

THE EFFECT OF COAL STRUCTURE ON THE
DISSOLUTION OF BROWN COAL IN TETRALIN

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INTRODUCTION

In much of the literature on coal dissolution in hydrogen donor systems the extent of the hydrogenation processes is assessed in terms of either the yield of liquid product or the conversion of coal to material soluble in a specified solvent, normally a solvent ineffective for coal. However, such approaches can not describe fundamental changes that occur within the coal material. To do this requires an experimental approach that allows coal conversion to be discussed in terms of the chemical changes that occur within the coal. This, in turn, requires a direct method of determining the structural features in coal.

In another paper presented at this Congress (1) we described the use of the acid-catalysed reaction of coal with phenol to study the structure of an Australian brown coal from Morwell, Victoria. The coal was solubilized by reacting it with phenol and then separated into four fractions, the first rich in aliphatics, the second rich in simple aromatics, the third rich in di-aromatics and polar groups, and the fourth rich in polyaromatics.

If these fractions are regarded as models of structural types within the coal, then reacting each fraction separately allows the role played by different chemical structures during the hydrogenation process to be examined. The effect that chemical type has on the coal hydrogenation reaction may then be studied directly and, in addition, the hydrogenation process may be represented by a composite process made up from the individual reactions of the different fractions.

The work now to be reported tested this hypothesis by reacting such fractions individually with tetralin, without any additions of catalyst or gaseous hydrogen. The untreated whole coal was also reacted to test whether phenol, present in the coal fractions as a result of the fractionation procedure, was having any significant effect on the reaction with the fractions.

EXPERIMENTAL

Experimental procedure

Morwell brown coal was solubilized by reacting with phenol, in the presence of para toluene sulfonic acid at 183°C and the reaction product was then separated into four fractions. The structural characteristics of the four fractions, as described in our other paper (1), are summarized in Table 1. As these characteristics are influenced to some extent by the presence of chemically combined phenol, the content of this in each fraction, as estimated in the present work and confirmed by reference to the literature (2,3) is also noted in Table 1.

Approximately 3g samples of the coal fractions and of the whole coal were then reacted separately with 25 - 30 ml of tetralin at 450°C in a type 316 stainless steel, sealed reactor, 13 cm high by 2 cm diameter. The reactor was heated by plunging it into a preheated fluidized sand bath; after 4 hours it was removed and quenched rapidly.

Table 1: Structural Characteristics of Coal Fractions Separated from Solubilized Brown Coal (1)

Fraction	Mass % Phenol	Structural Characteristics
A A liquid soluble in pentane	50	Mostly aliphatic material with some mono-aromatic parts broken off the coal by C-C cleavage. Apart from combined-phenol it has negligible polar material. It contains some free paraffinic material, but exists mostly as alkyl phenols and alkyl-aryl ethers
B A liquid insoluble in pentane but soluble in benzene	50	A mixture of alkyl side chains and aromatic fragments, predominantly di-aromatic. It exists either as alkyl phenols or as aromatic fragments attached to phenol by methylene bridges. It also contains other oxygen functional groups
C A pitch insoluble in benzene but soluble in benzene/ethanol azeotrope	25	Consists almost entirely of aromatic fragments attached to phenol by methylene bridges. These fragments are larger than in fraction B as they contain polyaromatic groups. It has more oxygen functional groups than B.
D A solid insoluble in ethanol/benzene azeotrope	10	Predominantly diaromatic and polynuclear perhaps combined through naphthenic bridges, with negligible aliphatic content

The temperature of the reaction mix was measured by a stainless steel-sheathed thermocouple inserted through the reactor cap. Heating up and cooling down times were small compared with the total reaction time. In all cases the free space in the reactor was flushed with nitrogen before sealing, and the reaction proceeded under a small initial nitrogen pressure.

After reaction, any solid residue was filtered off and the liquid product was separated by distillation into a bottoms product and a distillate that included unreacted tetralin and low-boiling products from both the coal and the tetralin. As tetralin breaks down under dissolution conditions to form mainly the tetralin isomer 1-methyl indan, naphthalene and alkyl benzenes (4) it was assumed that no compound with a higher boiling point than naphthalene was formed from the solvent, and the distillation to recover solvent was therefore continued until naphthalene stopped subliming. Some residual naphthalene remained in the bottoms product; its mass, as determined from nmr and elemental analysis, was subtracted from the mass of bottoms product recovered and included in the amount of distillate recovered. It was assumed that all naphthalene present came from the tetralin, not the coal. However, as the amount of tetralin reacted was 10 times the amount of coal this assumption appears reasonable.

