***The mobile phase in coals: Its
nature and modes of release: Part
2, Efforts to better define the
nature and magnitude of the
mobile phase: Final report***

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THE MOBILE PHASE IN COALS: ITS NATURE AND MODES OF RELEASE

P.H. Given, Principal Investigator

Final Report - Part 2

**EFFORTS TO BETTER DEFINE THE NATURE AND
MAGNITUDE OF THE MOBILE PHASE**

by

P.H. Given

Date Published April 1987

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FOREWARD

As originally conceived, this project has two major aspects. The objective of one was to strive to better understand the nature of the occluded or clathrated material in coals, which is characterized by the high rotational mobility of the protons. The other was more concerned with the relevance of this material in liquefaction processes and concentrated on catalytic hydrogenation without a donor solvent. It had been intended that the first two parts of this Final Report would be on the second aspect named above, and this is so stated. However, this Part, dealing with the first-named aspect, was ready for publication some time before the second report on the "dry" hydrogenation studies was expected, and so is published out of the order originally planned.

ABSTRACT

This project was based partly on two propositions: that coal should be regarded as a two-component system, consisting of a complex mixture of relatively small molecules filling interstices in a noncrystalline macromolecular network, some of them physically trapped and not extractable by ordinary solvents; and that the nature, mode and conditions of release will have an important influence on the kinetics and mechanism of liquefaction. Pulsed free-induction-decay ^1H NMR studies of 23 coals of different rank and from various basins showed that there are three distinct populations of protons in coals having quite different degrees of rotational mobility. Only about one-half of the molecules containing highly mobile hydrogen is extracted in long exposure to pyridine at room temperature, and they are more aliphatic than the molecules remaining trapped. The concept of a trapped mobile phase is confirmed, but it is considerably more complex than had been realized.

Several liquefaction conditions and many extracting solvents were used in attempts to set up conditions such that, as the conditions became more severe, progressively more hexane-solubles, analyzable by GC/MS, would be released. It was hoped to identify a threshold beyond which trapped mobile phase molecules would become evident. In fact, there proved to be little correlation between the yields of extracts and of that part of an extract that was soluble in hexane. Use of indoline as a donor solvent gave high conversion to THF-soluble products, but only a small fraction was soluble in hexane. The idea of a definite threshold is probably wrong.

A set of 10 hexane-soluble fractions, all obtained under various conditions from the same coal (a sample of Herrin No. 6 seam, Illinois), were subjected to analysis by tandem mass spectrometry (MS/MS). The yields ranged from 0.6 to 16% of the organic matter in the coal. Prominent constituents of all of the fractions were homologous series of alkyl aromatic hydrocarbons, phenols and heterocycles, notably alkylacenaphthenes. The alkyl chains were either unbranched or lightly branched. There was a striking similarity in the spectra of all of the fractions irrespective of yield. Evidently a given set of compounds can be partially released under a wide range of conditions. That is, the ease with which a certain homologous series can be released from a coal is highly variable. Thus the data are consistent with the concept of a mobile phase some components of which are trapped in cavities with entrances and exits of restricted size. Release of the various physically held species and the fragments from thermal breakdown of the structure will certainly present a very complex system for kinetic modeling.

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1. Evolution of the Mobile Phase Concept

(i) Introduction

It is widely conceded that coals behave, at least qualitatively, like highly cross-linked rubbery polymers, and so it is inferred that coal can usefully be described as containing a noncrystalline cross-linked macromolecular network (Green et al., 1982; Green and Larsen, 1984; Given, 1984). Such a network is likely to contain cavities due to imperfections of packing, in which relatively small molecules could be held. Jurkiewicz et al. (1982) and Marzec et al. (1983) performed pulsed, free-induction-decay, ^1H NMR experiments on a few coals previously swollen with various fully deuterated solvents, including pyridine- d_5 . The results were interpreted to mean that the coals contained two populations of protons of quite different rotational mobility. It was further proposed that the highly mobile protons were in relatively small molecules residing in cavities in the macromolecular network with some freedom to rotate, at least once any hydrogen-bonds linking them to the network had been broken by introduction of a strongly bonding solvent. The relatively small molecules appeared to represent a surprisingly high fraction by weight of the total organic matter. This two-component view of coal structure was advocated by Given (1984).

This view also constituted the starting point for the proposal that led to the funding of the project reported here. If much of the coal consists of trapped, rotating molecules, then a substantial part of the process of liquefaction could involve the release of

liquid by activated diffusion rather than chemical reaction, with important consequences for concepts of mechanisms and kinetics. This could account for the observations of Szladow and Given (1981) and Youtcheff and Given (1982) that the apparent activation energy of the interaction of a coal with tetralin increases with the degree of conversion.

(ii) The Mobile Phase Concept Disputed

In fact, the interpretation of the ^1H nmr studies by Marzec and her associates was disputed, and a "debate in print" was organized and published in FUEL (Given, Marzec, Barton, Lynch and Gerstein, 1986). The debate led to the conclusion that while Marzec's interpretation could be correct, it was not necessarily so if one considers only the nmr evidence. If, however, published work, using other approaches, is taken into account, then it seems that Marzec's view of the quantity of trapped molecules could well be justified. Thus, Rybicka (1959) claimed that 50-60% of certain bituminous coals was extracted by certain solvents (ethanolamine, a mixture of dimethylformamide and methylcyclohexanone; alternatively, a sequence of 5-6 solvents of increasing polarity applied successively). van Bodegam et al. (1984, 1985) more recently report very large amounts of extract (which in some cases they attributed to cleavage reactions by the solvent). Presumably extractable material consists largely of relatively small molecules that had been occluded in the network.

Youtcheff et al. (1983) reported that a much greater yield of alkanes (6-8x) was obtained by liquefaction of three coals than by

extraction with a benzene/ethanol mixture. Mudamburi and Given (1985a, 1985b) found homologous series of n. alkylaromatics in liquefaction products but not solvent extracts of the same coals. In all these cases the extra material released by liquefaction was believed to have been physically trapped within the macromolecular network.

Even so, the situation with regard to the mobile or molecular phase was thought to be unsatisfactory because so few coals had been studied by the free-induction-decay ^1H NMR technique.

(iii) New NMR Studies

Consequently, with support from this project and from the Penn State Cooperative Program in Coal Research, 23 U.S. coals were selected to cover a wide range of rank, sulfur content and geological history. After drying, these were weighed out in a glove box under nitrogen and samples placed in glass n.m.r. tubes freed from exchangeable ^1H . Pyridine- d_5 was then added, and the tube sealed while the contents were frozen at -78°C . The tubes were then subjected to pulsed free-induction-decay ^1H N.M.R. in the Ames Laboratory of Iowa State University by Dr. Bernard Gerstein, for whose cooperation we are grateful.

