standard " period of heating) and at 310° and 325° during 750 hours.

In Table I, the italicised figures in particular relate to the active-decomposition point. The high yields of oils on prolonged heating at 310°—higher yields than during the " standard " distillation at 320°—require explanation. For the most part, these are not products of decomposition of the main mass of the coal, but, as will be demonstrated in another communication, are derived

TABLE I.

The Active Decomposition of Wigan Six Foot Coal. Gaseous and Liquid Products.

(Gaseous products in c.c. per 100 g. Liquid products as percentages on the ash-free, dry coal.)

	At 300°, 120 hrs.	At 310°, 750 hrs.	At 320°, 120 hrs.	At 325°, 750 hrs.
Total gas	178	279	602	1140
Carbon dioxide	66	94	134	190
Higher olefins	3·5	20	38	90
Ethylene	2·4	3·3	14·7	—
Carbon monoxide	14	35	40	—
Paraffins	*89*	*126*	*363*	ca. *750*
Ratio C/A for paraffins	*1·05*	*1·16*	*1·51*	—
Water of decomposition	*0·29*	*0·35*	*0·79*	*1·52*
Total light oils	0·35	0·93	0·57	1·13
Total heavy oils	1·35	3·80	3·24	6·50
Phenolic oils	—	*0·26*	*0·37*	*0·95*
Saturated hydrocarbons	0·70	0·80	0·99	1·20
Unsaturated hydrocarbons	0·46	1·56	1·50	2·57
Oils soluble in ether and chloroform	0·13	0·57	0·17	1·30

from organised plant entities (mainly spore exines and cuticles), of which the Wigan Six Foot coal (mainly a clarain) contained about 4%. Such, in particular, are the unsaturated hydrocarbons. The oils soluble in ether and chloroform were derived from resins, which began to decompose slowly at 310°, whereas during the " standard " distillations they began to distil (with partial decomposition) at 325—330°.

The solid residues remaining after the distillation of coals at different temperatures undergo marked changes in character when the active-decomposition point has been passed. The principal changes in the residues are summarised in Table II, the Wigan Six Foot coal again being taken as an example.

TABLE II.

The Active Decomposition of Wigan Six Foot Coal. Solid Products.

	Sol. in C_5H_5N. Insol. in $CHCl_3$.	Sol. in $CHCl_3$. Insol. in light petroleum and Et_2O.	Reactivity with oxygen	Behaviour
	(% on ash-free, dry coal.)		(c.c. per g.).	on coking.
Original coal	12·34	3·14	11·1	Swollen
Residue at 250°	8·79	1·93	—	Less swollen
Residue at 280°	8·12	1·67	7·4	Shrunken
Residue at 300°	8·25	1·51	6·4	Shrunken
Residue at 320°	10·08	2·95	7·0	Much swollen
Residue at 350°	5·73	1·02	6·4	Incoherent

The material " soluble in pyridine but insoluble in chloroform " (termed β-compounds in the original coal, and regarded as ulmin

compounds that are dispersed rather than dissolved by pyridine) decreases in quantity in the residues obtained at temperatures below the decomposition point, but suddenly increases when that point has been passed. Similar remarks apply to the material soluble in chloroform but insoluble in light petroleum and ethyl ether. This material (termed γ_3- and γ_4-compounds in the original coal) behaves in some respects like the resins (see Cockram and Wheeler, J., 1927, 700), but in others, as this, like the ulmins. Simultaneously, therefore, with a marked evolution of gases and liquids, such as are known to be yielded on the break-down of the ulmin molecules, there is a marked change in the behaviour of the residues towards solvents, suggestive of a more comprehensive disruption than that of external groupings from the molecules. At lower temperatures, external groupings may be split off from the ulmin molecules, yielding water and the oxides of carbon (particularly from a partially oxidised coal), and causing a gradual decrease in reactivity.

