CHEMICAL NATURE OF SPECIES ASSOCIATED WITH MOBILE PROTONS IN COALS; A STUDY BY FIELD IONIZATION MASS SPECTROMETRY

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INTRODUCTION

Proton n.m.r. investigations of coals swollen in deuterated pyridine showed that the free induction decay /FID/ consists of Gaussian and Lorentzian components related to two populations of protons which have widely different degrees of rotational mobility (1-5). The Gaussian component of FID has been unanimously ascribed to the macromolecular part of the coal matter that is supposed to have very limited rotational mobility. These publications as well as the ensuing debates (6-8) however, reflected the controversy regarding the nature of the Lorentzian /mobile/ protons in coals.
One view is that all Lorentzian protons can be attributed to molecules that are free to rotate in cages of the macromolecular network. Since the free molecules may be differentiated in their sizes and may have restricted freedom of rotation, their spin-spin relaxation times may be also differentiated and account for numerous populations of various mobilities within the group of Lorentzian protons.
The other view is that a significant part of the Lorentzian protons, especially those of lower mobility, may be also associated with fragments of the macromolecular network that can rotate due to a single C-C or C-O bond linking such fragment to the network.
The controversy cannot be easily clarified; there is no experimental technique available that could isolate all the free molecules and would leave intact the macromolecular network.
A more realistic approach is a separation of a mixture of free molecules and structural units linked to the network by single bonds, after these bonds have been cleaved by heat treatment of the coal. An insight into the composition of such mixture can provide information on the nature of species that are likely to be associated with the mobile protons. It seems that pyrolysis-field ionization mass spectrometry can be used in order to attain this goal.

Recently, an improved experimental setup for time-resolved in-source pyrolysis /py./ field ionization /f.i./ mass spectrometry /m.s./ has been described (9) and examples of its application to studying various biomaterials have been shown. There is a number of characteristic features of the py.-f.i.m.s. that are relevant to coal studies. Due to an increase of temperature of a sample in the direct introduction system of the mass spectrometer at heating rates around 1 oC per second and recording magnetic scans in 10 oC intervals, the volatilized species are not effected by a

higher temperature than is needed for their volatilization and detection. High vacuum and short residence time of the volatiles in the ion source of the spectrometer also reduce significantly secondary reactions between the species. The volatiles undergo soft ionization in the high electric field to produce molecular ions, with essentially no fragmentation ions. Hence, the mode of heating and ionization coupled with frequent scanning, can provide information about the composition of the material.
When the py.-f.i.m.s. is applied to a coal, a mixture of free molecules as well as some parts of the macromolecular network is volatilized (10). Heating a coal to around 500 oC in the mass spectrometer should result in thermal decomposition of various single bonds that link structural units in the network (11).
Although it is difficult to ascertain whether all free molecules and the structural units in question are volatilized in the mass spectrometer, this volatilized material certainly represents a high proportion of them.

The present paper shows such py.-f.i.m.s. data for a low rank bituminous coal. More specifically, the molecular weight distribution of volatilized material as well as elemental composition of its major components, are determined.

EXPERIMENTAL

The coal studied, 78 % C and 15.8 % O daf, is derived from Carboniferous deposits from the Ziemowit mine in Poland. Its petrographic composition / % vol.dmmf/ is: vitrinite, 60; exinite, 12; and inertinite, 40.
Proton n.m.r measurements of Zeeman relaxation for the same coal showed (12) that the fraction of mobile protons is 32 % of all protons. Assuming that the content of hydrogen in the mobile and immobile phases of the coal is approximately the same, the relaxation measurements indicate that the coal mobile phase content is app. 32 wt % of organic material.

Previously the py.-f.i.m.s. of coals and their pyridine extracts has already been described (10) using this novel technique. About 100 micrograms of ground coal sample was heated in the high vacuum of a combined e.i/f.i./f.d. ion source of a double-focusing mass spectrometer (Finnigan MAT 731, Bremen, FRG). The sample was heated at a constant rate of 24 oC/min from 50 to 500 oC. The volatilization of the coal was 30 % daf.This end temperature had been selected in such way that the yield of volatilization of the coal in the mass spectrometer was comparable with the mobile phase content in the coal. The temperature also corresponds to a rapid decrease of volatilization that is shown in Figure displaying total ion current.
Forty spectra were recorded electrically in the whole temperature range. The f.i. signals of all the spectra were integrated, processed and plotted using the Finnigan Spectro-System 200 to give a summed spectrum. Five measurements of the sample were recorded and their averaged, summed spectrum was finally obtained which is reproducible and representative of the coal.
High mass resolution /h.r./ f.i. mass spectrography was carried

out using the same py. conditions as above. The photoplate (Q2, Ilford, England) was exposed to f.i.ions in the range m/z 60-500 for about 10 min. The resolution obtained was between 10,000 and 20,000 /50 % valley definition/ with an average mass accuracy of approximately 0.003 Dalton /3 mmu/. The photographic plate was evaluated with a Gaertner comparator. Mass measurements were calibrated using perfluorokerosene.The accurate mass determinations allow the calculation of the elemental composition of the f.i. ions.