This study of 23 coals has now been published (Kamienski et al., 1987). What purported to be a summary of the principal results has appeared in a Quarterly Progress Report on this project (Given and Derbyshire, 1985). However, the interpretation of the data has been extensively revised since then, and so the complete and recalculated set of figures, as they appear in the published paper,

is repeated here in Table 1. The interpretation turns out to be quite complicated.

If coals have not been swollen with pyridine-d₅, two populations of protons are seen, and at least 80% of the protons have very low rotational mobility, such as are commonly found with strongly bound molecular organic solids.

Barton et al. (1984) allowed quite short exposures (a few hours at most) to pyridine before making the n.m.r. measurements, whereas Jurkiewicz et al. (1982) allowed several days soaking. On the other hand, Kamienski et al. (1987) allowed 6 months or more, so that systems had presumably come to equilibrium. After the pyridine had been imbibed, three distinct relaxation times, rather than two, were observed. The protons of lowest mobility showed decay curves of Gaussian shape, had relaxation times of 12-15 μ sec, and accounted for about 40% of the protons in the coal (except for the two coals of highest rank: see Table 1). They must represent those hydrogen atoms in the macromolecular network that are close to cross-links.

The amount seen of the second population greatly increases on imbibition of pyridine, from 8-20% up to 30-35%. No doubt it is breaking of hydrogen bonds that permits the extra mobility. These protons are free to move anisotropically, and have relaxation times of about 35 μ sec; their decay curve is Lorentzian in shape. Kamienski et al. (1987) point out that the components to which these protons are attached are not necessarily extractable even in principle. They could be associated with hydrocarbon chains or methyl groups in the macromolecular framework, or with relatively large molecular fragments trapped in voids, as originally suggested

TABLE 1

Transverse Relaxation Times for coals After Inbibition of Pyridine-d₅

Sample Number	Seam, State, Prov. *	ASTM Rank	% C (dmmf)	T2 [μsec]			% of component		
				Fast	Medium	Slow	Fast	Medium	Slow
833	Fort Union, Mont., Gt. Pl.	L	70.0	13.6	34.3	680	47	37	16
1037	Unnamed, Tex., Gulf	subb c	73.1	13.1	32.7	540	40	31	29
1005	Canyon A, Wyo., Gt. Pl.	subb c	73.4	13.6	32.8	610	43	35	22
788	Lower, Tex., Gulf	subb c	73.5	13.4	36.0	490	41	32	27
626	Darco Tex., Gulf	L	74.9	13.8	35.2	620	45	35	20
844	Hanna 5, Wyo., R.M.	HVC	75.8	14.0	37.5	500	42	35	23
846	Brooks, Wyo., R.M.	HVC	77.8	14.4	36.6	640	43	34	23
1082	Ky. No. 11, Ky. Int.	HVC	78.6	14.0	36.0	330	43	20	28
938	Lower Blue, N.M., R.M.	HVC	78.7	14.4	38.2	510	39	33	28
684	Indiana No. 6, Ind., Int.	HVC	79.1	14.0	39.5	500	43	27	30
850	D., Colo., R.M.	HCV	79.6	14.0	33.2	580	40	32	28
1281	Lower Kitt., Ohio, East.	HVB	80.8	13.2	31.7	680	44	30	26
643	Ky. No. 6, Ky. Int.	HBV	81.1	13.8	4.2	620	43	29	28
857	Juanita C, Colo., R.M.	HVB	81.1	14.8	36.2	580	43	31	26
1289	L. Kitt., Ohio, East.	HVB	81.2	13.6	32.2	620	43	29	28
1098	Ill. No. 6, Ill., Int.	HVA	83.0	13.9	35.6	550	42	28	30
1116	U. Sunnyside, Utah, R.M.	HVA	83.7	13.6	33.7	520	43	28	29
1266	L. Kitt., Ohio, East.	HVA	83.7	13.5	31.2	680	44	28	28
1102	Pittsburgh, PA, East.	HVA	85.4	13.5	28.5	680	41	27	32
1336	L. Kitt., PA, East.	HVB	87.3	13.4	29.3	620	44	25	31
410	U. Hartshorne, Okla., Int.	LV	89.3	12.5	19.3	720	72	19	9
1197	L. Kitt., PA, East.	LV	91.0	12.2	2.3	950	89	6	5

* Provinces in which coals were found are indicated as follows: East = Eastern; Int. = Interior, R.M. = Rocky Mountain; Gt. Pl. = Great Plains; Gulf = Gulf.

for the "mobile phase" by Jurkiewicz et al. (1982). Long chain alkyl groups anchored to the network at one end of the chain and free to rotate in a cavity of restricted size, and segments of the macromolecular network remote from cross-links, are further possibilities (Given and Marzec, 1987).

A plot of the percentage of intermediate protons against carbon content is shown in Figure 1. The straight line put through the points is a least squares regression, for which the variance explained (R^2) is 70.7%; the points for the two coals of highest carbon content were omitted from the calculations. The equation of the line is:

$$(\% \text{ H}) = 78.6 - 0.604 (\% \text{ C})$$

The curved line represents a quadratic regression whose equation is:

$$(\% \text{ H}) = -356 + 10.6(\% \text{ C}) - 0.072 (\% \text{ C})^2$$

All points are included in this second regression, and the variance explained is 83.4%. Thus there seems to be a trend of decreasing content of intermediate protons, which is real but small until the carbon content is above about 85%.*

Thirdly, after imbibition of pyridine, 25-30% of the protons show much greater relaxation times (500-700 μ sec); the decay curve is of mixed Lorentzian-Gaussian shape. There may be a small trend of increasing total content of these isotropically highly mobile

*The authors are indebted to Mr. David Click for these calculations.

Figure 1. VARIATION WITH RANK OF PROTONS WITH INTERMEDIATE ROTATIONAL MOBILITY.
Lines represent linear and quadratic regressions: see text.

protons with rank, but the variance explained by a linear regression that omits the two coals of highest rank is only 51.7%. If these coals and the lowest rank lignite are omitted, the mean content is 27.5% with a standard deviation of 3.5%.

