XCI.—*Studies in the Composition of Coal. Plant Entities as Oil-yielding Constituents.*

By Ronald Holroyd and Richard Vernon Wheeler.

Morphologically organised plant entities, such as spore exines and cuticular and epidermal tissues, often form an important part of the coal conglomerate. For example, rational analyses of American bituminous coals (see Francis and Wheeler, J., 1928, 2967) have disclosed the presence of as much as 15%, and many of the

British bituminous coals that we have examined by similar methods have contained between 10 and 25% of spore exines and cuticles.

The exines of present-day spores, such as those of lycopodium, and the cuticles of present-day plants appear to be similar, both physically and chemically, to the corresponding plant structures in bituminous coals, the resistance of these parts of plants to the processes of decay, which enabled them to remain as entities in the coal-forming mass, having apparently been nearly proof against the processes of coalification. The results of an examination of modern plant cuticle have been published (Legg and Wheeler, J., 1925, **127**, 1412). A similar examination of modern spore exines and parallel studies of both exines and cuticles from coal, in accordance with the scheme outlined by Stopes and Wheeler ("The Constitution of Coal," H.M. Stationery Office, London, 1918), are in progress. An important property in relation to the present research is their decomposition at comparatively low temperatures, yielding a high proportion of their weight of oils.

In our previous papers (J., 1928, 2669, 3197), examples have been given of the behaviour of (1) hydrocarbons, (2) resins, and (3) ulmin compounds when a bituminous coal is destructively distilled in a vacuum, the yields of oils in particular being noted. Most of the coals we have examined have yielded a greater quantity of oils than can be accounted for by the distillation and decomposition of these constituents of the coal conglomerate, the excess of oils being generally unsaturated hydrocarbons. There remain the plant entities to be considered as oil-yielding constituents, the particular information required being the temperature range over which they decompose.

This information has been obtained by carrying out parallel distillations in a vacuum on samples of coal, from the same seam, devoid of plant entities and containing known proportions of them, *i.e.*, on samples of vitrains and durains from the same seams. The distillation of about 20 g. of spore exines separated from a bituminous coal has given supplementary information.

In summarising the results of the present work, it is necessary to recapitulate some of the information previously recorded (*loc. cit.*) regarding the behaviour of the hydrocarbons, resins, and ulmin compounds in the coal conglomerate during destructive distillation.

With most bituminous coals containing more than 80% of carbon, there is no extensive decomposition of any constituent below 300°. Occluded gases are driven off up to 150°, and slight changes in the external groupings of the ulmin compounds may occur at low temperatures, particularly if the coal has been "weathered," resulting in the evolution of water and oxides of carbon. Between

220° and 300°, the major part of the free hydrocarbons in the coal (γ_1-compounds, extractable by solvents) distils unchanged.

The present work shows that at 300°, or just above, any plant entities the coal may contain begin slowly to decompose. With clarains, this decomposition may be difficult to detect, but it is easily recognisable with durains. The gaseous products are rich in oxides of carbon, and the liquids consist of water with much heavy oil, containing mainly unsaturated hydrocarbons and neutral oxygenated compounds. The temperature range over which this decomposition occurs, *viz.*, 310—350° (or 300—320° if the duration of heating is prolonged much beyond the normal), is nearly the same with all bituminous coals.

Above 300°, marked decomposition of the ulmin compounds begins, the products being gaseous paraffins, water, phenolic oils, and liquid aromatic and hydroaromatic compounds. This "active-decomposition point," which is well defined, increases with the "rank" of the ulmin compounds, and marks the breakdown of their nuclear structures. Over the range of bituminous coals studied (of carbon content 77—90%) it increased from 290° to 365°. The production of oils from the ulmin compounds is confined mainly to a temperature range of 25—30° above the active-decomposition point.

