

DEDUCTION OF THE STRUCTURE OF BROWN COAL
BY REACTION WITH PHENOL

R.J. Hooper* and D.G. Evans[†]

* D.S.I.R. Industrial Processing Division, Private Bag, Petone, New Zealand

† Centre for Environmental Studies, University of Melbourne, Parkville, Victoria
3052, Australia.

INTRODUCTION

To make any real progress in the ability to predict and control the liquifaction of coal by hydrogenation it is necessary to know what chemical reactions are occurring. Modern preparative and analytical techniques such as elution chromatography, mass spectroscopy and proton nmr have made the task of characterizing the products of liquefaction reactions much easier than hitherto, but the task of characterizing the coal before reaction remains almost as intractable as ever, because these new methods depend on the analysis samples being in the liquid form (or in the case of mass spectroscopy, able to be completely vaporized).

This is not a new problem, of course. Over the years many solubilization techniques have been suggested as tools for deducing coal structure, e.g. oxidation, hydrogenation, alkaline hydrolysis, pyrolysis and extraction with powerful solvents (either alone or in conjunction with other methods such as thermal pre-treatment, use of ultrasonics, etc.). These suffer from one of two disadvantages: with the relatively mild physical methods insufficient coal is got into solution to be useful (less than 20% is typical); but with chemical methods, including pyrolysis, the treatment is so harsh that interpretation of the structure of the original coal in terms of that of the products is of dubious validity. In particular, use of elevated temperatures, as in pyrolysis or other thermal treatments, is to be avoided, as free radicals formed by cleaving fragments off the main body of the coal molecule may polymerize to form structures which were not present in the original coal.

If it is accepted that coal cannot be got into solution without altering its structure to some extent, we should look for methods in which these changes are not large enough to prohibit the drawing of adequate deductions about the structure of the original coal, while at the same time presenting the reacted coal in a form suitable for structural examination. This would require at least 80% of the coal to be solubilized, with the soluble material low enough in molecular weight to ensure that it in turn is soluble in mild organic solvents, as required for preparative techniques such as solvent fractionation or chromatography.

The methods we considered were Friedel-Crafts reactions of various kinds (alkylation and acylation) and depolymerization of the coal by using it to alkylate phenol, as first proposed by Heredy and co-workers (1), and extensively investigated by them (1-5) and by Ouchi and co-workers (6-11). From the recent review of these methods by Larsen and Kuemerrle (12) it appears that molecular weights of the coal fragments produced are higher for alkylation and acylation methods (typically several thousand, even after allowing for the added acyl or alkyl groups) than for the material depolymerized in phenol (less than a thousand). The only disadvantage of phenol depolymerization, compared with the other methods, was its relatively weak action on very high rank coals (< 90%C, daf). This did not concern us, as we were interested in examining brown coals from the Latrobe Valley, Victoria, Australia, with very low rank (65-70%C, daf). We therefore chose this method, which had already been shown by Ouchi and Brooks (9) to be very effective for this type of coal. We perhaps underestimated the difficulties that chemically combined phenol would cause us, as will be discussed later.

In our plan of attack we first depolymerized the coal using conditions suggested by Imuta and Ouchi (11), then divided it into five fractions of progressively increasing polarity, using solvent fractionation, then analysed these fractions separately by elemental and functional group analysis, and further characterized the fractions by running infrared and proton nmr spectra on them. After allowing for the effects of combined phenol these data were put together to build up a composite picture of the structure of the original coal. Heredy et al. (5) have carried out a similar investigation on a series of coals of different ranks. The present work differs from theirs in that it used a more powerful catalyst for the phenolation, a more decisive solvent fractionation scheme, and infrared as well as nmr analysis for characterizing the fractions. Also our coal was lower in rank than any of those they tested.

EXPERIMENTAL

Coal used

The coal tested was Morwell brown coal from Victoria, Australia. Its composition on a dry basis is shown in Table 1. This coal contains over 60% moisture as mined. It was ground wet to 80% < 25 mesh, and used in the wet state (60% moisture).

