109. *Studies in the Composition of Coal. The Thermal Decomposition of Lignites.*

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It has been shown (Holroyd and Wheeler, J., 1928, 3197) that, by slow distillation in a vacuum, the decomposition points of bituminous coals can be determined within narrow limits. The decomposition point, which marks the extensive breakdown of the main mass of the coal (the ulmins), is, in general, lower the lower the carbon content of the coal. For instance, the values determined for coals of carbon contents 82·8, 81·2, 78·3, and 77·0% were : 315—320°, 305—310°, 295—300°, and 290—300°, respectively.

The object of the work now to be described was to determine whether on passing out of the range of the bituminous coals to the lignites, of lower carbon content, the decomposition point would continue to be progressively lower; and whether these coals of low " rank," considered by some (*e.g.*, McKenzie-Taylor, *J. Inst. Pet. Tech.*, 1929, **15**, 372) to have been formed in a different manner from bituminous coals, would show significant differences on destructive distillation.

The coals used were : Colstrip (Montana), Beulah (N. Dakota), and Morwell (Australia). Their analyses (after having been dried at 105° in a vacuum oven during two days), together with, for comparison, that of a bituminous coal of low carbon content previously studied (*loc. cit.*, p. 3202), were :

Coal.	Moisture, %.	Ash, %.	Ultimate analysis, %, on " pure coal " basis.				
			C.	H.	O.	N.	S.
Hamstead Thick (Staffs) (Vitrain portion only)	13·4	1·3	78·3	5·1	14·6	1·0	1·0
Colstrip (Montana)	0·2	7·0	73·2	5·3	19·3	1·1	1·1
Beulah (N. Dakota)	2·5	8·4	68·9	5·3	23·5	1·2	1·1
Morwell (Australia)	7·5	3·0	67·2	4·9	26·9	0·5	0·5

For a series of bituminous coals it had been found, as already stated, that the temperature of decomposition was lower the lower the carbon content. Further, there was a general tendency for the coals of lower carbon content to give greater yields of (*a*) water and (*b*) phenolic compounds, and to evolve greater quantities of the oxides of carbon above their decomposition points.

The method of determining the decomposition points of the bituminous coals depended mainly upon observing at what temperature a sudden evolution of gases and oils, indicative of the general breakdown of the mass of the coal, occurred during the course of prolonged heating of the coal in a vacuum, the temperature being raised by 5° at intervals of not less than 24 hours. Additional evidence that the decomposition point had been correctly gauged could be obtained (*a*) by a comparison of the compositions of the gases and oils distilled below and above that temperature; and (*b*) by measuring the reactivity towards

oxygen of the solid residues obtained after distillation at temperatures below and above the presumed decomposition point, for a notable increase in the reactivity of the residue occurs just after the decomposition point has been passed (*loc. cit.*, p. 3199).

On applying these methods to the study of the lignites, it was found that vacuum distillation by itself could not be relied upon to determine the decomposition points with exactitude, for there was no sudden evolution of gases and oils at a definite temperature. Considerable volumes of the oxides of carbon were evolved throughout the distillations, masking the major breakdown of the ulmins. Significant changes occurred, however, in the character of the liquid and gaseous products of decomposition over certain temperature ranges, and the solid residues obtained below and above those temperature ranges exhibited marked changes in reactivity. The decomposition points could thus be gauged with fair accuracy. They were : Colstrip (73·2% C), 285—290° ; Beulah (68·9% C), 250—255° ; Morwell (67·2% C), 225—230°.

Bone, Horton, and Tei (*Proc. Roy. Soc.*, 1928, *A*, **120**, 523) have treated several lignites with boiling benzene under pressures of 40—48 atm. (corresponding with temperatures of 250—280°). Three had a carbon content (calculated on the ash-free dry basis) of about the same range as ours, namely : Rose Deer (Alberta), 72·6% C ; Cardiff (Alberta), 71·2% C ; Estevan (Saskatchewan), 67·7% C. A sample of the Morwell (Australia) coal, of which the carbon content was found to be 64·9%, was also treated with benzene.

The material removed by this treatment from the Estevan and the Morwell coal differed markedly in character from that obtained from lignites of higher carbon content (or from bituminous coals) inasmuch as it contained phenolic compounds amounting for the Estevan coal to about 2½% and for the Morwell coal to about 10% of the original coal substance. With regard to this, Bone, Horton, and Tei say (*loc. cit.*, p. 533) : " The extraction of so large a quantity of phenolic bodies from the coal substance of an immature brown coal is a remarkable circumstance. And the question naturally arose, were these bodies pre-existent as such in the original coal substance, or had they been produced from it by incipient thermal decomposition during the extraction process? Accordingly, experiments were carried out from which it was inferred that, although not present in the free state, these phenols were pre-existent in the coal substance in some loose ' molecular association,' rather than in firm chemical union, with the main coal-complex."