RESULTS AND DISCUSSION

The volatilization of the coal pyrolysed in the mass spectrometer to 500 oC corresponds to 30 wt % daf which is in accord with the mobile phase content of the coal, 32 wt % org. mat.
The molecular weights of the volatilized components were in the range of 80 to 800 Daltons. However, most intense f.i. signals were found in the much narrower range from 230 to 430 Daltons; abundances above this range quickly decreased to negligible values. The f.i. mass spectrum in question is not displayed here, since a similar one from another coal has been shown elsewhere (10).
High resolution f.i. data are shown in the Table.They are related to the major components of the volatilized material; the data for species for which intensities on the photoplate were below 5 % are not included, nor are the data for species above 300 Daltons that could not be accurately measured under the selected experimental conditions. Thus, the Table shows elemental composition of the species that account for app.50 wt % of the volatilized material.
The species represent all homolog series of hydrocarbons from C_nH_{2n} to C_nH_{2n-28} ; of compounds with one oxygen atom from $C_nH_{2n-2}O$ to $C_nH_{2n-30}O$; and with two oxygen atoms from $C_nH_{2n-6}O_2$ to $C_nH_{2n-26}O_2$. These formulae relate to compounds that contain one, two /such as naphthalene and indene/ and three aromatic rings /such as anthracene, cyclopentaphenanthrene and benzoacenaphthene/ as well as four aromatic rings /such as pyrene, chrysene/ and five aromatic rings as in benzopyrene.
There are from 1 to 8 carbon atoms in the alkyl substituents on the aromatic rings. It is worthy of note that the alkyl substituents are not long. Even if one assumes all alkyl carbons form one alkyl substituent on a ring, a substituent cannot be longer than C_8 for indenes, C_7 for acenaphthenes, fluorenes and anthracenes and C_6 for benzenes and naphthalenes. Essentially the same applies to alkyl oxygen compounds.
Under the same py.-f.i.m.s. experimental conditions, compounds with normal and branched alkyl chains up to C_{32} were easily detected in natural waxes (13). Thus, the present results indicate that long alkyl compounds are not major constituents of the coal and discussing the FID signals of coal in terms of its "polyethelene structures" (B.C. Gerstein in reference 8) is not correct for the coal studied and may be not correct for other coals.

In summarizing, the following statements can be made:

- Py.-f.i.m.s. of coal can provide information on chemical nature of species that most likely, contain protons detected by n.m.r. experiments as mobile protons.

- The results for a low rank bituminous coal show a high diversity of molecular weights for such compounds, from 80 to 800 Daltons.

- The high resolution f.i. data, although limited to major components, also show diverse structures: the number of aromatic rings is from 1 to 5; the number of carbon atoms in alkyl substituents is in the range from 1 to 8.

- This structural diversity must account for the wide range of rotational mobilities of the components of the mobile phase.

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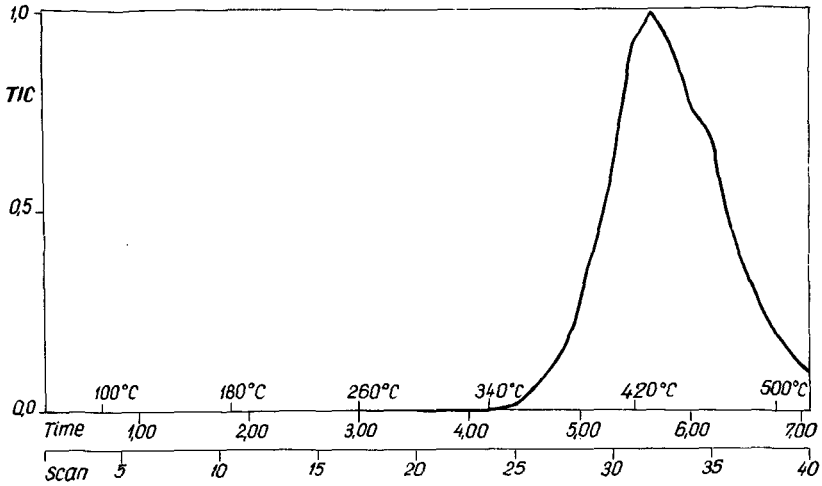
Table. ELEMENTAL COMPOSITION OF F.I. MASS SIGNALS DETECTED FOR A LOW RANK BITUMINOUS COAL, 78 %C daf