There are further complexities. Roughly one-half of the protons of high rotational mobility are attached to soluble molecules that are extracted by pyridine, and the other half remains trapped inside the solid coal. Thus, the percentage of the protons that appear highly mobile in these experiments approach the numbers indicated by Marzec and her associates considerably more closely than the data previously presented in a Quarterly Report, and about one-half of them seems to be present in molecules trapped in the network but quite free to rotate. Confirmation of this latter point comes from the observation of Kamienski et al. (1987) that all of the highly mobile protons are mobile enough for fine structure to be resolved in the ^1H n.m.r. spectra. From the spectra, it is clear that the extracted material is considerably more aliphatic than that also mobile but still retained in the coal.

(iv) Conclusions

We feel that these new results represent important contributions to ideas of coal structure. What strike us as highly significant points are the following:

1. There are indeed components of widely differing rotational mobility in coals, but the nature of the "mobile phase" is much more

complex than previously thought. Thus heterogeneity of coals is once more emphasized, very strongly, and from a new point of view.

2. The new data need to be built into concepts of the chemical structure of coals, but the surprisingly small variation of protons of differing levels of rotational mobility with rank makes it difficult to see how to do this.

3. It is likely that the liquefaction of coals does consist to a very significant extent of the release of relatively small occluded molecules.

4. The idea that 35-55% of a coal may be independent of the macromolecular network to the extent that it is extractable by certain specific solvents urgently needs testing by extractability experiments with a wider selection of coals than has been studied heretofore.

2. Solvent Extraction and Liquefaction Experiments

(i) Original Strategy

We started with the concept that any bituminous coal is a two-component system, consisting of an insoluble macromolecular network and a complex mixture of soluble, mostly fairly small, molecules, some of which are not extractable under the usual conditions because occluded within cavities having entrances and exits of restricted size. At higher temperatures, where larger activation energies could be available, the trapped material could escape. On the basis of previous observations (Youtcheff et al., 1983; Mudamburi and Given, 1985a, 1985b; Wood et al., 1984), we

believed that high molecular weight linear and cyclic alkanes and various homologous series of long-chain n. alkylaromatic compounds could serve as valid markers for the onset of the release of the trapped mobile components. In order to detect these substances, we wanted products analyzable by GC/MS using single ion monitoring. We assumed that solubility in hexane could usefully define analyzable material.

The plan was, therefore, to extract a suitable selection of coals with some of the common solvents at their atmospheric pressure boiling points, and then increase progressively the severity of the extraction conditions until the mobile phase markers were detected and then freely released. The later stages of the progression would employ liquefaction conditions. As it turned out, these ideas proved somewhat naive.

(ii) Experimental

The coals selected are listed in Tables 2 and 3 with some of their characteristics. In fact, PSOC 1098 was used in the bulk of the work.

Soxhlet extractions were carried out for 72 h. Liquefaction experiments were performed in the tubing bomb reactors previously described (Szladow and Given, 1981; Yarzab et al., 1980). Extractions at elevated pressures were also carried out in the liquefaction reactors. Liquefaction yields were defined in terms of material soluble in ethyl acetate under Soxhlet conditions.

A small point of disagreement on procedure between the two authors of this report should be noted. One (F.J.D.) believed that

TABLE 2
Characteristics of Coals Used

PSOC* No.	Seam, County, State, Province	ASTM Rank Class	% dmmf						% dry coal			
			Vitr.	C	H	N	S	O **	MM	S	S _p	S _{SO₄}
776	L. Kittanning, Hocking, Ohio, East.	HVB	87	79.0	5.7	1.5	1.7	12.1	14.5	6.1	4.4	0.33
1361P	U. Freeport, Lawrence, Pa, Eastern	HVA	79	84.2	5.7	1.9	1.0	7.0	10.5	2.1	1.1	0.1
1098	Ill. No. 6, Saline, Ill., Interior	HVA	90	83.0	5.6	1.5	1.9	7.9	19.0	4.0	2.2	0.27
1368P	Weir-Pittsburg, Henry, Missouri, Int.	HVA	84	83.9	5.6	1.9	3.9	4.6	23.7	10.2	7.3	0.0
1115	Blind Canyon, Emery, Utah, Rocky Mt.	HVA	87	82.0	5.8	1.4	0.5	20.4	6.2	0.6	0.1	0.01
1390P	Colorado B, Gunnison, Colo., Rocky Mt.	HVA	92	82.8	5.4	1.7	0.6	9.4	8.2	0.6	0.01	0.0
1403P	Anderson, Campbell, Wyo., N. Great Plains	sbbB	88	73.0	4.5	1.2	0.9	20.4	11.9	1.2	0.3	0.05

*The letter "P" after the sample number indicates that the sample was from the premium set, subject to special handling.

**By difference.

TABLE 3

Characteristics of Second Set of Coals Used in Extraction Studies

PSOC No.	Seam, State	% by vol.			% dry		% dmmf		
		<u>Vitr.</u>	<u>Lipt.</u>	<u>Inert.</u>	<u>MM</u>	<u>S</u>	<u>C</u>	<u>H</u>	<u>O (diff.)</u>
521	Rock Springs No. 7, Wyo.	94	1	5	4.6	0.78	79.0	5.2	13.8
592	Ill. No. 5, Ill.	52	16	32*	9.7	2.1	82.7	5.1	8.8
1082	Ky. No. 11, Ky.	90	2	8	19.9	6.3	78.6	5.4	11.5

*Includes 17% semifusinite.

drying a coal before liquefying or extracting it could well have a deleterious effect on the sample and degrade the behavior; better then to avoid the risk and not pre-dry (in the solvent-free liquefaction). The other author (P.H.G.) felt that the behavior of coals is complex enough without the added complication of possible interference by water; all coals discussed in this section of the report were dried at 100°C in vacuo in drying pistols overnight before use.

(iii) Some Analytical Considerations

Little solvent was retained by the products of extraction with benzene/ethanol or chloroform/acetone/methanol mixtures and material balances were good to about 1%. With pyridine and other powerful solvents, material balances were poor, as many others have found. Where it was necessary to correct yields for solvent retention, the excess weight was assigned to extract and insoluble residue in proportion to their yields. It was also assumed that retained pyridine was released during subsequent liquefaction and is removed in the distillation of the naphthalene and excess tetralin.

In a number of liquefaction experiments in the equipment used here, Neill (1984) collected and analyzed gaseous products. The sum, oil + asphaltene + gases, was usually in the range 93-96%. Presumably some volatile products are lost during the evaporation of the ethyl acetate and/or in the vacuum distillation of tetralin and naphthalene. In general, gases were not analyzed in the present series of experiments, and so stated "yields of liquids + gases" will include the losses. If the sum of (asphaltenes +

hexane-solubles) is deducted from total (liquids + gases), the difference will represent gases + losses; figures for this difference are shown.