Above the active-decomposition point of the coal, ulmin compounds, organised plant entities, and resins decompose and distil simultaneously, yielding a complicated mixture of liquid products. It is difficult to trace the exact contribution made by each ingredient of the coal to this distillate, but the simultaneous liquation and decomposition (yielding hydrocarbon oils) of resins can be detected at about 325°, continuing to about 375°. This temperature range, which is the same for all the bituminous coals examined, may be lowered slightly and narrowed if the duration of heating is much prolonged. The amount of resins distilled unchanged is usually less than that extractable from the coal by solvents (γ_2-compounds), but it may approach that quantity if the coal also contains a fairly high proportion of plant entities yielding much hydrocarbon oils on decomposition, the presumption being that some of the resins are then "vapour-distilled."

The amounts and descriptions of the primary gaseous and liquid products of resolution of bituminous coals by heat are shown in Table I.

As the distillation is carried beyond 400°, increasingly large quantities of gases are evolved, the proportion of hydrogen they contain rapidly increasing. Nitrogen- and sulphur-containing compounds appear in small quantity in both gaseous and liquid products at all temperatures of distillation.

TABLE I.

The Resolution of Bituminous Coals by Heat.

Constituent.	Principal gaseous products.	Principal liquid products.		
		Character.	Quantity.	Temperature range.
Free hydrocarbons.	Paraffins in small quantity.	Saturated and unsaturated hydrocarbons in nearly equal amount.	Equal to the original amount of free hydrocarbons in the coal.	225—300°
Resins	Paraffins and higher olefins.	Resins and unsaturated hydrocarbons.	Usually rather less than the original amount of resins in the coal.	325—375
Structured plant entities (*e.g.*, spore exines).	Oxides of carbon and some paraffins.	Unsaturated hydrocarbons, neutral oxygenated compounds, and water.	About 30% of the original amount of plant entities in the coal.	300—320
Ulmin compounds.	Paraffins and some oxides of carbon.	Phenolic and acidic oils, unsaturated hydrocarbons, aromatic and hydroaromatic compounds, and water.	Decreases with increase in "rank" of the ulmins; 6—1% water and 3—0·05% phenols and acids with coals ranging from 77—90% carbon.	Decomposition point increases with "rank" of the ulmins: from 290—365° with coals ranging from 77—90% carbon. All oils distilled below 400°.

EXPERIMENTAL.

(1) *Comparative Distillations of Vitrains and Durains.*—The apparatus used for the distillation of 250-g. charges of the coals in a vacuum was that described in J., 1928, 2669. Large blocks of coal from several seams were obtained, and the vitrain and durain carefully separated from them by hand. For each coal, parallel distillations of these distinct components of banded bituminous coals were then carried out simultaneously. Two examples are recorded : (*a*) the Thick Seam (Brazils), from Hamstead Colliery; and (*b*) the Barnsley Seam, from Brodsworth Colliery. Analyses of these coals are given in Table II.

(*a*) *The Thick Seam.* With both the vitrain and the durain the stages of heating adopted were : 15—100°, 100—200°, 200—275°, and 25° intervals thereafter up to 400°. The coals were maintained at the higher temperature of each stage during 120 hours. The gases and liquids distilled at each stage were collected separately and analysed in the manner described in J., 1928, 2669. The neutral hydrocarbon oils, soluble in light petroleum, were treated with concentrated sulphuric acid and subsequently with fuming sulphuric acid to determine roughly the proportions of unsaturated, aromatic, and saturated hydrocarbons they contained. The results are recorded in Tables III and IV.

Little gas (mainly oxides of carbon) was yielded by either the vitrain or the durain below 290°. With the vitrain, a well-marked decomposition point was observed between 295° and 300°, a sudden

Table II.

Analyses of the Coals Used.

Coal.	Proximate analysis, %.			Ultimate analysis, % on "pure coal."				
	Moisture.	Ash.	Volatile matter (ash-free, dry coal).	C.	H.	N.	S.*	O.
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 Seam, vitrain	6·4	1·3	33·0	81·2	5·31	1·34	1·03	11·12
Barnsley Seam, durain	3·5	4·0	36·1	82·7	5·23	1·42	1·06	9·59

Coal.	Rational analysis, %.				
	Hydrocarbons.	Resins.	Organised plant entities.	Ulmins.	Reactivity index for ulmins.
Thick Seam, vitrain	0·2	3·0	Nil	96·8	74
Thick Seam, durain	0·3	3·2	7·8	88·7	72
Barnsley Seam, vitrain ...	0·8	2·6	Nil	96·6	65
Barnsley Seam, durain ...	0·5	2·2	20·7	76·6	62

* Organic sulphur.

evolution of gaseous paraffins then occurring. With the durain, the evolution of gases increased between 290° and 310°, but the decomposition point was not well defined. A greater volume of gas was obtained from the durain than from the vitrain over this range, owing to the extensive evolution of carbon dioxide from the former. The durain yielded more carbon dioxide than the vitrain throughout the distillation, but much less paraffins below 350°.