Material formed from the coal which appears in the distillate is here called solvent-range material, following the terminology used by Whitehurst et al (5). Its mass was estimated by mass balance over the material recovered from the reaction as it could not be

separated from the large excess of tetralin and tetralin breakdown products also contained in the distillate. This procedure includes with the mass of solvent-range material any gases and water formed in the reaction.

Analysis techniques

The contents of the major breakdown products of tetralin (naphthalene and 1-methyl indan) present in the distillate were determined by gas-liquid chromatography using a Hewlett Packard Series 5750 Research Chromatograph with a 62m x 0.5mm diameter glass capillary SCOT column coated with non-polar SE 30 liquid phase (see Ref (4) for details).

Infrared spectra of the original coal, the original coal fractions, and all bottoms product and residues derived from them were measured on a Perkin Elmer 457 Grating Infrared Spectrophotometer. Liquid samples were analysed as a thin film or smear. Solid samples were prepared as a KBr disc containing approximately 0.3% by weight sample. The disc was prepared by grinding the KBr mixture for 2 minutes in a tungsten carbide TEMA grinding barrel, drying for 24 h in a vacuum desiccator over phosphorus pentoxide, then pressing into a disc at 10 tons force, at room temperature, but under vacuum.

Proton nmr spectra of fractions A, B and C and all bottoms products were recorded on a Varian HA 100nmr spectrometer using a solution of the sample dissolved in pyridine-d₅. Spectra were run at room temperature with tetra methyl silane (TMS) as an internal standard, with a sweep width of 0 to 1000 cps from TMS. Fraction D and the whole coal were only partly soluble in pyridine and it was therefore not possible to get representative spectra from them.

Carbon, hydron and oxygen contents of the original coal, original fractions, bottoms and residues were determined microanalytically by the CSIRO Microanalytical Service. Ash contents of samples were determined in a standard ashing oven (6). Phenolic and carboxylic oxygens were measured by the State Electricity Commission, using techniques developed by them for brown coals (7).

RESULTS

Recovery of coal material from the reaction with tetralin

The yields of the different products from the reactions of the various fractions with tetralin are summarized in Table 2.

Component	Fraction					Whole Coal				
	A		B		C		D		Composite	
	% of frac- tion	g/100g dry coal	% of frac- tion	g/100g dry coal	% of frac- tion	g/100g dry coal	% of frac- tion	g/100g dry coal	g/100g dry coal	
bottoms	47	13	56	37	37	29	30	9	88	46
residue	0	0	0	0	27	21	61	17	38	40
solvent range	53	15	44	29	36	28	9	2	74	14
total fraction	100	28	100	66	100	78	100	28	200	100

Table 2: Yields of original coal fractions and their products of reaction with tetralin, g/100g original dry coal.

These yields are also given on the basis of 100 g of original dry coal before fractionation. The bottom line of the table shows the mass of each fraction obtained from 100 g of dry coal. The masses include chemically combined phenol and residual solvent associated with the fraction as a result of the coal preparation and fractionation scheme. (For every 100g of original dry coal an additional 100g of extraneous material was present. Elemental balances and other evidence showed that about 70g of this was phenol and the remainder was excess solvent (benzene) never separated from the original fractions). Note that with fractions A and B no solid residue was obtained.

The amount of residue recovered from the other two fractions is almost the same as that recovered from the whole-coal reaction, suggesting that the combined phenol and residual solvent end up completely in the bottoms product and solvent-range product.

Composition of the coal products

Table 3 shows elemental compositions of the original coal fractions, the solid residues and the bottoms products, together with the portions of the total oxygen present as phenolic and carboxylic groups. Because of dilution with combined phenol and benzene solvent the composite analysis of the original fractions has higher carbon and lower oxygen contents than the original whole coal (note also the higher phenolic oxygen content).

As expected, both the bottoms products and the residues, when formed, have substantially higher carbon and lower oxygen contents than the original fractions, but whereas in the bottoms products the hydrogen contents have increased in the residues they are reduced. The bottoms products, including that from the whole coal, are remarkably similar in composition to each other. Likewise the residues are similar in composition to each other.

Figure 1 shows representative infrared spectra for the fractions before reaction and for bottoms products and residues. Although there were considerable differences in the spectra of the four original fractions the spectra obtained for their bottoms products were quite similar. The spectra show that significant amounts of aliphatic material (2850 and 2920 cm^{-1}) is present in the bottoms. An aromatic content is indicated by the aromatic C-H stretching vibration at 3030 cm^{-1} , but this is due in part, at least, to residual naphthalene and to phenol combined with the original fraction. Absorption at 3400 cm^{-1} (due to hydrogen bonded OH), present in both the coal fractions and the coal before reaction, has almost disappeared in the products from the coal fractions. The absorption does still occur in the bottoms product from the whole coal, although it is greatly reduced.