The experiments from which this inference is drawn are not described. It could be inferred, also, that because 285° is considerably higher than the decomposition temperature of a coal of 67% carbon content, which can be taken to be about 230°, extensive thermal decomposition had occurred.

Phenolic compounds (but not phenol itself) are characteristic decomposition products of the ulmins of bituminous coals (see Jones and Wheeler, *J.*, 1915, **107**, 1318), and, as noted earlier in this paper, the quantity yielded on distillation tends to be greater the lower the carbon content of the coal, being, for example, about 2¼% of the coal substance of the Hamstead Thick coal (78·3% C) as compared with about 1% of a coal of 86·6% carbon content distilled up to 350°. We therefore anticipated finding considerable quantities of phenols in the oils distilled from the lignites at temperatures between their decomposition points and 285°. This anticipation was not realised. The Morwell coal yielded no phenolic compounds until the range 275—300° was reached, whilst with the Beulah and the Colstrip coal the first appearance of phenols was at 250—275° and at 270—300° respectively. The total amounts yielded up to 350° were : Beulah, 0·12 ; Colstrip, 0·18% of the coal substance. The sample of heavy oil from the Morwell coal obtained over the range 300—325° was unfortunately lost before it was analysed, so that the total yield of phenols from that coal up to 350° can only be estimated ; it did not exceed 1% and was probably less than 0·2%.

The remarkably high yield of phenols (about 10%) obtained by Bone, Horton, and Tei on treating Morwell coal with benzene at 285° therefore cannot be explained as being due to decomposition of the coal substance, even though decomposition undoubtedly occurred. The yield is the more remarkable because more than half was found to be phenol, which was identified by conversion into its 3 : 5-dinitrobenzoate, m. p. 146°. We have suggested elsewhere (*J.*, 1933, 1405) that the possibility of the phenols having

been formed from the benzene used for the extraction of such a highly oxygenated coal as the Morwell cannot be ignored.

Our destructive distillations have not disclosed any abrupt change in general behaviour between the lignites and bituminous coals, such as might be expected were there an abrupt change in their character, unless the considerably smaller yield of phenols from the lignites than from the bituminous coals be so regarded. It is true that the liquid and gaseous products of distillation of the Morwell coal were markedly different from those of a bituminous coal of low carbon content, the Hamstead Thick coal (78·3% C) for example; but the Beulah and the Colstrip coal, of intermediate carbon content, yielded products of intermediate character. There was, in fact, a gradual change in the general character

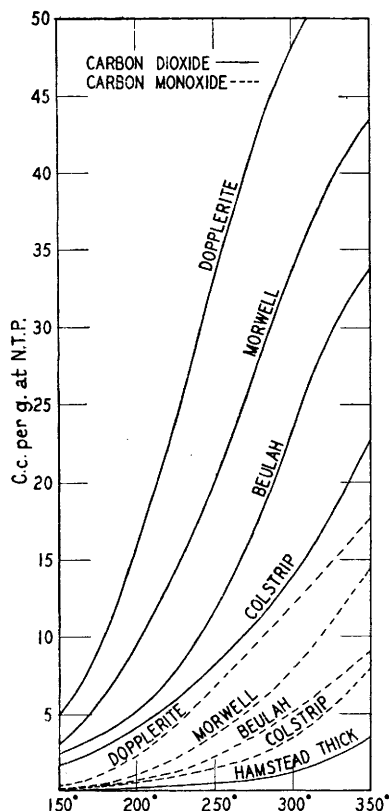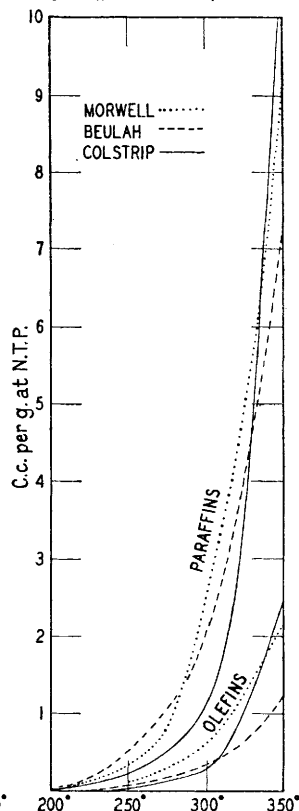FIG. 1. *The evolution of oxides of carbon.*

FIG. 2. *The evolution of paraffins and olefins.*

of the products the lower the carbon content of the coal, such as can readily be explained by a gradual change in the character of the ulmins.