Water of decomposition was evolved more freely by the durain than by the vitrain below 300°, but the reverse occurred above 310°.

Hydrocarbon oils were distilled from both coals below the active-decomposition point in quantities corresponding with their contents of free hydrocarbon (γ_1-compounds). The evolution of oils was accelerated just below 300°, above which the durain yielded more than the vitrain by reason of an extensive production of hydrocarbon oils between 300—350°. The vitrain yielded more phenolic oils. Analysis of the hydrocarbon oils from the two coals showed that in those from the vitrain aromatic hydrocarbons predominated, whilst those from the durain contained a high proportion of unsaturated hydrocarbons.

(*b*) *The Barnsley Seam.* The stages of heating adopted were 15—100°, 100—200°, 200—280°, 280—300°, thence 10° intervals up to 350°, and finally 350—375° and 375—400°. The coals were maintained at the higher temperature of each stage during 120 hours

TABLE III.

Gaseous Products of Distillation of Vitrain and Durain from Thick Seam.

(Volumes in c.c. per 100 g. of ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—300°.		300—325°.		325—350°.		350—375°.		375—400°.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
CO_2 (and H_2S)	6	20	19	35	99	317	118	396	89	759	90	1334	41	1375
Olefins	—	—	—	—	24	20	73	46	93	84	103	77	22	19
CO	1	3	4	10	42	52	62	44	88	57	134	69	135	45
H_2	—	—	—	—	—	—	—	—	36	48	77	91	117	140
Paraffins	—	1	1	4	110	65	329	74	628	408	1117	936	1332	1100

TABLE IV.

Liquid Products of Distillation of Vitrain and Durain from Thick Seam.

(% on ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—275°.		275—300°.		300—325°.		325—350°.		350—375°.		375—400°.		Total.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
Water	2·28	1·60	0·14	0·23	0·54	0·59	0·59	0·59	1·36	0·77	1·36	0·87	1·15	1·32	0·84	1·03	8·20	6·98
Light oils	—	—	0·05	0·04	0·18	0·16	0·19	0·16	0·33	0·32	0·33	0·32	0·23	0·32	0·19	0·16	1·50	1·48
Heavy oils	—	—	—	—	0·23	0·29	0·65	1·00	2·43	2·28	1·41	2·49	0·92	1·15	0·18	0·53	5·82	7·74
Fractionation of heavy oils.					V.		D.											
Sat. hydrocarbons	—	—	—	—	0·18		0·30		0·19	0·20	0·09	0·26	0·04	0·09	Trace	0·02	0·50	0·87
Unsat. hydrocarbons	—	—	—	—	0·15		0·34		0·43	0·84	0·07	0·76	0·13	0·08	0·02	0·05	0·80	2·07
Aromatic hydrocarbons	—	—	—	—	0·19		0·29		0·33	0·41	0·25	0·42	0·13	0·30	0·06	0·02	0·95	1·62
Acidic oils	—	—	—	—	0·08		0·04		0·28	0·08	0·05	0·13	0·10	0·05	0·05	0·13	0·56	0·30
Phenolic oils	—	—	—	—	0·14		0·14		0·71	0·24	0·53	0·29	0·29	0·26	—		1·67	1·06
Bases	—	—	—	—	0·02		0·02		0·07	0·04	0·04	0·04	0·04	0·04	0·01	0·02	0·18	0·16
Ether-sol. oils	—	—	—	—	0·03		0·04		0·12	0·35	0·20	0·43	0·09	0·15	0·02	0·08	0·46	1·05
$CHCl_3$-sol. oils	—	—	—	—	0·01		—		0·04	0·06	0·05	0·10	0·03	0·03	Trace		0·13	0·19
Loss during fractionation	—	—	—	—	0·09		0·12		0·26	0·06	0·13	0·06	0·07	0·15	0·02	0·03	0·56	0·42

TABLE V.

