327. *Studies in the Composition of Coal. The Action of Solvents.*

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If the coal conglomerate could readily be separated into its constituents by the use of organic solvents, the study of the composition of coal would be simplified. A method of resolution by pyridine and chloroform, followed by separation of the extract into portions soluble in light petroleum and in ethyl ether (see Cockram and Wheeler, J., 1927, 700), is widely used. This treatment yields fractions, γ_1, mainly hydrocarbons, γ_2, resinols, resines and resenes, and γ_3, resin-like compounds, the separation of which is informative. It is by no means certain, however, that the initial treatment with pyridine and chloroform invariably effects removal of the whole of the free hydrocarbons and resins from the coal conglomerate.

Fischer and Gluud (*Ges. Abh. Kennt. Kohl*, 1916, **1**, 54) originated a treatment with benzene boiling under pressure at 200—285° (adopted by Bone, Pearson, and Quarendon, *Proc. Roy. Soc.*, 1924, *A*, **105**, 608) which usually yields more " extractable matter " from a bituminous coal than does the treatment, at low temperatures, with pyridine and chloroform. This method is unsuited for coals of low carbon content, since they begin to decompose on heating above about 250°.

Within recent years, two new methods of solvent analysis of coal have been suggested. Hankiss and Péter (*Szénkisérleti Köslemények*, 1927, **2**, 45) of the Hungarian Fuel Research Station, Budapest, have recorded that mixtures of two or more low-boiling solvents could extract considerably more from certain Hungarian coals than could any one of the solvents alone. The most striking results were obtained with equal volumes of either ethyl alcohol and carbon tetrachloride or ethyl alcohol and benzene. A more suggestive method is that due to Fischer, Peters, and Cremer (*Brennstoff Chem.*, 1932, **13**, 364), the feature of which is the grinding of the coal in a vacuum ball-mill until the average size of the particles is 1 μ. A German bituminous coal reduced to such a degree of fineness readily yielded ten times as much extractable matter to a low-boiling solvent (*e.g.*, trichloroethylene) as it did when in the form of a comparatively coarse power. The suggestion is that mechanical disintegration of the coal performs the same function, of rendering the soluble matter accessible to the solvent, as does the colloidal dispersion effected by pyridine. We intend, with Dr. Fischer's permission, to apply this method of study to British coals.

The experiments we have made during the past four years on the treatment of coal with mixtures of solvents have not been successful in evolving a method of resolution superior to that of extraction with pyridine, followed by chloroform. They have disclosed, however, a source of fallacious results, to which we wish to direct the attention of other workers, which must render suspect some of the work that has been published on the treatment of coal by solvents.

Briefly, our experiments, some of which are recorded later, show that coal can exert a powerful catalytic action; for example, in promoting the condensation of xylene with amyl alcohol, with or without simultaneous oxidation, the result being a " resinic " material difficult to distinguish from a coal extract.

The oxygen that a coal contains can be highly reactive; for example, ethyl alcohol is changed to aldehyde when it is boiled with a finely divided lignite. On the other hand, a warm dilute acid solution of potassium permanganate is rapidly decomposed, with evolution of oxygen, by the catalytic action of finely divided bituminous coal suspended in it.

The synthesis of solid " extractable matter " when coal is treated with organic solvents is promoted, the catalytic action of the coal being enhanced, by increase of temperature. For this reason alone we should distrust results obtained with benzene boiling under pressure at a temperature as high as 280°. In this connexion, reference may be made to the observation by Newitt and Szegö (*J. Soc. Chem. Ind.*, 1933, **52**, 645) relative to the oxidation of aromatic hydrocarbons under pressure, that : " In the case of benzene there is little doubt but that the initial product of oxidation is phenol and references are repeatedly found in the literature to the detection of this compound amongst its oxidation products." Bone, Horton, and Tei (*Proc. Roy. Soc.*, 1928, *A*, **120**, 523) have recorded the presence of as much as 25% of phenol (which is not to be expected either as an original constituent or as a product of decomposition of coal) in the " extract " obtained on treating a lignite, of high oxygen content (29·5%), with benzene at 280° under 48 atm. pressure.

None of our experiments suggests that the substances obtained by extracting coal with pyridine (b. p. 115°), followed by treatment of the extract with chloroform (b. p. 61·2°), are vitiated by material synthesised from the solvent.

EXPERIMENTAL.

Preliminary experiments on the treatment of coal with mixed solvents were made with Silkstone (Yorkshire) coal (C, 83·6; H, 5·4%) ground to pass a 20- and remain on a 100-mesh I.M.M. standard sieve. The extractions were made on 20 g. charges of the coal by boiling in flasks during three periods, each of 12 hours duration, fresh solvent being used for each period. The boiling flasks were fitted with ground-in glass condensers and air was excluded. The amounts extracted by different solvents were, % on the ash-free dry coal: ethyl alcohol, 0·18; benzene, 0·19; carbon tetrachloride, 0·08; benzene–carbon tetrachloride, 0·10; ethyl alcohol–benzene, 1·46; ethyl alcohol–carbon tetrachloride, 2·02; ethyl alcohol–benzene–carbon tetrachloride, 0·92. The mixed solvents in these and all subsequent experiments were in equal parts by volume.