The very reasonable assumption was made that, during, liquefaction, all pyrite was reduced to pyrrhotite of composition $\text{FeS}_{1.1}$, and the associated loss in weight by mineral matter was allowed for calculating yields.

(iv) Results of Liquefaction Experiments in Tetralin

If a substantial part of the liquefaction process consists of the activated diffusion of trapped molecules into the donor solvent, one might expect that prior extraction with such solvents as pyridine would decrease liquefaction yields while leaving the sum of extraction + liquefaction yields equal to the liquefaction yield of the unextracted coal. On the other hand, prior extraction with pyridine might swell and open up the coal structure, rendering it more accessible to donor solvent and hydrogen, and to product removal. Thus the experiment would be ambiguous, but even so, was thought worth performing. The results are collected in Table 4.

The most interesting observation is that the sum of (oil + asphaltene + solvent extracts) when the coal was pre-extracted is not very different from the sum (oil + asphaltene) in the nonextracted case. The oil and asphaltene yields are diminished by prior extraction, but (gases + losses) are increased. This seems to suggest that prior extraction promotes the formation of either gases or volatile organic compounds; a suggestion that is not in accord with either of the above expectations.

TABLE 4

Liquefaction of PSOC 1098 With and Without Prior Extraction

Liquefaction in tetralin; 425°C for 30 min; 1000 psi (cold) of H₂

Yields from 100 gm. coal organic matter

	<u>Not solvent- extracted</u>	<u>Prior Extraction with bz./EtOH and pyridine</u>
Total extracts	--	14.4 gm
Wt. after extraction	100 gm	87.2
Total liqn. + gases + losses	63.7	57.7
Asphaltenes	33.2	24.8
Hex. solubles	16.7	12.3
Σ (hex. sol. + insol.)	49.9	37.2
Σ (extrs. + hex. sol. + hex. insol.)	49.9	48.1
gases + losses (by diff.)	13.8	19.8

N.B. Data corrected as explained in text.

TABLE 5

Liquefaction of PSOC 1098 at Low Temperature

Liquefaction in tetralin at 350°C for 120 min.; 1000 psi (cold) H₂

Percent dmmf

<u>Total conversion to liqn. + gases</u>	<u>asphaltenes</u>	<u>Hex. sols.</u>	<u>Σ</u>	<u>Gases + losses (diff.)</u>
35.2	24.6	7.5	32.1	3.1

Note: Σ = sum of asphaltenes and hexane-solubles.

A further liquefaction run (without prior extraction) was performed with the same coal at 350°C, with results shown in Table 5. The most significant differences from the 425°C run are the lower yield of hexane-solubles and the drastically reduced figure for gases + losses. As will be discussed later, products from these liquefaction experiments and from the solvent extractions still to be described were analyzed by tandem MS.

Liquefaction experiments and benzene/ethanol extractions were performed on the other coals of the sample set, with results shown in Table 6. As would be expected from previous work, two of the highest total yields were found with coals of very high sulfur content (PSOC 776 and 1368P). PSOC 1098 (from Illinois) has a high sulfur content but gave a smaller total yield; however, the sum of asphaltene + hexane-solubles was nearly equal to that from the Ohio and Missouri coals (PSOC 776 and 1368P). The Missouri coal was notable also in giving a high yield on extraction with the benzene/ethanol mixture.

The anomaly in this set is the Wyoming coal, PSOC 1403P. It is the coal of lowest rank in this set. Previous results indicate that the low-sulfur, relatively low rank coals of the Western U.S. are likely to give poor liquefaction yields. However, inspection of the data show that the yields of asphaltenes and hexane-solubles are indeed small, and it is the figure for gases + losses that is specially high. This suggests that this subbituminous coal gives particularly high yields of volatile liquids. The reasonably good material balances obtained in the solvent extraction of the other coals suggests that the yield calculated by difference for the

TABLE 6

Yields from Liquefaction of a Set of Coals
(coals arranged by province; data for PSOC 1098 repeated for comparison)

<u>Sample PSOC No.</u>	<u>State</u>	<u>Total liqs. + gases</u>	<u>Asphaltenes</u>	<u>Hexane- sol.</u>	Σ^*	<u>Gases + losses</u>	<u>Ratio/asph./ hex.-sol.</u>
776	Ohio	73.0	36.9	14.5	51.4	21.6	2.5
1361P	Pa.	61.2	34.0	12.2	46.2	15.0	2.8
1098	Ill.	63.7	33.2	16.7	49.9	13.8	2.0
1368P	Missouri	72.0	39.6	11.8	51.4	24.3	3.4
1115	Utah	62.9	28.6	10.7	39.3	23.6	2.7
1390P	Colo.	60.6	31.5	13.2	44.7	15.9	2.4
1403P	Wyo.	73.0	24.2	10.8	35.0	38.0	2.2

* Σ = sum of asphaltenes + hexane-solubles

Wyoming coal should be close to the truth; it is in fact very high, consistently with the inferred high yield of volatile liquids. The mobile phase in this coal seems relatively highly accessible.

(v) Liquefaction in Indoline

Padrick and Lockwood (1984) have reported that indoline (dihydroindole) is a more effective donor solvent than tetralin for a sample of coal from the Wyodak seam, particularly at lower temperatures. It seemed that this solvent might be specially useful to us in defining the mildest conditions under which the trapped part of the mobile phase can be released.

In the first experiments (PSOC 1098, 375°C, 10 min, 1000 psi H₂, cold), attempts to rinse out the products from the reactor with our usual solvent, ethyl acetate, caused some precipitation. This problem was not encountered if, following Padrick and Lockwood, THF was used as solvent, and conversion was then 79.1%.

Further experiments were made with PSOC 1098 (Soxhlet, 24 h) and two of the coals listed in Table 3. PSOC 521 and 592 were selected because Mudamburi and Given (1985b) had previously found them to yield homologous series of n. alkylaromatics on liquefaction, which were thought to be useful markers for the appearance of the trapped part of the mobile phase. THF was successfully used for recovering the products, with the following dmmf values of total conversion to THF-solubles + gases + losses:

PSOC 1098,	79.2%
521,	97.0%
592,	19.2%

These values were, of course, highly satisfactory. However, attempts to get a major part of the products into solution in milder solvents were unsuccessful. Evaporation of the THF from the PSOC 1098 product, extraction of the residue with toluene and filtration showed that the material insoluble in toluene represented 55.4% of the organic matter of the coal. Addition of much hexane to the toluene-solubles caused deposition of a tar on the walls of the vessel and separation of two liquid layers.