homolog series $C_nH_{2n+z}O_x$ and proposed structure	elemental compositon of ions								
C_nH_{2n};olefins/monocyclic alkanes	C_6H_{12}	C_7H_{14}	C_8H_{16}	C_9H_{18}	-	-	-	-	-
C_nH_{2n-2};diolefins/dicycloalkanes	C_6H_{10}	C_7H_{12}	C_8H_{14}	C_9H_{16}	-	-	-	-	-
$C_nH_{2n-2}O$;	$C_6H_{10}O$	$C_7H_{12}O$	-	-	-	-	-	-	-
C_nH_{2n-4};triolefins/tricycloalkanes	C_6H_8	C_7H_{10}	C_8H_{12}	C_9H_{14}	$C_{10}H_{16}$	-	-	-	-
$C_nH_{2n-4}O$;	C_6H_8O	$C_7H_{10}O$	$C_8H_{12}O$	$C_9H_{14}O$	-	-	-	-	-
	Number of carbon atoms in alkyl substituents								
	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
C_nH_{2n-6};benzenes	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	$C_{10}H_{14}$	$C_{11}H_{16}$	$C_{12}H_{18}$	-	-
$C_nH_{2n-6}O$;hydroxy benzenes	C_6H_6O	C_7H_8O	$C_8H_{10}O$	$C_9H_{12}O$	$C_{10}H_{14}O$	$C_{11}H_{16}O$	$C_{12}H_{18}O$	-	-
$C_nH_{2n-6}O_2$;dihydroxybenzenes	$C_6H_6O_2$	$C_7H_8O_2$	$C_8H_{10}O_2$	-	$C_{10}H_{14}O_2$	$C_{11}H_{16}O_2$	-	-	-
C_nH_{2n-10};indenes	C_9H_8	$C_{10}H_{10}$	$C_{11}H_{12}$	-	$C_{13}H_{16}$	$C_{14}H_{18}$	-	$C_{16}H_{22}$	$C_{17}H_{24}$
$C_nH_{2n-10}O$; hydroxyindenes	C_9H_8O	$C_{10}H_{10}O$	-	$C_{12}H_{14}O$	$C_{13}H_{16}O$	$C_{14}H_{18}O$	$C_{15}H_{20}O$	-	$C_{17}H_{24}O$
$C_nH_{2n-10}O_2$; dihydroxyindenes	-	$C_{10}H_{10}O_2$	-	$C_{12}H_{14}O_2$	$C_{13}H_{16}O_2$	$C_{14}H_{18}O_2$	-	$C_{16}H_{22}O_2$	-

	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
C_nH_{2n-12};naphthalenes/ -tetrahydrofluorenes	$C_{10}H_8$	$C_{11}H_{10}$	$C_{12}H_{12}$	$C_{13}H_{14}$	$C_{14}H_{16}$	$C_{15}H_{18}$	$C_{16}H_{20}$	-	-
$C_nH_{2n-12}O$;hydroxy-naphthalenes/ -tetrahydrofluorenes	-	$C_{11}H_{10}O$	$C_{12}H_{12}O$	$C_{13}H_{14}O$	-	$C_{15}H_{18}O$	$C_{16}H_{20}O$	$C_{17}H_{22}O$	$C_{18}H_{24}O$
$C_nH_{2n-12}O_2$;dihydroxy-naphthalenes/ -tetrahydrofluorenes	$C_{10}H_8O_2$	-	$C_{12}H_{12}O_2$	$C_{13}H_{14}O_2$	$C_{14}H_{16}O_2$	$C_{15}H_{18}O_2$	$C_{16}H_{20}O_2$	-	-
C_nH_{2n-14};acenaphtenes	$C_{12}H_{10}$	$C_{13}H_{12}$	$C_{14}H_{14}$	$C_{15}H_{16}$	$C_{16}H_{18}$	$C_{17}H_{20}$	$C_{18}H_{22}$	$C_{19}H_{24}$	-
$C_nH_{2n-14}O$; hydroxyacenaphtenes	$C_{12}H_{10}O$	$C_{13}H_{12}O$	$C_{14}H_{14}O$	$C_{15}H_{16}O$	$C_{16}H_{18}O$	$C_{17}H_{20}O$	-	-	-
$C_nH_{2n-14}O_2$; dihydroxyacenaphthenes	$C_{12}H_{10}O_2$	-	$C_{14}H_{14}O_2$	$C_{15}H_{16}O_2$	-	$C_{17}H_{20}O_2$	-	$C_{19}H_{24}O_2$	-
C_nH_{2n-16};fluorenes	$C_{13}H_{10}$	$C_{14}H_{12}$	$C_{15}H_{14}$	$C_{16}H_{16}$	$C_{17}H_{18}$	$C_{18}H_{20}$	$C_{19}H_{22}$	$C_{20}H_{24}$	-
$C_nH_{2n-16}O$;hydroxyfluorenes	$C_{13}H_{10}O$	-	$C_{15}H_{14}O$	$C_{16}H_{16}O$	$C_{17}H_{18}O$	$C_{18}H_{20}O$	$C_{19}H_{22}O$	$C_{20}H_{24}$	$C_{21}H_{26}O$
$C_nH_{2n-16}O_2$ dihydroxyfluorenes	-	$C_{14}H_{12}O_2$	$C_{15}H_{14}O_2$	-	$C_{17}H_{18}O_2$	$C_{18}H_{20}O_2$	$C_{19}H_{22}O_2$	-	
C_nH_{2n-18};anthracenes	$C_{14}H_{10}$	$C_{15}H_{12}$	$C_{16}H_{14}$	$C_{17}H_{16}$	$C_{18}H_{18}$	$C_{19}H_{20}$	$C_{20}H_{22}$	$C_{21}H_{24}$	-
$C_nH_{2n-18}O$; hydroxyanthracenes	-	$C_{15}H_{12}O$	-	$C_{17}H_{16}O$	$C_{18}H_{18}O$	$C_{19}H_{20}O$	$C_{20}H_{22}O$	-	
$C_nH_{2n-18}O_2$; dihydroxyanthracenes	$C_{14}H_{10}O_2$	$C_{15}H_{12}O_2$	$C_{16}H_{14}O_2$	-	$C_{18}H_{18}O_2$	$C_{19}H_{20}O_2$	-		
C_nH_{2n-20}; cyclopentaphenanthrenes	$C_{15}H_{10}$	$C_{16}H_{12}$	$C_{17}H_{14}$	$C_{18}H_{16}$	$C_{19}H_{18}$	$C_{20}H_{20}$	-	-	