Phenolation reaction

179 g of wet ground coal, 75 g of p-toluenesulfonic acid catalyst and 1300 g of laboratory grade phenol were heated under nitrogen, and the water was removed from the coal by boiling at 183°C (the boiling point of phenol is 181.8°C). The remaining mixture was refluxed at 183°C for 4h, after which the phenol was removed by steam distillation, leaving a solid, black, tarry material of low melting point, which was separated by decantation, and extracted by refluxing for 2h with 1200 ml of ethanol/benzene azeotrope (65% benzene, 35% ethanol). The insoluble material was filtered off and dried in a vacuum oven for 12h at 50°C and 16kPa pressure (these conditions were later used to remove excess solvent from all the fractions - see Figure 1 below).

Solvent fractionation

To facilitate later structural analysis the coal was separated into structural types using the solvent fractionation scheme shown in Figure 1.

Analysis

The original coal and the various fractions were analysed for carbon, hydrogen and oxygen by the C.S.I.R.O. Microanalytical service. Ash contents were determined in a standard ashing furnace (13). Phenolic, carboxylic and carbonyl oxygen contents were determined by the State Electricity Commission of Victoria, using methods developed by them for brown coals (14).

Infrared spectra of the original coal and the fractions were measured on a Perkin Elmer 457 Grating Infrared Spectrophotometer. Liquid samples (fractions A and B) were analysed as a thin film or smear. Solid samples (C, D and original coal) were analysed in KBr discs containing 0.3% by mass of sample. These were prepared by grinding the KBr mixture for 2 minutes in a tungsten carbide TEMA grinding barrel, drying for 24h in a vacuum desiccator over phosphorus pentoxide, then pressing into discs at 10 tons force, at room temperature but under vacuum. Because fraction A was dominated by phenol a sample of it was further separated by elution chromatography in an attempt to separate from it material less dominated by phenol. Elution was carried out in a silica column, using elutants in the following order:

hexane, chloroform, methanol.

Proton nmr spectra were recorded on a Varian HA 100 nmr spectrometer at room temperature, with tetramethylsilane (TMS) as internal standard, with a sweep width of 0 to 1000 Hz from TMS. For fraction A a solution of deuterated chloroform was used; fractions B and C were not soluble in CDCl_3 and pyridene $-d_5$ had to be used; fractions D and the whole coal were barely soluble even in pyridene $-d_5$, but enough dissolved to get spectra. These will not, of course, be representative of the whole material.

RESULTS

Yields and compositions

Table 1 shows the yields of the five fractions per 100 g of original dry coal and their compositions, including a breakdown of the oxygen into carboxylic, phenolic and other oxygen. Note that part of the ash-forming material has been removed by the solubilizing process (much of the non-organic material in Morwell coal is ion-exchangeable, and would have been replaced by hydrogen ions from the p-toluene-sulfonic acid; this was confirmed by ash analysis: e.g. ash from the original coal contained 50% SiO_2 and 10% MgO, whereas fraction D ash contained 80% SiO_2 and only 1% MgO). As the total yield of fractions was 202 g/100 g of original coal 102 g must have been added. This consists of combined phenol and unseparated solvents, as will be discussed later. This dilution results in the fractions having higher carbon contents and lower oxygen contents than the original coal. The hydrogen content decreases from A to D as the fractions become less aliphatic and more aromatic and polar.

Infrared spectra

The infrared spectra of the fractions and the original coal are shown in Figure 2. The spectra of the eluted sub-fractions of fraction A are not given here.

As already mentioned fraction A is dominated by phenol; nevertheless strong aliphatic absorptions can be seen at 2920, 2850, 1460 and 1380 cm^{-1} . The spectra of subfractions A1 (eluted by hexane, a very small part of A) and A2 (eluted by chloroform, about a quarter of A) showed these aliphatic absorptions very strongly. The spectrum for A1 showed little else, and this sub-fraction is probably virtually pure paraffins. The spectrum for A2 resembled the spectra for phenol ether and phenetole ($\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$). Absorption due to hydrogen-bonded hydrogen is negligible, showing that all the phenol in this sub-fraction has been converted to ethers. The spectrum for subfraction A3 (which constitutes about three quarters of A) was dominated by phenol, but some aliphatic absorptions still showed, and this sub-fraction may well consist of phenol bonded to small coal fragments by methylene bridges. The absorptions for A, A2 and A3 at 1250 cm^{-1} are probably due to ether oxygen.