In this connexion, it is of interest to compare the behaviour of an ulmin from peat, namely, dopplerite (56·7% C). Tideswell and Wheeler (J., 1922, **121**, 2345) distilled dopplerite in a vacuum in a manner similar to that employed by us for the lignites. Briefly, the results, which are summarised later, fall into line with those obtained with the lignites, the inference being that, throughout the series of fuels from peat to anthracite, the change in their character is due primarily to a gradual polymerisation and dehydration of the ulmins with the elimination of carboxylic and hydroxyl groupings.

The principal differences in behaviour between bituminous coals and the lignites, representing a gradation of properties, can be set forth as follows :

The evolution of gases. Curves showing the evolution of the principal gases are given in Figs. 1 and 2. The yields of " total gas " from the lignites up to 350° were considerably higher than for bituminous coals, the amounts increasing with their decreasing rank.

There was no sudden increase at the decomposition point in the production of carbon dioxide, as there is with bituminous coals, and the yield of that gas, though always large, decreased markedly above 350°. With bituminous coals, carbon dioxide is evolved in increasing quantity up to 400°. Curves relating volumes of carbon monoxide evolved to temperatures of distillation are fairly smooth, though with the Colstrip coal there was a slightly increased evolution above 300°. The oxides of carbon are mainly responsible for the high yields of " total gas " from the lignites.

The evolution of paraffins from the Morwell and the Beulah coal was fairly regular throughout up to 400°, there being no sudden evolution at the decomposition point as there is with bituminous coals. With the Colstrip coal, however, an increased evolution of paraffins was noticeable at 300°. Similarly, the Colstrip differed from the other lignites in that the evolution of unsaturated hydrocarbons showed a marked increase at about 300°.

The evolution of water and light oils. The amounts of water of decomposition and light oils (light petroleum) evolved up to 350° (% on the ash-free dry coals) were : Water, Colstrip, 8·2 ; Beulah, 10·4 ; Morwell, 9·0. Light oils, Colstrip, 0·8 ; Beulah, 2·1 ; Morwell, 2·1. By comparison, the Hamstead Thick coal yielded 6·2% of water and 1·8% of light oils.

Some of the light oils from the Morwell coal was evolved suddenly over the range 275—325°, but with the Beulah and the Colstrip coal their rate of evolution increased regularly as the temperature was raised.

The evolution of heavy oils. The percentage amounts of heavy oils evolved up to 350° were : Colstrip, 2·9 ; Beulah, 2·6 ; Morwell, 2·0. The Hamstead Thick coal yielded 4·7%. The oil evolved from the Beulah coal between 200° and 250° was pale yellow and consisted mainly of waxy hydrocarbons ; the Colstrip coal yielded no oils below 250° ; the Morwell coal yielded no waxy solids, and the production of heavy oils was not observed below 260°. The heavy oils were analysed (see J., 1928, 2672) with respect to their contents of (*a*) hydrocarbons, (*b*) resins (soluble in chloroform and ethyl ether), and (*c*) phenolic and acidic compounds.

The general results of the distillations, details of which are given under " Experimental," are summarised in Table I, which includes, for comparison, the results of vacuum distillations of (*a*) dopplerite and (*b*) a bituminous coal of low carbon content.

TABLE I.

Vacuum Distillations of Coals. Yields of Liquid and Gaseous Products up to 350°.

Liquids, % on ash-free dry coal.

Coal.	Carbon content, %.	Water.	Light oil.	Total heavy oil.	Hydrocarbons.	Phenols and acids.	Gases, c.c. per g.	Decomposition point.
Dopplerite	56·7	24*			0·02*	trace †	78	uncertain
Morwell	67·2	9	2·1	2·0			67	225°
Beulah	68·9	10·4	2·1	2·6	1·5	0·12	52	255
Colstrip	73·2	8·2	0·8	2·9	1·7	0·18	44	285
Hamstead Thick......	78·3	6	1·1	4·7	1·9	1·8	18	300

* Up to 410°.   † No phenol.

EXPERIMENTAL.