In a further experiment with products from PSOC 1098, THF was removed and toluene extraction followed by filtration were performed as before. Toluene was next evaporated from the soluble fraction, and then indoline was removed as completely as possible by vacuum distillation in a spinning band micro-column. Attempts to further work-up the involatile residue gave little hexane-soluble material, and indicated that much indoline remained. Poor material balances indicated that some of the indoline evidently decomposed to volatile products during the liquefaction. Thus the use of indoline does indeed, with several coals, lead to high conversions to THF-soluble material at low temperatures, but the major part of the product is soluble only in powerful solvents, work-up is difficult, and very little of the product is likely to be analyzable by GC/MS. We have not further pursued its use.

(vi) Solvent Extraction

It was assumed (without experimental test) that a greater yield of hexane-solubles would be obtained by first extracting a coal with

a more powerful solvent, and then extracting the extract with hexane, than by extracting the coal directly with hexane (which has little or no swelling action).

The most extensively used solvent was the azeotropic mixture of benzene and ethanol (70:30 by weight). The results are collected in Table 7. The extractions at elevated temperatures and pressures were performed in the tubing bombs used as liquefaction reactors, with agitation as for liquefaction. It was hoped that extractions at a series of increased temperatures and extraction times would provide a progressively increasing amount of extract and mobile phase (molecular component). In fact, the yields of extract with benzene/ethanol vary little with conditions or even with which of the three coals was selected (no explanation for the large loss with PSOC 521 at 200°C was found). Yet with the Illinois coal, PSOC 1098, the yield of hexane-solubles did increase with severity of conditions except for the run at 200°C for 96 h.

The existence of an azeotrope formed by a mixture of benzene and ethanol implies some kind of interaction between the components which is greatest at the composition of the azeotrope. This interaction might have something to do with the effectiveness of the mixture as a solvent for coal. At 427 psi pressure, the azeotrope contains 85% ethanol by weight and boils at 200°C (Horsley and Tamplin, 1962). At this temperature the mixture having the atmospheric pressure composition (31.7% ethanol) would still be partly liquid: the critical temperature of benzene is 289° and of ethanol 243°, while the critical temperature of a mixture containing 31.7% ethanol is 258°C (Hicks and Young, 1975). An extraction of

TABLE 7

Extractions with Benzene/Ethanol and Hexane

PSOC No.	Conditions	% of dmmf coal					
		extract	residue	Σ_1^{**}	hex.-sols.	hex.-insols.	Σ_2^+
1098	Soxhlet, 1 atm, 48 h	6.5*	93.6	100.1	1.67	4.2	5.87
1098	same	7.5*	93.0	100.5	1.06	5.8	6.9
1098	200°C, 3 h	6.7	93.5	100.2	2.7	3.1	6.8
1098	200°C, 24 h	7.1	90.0	97.1	6.0	2.8	8.8
1098	200°C, 96 h	7.5	92.6	100.1	2.5	4.35	6.85
521	Soxhlet, 1 atm, 48 h	4.1	97.0	101.1	2.10	1.72	3.82
521	200°C, 24 h	4.8	62.8	67.6	--	--	--
592	Soxhlet, 48 h	7.7	96.6	104.3	1.40	4.39	5.79
592	200°C, 24 h	5.5	98.8	104.3	--	--	--

*10.4% in earlier experiment

** Σ_1 = sum of material soluble and insoluble in benzene/ethanol under stated conditions

+ Σ_2 = sum of hexane-solubles and hexane-insolubles; should be equal to material extracted by benzene/ethanol

PSOC 1098 was made at 200°C with a mixture containing 80% ethanol; the yield was much the same as when the 31.7% mixture was used.

(vii) Other Solvents

In the hope of obtaining larger amounts of extract, and in particular, larger amounts of hexane-solubles, a number of other solvents and solvent mixtures were tested with the Illinois coal, PSOC 1098, with results shown in Tables 8 and 9.

Experiments 1 and 2 in Table 8 were part of the large experiment whose results were collected in Table 4. However, the data in Table 4 had been corrected for the weight of pyridine retained, whereas those in Table 8 have not. It should be noted that all figures are percentages of the original organic matter in the coal. Thus, if no pyridine had been retained, s, for experiment 2 would have been 90.9% instead of 97.1%. Later extractions of the same coal with benzene + ethanol gave lower yields (see Table 7).

The ternary azeotrope of methanol, chloroform and acetone (23:47:30; b.p. 57.5°C) gave a moderately good yield of extract under Soxhlet conditions, with an excellent material balance. Extraction of the residue from this with pyridine gave much product, though with much retention of solvent. However, very little of the extract was solubilized by hexane. The yield of pyridine extract, corrected for retention of solvent and expressed as a percentage of the organic matter in the original coal was 19.9%. Attempts to extract with the ternary azeotrope under pressure at 200°C were unsatisfactory because components of the mixture partly decomposed.

TABLE 8

Extraction of Illinois No. 6 Coal, PSOC 1098, with Various Solvents

Exp. No. Extractant	Yield extract	Yield insol.	Σ_1^a	hex. sols.	hex. insols.	Σ_2^b	Δ^c
1. bz. + EtOH	10.4	90.9	101.3	2.3	8.2	10.5	-0.1
2. pyridine ^d	4.0	93.1	97.1	--	--	--	--
3. CH ₃ OH/CHCl ₃ /(CH ₃) ₂ CO, Sox.	7.8	93.6	101.4	3.1	3.8	6.9	0.9
4. pyridine ^e	24.4	90.6	115.0	0.6	26.5	27.1	-2.7
5. pyridine/CS ₂	18.8	89.3	108.1	5.7	19.6	25.3	-6.5
6. pyridine, Sox., undried coal	28.4	90.3	118.7	0.8	9.7	10.5	17.9

Notes: ^a Σ_1 = sum of extract + residue in primary extraction

^b Σ_2 = sum of hexane-solubles and insolubles; should equal yield from primary extraction if material balance is fully closed