Fraction B is in many ways similar to fraction A, but with much weaker aliphatic absorption. It has a strong absorption due to hydrogen-bonded hydrogen at 3400 cm^{-1} , a weak aromatic absorption at 3030 cm^{-1} and many other absorptions characteristic of phenol. It also shows weak aliphatic absorptions at 2920, 1460 and 1380 cm^{-1} , and ether oxygen absorption at 1250 cm^{-1} .

Fractions C, D and E have spectra similar to those of the original coal. Phenol no longer dominates, although the hydrogen bonded -OH absorption at 3400 cm^{-1} is still strong. Aliphatic absorption is weak in C and E and negligible in D. The shoulder at 1700 cm^{-1} due to carboxylic oxygen, which was quite strong for the whole coal, is also quite pronounced for fractions C and D. (It was absent from fractions A and

B). This checks well with the data in Table 1 obtained by chemical analysis. The broad absorption from $1200-1000\text{ cm}^{-1}$ present in the whole coal is also present in fractions C and D although absent from A, B and E. Doubtless oxygen groups contribute to this, but we believe it is mainly due to silica, which is a major constituent of the ash. It could be virtually removed by deashing the coal with strong acids or by float/sink separations.

Nmr spectra

Figure 3 shows nmr spectra for fractions A, B, C and E.

Table 2 shows the forms the protons are present in, as determined from these spectra. The data for fraction D and the whole coal are shown in brackets, as these samples were virtually insoluble in pyridine, and the spectra represent only the small soluble portions. This table demonstrates the difficulties the coal chemist faces in trying to use proton nmr on physical solutions of coal: e.g. the soluble part of the whole coal shows no hydrogen-bonded protons despite the evidence of table 1; it shows no triaromatic or methylene bridge protons, despite the presence of appreciable amounts of these in the fractions; on the other hand it shows far more methylene α and methylene β than do the fractions.

The nmr data confirm and amplify the infrared data: hydrogen bonded protons are present from phenolic and carboxylic groups in the coal and phenol groups added into the chemically combined phenol. The monoaromatic content (of fractions A and B especially) is high, also because of added phenol, but di-ring aromatic material is also present in all fractions (even triaromatic in C), which must have come from the original coal. The aliphatic material observed in the infrared spectra of A, B and C is now seen to consist principally of methylene bridges and short, branched aliphatic chains (α and β - methyl predominate).

DISCUSSION

Combined phenol

The total combined phenol was estimated as follows:

Using the yield and composition data of Table 1 elemental balances were drawn up, as in Table 3. The third last line gives the masses of the various constituents of the added material. The second last line gives the amount of phenol this would account for, assuming all the added oxygen was from phenol (none from ethanol or methanol). The last line gives the remainder, which is close in composition to benzene (which could be present as a contaminant in fractions B and C). In the fractionation scheme shown in Figure 1 ethanol contamination of any fraction is unlikely, but pentane contamination of fraction A and methanol contamination of D and E are possible. We rejected these because pentane was not picked up from fraction A by hexane elutriation while preparing subfraction A1 (this was negligible in mass), and D was too deficient in hydrogen and oxygen to contain any appreciable amount of methanol. Methanol could have been present in E, but the mass of this fraction was so small that any such effect would be negligible.

Distribution of hydrogen on a phenol - and solvent-free basis

We can now determine the distribution of hydrogen in the original coal, but first we have to estimate the hydrogen distribution in fraction D, which could not be determined by nmr analysis. In another paper presented to this Congress (15) we reported results of the hydrogenation of fractions A to D in tetralin. Fraction D yielded a low-hydrogen residue, which still could not be analysed by nmr, and a high-hydrogen

liquid product separated by boiling off excess tetralin. From its nmr analysis and the known amount of functional group hydrogen in the original fraction (0.05 g/100 g original coal) we concluded that the aliphatic hydrogen in the original fraction was about 0.3 g/100 g, and the remaining 0.8 g of hydrogen/100 g was aromatic hydrogen of various kinds.

In Table 4 the results of the nmr analyses (Table 2), the estimates of combined phenol and contaminant benzene (Table 3), and the above estimates of the distribution of hydrogen in fraction D are manipulated to give a composite estimate of hydrogen in various forms in the original coal (the aromatic hydrogen in fraction D is assumed to follow the same pattern as in A, B and C, and the aliphatic hydrogen is also assumed to be distributed as in A, B and C). From this we can calculate by difference the hydrogen present in various forms in the original coal (second last line of Table 4).

