167. *Studies in the Composition of Coal: Extraction of Coal with Quinoline.*

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The estimation of the proportion of resins and hydrocarbons in coal is hindered by the difficulty of extracting them completely. Quinoline as a primary solvent is found to have no advantage over pyridine in either the rapidity or the completeness of extraction. If technical quinoline is used in daylight, there is introduced a liability to photochemical synthesis of material likely to be confused with the true extract.

RESINS and hydrocarbons form only a small proportion of the material of coals but their effects on the properties of coals, *e.g.*, caking properties, are disproportionately great. In the rational analysis of coals (Cockram and Wheeler, J., 1937, 700) the resins and hydrocarbons are extracted with pyridine, and the crude extract is resolved by further extractions with chloroform, ether, and light petroleum. The purpose of the preliminary extraction with pyridine is to set free the resins and hydrocarbons, which cannot be extracted directly by highly discriminating solvents. The pyridine is believed to exert more than a purely solvent action and to peptise much of the ulmin component of the coal.

A common alternative method of resolving the coal is by extraction with benzene under pressure, at, say, 275°. This method has been criticised on the ground that coals of low carbon content may decompose to some extent during the extraction.

It seems that neither process extracts the resins and hydrocarbons completely, for the amount of these materials extracted is increased by grinding the coal very finely, to micron size (Fischer *et al.*, *Brennstoff-Chem.*, 1932, **13**, 364; Sherburn, Safety in Mines Research Board Annual Report, 1934, p. 58). Also, Bakes has obtained resin and hydrocarbons from that fraction of a coal undissolved by pyridine by subsequent extraction with benzene under pressure (Fuel Research Board Technical Paper No. 37).

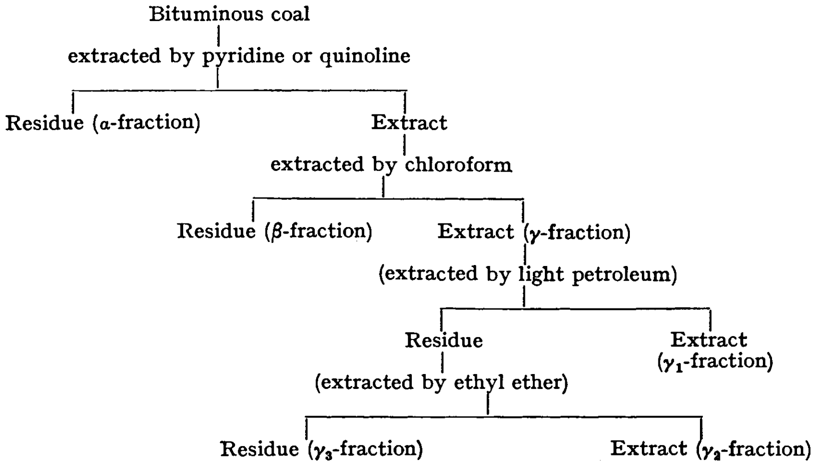
The residue after extraction by pyridine or benzene may be from 60 to nearly 100% according to the nature of the coal. It would be an advantage, in order to ensure the complete extraction of the resins and hydrocarbons, to bring as much as possible of the coal into solution or pseudo-solution before resolving the extract into these constituents. Attempts have been made to complete the solution of the coal by the use of high-boiling solvents. Vignon (*Compt. rend.*, 1914, **158**, 1421) reported a yield of 47% of soluble material by treating a certain coal with boiling quinoline, whereas pyridine extracted only 17%. The greater extractive power of quinoline than of pyridine, and the apparent inability of pyridine to extract the whole of the resins and hydrocarbons from coal of convenient fineness, suggested that quinoline might prove a more efficient preliminary solvent than pyridine.

EXPERIMENTAL.

Extractions have been made both with " technical " quinoline and with pure quinoline (for which we are indebted to Dr. E. Moehrle, of Duisberg-Meiderich). Before use, the " technical " quinoline was dried over sodium hydroxide and distilled; the fraction of b. p. 230—240° was redried and redistilled. The pure quinoline was used without any pre-treatment.

The coal to be extracted, after partial drying by exposure to the air, was carefully ground so as just to pass through a 20-mesh I.M.M. sieve, that part remaining on a 100-mesh sieve being used. Before extraction, the ground coal was dried for 8 hours in a vacuum oven at 100°. 20 G. were weighed into a stoppered jar, covered with quinoline, and kept overnight. The coal (which had not swelled appreciably) was then transferred to an alundum thimble, which was plugged with glass-wool and immersed, to above the level of the coal, in 500 c.c. of quinoline boiling in an atmosphere of carbon dioxide. The solvent was changed periodically, and the coal in the thimble was well stirred at each renewal.

The quinoline extract was fractionated by the scheme elaborated by Cockram and Wheeler (*loc. tit.*), which may be represented as follows :



The first experiments were made with the technical quinoline. The yield of extract was notably high, amounting, with coal from the upper Bright Bench of the Barnsley seam from the Hatfield Main Colliery, Yorkshire, to 84% of the original coal, as compared with only 26% extracted by pyridine. A weight balance was not struck in this experiment, but in a subsequent experiment on the same coal, extracted by quinoline at a temperature of only 120°, the recovered extract weighed 90% and the residue 60% of the weight of the original coal. This showed that synthesis was occurring during the extraction of the " soluble " material.