^c Δ = yield of primary extract - Σ_2

^dpyridine extract of residue from experiment 1

^eSoxhlet extract of residue from experiment 3

TABLE 9

Extraction of Some Coals with Dimethylsulfoxide

PSOC No.	Seam, State	percent							
		<u>Yield extract</u>	<u>Yield residue</u>	<u>Σ_1</u>	<u>THF- insols.</u>	<u>THF-sols. (by diff.)</u>	<u>Hex.- sols.</u>	<u>Hex.- insols.</u>	<u>Σ_2</u>
680	Indiana No. 6 ^a	--	93.4	--	--	--	--	--	--
534	Kentucky No. 11 ^b	--	80.5	--	--	--	--	--	--
1082	Dietz, Montana	--	111.2	--	--	--	--	--	--
1082	Same	18.7	80.6	99.3	16.1	2.6	1.3	1.06	2.45

Notes: ^a80.0% C dmmf, HVC^b75.0% c, sub. B

Iino and Matsuda (1983) have reported that a 1; 1 mixture of pyridine and CS_2 at room temperature is an excellent extractant for a coal of fairly high rank (86% C), though much less good for a subbituminous coal. It is only very moderately effective with the Herrin No. 6 sample (PSOC 1098). The material balance for the extraction is rather poor, and, surprisingly, also for the hexane extraction.

It has been alleged that drying a coal causes some chemical deterioration. In one experiment (Table 8), undried coal (4.2% moisture) was extracted with pyridine. In calculating yields, the weight of coal taken was corrected for the moisture. Presumably all the moisture was extracted by the pyridine and distilled out as the azeotrope when the pyridine was evaporated, so that its weight did not have to be subtracted from the weight of extract. The yield of extract was a little higher than when dried coal was extracted. The material balance was again poor, and a large and inexplicable loss was observed in the hexane extraction.

It is well known that the extractability of coals by pyridine falls off sharply as rank decreases from the level of 86-87% C. We were concerned to find a solvent or solvent mixture that was reasonably effective with lower rank coals. Dimethylsulfoxide seems to be effective with lignites (Mallya et al., 1983). In preliminary trials, three coals of carbon content 75, 79 and 80% were extracted with stirred dimethylsulfoxide at 120°C for 24 hours (the boiling point of the solvent at atmospheric pressure is 189°C). After cooling, the suspension was filtered and the residue washed with fresh solvent and then with toluene. Attempts to evaporate solvent

from the extract in a rotary evaporator with the aid of a vacuum pump were unsuccessful. The fact that one residue weighs more than the weight of coal taken (Table 9) indicates that the completeness of solvent removal (estimated from the weight of residue) is suspect in the other cases. Thus the apparent yields of extract (6.6 and 14.5%, respectively) are minimum values. The latter value encourages continued effort with this solvent.

In a further experiment, a coal (PSOC 1082) was heated with stirring at 120°C with dimethylsulfoxide. The filtered residue was washed with solvent, toluene and water, and dried in vacuo. The solvent was successfully evaporated from the extract, which was then stirred at room temperature with THF. The recovered THF extract (a pasty solid) was refluxed with hexane for 24 hours; and the final residue and extract recovered. The various yields are assembled in Table 9. The material balance in the DMSO extraction is remarkably good, and the yield of extract quite impressive. However, the yields of material soluble in either THF or hexane were quite small.

The final experiments in this phase of the work involved extraction in a Soxhlet apparatus with a 50:50 mixture of 3-methylcyclohexanone and N,N-dimethylformamide. This mixture forms an azeotrope of boiling point 150°C (P. H. Given, 1953, unpublished). Rybicka (1959) reported that under Soxhlet conditions the mixture solubilizes about 50% of a vitrain (about 84% C). PSOC 521 and 592 (see Table 3) were extracted for 108 h under nitrogen with this mixture, using 15:1 ratio of solvent to coal. The coals were allowed to soak in solvent for 2 h at room temperature before being subjected to Soxhlet conditions. Finally, the thimbles were

drained, and the solid residue was stirred overnight with a 10:1 excess of the benzene/ethanol mixture, and further washed on the filter. After drying in a vacuum oven, the weights of residue recovered were, for PSOC 521, 97.5%, and, for PSOC 592, 91.6%, implying minimum extract yields of 2.5 and 8.4%, respectively. These results were so disheartening that this line of investigation was not pursued further. No doubt the residues retained solvent, but not enough, surely, for extract yields to be anything approaching 50%. It is true that Given et al. (1982) found bituminous coals of Cretaceous age from the western U.S. to give considerably lower yields of extracts in pyridine than Carboniferous coals of the same rank range (perhaps by a factor of 2), and PSOC 521 is a Cretaceous, western coal. Even so, the very low yields here were disappointing.

Ethylene diamine was found by Dryden (1952) to extract substantial quantities of bituminous coals. van Bodegom et al. (1984, 1985) have documented the phenomena in some detail recently; they claim particularly large solubilization of lignites, and attribute this to chemical reactions of the solvent. Ethylene diamine liquid rapidly attacks skin, and the vapor attacks lung tissue. Prolonged exposure can set up allergies. Thus it is unpleasant to work with, and we did not in fact use it. It can be handled safely with proper precautions, and should be further investigated in the future.

(viii) Product Analysis by HPLC

Some analyses have been performed on the hexane-soluble parts of a number of products obtained from the Herrin No. 6 coal (Illinois; PSOC 1098). The nature of the products, their yields based on the organic matter content of the original coal, and the tables of this report in which more information on the source of the samples may be found are shown in Table 10.

A Waters instrument was used, equipped with a semi-preparative column of Whatman "Partisil" and an absorption detector set for 254 nm. The sample in hexane was injected through a guard filter. Nonpolar material was eluted with hexane, and then polar material was back-flushed out with methylene chloride. Products were collected in 4-6 fractions, with guidance from the record of the detector response. The refractive index detector was not used, so that alkanes were recovered with the first aromatic fraction, which in the case of liquefaction products consisted chiefly of tetralin and naphthalene that the vacuum distillation had failed to remove.