Similarly, as the temperature of distillation was raised, the reactivity of the residues with oxygen gradually decreased, to increase suddenly as soon as the point of marked decomposition had been passed. The reactivity measurements recorded in Table II (made for us by Dr. A. L. Godbert) are expressed in terms of the volume of oxygen combining with the material at 150° under standard experimental conditions. They confirm observations, made by Graham and Coles (*Fuel*, 1928, 7, 21), that the rate of oxidation of certain coals was considerably increased by preheating them in a vacuum at " critical " temperatures, between 300° and 400°, dependent on the character of the coals. These critical temperatures were, we conclude, the active-decomposition points of the coals. The compounds responsible for the reactivity of coal with oxygen have been shown by Francis and Wheeler (*Safety in Mines Research Board Paper* No. 28, 1926) to be the ulmin compounds.

Finally, the results of coking tests, carried out by heating in small crucibles at 900°, during $7\frac{1}{2}$ minutes, 2-g. samples of the coals and residues from the distillations at different temperatures, revealed a marked change in this characteristic property of coal by preheating at the decomposition point, the coke produced from that residue being considerably more swollen than the coke from the original coal.

Such fundamental changes in the properties of the coal on being heated at a given temperature clearly mark the beginning of extensive molecular disruption. Francis and Wheeler (*loc. cit.*) conclude from their work that the nuclei of the ulmin molecules are compact systems of six-membered annular groupings connected together by

heterocyclic structures such as pyrrole and furan. Compounds having such structures might be expected to yield alkylised phenolic compounds and complex hydroaromatic hydrocarbons on decomposition (see Schrauth, *Brennstoff-Chem.*, 1923, **4**, 161). Such compounds have, in fact, been found to be characteristic decomposition products of the coal ulmins.

The Decomposition Points of Different Coals.

The active-decomposition points of a number of different coals, with data regarding the characteristic products of decomposition of most of them, have been determined. The results are summarised in Table III.

TABLE III.

Active-decomposition Points of Coals.

Description of coal.	Carbon content.*	Decomp. point.	Water of decomp., % (up to 400°).	Phenols and acids, % (up to 400°).
Seven Foot (Kingsbury)	77·0	290—300°	—	—
†Thick Seam, Brazills (Hamstead)	78·3	295—300	5·97	2·23
‡Ditto	80·9	(300)	5·40	1·36
†Barnsley (Brodsworth)	81·2	305—310	4·07	0·91
‡Ditto	82·7	(310)	4·08	0·85
Wigan Six Foot (Maypole)	82·8	315—320	4·09	1·94
Parkgate (Cadeby)	83·4	325—330	—	—
Silkstone (Rockingham)	83·7	325—330	1·82	0·83
Six-Quarter (Haig)	86·6	320—325	2·29	1·06
Busty (Tudhoe)	87·4	335—340	—	—
Busty (Beamish Mary)	88·4	340—345	—	—
Black Vein (Celynen)	88·5	340—345	1·51	0·56
Two Foot Nine (Ferndale No. 7) ...	89·8	360—365	0·81	0·06

* Calculated on the " pure coal " basis; see Table IV.
† Vitrain portion.   ‡ Durain portion.

In the descriptions of the coals, the name of the seam is given first, with the name of the colliery or pit at which the seam was worked in parentheses. All the coals except those specified were clarains. With the two durains, the decomposition point could not be determined precisely, since there was incipient decomposition of a minor ingredient of the coal at a lower temperature. It will be seen that, in general, the decomposition point increased with the carbon content of the coal, a result to be expected if the decomposition is that of the ulmin constituents. There is a general tendency for the yields of water and phenolic compounds (expressed in Table III as percentages on the ash-free, dry coals) to be greater from the coals of lower carbon content. The yields of oxides of carbon above the decomposition point were also greater from the coals of lower carbon content.

In a paper entitled " The Primary Decomposition of Coal. I.

The Temperature of Initial Decomposition," King and Willgress (*Dept. Sci. Ind. Res., Fuel Res. Tech. Paper No.* 16, 1927) record results for three bituminous coals showing that, when they were heated in a stream of nitrogen, traces of oils were carried over at lower temperatures from the coals of higher carbon content, as follows : C, 74·5%, first appearance of oil at 245° ; C, 83·87%, 230° ; C, 85·43%, 215°. They say : " With bituminous coals the temperature of initial decomposition appears to increase with increasing oxygen content and decreasing carbon content." We are satisfied that the temperature at which oils first make their appearance when a bituminous coal is heated is not the temperature of initial decomposition of the coal, but that such oils are distilled unchanged. In our experience, the temperature at which such oils

TABLE IV.