The synthesis appeared to be the result of a photo-chemical reaction between the quinoline and its impurities. Synthesis occurred during the extraction with the technical quinoline in the daylight, but not in the dark; it did not occur with pure quinoline either in the dark or in daylight (see note, p. 868).

A sample of the same coal was extracted exhaustively in parallel tests with pure quinoline and with pyridine to assess the relative efficacies of the solvents. Each extract was fractionated by light solvents in the usual way. The γ_1-fractions were treated with Robinson's reagent (J., 1925, **127**, 68) to separate oxygenated material from hydrocarbons. The residual hydrocarbons were then treated with Manning's reagent (J., 1929, 1014), to remove unsaturated and aromatic hydrocarbons. The carbon and hydrogen contents of the recovered fractions were determined. The results of the extraction and analyses are given in the tables.

Discussion.—It is evident that the greater amount of extract obtained by means of quinoline as compared with pyridine lay in an increased yield of the β-fraction (which is ulmic in nature), and was presumably the result of its greater peptising action. The γ_1- and γ_2-fractions (hydrocarbons and resins) were similar in amount to those obtained when pyridine was the primary solvent. The ultimate and chemical compositions of the γ_1-fraction yielded by the two extractions were similar, but the γ_2-fraction in the quinoline extract contained about 1% less carbon than the same fraction in the pyridine extract.

The extractions, by either primary solvent, of resins and hydrocarbons appeared to be equally complete, for when the residue from the pyridine extraction was further extracted by quinoline, or *vice versa*, no additional extract was obtained.

Comparison of weights of extracts obtained by pyridine and quinoline, % of original coal.

Duration of extraction, hrs.	Crude extract.	Fraction. β- (by diff.).	γ-.	γ_1-.	γ_2-.	γ_3- (by diff.).
Pyridine.						
20	15·35	9·01	6·34	—	—	—
40	18·67	—	—	—	—	—
120	20·92	13·80	7·12	2·42	2·19	2·51
Quinoline.						
20	14·0	10·6	3·4	—	—	—
40	23·25	17·45	5·8	—	—	—
80	30·0	—	—	—	—	—
200	34·6	26·89	7·71	2·59	2·40	2·72

Composition of γ_1-fractions, % of original coal.

Primary solvent.	Total γ_1-fraction.	Oxygenated material.	Unsat. and aromatic hydrocarbons (by diff.).	Sat. hydrocarbons.
Pyridine	2·42	0·48	0·93	1·01
Quinoline	2·59	0·68	1·21	0·7

Ultimate analysis of extracts.

	Pyridine. C, %.	Pyridine. H, %.	Quinoline. C, %.	Quinoline. H, %.
γ_1-Fraction :				
Oxygenated material	84·3	7·0	84·5	7·2
Residue after removal of oxygenated material	87·2	8·7	86·9	9·0
Saturated hydrocarbon	87·4	12·0	87·2	12·1
γ_2-Fraction	85·2	6·5	84·0	6·6

Quinoline has therefore no advantage as a primary solvent over pyridine as regards the extraction of resins and hydrocarbons from coal. Indeed, in spite of its higher boiling point, it is somewhat slower than pyridine in extracting these materials from coal. Moreover, if impure, it may give erroneous results due to photochemical synthesis.

Note on the Photochemical Synthesis in Quinoline.—That in the extraction of coal with technical quinoline the total amount of extract and residue was much greater than the amount of coal extracted shows that part of the " extract " must have been synthesised from the solvent. John (*Ber.*, 1926, **59**, 1) obtained (presumably at room temperature) a small yield of resin when quinoline was exposed to light in the presence of anthraquinone. His work suggested that the explanation of the synthesis during extraction with quinoline might be sought in a photochemical reaction between the quinoline and its impurities.

To verify whether the technical quinoline of itself would react photochemically, presumably with its impurities, 500 c.c. of each of several samples were heated for a week, in the dark and in daylight, at 120° and 240°. The effect of adding calcined anthracite (which itself can exert catalytic action) was also investigated. The results are given in the following table.

Temp.	Calcined anthracite.	Conditions.	Material synthesised, g.	Portion soluble in $CHCl_3$, g.
120°	Absent	Exposed to light	2	—
240	,,	,, ,,	5	4·8
120	Present	,, ,,	2·8	2·7
120	Absent	In dark	0·11	0·11
240	Present	,,	0·12	0·10

The quantity of material synthesised in the light is appreciable even at 120°, and rise of temperature to 240° more than doubled the amount. When calcined anthracite was present the yield was increased, but the effect may have been due to variation in the intensity of the light between the different experiments. The amount of synthesis in the dark was small and was not significantly affected by the presence of anthracite.

The material synthesised at 240° in the presence of light was fractionated by the Cockram–Wheeler method, with the following results, expressed as % of the synthesised material.

γ-Fraction.	γ_1-Fraction.	γ_2-Fraction.	γ_3-Fraction.
98·0	4·8 3·2 * 1·6 †	13·8	79·4

* Oxygenated material. † Residual γ_1-fraction.

Experiments with pure quinoline. The above experiments were repeated on 500 c.c. of a sample of pure quinoline, with the following results:

Temp.	Calcined anthracite.	Conditions.	Product, g.	Portion soluble in $CHCl_3$, g.
120°	Absent	Light	0·12	0·12
240	,,	,,	0·17	0·17
240	Present	,,	0·17	0·17

It is evident that inappreciable photochemical synthesis occurs with the pure quinoline. The synthesis from the technical quinoline must therefore be due to impurities. Which of them caused the synthesis has not been ascertained.

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