	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
$C_nH_{2n-20}O$;hydroxycyclo-pentaphenanthrenes	-	$C_{16}H_{12}O$	-	-	$C_{19}H_{18}O$	-	-		
$C_nH_{2n-20}O_2$;dihydroxycyclo-pentaphenanthrenes	-	-	-	$C_{18}H_{16}O_2$	-	-			
C_nH_{2n-22};pyrenes/ fluoranthenes	$C_{16}H_{10}$	$C_{17}H_{12}$	-	$C_{19}H_{16}$	$C_{20}H_{18}$	-	-		
$C_nH_{2n-22}O$;hydroxypyrenes/ -fluoranthenes	$C_{16}H_{10}O$	-	-	-	-	-			
C_nH_{2n-24};chrysenes	-	$C_{19}H_{14}$	$C_{20}H_{16}$	$C_{21}H_{18}$	$C_{22}H_{20}$	-			
$C_nH_{2n-24}O$; hydroxychrysenes	-	$C_{19}H_{14}O$	-	$C_{21}H_{18}O$					
$C_nH_{2n-24}O_2$; dihydroxychrysenes	$C_{18}H_{12}O_2$	-	-	-					
C_nH_{2n-26};cyclopentapyrene	$C_{18}H_{10}$	$C_{19}H_{12}$	$C_{20}H_{14}$	$C_{21}H_{16}$	$C_{22}H_{18}$	-			
$C_nH_{2n-26}O$;hydroxy-cyclopentapyrenes	$C_{18}H_{10}O$	-	$C_{20}H_{14}O$	-	-				
$C_nH_{2n-26}O_2$;dihydroxy-cyclopentapyrenes	-	$C_{19}H_{12}O_2$	-	-	-				
C_nH_{2n-28}; benzofluoranthenes	$C_{20}H_{12}$	-	-	$C_{23}H_{18}$	-				
$C_nH_{2n-28}O$;hydroxy-benzofluoranthenes	-	$C_{21}H_{14}O$	-	-	-				
$C_nH_{2n-30}O$;hydroxy-dibenzoanthracenes	$C_{22}H_{14}O$								



TOTAL ION CURRENT TIC /arbitrary units/ VERSUS TEMPERATURE AND TIME OF HEATING /minutes/ THE SAMPLE IN THE DIRECT INTRODUCTION SYSTEM OF THE MASS SPECTROMETER, AND SCAN NUMBER

EXPERIMENTAL OBSERVATIONS CONCERNING THE TWO-COMPONENT CONCEPT OF COAL STRUCTURE

by

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Abstract

The hypothesis that coals can be considered to consist of two component groups has its origins in observations of coal behaviour as well as deriving from the analysis of coals and attempts to define their structure. The results of extensive studies of untreated, preheated and hydrogenated coals, using analytical and microscopic techniques, have allowed some insight into the association between the so-called mobile phase and macromolecular network, and have provided information upon differences in their chemical properties.

The yield of chloroform-soluble extract has been used to indicate the extent of the mobile phase. In untreated coals, only a portion of the mobile phase is readily removable. After mild preheating or mild hydrogenation, there are sharp increases in the yield of extract and accompanying changes in properties. Under these conditions, it is believed that weak binding between the mobile phase and network is disrupted. The solubilisation of the network requires much higher energy input and necessitates the consumption of hydrogen. The properties of the network components differ significantly from those of the mobile phase and both are coal rank-dependent.

Introduction

Much of the research pursued jointly by the authors and their associates has involved studies of the catalytic hydrogenation of coals in the absence of solvent. The aims have been to utilise this technique to try to elucidate the mechanisms of catalytic coal liquefaction and simultaneously to provide some insight into coal structure. The concept that, in broad terms, coals can be considered to consist of two distinct groups of constituents has been a particular focal point. The hypothesis is not new and has been advanced in a number of ways since the early part of this century. Its revival in recent years is largely attributable to the efforts of the late Peter Given to whom is also owed the now wide usage of the expressions 'mobile phase' and 'macromolecular network' (1,2).

To allow some clarification for a general readership, brief definitions of these terms will be attempted. The mobile phase comprises the smaller molecules in coals, some of which are extractable in solvents. The insoluble portion of coal is primarily a three-dimensional cross-linked macromolecular network or matrix. The mobile phase is attached to or held with the network by physical contraints and weak chemical bonds.

Peter Given was directly instrumental in providing the initiative and impetus which originated the authors' research. These efforts have extended since 1983. Previous findings were disseminated through several publications (3-7). In this paper, some of the earlier data have been collated with more recent (8) and hitherto unpublished results to provide an account of the relevance of these studies to the two-component concept.

Experimental

Coals covering a range of rank downwards from low-volatile bituminous were examined in solvent-free catalytic hydrogenation over the temperature range 300-400°C and for reaction times up to 60 min. The work discussed here specifically involved four coals which were obtained from the Penn State Coal Sample Bank. These were a subbituminous coal (PSOC-1403) and three hvAb bituminous coals, PSOC-1168, PSOC-1266 and PSOC-1510. Characteristics of the coals are summarised in Table 1. The reactors were of the tubing bomb type and the initial (cold) hydrogen pressure was 7 MPa. A sulphided Mo catalyst was introduced to the coal by impregnation from an aqueous solution of ammonium tetrathiomolybdate.