After sharp peaks due to naphthalene and tetralin, the hexane-solubles from liquefaction runs showed a broad composite peak presumably containing aromatic hydrocarbons and heterocycles, before a sharp peak containing the back-flushed polars. In the case of the two 425° runs, the polars accounted for over 50% of the eluates, but the aromatic fraction (26-36%) eluted at longer retention times in the case of the liquefaction of the solvent extraction residue. This slow elution was also observed with the aromatic fraction of

TABLE 10

Hexane-Soluble Fractions of Illinois Coal (PSOC 1098) Studied by HPLC and Tandem Mass Spectrometry

Sample No.	Source of Fraction	Yield % of dmmf coal	Further info. in Table No.
1	Liquefaction in tetralin/H ₂ , 425°C, 30 min	16.7	4
2	Liquefaction in tetralin/H ₂ , 350°C, 120 min	7.5	5
3	Liquefaction, 425°C, 30 min, of residue after successive extraction with benzene/ethanol and pyridine	12.3*	4
4	Benzene/ethanol extract, 200°C, 3 h	3.7	7
5	As 4, but 200°C, 24 h	6.0	7
6	Pyridine/CS ₂ extract, about 25°C	5.7	8
7	Pyridine extract of undried coal (Soxhlet)	0.80	8
8	Extraction with CH ₃ OH/CHCl ₃ /(CH ₃) ₂ CO azeotrope (Soxhlet)	3.1	8
9	Pyridine extract (SOxhlet) of residue from 8	0.60	8

*% of extracted residue

the products of the 350° run, but here the polar fraction represented only 37% of the whole.

Of the solvent extracts, the elution behavior of the benzene/ethanol (200°, 3 h) and $\text{CH}_3\text{OH}/\text{CHCl}_3/(\text{CH}_3)_2\text{CO}$ products was quite similar, except that the latter showed a large sharp peak at low retention times accounting for 16% of total eluate. In both cases a broad peak at fairly early times accounted for about 5% of the material and a larger peak (20-30% by weight) was separated from this and the polars (54%, 50%). The product of the 24 h extraction with benzene/ethanol at 200° was similar, but the polar fraction was appreciably smaller (38%).

Further extraction with pyridine of the residue from the methanol/chloroform/acetone extraction afforded little hexane-soluble material. In HPLC this showed, surprisingly, an unusually strong polar peak, at relatively low retention time, although the proportion of the whole extract that eluted in this fraction was not unusual (53%). In contrast, the pyridine/ CS_2 extraction gave a high yield of hexane-solubles, with a low concentration of polars (25%); much of the eluate was in two fractions of, presumably, neutral, aromatics (39 and 17%, respectively).

Thus HPLC under the conditions selected appears to be an effective means of achieving a preliminary separation into a number (3-5) of well-resolved fractions that may well contain appreciably different structural types. Moreover, there are indications that, in some case at least, different conditions of extraction lead to a somewhat different product distribution.

(ix) Product Analysis by Tandem MS (MS/MS)

The same set of hexane-solubles (Table 10) was analyzed at Purdue University by Singleton, Cooks and Wood by tandem mass spectrometry. Their work has now been published (Singleton et al., 1987), and we are grateful for their cooperation.

The several variants of this technique are highly sophisticated, and the data require skilled and detailed interpretation. Only an outline of the most significant findings will be given here.

A number of homologous series of alkyl aromatics were found in all samples; they are shown in Table 11.

In most cases the acenaphthene series seems to have been the most prominent, together with bipyridyl when pyridine had been used as a solvent. However, the acenaphthene series was weak in the spectra of sample 10 (pyridine extract of residue from extraction with the ternary azeotrope). The expression "cyclized acenaphthene" refers to a series formed from long chain alkyl acenaphthenes by cyclization of the first four carbon atoms to form a new six-membered ring. These techniques incidentally, cannot prove that homologues with many aliphatic C atoms have them all in a single unbranched chain, but it appears that we do have few long chains rather than many short chains, which, if branched at all, are only lightly so. The maximum alkyl chain lengths shown in Table 11 are considerably shorter than Mudamburi and Given (1985a, 1985b) found in liquefaction products. On the other hand, these authors did not find long chain alkyl aromatics in the two solvent extracts they

TABLE 11

Alkylaromatic Series Identified in Coal Liquefaction
and/or Extraction Samples by Tandem MS

<u>Initial series member</u>	<u>(M+H)⁺</u>	<u>Alkyl chain length (scan used)</u>
Naphthalene	129 ⁺	C ₇ (parent scan of 142 ⁺)
Acenaphthene	155 ⁺	C ₈ (parent scan of 155 ⁺)
Methylhydroxy(iso)- quinoline	160	(inconclusive)
Fluorene/phenalene	167 ⁺	C ₇ (parent scan of 167 ⁺)
Anthracene/phenanthrene	179 ⁺	C ₈ (parent scan of 179 ⁺)
Cyclized acenaphthene	155 ⁺	C ₉ (parent scan of 155 ⁺)
Naphthylphenol	221 ⁺	C ₃ (parent scan of 179 ⁺)

examined, whereas Singleton et al. found them in all extracts as well as liquefaction products. Moreover, Singleton et al. found many more homologous series than did Mudamburi and Given.

Apparently it is of the nature of the tandem MS techniques to be more sensitive than the GC/MS with single ion monitoring used by Mudamburi and Given.

The most surprising finding of Singleton et al. was that, in spite of the widely differing methods used and yields achieved, the parent spectra obtained for the ten hexane-soluble fractions were remarkably similar. Such differences as were noted were in the relative intensity of the ions in a particular series. Thus the relative ion intensities shown by the product of the first liquefaction run (sample 1 in Table 10) tended to be slightly greater than those shown in spectra from sample 2 (350°C) and sample 3 (liquefaction at 425°C of previously extracted coal). There were notable differences in the length of the homologous series. In the series of benzene/ethanol extracts prepared at 200° for 3, 24 and 96 h, the spectra of the 96 h sample tended to show greater intensities at higher masses (and poorer signal-to-noise ratio). Thus with increasingly severe conditions, the primary difference is in the total amount and not the nature of the alkyl aromatics released from the coal. Of course, all of the products contained components other than members of the homologous series named. These were unidentified and may differ between products.

The authors compare their observations with those of Youtcheff et al. (1983), who found the distributions of linear and cyclic alkanes from solvent extracts of three coals to be very similar to

the distributions in the much greater yields obtained by liquefaction of the same coals. They accept for their own observations an interpretation analogous to that proposed by Youtcheff et al., that the additional alkanes released were physically trapped inside the coal macromolecular network and released by disruption of the network.

3. Discussion

The first point we feel we should make is that in spite of all the work described in the literature over the last 90 years or so, it is our belief that knowledge of the behavior of coals with organic solvents is still quite inadequate (we are here considering only extractability). Pyridine is the solvent that has been studied most extensively, but even here we do not know much about the behavior of low rank coals or of bituminous coals from basins other than those of Carboniferous age in Europe and North America. Ethylene diamine has also been much studied, and the same comments apply. If we turn to the various solvent mixtures used by Rybicka and later workers, we find knowledge far more limited still. Yet the subject is of great theoretical and practical interest. Systematic studies covering wide ranges both of rank and of geological history are badly needed, for a number of solvents and solvent mixtures.