The spectra show that carbonyl groups (absorption at 1700 cm^{-1}) and the broad absorption in the region $1000 - 1200\text{ cm}^{-1}$ due to oxygen functional groups, both normally present in coal, have been destroyed, indicating, as would be expected, that functional groups are destroyed during the reaction. The absence of a large hydrogen-bonded OH peak at 3400 cm^{-1} indicates that the remaining oxygen absorption at 1250 cm^{-1} is not due to phenol. This absorption may be due to ether absorption, but this assignment is by no means certain, as normally ether absorption in this region is broad whereas the spectra show sharp absorption.

Aliphatic material still remains in the residue from the whole coal, but is virtually eliminated in the residue from fraction C. The absorption at 1170 cm^{-1} in the spectra of both residues may be due to benzofuran type structures (8), but it is felt that the strong absorption in the region $1000-1200\text{ cm}^{-1}$ may have been enhanced by the presence of silica, a major component of the ash content in this coal.

	fraction					Whole Coal
	A	B	C	D	composite	
<u>original fraction</u>						
C	76	74	69	71	72	63
H	7	6	5	4	5	5
O phenolic	8	8	7	11	8	5
O carbolic	0	3	5	4	4	5
O total	17	16	21	18	18	25
ash	-	-	2	3	2	4
unaccounted	1	4	3	4	3	3
<u>residue</u>						
C			89	86	88	85
H			4	4	4	4
O			3	3	3	5
ash			N.D.	7	N.D.	8
unaccounted			N.D.	0	N.D.	-2
<u>bottoms</u>						
C	86	83	86	83	85	85
H	7	7	7	7	7	8
O	7	10	7	10	8	7

Table 3: Composition of the fractions and their reaction products, mass %. N.D. means not determined (in the case of the residue from fraction C insufficient sample was available for an ash determination). Note that the method for backing out naphthalene from the bottoms involves normalizing the composition to $C + H + O = 100\%$.

Table 4 shows the proton ratios obtained from the nmr spectra on the original fractions A, B and C and all the bottoms products. The proton ratios for the bottoms products have been adjusted to eliminate absorptions due to residual naphthalene. Note that the original fractions contained hydrogen present from combined phenol. Most of this hydrogen appears as monoaromatic hydrogen, but when the phenol -OH is still intact, one proton will appear as OH hydrogen.

ratio of protons present in various forms to total protons, %	fraction								
	A		B		C		D	comp- osite	Whole Coal
	orig frac- tion	bottoms	orig frac- tion	bottoms	orig frac- tion	bottoms	bottoms	btms	bottoms
OH hydrogen	7	0	17	0	19	0	0	0	0
polyaromatic	0	0	0	0	6	0	0	0	0
diaromatic	6	0	10	0	8	0	0	0	0
monoaromatic	63	46	58	54	44	42	43	48	33
olefinic	1	0	0	0	0	0	0	0	0
methylene bridge	4	5	9	4	17	1	1	3	0
α methine and methylene	(3	15	0	17	0	21	21	18	24
α methyl	(8	1	8	4	11	11	9	8
β methylene	3	10	1	13	0	14	16	13	20
β methyl	13	12	4	5	1	10	7	8	12
γ aliphatic	0	4	0	0	0	0	0	1	4
Har/Hal	2.8	0.9	4.5	1.2	2.7	0.7	0.8	0.9	0.5

Table 4: Distribution of protons by type and overall aromatic/aliphatic proton ratios for the original fractions and bottoms products, as determined by proton nmr.

The nmr analyses of the bottoms products given in Table 4 show the material to have a large aliphatic content. The aromatic/aliphatic ratios of the fractions are higher than for the whole coal because of the presence of combined phenol and unseparated benzene solvent; reaction with teralin reduces these ratios considerably, presumably by transfer of much of this material to the solvent-range product, but some of it must remain in the bottoms as the aromatic/aliphatic ratio of the composite bottoms product from the fractions is higher than that from the whole coal. It was not possible to calculate the contribution that the diluents, excess solvent and combined phenol, made to the aromatic H, but the large monoaromatic content of the bottoms product must be due, in part, to these.