The gaseous products, chloroform-soluble extracts and chloroform-insoluble residues were characterised using a range of analytical techniques. A particular advantage of conducting the hydrogenation reactions in the absence of solvent is that microscopy can be used to observe directly the changes wrought in the whole reacted coals and in the extracted residues. Considerable emphasis was placed on this method of analysis using both visible light microscopy and quantitative fluorescence microphotometry. Detailed descriptions of the procedures and techniques have been given earlier (3-7).

Results and Discussion

Catalytic Hydrogenation

Detailed examinations of the composition and distribution of the reaction products over a range of reaction conditions showed that the four coals exhibited certain common trends. Of particular note, there was in each case, a sharp distinction between the events which took place at low and high conversions. The division occurred at a chloroform-solubles yield of approximately 25% wt dmmf coal.

Low extract yields were obtained either by short reaction times at high temperatures or by more extended reaction at low temperatures. The designations of high and low temperature depend upon the individual coal and, more especially upon the coal rank. The evidence accrued in this research has shown that there exists a threshold temperature below which the potential for liquids formation is minimal and above which conversion can proceed at an appreciable rate.

It is supposed that this temperature is essentially determined by the density and nature of the crosslinks in the macromolecular network. This is consistent with evidence showing that the ease of conversion and the selectivity to lower molecular weight liquids increases with decreasing coal rank (8,9). For the subbituminous coal, the rate of liquids formation was negligible at 300°C and became appreciable at 350°C and higher. The bituminous coals began to

respond only at temperatures around 400°C. Similar observations have been made in experiments which compared the solvent-free hydrogenation of a lignite and a bituminous coal (10).

During the initial stages of conversion, as the liquid yield increased there were radical changes in the properties of the chloroform-soluble extracts. The H/C atomic ratio, aliphatic hydrogen content and oil to asphaltene (O/A) ratio each increased rapidly at first, passed through a maximum and decreased equally precipitately to a lower value, as illustrated in Figure 1. The curve shown for the O/A ratio is typical of the behaviour exhibited by the other coals.

A notable distinction was that the magnitudes of the changes were different for the subbituminous coal and the group of bituminous coals. Examples of the differences between the values for the parent coal extracts and the maxima are: H/C ratio 1.46 to 1.60 for the subbituminous coal, PSOC-1403, and 1.01 to 1.06 for the bituminous coal, PSOC-1266; O/A ratio 0.8 to 8.0 for PSOC-1403 and 0.25 to 1.5 for PSOC-1266.

At the maxima, ^1H n.m.r. and elemental analyses showed that the greater proportion of the extract hydrogen was aliphatic: 10.5% for PSOC-1403 and 6.9% for PSOC-1266. In all cases over 90% of the total hydrogen content was aliphatic at this point. The high aliphatic hydrogen content was associated with the presence of polymethylene chains. The early release of paraffinic material, as n-alkanes and as long chain substituents to aromatic structures, under conditions of mild pyrolysis has been observed in other research (11-13). Over the initial period of conversion, it was also observed that only small quantities of light hydrocarbon gases were produced.

For the four coals, the maxima occurred between 5-10% wt extract yield and the subsequent decreases were arrested between 20-35% extract yield. No distinction could be made on the basis of coal rank although, admittedly, the number of coals is small.

The production of extract yields in excess of 20-35% wt marked the second stage of conversion. Over this period, the H/C atomic ratio and the total aliphatic hydrogen content remained approximately constant or decreased only gradually while the O/A ratio passed through a shallow minimum, Figure 1. The secondary gain in selectivity to oils at high conversions may represent the interconversion of asphaltenes to oils after extended reaction of the primary dissolution products. Other phenomena associated with the progress of the second stage were that the production of light hydrocarbon gases increased, the aromaticity of the extract progressively increased and oxygen functionalities were eliminated.

The consumption of gaseous hydrogen mirrored the changes described above, Figure 1. For the bituminous coals at 400°C, the initial rate of hydrogen uptake was very low. With further reaction, it accelerated, passed through a maximum, and then fell to a lower, more steady value. After about 60 minutes reaction, the total consumption was about 1.5% wt dmmf coal (about 2.0% wt for the subbituminous coal). At the point of transition from the slow initial rate to the accelerating rate, the liquid yields were between 5-15% wt dmmf coal. The acceleration in hydrogen uptake coincided with the end of the first phase of conversion. At this juncture, the total hydrogen consumed was 0.1-0.2% wt. The corresponding figure for the subbituminous coal was about 0.3% wt.

The existence of two stages of conversion has been separately demonstrated in studies by Mobil R & D Corporation where, in non-catalytic solvent liquefaction, two kinetic regimes were distinguished. Initial conversion was rapid with low attendant hydrogen consumption while subsequent conversion was slower and created a much greater demand for hydrogen (14). These findings were re-confirmed in later studies by the same group, when it was further shown that the products first formed were of higher H content and more aliphatic than those generated in the second regime. A subbituminous coal was found to consume more hydrogen than a bituminous coal at the same level of conversion (15).