Distribution of structural types

The distribution of hydrogen calculated above, together with the distribution of functional group oxygen (Table 1), between them define a statistically probable structure for Morwell brown coal. Rather than attempt to draw a structure we give in Table 5 estimates of the numbers of carbon atoms associated with each type of hydrogen atom that not only predict approximately the correct mass of carbon per 100 g of coal but also allow for approximately the required number of substituents in the aromatic groups, and for the bridges connecting the groups. There may, of course, also be some carbon not associated with hydrogen, such as acyl bridges and tertiary carbons in side chains (see later). We note in passing that the greatest difficulty in meeting the above requirements is in accommodating the oxygen not accounted for in functional groups.

We will conclude with a brief discussion of the forms taken by the three main structural groups: oxygen groups, aromatic groups and aliphatic groups.

Oxygen groups: As seen from Table 1, 25% of the dry coal was oxygen, 5% in the form of phenolic groups, 5% carboxylic, and 3% carbonyl. The present work throws little light on the remaining 12%. Some ethers are thought to be present, but we cannot confirm this: ethers noted in fractions A and B could have come from the phenolation reaction. There was some indication of the presence of benzofuran groups from the infrared spectra of residues left after the reaction of fractions C and D with tetralin (15). No doubt other heterocyclic oxygen is present also.

Aromatics: The presence of relatively large proportions of higher aromatic structures (diphenyl, naphthalene and polynuclear) is noteworthy, and unexpected from previous studies on brown coal (16, 17). The total aromatic content may have been overestimated slightly by the procedure used to estimate the hydrogen distribution of fraction D, but this would make little difference to the contents of the higher aromatics.

Aliphatics: The most surprising result of this work is the high methylene bridge content (more than 25% of all hydrogen), which again was not expected from earlier models (16). However it should be noted that in the study by Heredy et al. (5) similar to the present one 12% of the hydrogen in a lignite was found to be in the form of methylene bridges. It seems unlikely that these bridges were formed by the phenolation reaction (indeed Heredy's favored mechanism requires the prior presence of such bridges, and the large content found in this work appears to confirm his mechanism as being the most important one in the phenolation reaction). If the quantities in Table 5 are calculated out in terms of the numbers of structures rather than their masses, we get 0.45 mole of aromatic groups per 100 g of coal and 0.65 mole of methylene bridges per 100 g. This means that there is more than one bridge per aromatic group, i.e. a high degree of crosslinking must be present, probably in

a three-dimensional network. Possibly dihydroanthracene structures may also be present.

Another surprising result is the high number of β -methyl and β -methylene groups (0.23 mole/100 g coal) without corresponding α -methylenes (only 0.02 mole/100 g). This could be explained only by the presence of tertiary butyl groups (note that Swann et al. (18) recovered 2,6-di-*t*-butyl-4-methylphenol from a similar brown coal by evacuation at 35°C). The material reported here as β -methyl occurred at $\delta = 1.2$ (Figure 3), which Heredy et al. (5) interpret as β -methylene groups in naphthenic rings. If they are right this would put quite a different complexion on this finding; however their interpretation differs from those of other authorities (e.g. Ref. (19)), and would require a simultaneous occurrence of α -methylene groups, which is not borne out by our Figure 3.