Solvent mixtures seem to be specially valuable, no doubt because their physicochemical properties match those of a coal more closely than do those of pure solvents. The mixture of benzene and ethanol seems of general utility; it appears to be stable at 200°C

under pressure, though we found the yield of extract surprisingly little improved by the increase in temperature.

As pointed out earlier, we have assumed that the homologous series we had proposed to use as markers of the mobile phase would be in the hexane-soluble fraction. This is a reasonable assumption, and, most probably, justified. It was also assumed that a graduated series of increasingly severe conditions could be set up that would contain a threshold beyond which the markers for the mobile phase would become very evident. This last assumption has turned out to be naive and simplistic. Youtcheff et al. (1983) found the content of alkanes to be 6-8 times greater in liquefaction products than in solvent extracts. Mudamburi and Given (1985a, 1985b) found homologous series of n. alkylaromatics in liquefaction products but could not detect them in solvent extracts of three coals. It was these earlier results that promoted the idea that a definite threshold of release existed. The hexane-soluble fractions of PSOC 1098 analyzed by Singleton et al. represented between 0.6 and 16.7% of the organic matter of the coal. Several series of alkylaromatics were prominent constituents of all of them, though of course representing widely differing fractions by weight of the coal.

Youtcheff et al. (1983) argued that it was difficult to imagine pyrolysis reactions in liquefaction generating essentially the same complex mixture as was physically held and extractable by solvents at low temperatures. They concluded, therefore, that the alkanes released during liquefaction had been physically trapped and had not been chemically bound into the network. Mudamburi and Given (1985a, 1985b) used a similar argument: it is very difficult to imagine

extensive homologous series of n. alkylaromatics being combined chemically in the network structure and being released as such by pyrolysis or hydrogenation. The same reasoning applies to the more comprehensive data of Singleton et al. for a single coal. It appears securely established that certain compounds can be present in the macromolecular network of coals in cavities of a wide range of accessibilities. Thus, for example, a physically-held series of long chain alkylacenaphthenes is released into a $\text{CH}_3\text{OH}/\text{CHCl}_3/(\text{CH}_3)_2\text{CO}$ mixture boiling at 57° , more of the same mixture is released by benzene/ethanol at 200°C for 24 h, and more still in liquefaction at 425°C . Such compounds would surely exhibit a fair degree of rotational mobility, though we cannot say whether in the high or intermediate range of mobility or some part in both.

In a discussion of the concept of the mobile phase as proposed originally by Jurgiewicz et al. (1982), it was concluded that while the concept was consistent with their ^1H NMR data, the NMR data alone could not unequivocally validate the concept (Given et al., 1986). We now suggest that a further measure of validation of the concept is contributed by the data (admittedly for only one coal) published by Singleton et al. (1987).

The findings of Singleton et al. also raise fresh problems: what is the origin of the homologous series of alkylaromatics they identify. Of course, Baset et al. (1980) and Gallegos (1981) in the case of alkylbenzenes, and Mudamburi and Given (1985a, 1985b) in the case of alkylnaphthalenes, furans, phenols and isophorone analogs, had to face the same problem, but at least the homocyclic or heterocyclic ring in each case is common enough in constituents of

organisms, and some means of alkylation by reaction with fatty acids could be suggested. But most of the cyclic structures identified by Singleton et al. are not known to occur to significant extents, or at all, in organisms (phenanthrene derivatives related to cyclic terpenes are the main exception). It would seem that the cycles are generated after burial of peat and exposure to elevated temperatures, and alkylation also occurs then or later still.

The recent study by Kamienski et al. (1987) of coals swollen by pyridine- d_5 , using pulsed 1H NMR, shows that the nature of the components of high rotational mobility is considerably more complex than had been thought. It appears that there are two sets of components whose protons have very high mobility, one extractable by pyridine in long periods at room temperature and of more aliphatic character, and the other not extracted under these conditions and of more aromatic character. In addition, there are components whose protons are of intermediate mobility; an unknown proportion of these may be attached to parts of the macromolecular network remote from cross-link but not to aromatic rings, while the rest are probably attached to molecules physically trapped in cavities in the network and enjoying only restricted mobility. We regard these findings as an important contribution to coal structural studies. One consequence of the findings is to cast still further doubt on the utility of attempting to represent the structure of a vitrinite by a single "average" structural model (Given, 1984).

It was suggested above that the importance of the mobile phase concept to liquefaction was that its loss by activated diffusion, added to chemical decomposition of the network, would complicate

treatment of the kinetics of the process. With the increased complexity of the mobile phase concept, the complexities of kinetic modeling become even more severe. For one thing, a range of activation energies for diffusion is now called for and for another break up of mobile parts of the network will have at least entropies of activation different from those of the highly cross-linked parts. Modeling coal liquefaction as if coal were a single pure substance as has so often been done in the literature, becomes an even more dubious operation.

The kinetic model of Szladow and Given (1981) is based on the premise that in liquefaction, many reactions of different activation energy proceed in parallel. The model was further exploited by Youtcheff and Given (1982). There seems to be no reason why this model should not be modified to accomodate participation of diffusion processes as well as chemical reactions, and perhaps the arbitrary "lumps" used by Szladow as reacting species could now be more specifically identified.

4. Summary

The principal findings are:

(i) Coals are extremely complex materials, in ways that have not adequately been considered before. The concept that we are dealing with multicomponent systems containing at least two kinds of component seems well established. These components consist of a large number of relatively small molecular, some extractable at low temperatures, imbibed in a cross-linked macromolecular network. As

a consequence, the kinetics of thermal processes will be extremely complex, and need to take account of a number of both physical and chemical processes.

(ii) Much more work still needs to be done before we can claim to understand the extractability of coals with solvents, particularly with mixtures of solvents. There is little correlation between the yield of extract with various solvents and the percentage of the extract that will dissolve in hexane.

(iii) Homologous series of alkyl aromatic substances are prominent constituents of the hexane-solubles of many different solvent extracts and liquefaction products of a coal. It looks as if further increments of the same series are released wherever conditions of processing are such that the gross yield of hexane-solubles is increased. That is, varying amounts of a given set of physically trapped compounds can be released according to the conditions used. Thus the concept of a trapped mobile phase is confirmed, though in a modified and elaborated form.

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