The foregoing observations have direct implications to coal structure. In the present work, the production of liquids is facile below about 15% liquids yield and requires little hydrogen consumption. The processes most probably involve the release of species which are physically trapped or are weakly bonded to the insoluble matrix. At high conversions, the products are derived from the breakdown of the macromolecular network. This phase of conversion requires the cleavage and stabilisation of strong bonds, thereby creating an appreciable demand for hydrogen.

The products formed during the two stages are quite different in composition which can account for the rather dramatic swings observed in the extract properties with increasing conversion. The hydrogen-rich aliphatic products, which are first liberated, are responsible for the initial increases in the measured parameters. Later, as they become progressively diluted by more aromatic materials emanating from the network, the properties pass through a maximum and then decrease.

Fluorescence Microscopy

The phenomenon of vitrinite fluorescence has been described for 76 humic and vitrinitic materials with levels of organic maturation ranging from peat to low volatile bituminous coal (5,6). Figure 2a shows that fluorescence intensity decreases sharply through the series peat - peat/lignite transitional materials - lignite - subbituminous coal. The so-called primary fluorescence within this range is believed to be due to the presence of fluorophors derived from biopolymers, especially lignin. A second peak in fluorescence intensity (Fig. 2b) commences at about subbituminous rank, is reached in coals with a vitrinite maximum reflectance of about 0.9%, and is largely lost by medium volatile bituminous rank. This "secondary fluorescence" is attributed mainly to the presence of the mobile phase, a conclusion which is supported by a notable parallelism among the trends, in this rank range, of fluorescence intensity, chloroform-solubles yield and Gieseler maximum fluidity (5). The spectral distributions of the secondary fluorescence undergo a red shift due to the increasing conjugation of double bonds which accompanies coalification.

After chloroform extraction, coals still demonstrate low levels of residual fluorescence (Fig. 3), interpreted as being due to entrapped portions of the mobile phase. The figure also shows that mild thermal pretreatment (350°C for 3 min; N_2 atmosphere) considerably enhanced the intensity of fluorescence which subsequently was entirely removed by extended chloroform extraction (6). Apparently the heat treatment disrupts the bonding between network system and mobile phase, resulting in increased yield; with reduced energy transfer between the two phases, there is less possibility for intermolecular quenching, so that fluorescence intensity is enhanced.

Brown and Waters (16) showed that the yield of chloroform-soluble extract could be increased several-fold by coal pretreatment which involved rapid heating and cooling. The liberation of additional extract by this means is identical to the situation described above. The enhanced yields reported by Brown and Waters are of the same order as those corresponding to the initial conversion stage in the catalytic hydrogenation experiments. As this first stage incurred little or no net consumption of hydrogen external to the coal, it is believed that the effects of preheating and of low severity catalytic hydrogenation are equivalent. Brown and Waters concluded that the material derived by preheating was originally present as such in the coals and was not a product of pyrolysis. This is more or less the same definition of the mobile phase as it is understood in the present research.

Just as the untreated bituminous coals showed a parallelism among chloroform-solubles, vitrinite fluorescence intensity and Gieseler plasticity, the products of a single hvAb coal (PSOC-1510), hydrogenated for varying reaction times with a sulfided molybdenum catalyst, showed similar interrelations (Fig. 4). These results, together with the observation that chloroform-extracted coals lose their capability to become thermoplastic (17), are convincing evidence that the mobile phase is a necessary agent in promoting fluid behaviour.

Chloroform extraction of the whole products of dry hydrogenation (400°C; 60 min; 5% Mo; 7 MPa H_2) of PSOC-1266 produced a strongly fluorescent extract and non-fluorescent residue. After drying, the extract was seen under the microscope to contain two components with distinctive fluorescence characteristics (Fig. 5). Component 1 had a fluorescence spectrum very similar to that of the oil (hexane-soluble) fraction of the same hydrogenation products; component 2 had a spectrum like that of the corresponding asphaltene fraction, which, in addition to a higher peak wavelength, had a very much lower fluorescence intensity than the oil fraction. The observed differences in the fluorescence characteristics of the oil and asphaltene fractions are believed to be due to the more highly condensed materials which constitute the latter.

As reaction conditions became more severe, the fluorescence spectra of the hydrogenated vitrinite underwent a red shift (Fig. 6) from around 600 nm at 350°C to around 680 nm at 400°C. The trend is believed to be due to the production of a higher proportion of asphaltenic material from the vitrinite network, as shown earlier by the reduction in O/A ratio with increasing conversion.

Synopsis

The liquefaction behaviour to the four coals investigated allows a general definition of the mobile phase as that material which is readily liberated by mild thermal treatment. The mobile phase components are richer in hydrogen and significantly more aliphatic than the structural units which comprise the network. The latter are connected by much stronger bonds, necessitating more severe reaction and higher hydrogen consumption to secure their release. The compositions of the mobile phase and network are also dependent upon coal rank.

Fluorescent light microscopy allowed a distinction between the extractable liquids, which fluoresce strongly, and the matrix, which does not. The disruption of weak bonding effected by thermal treatment, which increased the

extract yield, was paralleled by changes in fluorescence intensity. The fluorescence spectra of the extracts also reflect the compositional differences between the mobile phase and the solubilised coal network.

Based upon solubility in chloroform, the mobile phase is estimated to constitute 5-15% wt of the coal. Obviously, this amount will vary if other characterising solvents are used.