Gaseous Products of Distillation of Vitrain and Durain from Barnsley Seam.

(Volumes in c.c. per 100 g. of ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—280°.		280—300°.		300—310°.		310—320°.		320—330°.		330—340°.		340—350°.		350—375°.		375—400°.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
CO_2 (and H_2S)	8	6	17	17	25	29	23	42	22	75	28	53	41	33	42	26	39	30	72	71	50	42
Olefins	—	—	—	—	3	3	9	11	20	31	25	45	49	42	41	35	34	33	58	46	20	15
CO	4	1	8	1	10	11	8	18	13	33	19	20	23	11	31	15	32	20	73	43	57	37
H_2	—	—	—	—	—	—	—	—	—	—	2	4	2	3	4	9	8	17	65	92	124	175
Paraffins	36	24	9	8	12	10	34	45	90	174	159	217	300	243	455	280	503	322	1230	895	1440	1060

TABLE VI.

Liquid Products of Distillation of Vitrain and Durain from Barnsley Seam.

(% on ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	100—200°.		200—280°.		280—300°.		300—310°.		310—320°.		320—330°.		330—340°.		340—350°.		350—375°.		375—400°.		Total.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
Water	0·13	0·21	0·23	0·35	0·14	0·29	0·22	0·60	0·35	0·54	0·39	0·22	0·56	0·27	0·43	0·21	0·84	0·60	0·78	0·79	4·07	4·08
Light oils	0·05	0·15	0·29	0·08	0·17	0·11	0·13	0·32	0·14	0·40	0·24	0·22	0·22	0·17	0·18	0·22	0·30	0·27	0·17	0·20	1·89	2·14
Heavy oils	—	—	0·15	0·23	0·25	0·65	0·48	3·36	0·58	4·43	0·73	1·47	0·65	0·90	0·37	0·62	0·32	0·72	0·10	0·14	3·60	12·52
Fractionation of heavy oils.			V.		D.																	
Sat. hydrocarbons	—	—	0·10		0·12		0·07	0·19	0·06	0·22	0·03	0·11	0·02	0·06	Trace	0·04	Trace	0·02	—	Trace	0·28	0·75
Unsat. hydrocarbons	—	—	0·14		0·30		Trace	1·24	0·03	1·67	0·06	0·34	0·07	0·24	0·06	0·17	0·06	0·14	—	0·05	0·44	4·15
Aromatic hydrocarbons	—	—	0·08		0·12		0·10	0·28	0·11	0·35	0·09	0·16	0·03	0·12	0·02	0·10	0·03	0·06	0·02	Trace	0·45	1·19
Acidic oils	—	—	—		0·01		0·02	0·05	0·04	0·04	0·06	0·04	0·06	0·01	0·02	—	0·10	—	—	—	0·20	0·15
Phenolic oils	—	—	—		0·04		0·08	0·19	0·12	0·19	0·16	0·10	0·14	0·06	0·11	0·03		0·09	—	—	0·71	0·70
Bases	—	—	—		0·01		0·01	0·04	0·01	0·04	0·02	0·03	0·01	0·01	0·01	—	—	0·06	—	—	0·06	0·19
Oxygenated compounds	—	—	0·04		0·13		0·05	0·43	0·04	0·50	0·05	0·22	0·03	0·10	0·02	0·08	0·02	0·14	—	0·04	0·25	1·64
Ether-sol. oils	—	—	—		0·07		0·06	0·40	0·06	0·63	0·14	0·19	0·20	0·15	0·08	0·06	0·05	0·10	0·08	0·02	0·67	1·56
$CHCl_3$-sol. oils	—	—	—		0·03		0·03	0·19	0·02	0·30	0·06	0·07	0·04	0·07	0·02	0·02	0·01				0·18	0·74
Loss during fractionation	—	—	0·04		0·05		0·03	0·35	0·09	0·49	0·06	0·22	0·05	0·08	0·03	0·12	0·05	0·11	—	0·03	0·35	1·55

except at 300—310° and 310—320°, for which the duration was 240 hours, the shorter time being insufficient to distil all the oils from the durain at those temperatures. The gases and liquids evolved at each stage were collected separately. In the examination of the neutral hydrocarbon oils, oxygenated compounds were removed by treatment with ferric chloride, according to Robinson's method (J., 1925, **127**, 768). The results are recorded in Tables V and VI. They were similar to those obtained with the Thick Seam, but there was a greater contrast between the behaviour of the vitrain and the durain because the latter contained a higher proportion of plant entities than did the durain of the Thick Seam.