Vacuum Distillations.—The apparatus and method of experiment were as described by Holroyd and Wheeler (J., 1928, 2669). A charge of 250 g. of the coal, dried and ground to pass through a 20- and remain on a 100-mesh sieve, was heated in a cylindrical retort of Jena glass fixed vertically with its mouth downwards. A series of condensers was attached to the retort by a ground-glass joint, and a vacuum, within 2 mm., was maintained by an automatic mercury Sprengel pump. Heating was effected slowly by stages and the gases and liquids evolved at each stage were collected separately. The stages of heating were : (1) At atmospheric temperature during 50 hours ; (2) up to 100° ; (3) 100—150° ; (4) 150—200° ; (5) 200—225°, and thereafter by 20—30° intervals up to 350°. The heating lasted 5 days for stage 2, and 7 days for the other stages. During the later stages, the temperature at the beginning of each of the first 5 or 6 days was raised 5°.

Colstrip (Montana). Solvent analysis (see Cockram and Wheeler, J., 1927, 700) : β-fraction, 4·3 ; total γ-fraction, 3·0 ; γ_1, 1·03 ; γ_2, 1·88 ; γ_3, 0·09%. The principal results of the vacuum distillation are recorded in Table II.

TABLE II.

Vacuum Distillation of Colstrip Coal.

(i) *Gaseous products, c.c. per 100 g. of coal.*

					Temperature range.			
	Up to 150°.	150—200°.	200—230°.	230—250°.	250—270°.	270—300°.	300—330°.	330—350°.
CO_2 and H_2S	150·6	278·9	228·6	166·0	200·0	332·0	535·4	383·0
C_nH_{2n}	—	—	0·9	1·6	3·1	9·1	58·9	63·4
C_2H_4	—	—	0·7	2·2	3·5	9·6	39·2	47·5
CO	21·4	46·6	47·4	40·0	55·1	111·0	250·8	210·2
H_2	—	—	—	—	—	—	—	66·7
C_nH_{2n+2}	—	2·5	9·4	10·0	23·2	73·5	351·2	556·0
Total gas	172·0	328·0	287·0	219·8	284·9	535·2	1235·5	1326·8

(ii) *Liquid products.*

(a) *Water and light oils, c.c. per 100 g. of coal.*

			Temperature range.			
	Up to 225°.	225—250°.	250—270°.	270—300°.	300—325°.	325—350°.
Water	3·6	0·4	0·5	1·0	1·5	1·4
Light oils	nil	trace	0·1 (colourless)	0·1	0·2 (yellow)	0·4 (brown)

(b) *Heavy oils, g. per 100 g. of coal.*

		Temperature range.		
	250—270°.	270—300°.	300—325°.	325—350°.
Total heavy oils	0·156	0·510	1·620	0·635
Sat. hydrocarbons	0·086	0·154 ⎫	0·910	0·148
Unsat. and aromatic hydrocarbons	0·070	0·176 ⎭		0·142
Phenolic oils	trace	0·016	0·092	0·075
Oxygenated oils	—	0·035	0·138	0·066
Ether-sol. oils	—	0·029	0·110	0·047
Chloroform-sol. oils	—	0·002	0·035	0·020

A trace of acids could be detected in the fraction collected over 300—325°, but no bases were present in any fraction.

Beulah (N. Dakota). Solvent analysis : β-fraction, 2·3 ; total γ-fraction, 3·8 ; γ_1, 1·67 ; γ_2, 1·64 ; γ_3, 0·49%. The principal results of the vacuum distillation are recorded in Table III.

TABLE III.

Vacuum Distillation of Beulah Coal.

(i) *Gaseous products, c.c. per 100 g. of coal.*

					Temperature range.				
	Up to 100°.	100—150°.	150—200°.	200—225°.	225—250°.	250—275°.	275—300°.	300—325°.	325—350°.
CO_2 and H_2S	36	209	286	266	401	497	622	691	374
C_nH_{2n}	—	—	—	1	6	11	18	29	56
CO	—	22	52	60	95	137	166	167	202
H_2	—	—	—	—	—	—	—	13	76
C_nH_{2n+2}	—	—	4	11	34	54	105	206	307
Total gas	36	231	342	338	536	699	911	1106	1015

(ii) *Liquid products.*

(a) *Water and light oils, c.c. per 100 g. of coal.*

				Temperature range.			
	Up to 200°.	200—225°.	225—250°.	250—275°.	275—300°.	300—325°.	325—350°.
Water	6·25	0·65	0·7	1·0	1·3	1·5	1·45
Light oils	nil	trace	0·1	0·25	0·4	0·55	0·75

The water evolved at the lower temperatures had an odour of terpenes. The oil first evolved had a yellow colour, that obtained at higher temperatures was brown.

(b) *Heavy oils, g. per 100 g. of coal.*

Temperature range.