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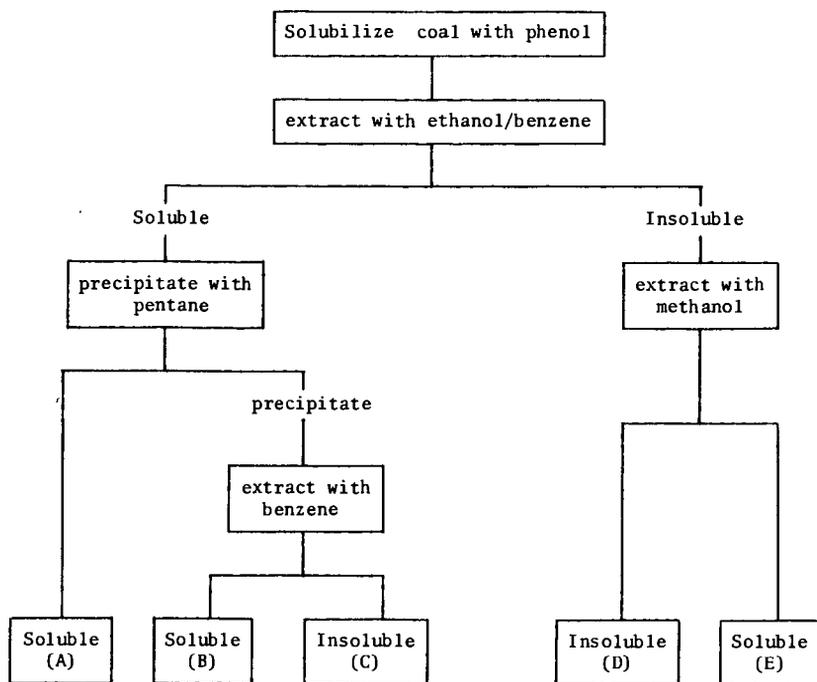


Figure 1: The fractionation scheme used to separate coal into four soluble fractions and an insoluble residue.

	fraction						Whole Coal
	A	B	C	D	E	Composite	
yield, g/100g original coal	28	66	78	28	2	202	100
composition, mass %							
C	76	74	69	71	56	72	63
H	7	6	5	4	6	5	5
O phenolic	4	4	3	6	ND	(4)	5
O carboxylic	0	1	3	2	ND	(2)	5
O carbonyl	ND	ND	ND	ND	ND	ND	3
O total	17	16	21	18	24	18	25
ash	ND	ND	2	3	ND	(1)	4
unaccounted	1	4	3	4	14	4	3

Table 1: Yields and compositions of the fractions. ND means not determined. Ash contents were not determined on fractions A, B and E, which were liquids. Functional group oxygen was not determined on fraction E because insufficient of it was available. The figures in brackets for the composition of the composite should be little affected.