The extractions were incomplete (pyridine–chloroform yielded 7·1% extract), but confirmed the observations of Hankiss and Peter.

A second series of extractions of the Silkstone coal was made in the same way, but with four 44-hour periods. The extracts were fractionated with light petroleum and ethyl ether for comparison with the "γ-fractions." The results are in Table I.

TABLE I.

Extracts from Silkstone Coal, % on Ash-free Dry Coal.

Solvent.	Total extract.	Sol. in light petroleum.	Sol. in ethyl ether.	Insol. in ethyl ether.
Chloroform	2·0	1·0	0·6	0·4
Chloroform–ethyl alcohol	2·9	0·9	1·0	1·0
Benzene–ethyl alcohol	3·6	1·2	1·4	1·0
Ethyl alcohol–carbon tetrachloride	5·9	1·3	1·3	3·3
(Pyridine–chloroform)	7·1 (γ)	1·8 (γ_1)	1·8 (γ_2)	3·5 (γ_3)

It will be noted that, although the extractions were incomplete, the relative proportions of the extracts soluble in light petroleum and ethyl ether corresponded approximately with the γ_1 and γ_2 fractions. The corresponding extracts were of similar appearance.

For the third series of extractions, Cockshead (Staffordshire) coal (C, 85·1; H, 5·3%) was used, there being four 100-hour periods. In an attempt to expedite extraction, a mixture of xylene and amyl alcohol was tried in addition to the mixtures previously used. The results are in Table II.

TABLE II.

Extracts from Cockshead Coal, % on Ash-free Dry Coal.

Solvent.	Total extract.	Sol. in chloroform.	Sol. in light petroleum.	Sol. in ethyl ether.	Insol. in ethyl ether.
Benzene–ethyl alcohol:					
1st period	2·3	1·9	1·2	0·4	0·3
2nd ,,	2·3	1·3	0·9	0·3	0·1
3rd ,,	2·1	1·2	0·4	0·3	0·5
4th ,,	2·4	1·3	0·4	0·3	0·6
Total	9·1	5·7	2·9	1·3	1·5
Chloroform–ethyl alcohol:					
1st period 2nd ,,	1·9 1·7	1·4 1·4	0·9	1·0	0·9
3rd ,,	0·9	0·9	0·3	0·3	0·3
4th ,,	1·0	0·9	0·1	0·3	0·5
Total	5·5	4·6	1·3	1·6	1·7
Ethyl alcohol–carbon tetrachloride:					
1st period 2nd ,,	4·6 2·0	2·7 1·6	0·7	2·1	1·5
3rd ,,	1·9	1·7	0·5	0·5	0·7
4th ,,	1·7	1·2	0·4	0·4	0·4
Total	10·2	7·2	1·6	3·0	2·6
Xylene–amyl alcohol:					
1st period	21·6	21·0	9·4	11·5	0·1
2nd ,,	22·3	21·1	6·5	13·8	0·8
3rd ,,	8·7	8·0		not determined	
4th ,,	10·0		not determined		
Total	62·6				
Pyridine:					
1st period	17·6	6·4	2·4	2·9	1·1
2nd ,,	4·6	1·0	0·3	0·2	0·5
3rd ,,	0·8 0·3	0·5		not determined	
Total	23·3	7·9 (γ)	2·7 (γ_1)	3·1 (γ_2)	1·6 (γ_3)

That the mixture of xylene and amyl alcohol (b. p. 140°) would yield the most extract was not unexpected, but the actual amount was as surprising as was the fact that most of the extract was soluble in chloroform with high proportions soluble in light petroleum and ethyl ether. These observations caused us to suspect that the solid matter recovered was derived from the solvents and not from the coal, and the suspicion was confirmed by the fact that the coal extracted was found not to have lost in weight.

Proof of the synthesis of "extractable matter" from the solvents was obtained by treating anthracite calcined at 1000° (which yields nothing to organic solvents) with the mixture of xylene and amyl alcohol. After 100 hours, a solid in amount representing 18·2% on the weight of the anthracite was obtained. This was nearly all soluble in chloroform; half of it was soluble in light petroleum and half in ethyl ether.

The "extracts" obtained with the other mixed solvents were also in large part synthesised from the solvents, for the samples of coal extracted had gained in weight despite the fact that they had apparently yielded from 5 to 10% of extractable matter (see Table II). Only the residue from extraction by pyridine was in correct proportion.

The fractions of the "extracts" of the coal by mixed solvents obtained by successive treatment with chloroform, light petroleum, and ethyl ether were indistinguishable in appearance from the corresponding γ-fractions of the coal, and the similarity extended to their ultimate analyses. The synthetic material obtained by treating anthracite with xylene and amyl alcohol, however, differed from coal extracts in that the fraction soluble in chloroform and light petroleum (corresponding with the γ_1 fraction of a coal) consisted wholly of saturated compounds. The γ_1 fraction of a coal, when freed from oxygenated compounds, is a mixture of saturated and unsaturated hydrocarbons, usually in nearly equal amounts (Cockram and Wheeler, *loc. cit.*, p. 705).

This work is being continued with a view to determine the nature of the synthetic products. The observations here recorded demonstrate a possible source of error in studies of the extraction of coal by solvents.

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