It is to be expected there will be a gradation in the manner in which the smaller molecules are associated with the network. This may involve both physical and chemical forces such as covalent bonds; dispersion forces; hydrogen bonding; and could involve physical entrapment. It is doubtful whether any single technique can distinguish between these different modes of attachment sufficiently clearly to establish a precise boundary. Different energies will be required to disrupt the different types of attachment. It may be significant that Brown and Waters (16) found that the increase in chloroform-soluble yield upon coal preheating was dependent upon the pretreatment temperature. A minor peak in the yield was observed at temperatures in the region of 300°C and a second major one at 400-450°C.

The particular experimental studies, which have been described here, have provided a basis for a practical definition of the boundary of the mobile phase in coals and some tentative clues to the nature of its association with the network. Inevitably, other research techniques will provide a different perspective.

Acknowledgement

The authors wish to acknowledge Peter Stansberry and Maite Terrer whose individual and collaborative research work provided the basis for this contribution.

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Table 1. Coal Properties

Penn State Sample Bank No.	PSOC-1403	PSOC-1266	PSOC-1168	PSOC-1510
Seam	Anderson	L. Kittanning	L. Kittanning	L. Kittanning
County	Campbell	Mahoning	Lawrence	--
State	Wyoming	Ohio	Pennsylvania	Pennsylvania
ASTM rank	sub B	hvAb	hvAb	hvAb
Mean maximum reflectance of vitrinite (%)	0.40	0.83	0.83	0.89
Moisture (a.r. wt%)	23.3	3.4	2.4	1.4
Mineral Matter (a)	--	--	--	--
(dry, wt%) (c)	11.9	6.1	14.5	7.2
	Elemental Composition (% dmmf)			
Carbon	72.9	83.2	71.8	77.4
Hydrogen	4.5	5.0	4.9	4.9
Oxygen (b)	20.4	8.6	18.8	15.2
Nitrogen	1.2	2.1	1.6	1.7
Organic sulfur	0.9	0.5	2.9	0.8
	Petrographic Composition (Mineral-Free, vol %)			
Vitrinite	88	91	88	83
Exinite	2	3	4	10
Inertinite	11	6	7	7

(a) reported as ASTM ash
(b) by difference
(c) by low-temperature ashing

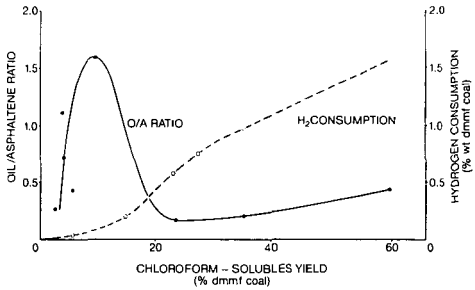

Figure 1. RELATIONSHIP OF H_2 CONSUMPTION AND O/A RATIO FOR hvAb COAL, PSOC-1266 (solvent-free hydrogenation; 400°C; 1% wt sulfided Mo; 7 MPa H_2)

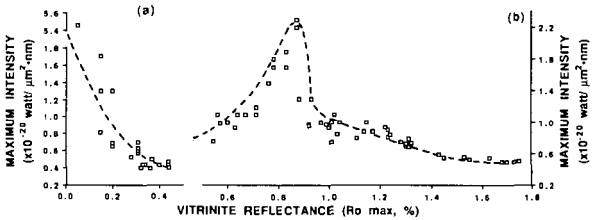

Figure 2. PRIMARY AND SECONDARY VITRINITE FLUORESCENCE (Absolute Units)
(a) PRIMARY FLUORESCENCE IN U-V IRRADIATION
(b) SECONDARY FLUORESCENCE IN BLUE-LIGHT IRRADIATION

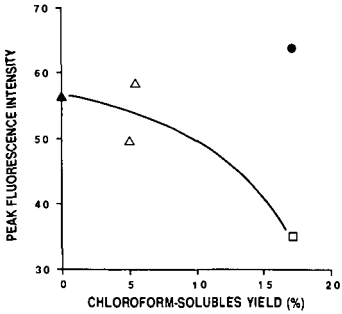

Figure 3. PEAK FLUORESCENCE INTENSITY OF RAW (▲) AND EXTRACTED VITRINITES (△) VERSES YIELD OF CHLOROFORM-EXTRACTABLES.
Also shown are data for thermally pretreated vitrinite before (●) and after (◻) prolonged chloroform extraction (ref.6)

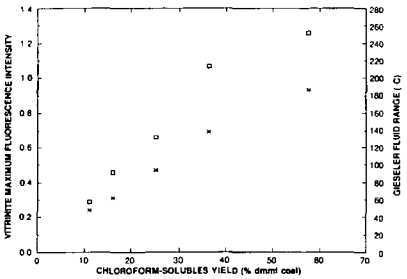

Figure 4. RELATIONS AMONG FLUORESCENCE INTENSITY, CHLOROFORM-SOLUBLES YIELD AND GIESELER PLASTICITY FOR HYDROGENATED COAL (PSOC-1510; solvent-free; 400°C; 5-60 min; 1% wt sulfided Mo; 7 MPe H_2 cold)