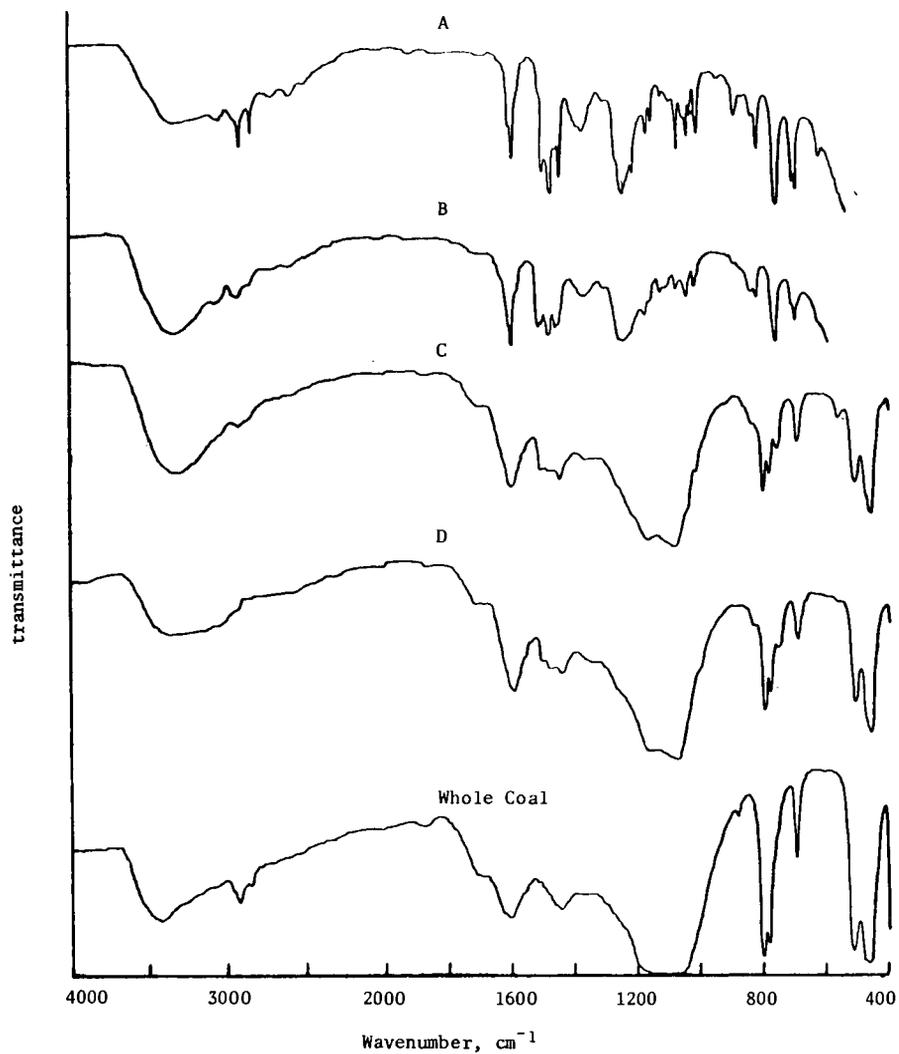


Figure 2: Infrared spectra for the original coal and the fractions A to D separated by the fractionation scheme shown in Figure 1. Fractions A and B, thin film; C, D and whole coal, KBr disc.

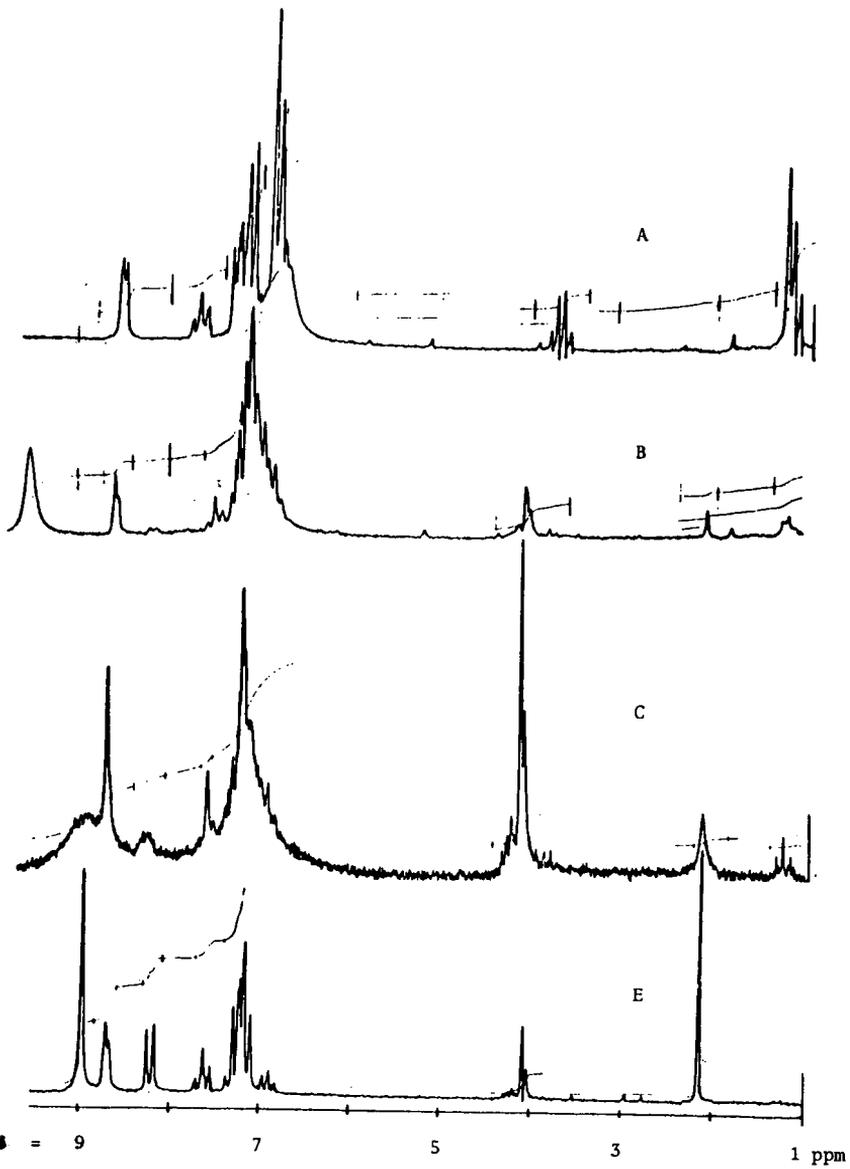


Figure 3: Nmr spectra for fractions A, B, C and E.
 A is dissolved in CDCl_3 ; B, C and E in pyridene $-d_5$.