Proximate and Ultimate Analyses.

Proximate analysis.

Coal.	Moisture, %.	Ash, %.	Volatile matter, %, ash-free, dry.	Ultimate analysis, % on " pure coal " basis.				
				C.	H.	N.	S.*	O.
Seven Foot	5·5	8·7	41·9	77·0	5·55	1·19	1·00	15·26
Thick Seam, vitrain	13·4	1·3	37·5	78·3	5·15	1·02	1·01	14·52
Thick Seam, durain	6·4	6·0	35·1	80·9	4·71	1·08	0·97	12·34
Barnsley, vitrain ...	6·4	1·3	33·0	81·2	5·31	1·34	1·03	11·12
Barnsley, durain ...	3·5	4·0	36·1	82·7	5·23	1·42	1·06	9·59
Wigan Six Foot ...	1·7	2·7	37·6	82·5	5·55	1·53	0·90	9·52
Parkgate	2·7	3·4	36·1	83·4	5·13	(Not determined)		
Silkstone	1·2	1·5	34·1	83·6	5·38	1·82	1·43	7·77
Six-Quarter	1·4	12·2	37·0	86·6	5·08	1·61	0·39	6·32
Busty (Tudhoe) ...	0·6	6·3	27·7	87·4	4·72	0·89	1·04	5·95
Busty (Beamish Mary)	0·8	7·9	28·7	88·3	5·27	1·58	0·57	4·28
Black Vein	0·9	6·8	30·8	88·5	5·02	1·53	0·83	4·12
Two Foot Nine	0·6	5·6	16·7	89·8	4·18	1·39	0·88	3·75

* Organic sulphur.

Rational Analyses, %.

Coal.	Hydrocarbons and resins.	Organised plant entities.	Ulmins.	Reactivity index for ulmins.
Seven Foot	—	2·8	—	76
Thick Seam, vitrain	3·2	Nil	96·8	74
Thick Seam, durain	3·5	7·8	88·7	72
Barnsley, vitrain	3·4	Nil	96·6	65
Barnsley, durain	2·7	20·7	76·6	62
Wigan Six Foot	3·0	4·1	92·9	50
Parkgate	4·8	2·0	93·2	61
Silkstone	3·6	4·0	92·4	52
Six-Quarter	4·0	7·2	88·8	55
Busty (Tudhoe)	4·3	7·4	88·3	45
Black Vein	—	6·6	—	39
Two Foot Nine	Trace	12·0	88·0	16

first appear bears no direct relation to the carbon content of the coal. It has, however, a tendency to be lower the greater the proportion of free hydrocarbons in the coal. Some decomposition of part of the coal substance undoubtedly occurs at a lower temperature than that specified as the "active-decomposition point." As already stated, the external groupings of the ulmin compounds may yield water and oxides of carbon in small amount at quite low temperatures (from about 150° upwards), whilst other parts of the coal conglomerate, such as the resins, spore exines, and cuticles, yield oils slowly at about 300°. Such decompositions do not materially affect the character of the coal, a loss of reactivity of the ulmin compounds being the most noticeable result. Marked changes of character only begin when the breakdown of the nuclear structure of the ulmin compounds begins.

Proximate, ultimate, and rational analyses of the coals referred to in this paper are given in Table IV. For the ultimate analyses, the usual calculations on an "ash-free, dry" basis have not been made; instead, allowance has been made for the fact that the mineral matter contained in a coal differs in composition and amount from the ash it yields on incineration. For the rational analyses, the methods described by Francis and Wheeler (this vol., p. 2967) were used.

NOTE.—Through an error in transcription, the figures in the first column of Table III of our previous paper (*loc. cit.*, p. 2675) were wrongly given. They should read : 81·54, 85·5, 86·1, 85·4, 79·0, 77·5.