The remarkable feature in Table 4 is that after the spectra are adjusted for naphthalene, none of the bottoms products show the diaromatic or polyaromatic material which were present in the original materials. In the case of fractions C and D one might expect this material to end up in the solid residue, but in the reactions of fraction A and especially with fraction B, where a large diaromatic content existed before reaction, no residue was formed; thus suggesting that aromatic rings must be broken during the reaction. In addition, none of the OH hydrogen present in the original coal fractions appears in the bottoms product.

The solvent-range product was not separately analysed as it was not able to be separated from the recovered solvent in the distillate. However, GLC examination of the distillate indicated that the solvent-range product was derived mainly from aliphatic side chains

in the coal (9). Note that virtually no solvent-range product was derived from fraction D. Naphthalene and 1-methyl indan contents in the distillate were measured by GLC in order to calculate the amount of hydrogen transferred to the coal material from the solvent. It is beyond the scope of this paper to discuss in detail the results that were obtained, but it is interesting to compare the naphthalene content of the solvent recovered from the reactions between tetralin and the coal fractions with the naphthalene content of the solvent when tetralin is heated alone (Table 5). The large increase in naphthalene content when tetralin is reacted in the presence of coal material can only be explained by a reaction mechanism involving free radicals.

Fraction	A	B	C	D	Whole Coal	Tetralin heated alone at 450°C 4h.*
wt% naphthalene in recovered solvent	12.9	16.9	23.8	17.1	11.1	4.3

* From reference (4)

Table 5: Naphthalene content of recovered solvent from reaction for 4 h at 450°C.

DISCUSSION

The effect of phenol

Three types of phenol compounds have been identified in the fractions derived from the product of the phenolation reaction (1,2): alkyl phenols and alkyl-aryl ethers, both formed by combining phenol with alkyl side chains cleaved from the coal molecule, and compounds made up of aromatic fragments attached to phenol by a methylene bridge, formed by cleaving aromatic-aliphatic linkages in the coal and exchanging the aromatic structures with phenol. For the hydrogenation of coal fractions separated from the phenolated product to simulate the hydrogenation of the whole coal the removal of coal fragments from the coal molecule during the phenolation reaction must involve similar C-C cleavage processes as would occur by the thermal breakdown of coal during a hydrogenation reaction. For example, one would expect alkyl side chains to be cleaved off under hydrogenation conditions, in much the same way as has been seen to occur in the phenolation reaction. Moreover other workers have shown that the molecular weights of coal fragments from the phenolation reaction are in the region 300 - 1000 (3) which is the same molecular weight range as for products from a coal dissolution reaction (4). Thus, both processes, one involving C-C cleavage by phenolation, the other by thermal breakdown, produce coal fragments of the same size. The hydrogenation of the coal fragments can therefore be considered to simulate the reaction of the whole coal, providing appropriate allowance is made for the movement of the phenol groups themselves.

The nature of the products

The composition of the bottoms products from the various reactions were all similar, regardless of the original material. Elemental composition ranged from 83.3% to 86.4% carbon, from 6.6% to 7.2% hydrogen, and from 6.7% to 10.1% oxygen. Infrared and nmr analysis show the material to be largely aliphatic, with hydrogen bonding in the product almost destroyed. Similarly, the residue in a carbon-rich material with very little oxygen were all similar. Its elemental composition ranged from 86.1% to 89.3% carbon, 3.8% to 4.2% hydrogen, and 2.6% to 2.9% oxygen. The material is mainly

aromatic with perhaps some benzofuran type structures, suggesting that condensation reactions may be involved in its formation. Most importantly, a solid residue was shown to form only from fractions C and D. As fraction C was completely soluble in tetralin and the reactor feed before reaction was therefore liquid, the solid material present after reaction was, in the case of fraction C at least, not present in the original coal and must therefore be a product of the reaction.

Although we have followed the usual nomenclature in calling this solid a "residue", such nomenclature is misleading in terms of reaction mechanism. Presumably some of the "residue" formed in the reaction of the whole coal is genuine unreacted residue and some is a reaction product, and one of the aims of liquefaction research must be to learn how to minimize the formation of such solid products (10).

The mechanism of coal dissolution

The classic view of the mechanism for the reaction between coal and a hydrogen-donor solvent involves the thermal breakdown of the single carbon-carbon bonds within the coal to produce reactive fragments in the form of free radicals which are then stabilized by hydrogen transferred from the solvent or elsewhere in the coal. If insufficient hydrogen is available the aromatic fragments can polymerize yielding chars or coke. Another view of coal dissolution, but much less widely held, is that oil is produced from coal via an asphaltene intermediate (11).