	200—225°.	225—250°.	250—275°.	275—300°.	300—325°.	325—350°.
Total heavy oils	0·116	0·212	0·336	0·538	0·620	0·750
Sat. hydrocarbons	0·031	0·015	0·013	0·009	0·061	0·110
Unsat. hydrocarbons	—	0·065	0·101	0·242	0·212	0·192
Aromatic hydrocarbons	0·051	0·037	0·064	0·078	0·121	0·096
Phenolic oils	—	—	0·003	0·019	0·028	0·038
Oxygenated oils	—	—	0·052	0·085	0·057	0·091
Ether-sol. oils	—	—	0·050	0·040	0·041	0·055
Chloroform-sol. oils	—	—	0·011	0·008	0·006	0·190
Acids	—	trace	0·008	0·009	0·014	trace

No bases could be detected in any fraction.

It should be noted that the γ_2-fractions (resinic) of the Colstrip and the Beulah coal have not distilled unchanged, but have yielded hydrocarbons and ether-soluble oxygenated compounds.

Morwell (Australia). Solvent analysis : β-fraction, 10·9; total γ-fraction, 4·6; γ_1, 1·4; γ_2, 1·84; γ_3, 1·36%. The principal results of the vacuum distillation are recorded in Table IV.

TABLE IV.

Vacuum Distillation of Morwell Coal.

(i) *Gaseous products, c.c. per 100 g. of coal.*

Temperature range.

	Up to 150°.	150—200°.	200—250°.	250—280°.	280—300°.	300—325°.	325—350°.
CO_2	326	684	1028	869	369	649	447
C_nH_{2n}	—	—	4·9	12·8	12·1	36·8	56·5
C_2H_4	—	—	6·9	10·1	11·3	30·6	38·0
CO	31·2	70·0	260·3	250·0	152·5	342	356·5
H_2	—	—	—	—	—	38·2	145·9
C_nH_{n+2}	—	3·0	28·1	75·2	136·2	236·5	429·5
Total gas	357·2	757·0	1328·2	1217·1	681·1	1333·1	1473·4

None of the samples contained H_2S.

(ii) *Liquid products.*

(a) *Water and light oils, c.c. per 100 g. of coal.*

Temperature range.

	Up to 250°.	250—280°.	280—300°.	300—325°.	325—350°.
Water	11·0	1·5	1·1	1·9	1·4
Light oils	nil	0·1	0·7	0·8	0·5

The oil was brown, and darkened on exposure to air.

(b) *Heavy oils, g. per 100 g. of coal.*

Temperature range.

	260—275°.	275—300°.	300—325°.	325—350°.
Total heavy oils	0·505	0·389	0·727	0·485
Sat. hydrocarbons	0·303	0·114		0·127
Unsat. and aromatic hydrocarbons	0·202	0·082		0·105
Phenolic oils	—	0·016	(Sample lost)	0·027
Oxygenated oils	—			0·066
Ether-sol. oils	—	0·139		0·011
Chloroform-sol. oils	—			

A trace of acids was found in the fraction collected over 325—350°.

Reactivity Measurements.—With bituminous coals, the reactivity towards oxygen of the solid residue obtained on heating usually gradually decreases with temperature so long as the decomposition point is not exceeded, to increase suddenly so soon as that point has been attained. A check on the decomposition point of each of the lignites was therefore sought by

determining the reactivities of residues obtained on heating samples at a series of temperatures below and above the presumed value. Each sample (20 g., through 20- and on 100-mesh sieve) was heated in a vacuum at the required temperature during 3 days, 2 days having been taken to reach that temperature. The results are recorded in Table V, the reactivity measurements being expressed in terms of the volumes of oxygen combining with the residues at 100° under standard experimental conditions.

TABLE V.

Reactivity Measurements for Residues of Lignites heated at Different Temperatures.

C.c. of oxygen absorbed per g. per hr. at 100°.

Colstrip.		Beulah.		Morwell.	
Temp. of original coal.	Reactivity.	Temp. of original coal.	Reactivity.	Temp. of original coal.	Reactivity.
	1·83		1·53		1·50
260—265°	1·54	235—240°	0·72	210—215°	1·52
270—275	1·07	250—255 *	0·93	220—225 *	2·20
275—280	0·86	265—270	0·70	225—230	1·46
285—290 *	1·32			280—285	1·42
295—300	0·80				

* Decomposition point.

With the Colstrip and the Beulah coal the decomposition points indicated by these measurements corresponded with the temperatures at which phenols first appeared in the oils, but with the Morwell coal no phenols appeared until 275—300°.