δ ppm	proton type	fraction					Composite	Whole Coal
		A	B	C	D	E		
> 8.0	hydrogen bonded	7	17	19	(0)	27	(15)	(0)
8.7-8.0	triaromatic (5)	0	0	6	(10)	0	(3)	(0)
8.0-7.2	two-ring aromatic (5)	6	10	8	(48)	13	(63)	(46)
7.2-6.2	monoaromatic	63	58	44	(35)	37		
5.8-4.3	olefinic	1	0	0	(0)	0	(0)	(0)
4.3-3.4	methylene bridge	4	9	17	(trace)	9	(10)	(0)
3.4-3.2	acetylinic	0	0	0	(0)	trace	(0)	(0)
3.2-2.4	methin, methylene α	3	0	0	(0)	0	(3)	(11)
2.4-2.0	methyl α		1	4	(4)	15		
2.0-1.4	methylene β	3	1	0	(0)	0	(1)	(4)
1.4-1.0	methyl β	13	4	1	(4)	0	(5)	(39)
1.0-0.6	aliphatic γ	0	0	0	(0)	0	(0)	(3)

Table 2: Distribution of protons by type in the various fractions as measured from nmr spectra. Figures are % of the total protons in the particular fraction. Allowance has been made for residual protons in the deuterated solvents (CDCl_3 for A, pyridene- d_5 for others). The figures for fraction D and the whole coal are put in brackets to indicate that these samples were barely soluble and the spectra do not represent the whole material, only the small soluble part. α , β , γ refer to the positions of these protons with respect to aromatic rings.

fraction	C	H	O	ash	un- accounted	total
A	21	2	5	0	0	28
B	49	4	11	0	2	66
C	54	4	16	1	3	78
D	20	1	5	1	1	28
E	1	0	0	0	1	2
total original coal	145	11	37	2	7	202
added material	63	5	25	4	3	100
added phenol	82	6	12	-2	4	102
remainder	54	4	12	0	0	70
	28	2	0	-2	4	32

Table 3: Materials balances on material added to the coal by phenolation and fractionation. All figures are g/100 g of original dry coal.

	hydrogen bonded	aromatic			meth. bridge	aliphatic				total
		tri	di	mono		α CH ₂	α CH ₃	β CH ₂	β CH ₃	
A	0.14	0.00	0.12	1.23	0.08	(0.02	0.04)	0.06	0.25	1.94
B	0.67	0.00	0.40	2.30	0.36	0.00	0.04	0.04	0.16	3.97
C	0.74	0.23	0.31	1.72	0.66	0.00	0.16	0.00	0.04	3.86
D	(0.05)	(0.03	0.10	0.65)	(0.16	0.00	0.04	0.02	0.07)	1.12
E	0.03	0.00	0.02	0.04	0.01	0.00	0.02	0.00	0.00	0.12
total	1.63	0.26	0.95	5.94	1.27	0.02	0.30	0.12	0.52	11.01
phenol	0.74	-	-	3.01	-	-	-	-	-	3.75
benzene	-	-	-	2.46	-	-	-	-	-	2.46
coal	0.89	0.26	0.95	0.47	1.27	0.02	0.30	0.12	0.52	4.80
total	1.63	0.26	0.95	5.94	1.27	0.02	0.30	0.12	0.52	11.01

Table 4: Hydrogen present in various forms in fractions, original coal, combined phenol and benzene contaminant, g/100 g original dry coal (figures in brackets have involved making some assumptions about the distribution).

hydrogen type	atomic C/H	mass C/H	H (Table 4) g/100 g coal	C g/100 g coal
monoaromatic	6/2	36	0.47	17
two ring aromatic	10/4	30	0.95	28
triaromatic	14/4	39	0.26	10
α methylene	1/2	6	0.02	0
β methylene	1/2	6	0.12	1
methylene bridge	1/2	6	1.27	8
α methyl	1/3	4	0.30	1
β methyl	1/3	4	0.52	2
carboxyl	1/1	12		2
total				69

Table 5: Calculation of carbon in various structural forms, g/100 g dry coal.