The active-decomposition point, well marked with the vitrain but less distinct with the durain, was at 305—310°. Above this temperature the evolution of gases rapidly increased, paraffins predominating. Between 300—320° the durain yielded considerably more gases than the vitrain, the excess being due to carbon dioxide. The durain also yielded much more water of decomposition than the vitrain over this range. Above 320°, the evolution of gases, particularly of the paraffins, increased more rapidly with the vitrain than with the durain, and the former yielded the greater quantity of water.

The yields of oils from the two coals were markedly different, the durain producing the greater quantity, particularly over the range 300—320° (*i.e.*, the range over which it evolved the greater quantities of gases and water). The oils from the vitrain, apart from phenolic compounds, consisted mainly of aromatic hydrocarbons. The oils from the durain contained less phenolic compounds and the hydrocarbons were mainly unsaturated.

(2) *Distillation of Spore Exines from Bituminous Coal.*—We are indebted to Dr. V. H. Legg for a supply of megaspore exines separated by him from the durain of the Top Hard Seam, East Kirkby. The mode of separation involved the gradual oxidation by hydrogen peroxide, and subsequent dissolution in potassium hydroxide solution, of the matrix of ulmin compounds in which the megaspores were embedded. Partial oxidation of the megaspores must be presumed, though their appearance was unchanged by this treatment. The retort when filled contained 17 g. of spore exines. The distillation was carried out by stages as recorded in Table VII, the duration of heating at the higher temperature of each stage being 120 hours.

Heavy oils began to distil at 280° and appeared in greatest quantity over the range 300—360°. Water and large volumes of gas, containing a high proportion of paraffins and carbon dioxide, accompanied the oils, which consisted mainly of unsaturated and aromatic hydrocarbons and oxygenated compounds. The hydrocarbon oils,

TABLE VII.

Gaseous and Liquid Products of Distillation of Megaspore Exines.

(Gases : c.c. per 100 g. Liquids : % by weight.)

Temp. range.	100—200°.	200—300°.	300—330°.	330—360°.	360—400°.	Total.
CO_2 (and H_2S)	1170	1269	177	209	179	3004
Olefins	7	34	66	273	299	679
CO	112	277	155	190	188	922
H_2	—	—	42	185	624	851
Paraffins	12	122	522	1440	1390	3476
Water	2·9	3·5	5·3	1·5	0·7	13·9
Light oils	0·3	0·3	1·4	1·2	1·0	4·2
Heavy oils	Nil	1·5	6·7	5·5	3·0	16·7
Fractionation of heavy oils.						
Sat. hydrocarbons ...	—	Trace	0·5	0·4	0·2	1·1
Unsat. hydrocarbons	—	0·8	2·7	1·7	0·9	6·1
Aromatic hydrocarbons....................	—	0·2	0·9	0·7	0·4	2·2
Phenolic and acidic oils	—	Trace	0·3	0·3	0·1	0·7
Bases	—	,,	0·2	0·2	0·1	0·5
Oxygenated compounds	—	0·2	1·2	0·7	0·4	2·5
Ether- and chloroform-soluble oils......	—	Trace	0·3	1·1	0·5	1·9
Loss during fractionation	—	0·3	0·6	0·4	0·4	1·7

like those from the two durains, darkened on exposure to the air, oxygenated compounds being readily formed from them.

The products of distillation of megaspore exines thus provide, over the significant temperature range, the difference in character between the gaseous and liquid products of distillation of durain and vitrain from the same coal.

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.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD.

[*Received, January* 30*th*, 1929.]