A most striking result from the work described above is that the composition of the bottoms product from the dissolution reaction did not depend on the chemical structure of the original coal material; only their relative quantities differed. This supports the view of a free-radical mechanism rather than an asphaltene-intermediate mechanism. The greatly increased formation of naphthalene during the reaction further supports this view.

Perhaps the greatest difference between the present work and more conventional work on higher-rank coals is the important role of the functional-group oxygen. The importance of oxygen groups is stressed, as the predominant process during the dissolution reaction was the destruction of functional groups within the coal. The role of oxygen in the reaction was not clearly defined by the present work, but quinone groups, for example, are thought to play a role in the liquefaction of high-oxygen-content coals (12), and their effectiveness in the free radical abstraction of hydrogen from hydrogen-donor compounds is well known (13).

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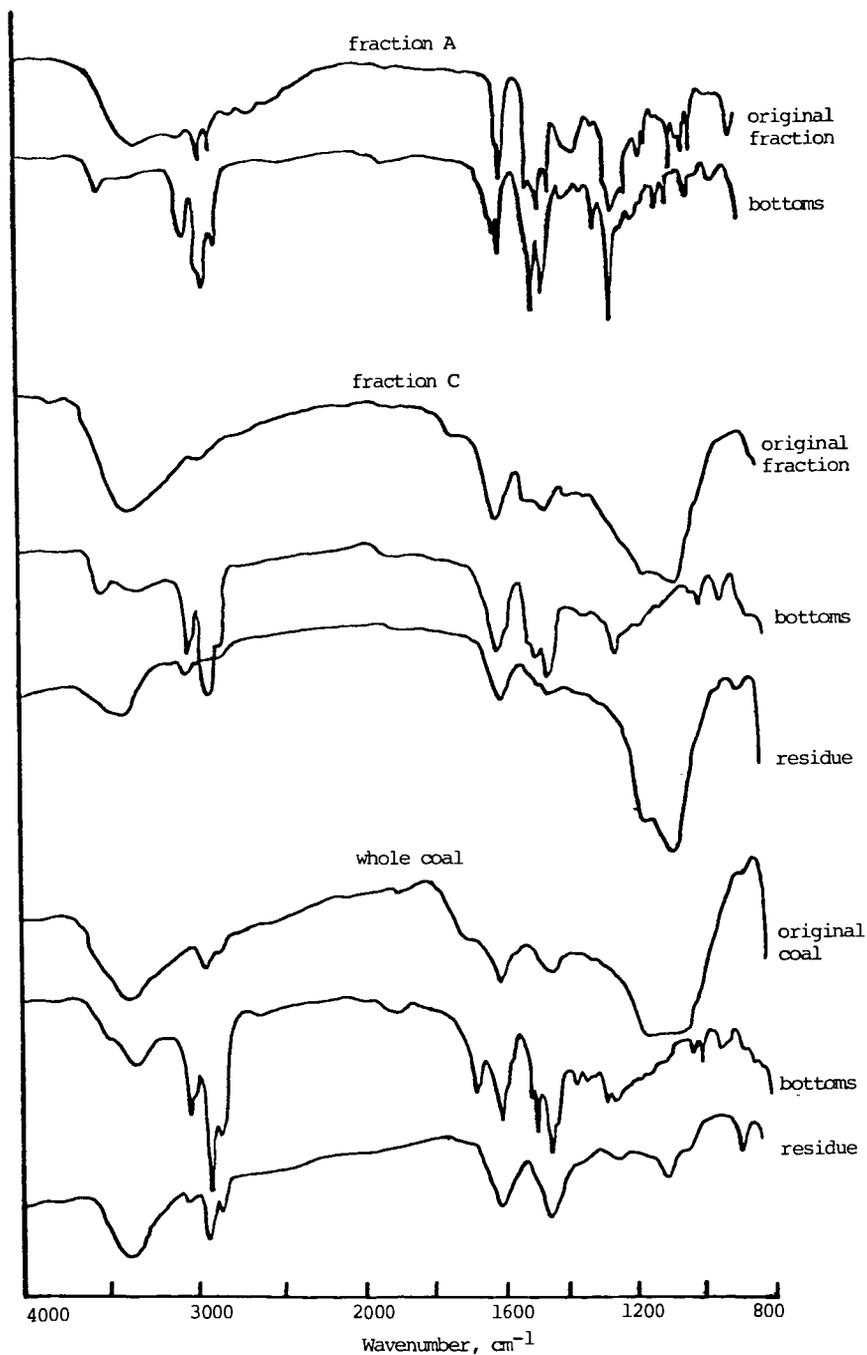


Figure 1: Infrared spectra for typical fractions and their products