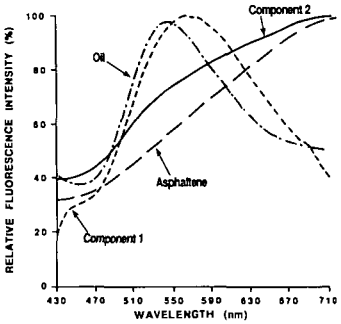

Figure 5. COMPARISON OF FLUORESCENCE SPECTRA OF TWO COMPONENTS IN CHLOROFORM-SOLUBLES FRACTION WITH OIL AND ASPHALTENE FRACTIONS OF HYDROGENATED COAL (PSOC-1266; solvent-free; 400°C; 60 min; 5% wt sulfided Mo; 7 MPe H_2 cold)

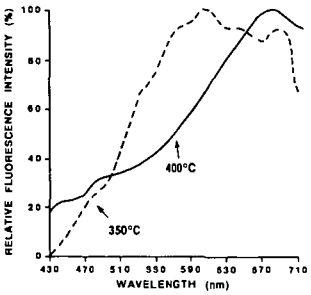

Figure 6. FLUORESCENCE SPECTRA OF VITRINITE FOLLOWING HYDROGENATION AT 350 AND 400°C (PSOC-1266; solvent-free; 60 min; 5% wt sulfided Mo; 7 MPa H_2 cold)

A Study of the Proposed Two Phase Model for High-Volatile Bituminous Coals

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Introduction

It has been proposed that coal is composed of macromolecular networks and relatively small molecules occluded in macromolecular networks.[1,2] This idea is known as a so-called two phase or host-guest model, which states that a mobile (molecular) phase or a "guest" of relatively low molecular weight such as a pentacyclic triterpane and various long chain alkyl aromatics is physically held inside an immobile (macromolecular) phase or a host of relatively high molecular weight. This is alternatively interpreted as a modified model in which some portions of the mobile phase are bonded to the immobile phase, however, it is thought that a substantial portion of the mobile phase is clathrated within the immobile phase.[3,4]

Although low-molecular-weight (extractable) compounds with difficulty in extraction were investigated in 1960 to early 1970[5,6] they were reestimated in late 1970 to early 1980 as components with mobile protons since the ^1H NMR free-induction decay was applied for coal to distinguish between mobile protons and immobile protons.[7-13] Many works have been recently reported to characterize the two phase model,[14-20] and there seems to be consensus by them that only some portions of a mobile phase can be extracted using conventional extraction procedures because of restricted orifice sizes of immobile phases or networks. However, there is no direct evidence to prove the two phase model.

In this paper, the two phase model was studied by two sets of experiments. One used a combination of chemical class fractionations of coal extracts and mild pyrolyses of coals and extracts. Another used an n-butylamine treatment[22] of coal followed by two different pyrolyses. The concentrations of n-alkanes, polycyclic aromatics (PAH), and pentacyclics, regarded as representative compounds in the mobile phase, were carefully determined. It is concluded that the two phase model is not applicable for high-volatile bituminous coal. It is also inferred that major constituents of coal are uniformly abundant in both extracts and residues.

Experimental Section

Five different rank coals were obtained from Exxon Research and Engineering Co. (Annandale, NJ). ACS reagent and HPLC grade solvents were used. Palladium on activated carbon (10%) was obtained from Alfa Products (Danvers, MA). Tetrahydrofuran (THF) was distilled before use, but other materials were used without purification.

Illinois No. 6 coal was treated as outlined in Figure 1. The coal (6g) was put into a 300 mL bomb (Parr Instrument Co., Moline, IL) in a removable Pyrex liner. After adding n-butylamine (25 mL), evacuating, and purging with N_2 five times, the bomb was heated to 350°C within 10 min with a Parr bomb heater, held at 350 ± 3°C for 4 h with agitation with a magnetic stirrer.

After treatment, the products were washed out with THF, filtered, and Soxhlet-extracted with THF. One part of the THF extract was hydrotreated

following the Mudamburi and Given's procedure.[22,23] A sample (2g) was heated with tetralin (5.6 mL) and H_2 (initial pressure 6.5 MPa) in a tubing bomb heated by immersion in a preheated fluidized bed sand bath for 30 min at 425°C. Another sample (2g) was pyrolyzed in cyclohexane (30 mL) and 3% aqueous H_2O_2 (3 mL) at 350°C for 30 min in a bomb. The sample (0.3g) after H_2O_2 treatment was further refluxed in decalin (50 mL) with Pd (10%) on activated carbon (300 mg) at 190°C for 24 h.

Five different rank coals were put into Pyrex glass flasks under a dry N_2 atmosphere and were heated at 250 ± 1 °C and about 660 mmHg pressure under N_2 flow in a Forma Scientific high-temperature vacuum oven 24 h as shown in Figure 2. Starting and pyrolyzed samples (2 - 3 g) were extracted with 200 mL of THF for 24 h in a Soxhlet apparatus under N_2 atmosphere. These extracts were fractioned into chemical classes by column adsorption chromatography on neutral alumina.[24] The fractionation sheme is summarized in Figure 2. The aliphatic and neutral aromatic fractions were analyzed in this study.

Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with a flame ionization detector was used. Sample injection was made in the splitless mode, and helium carrier gas was set at a linear velocity of 50-60 cm s^{-1}. The fused silica capillary tubing (30 m x 0.25 mm i.d.) coated with SE-54 (film thickness of 0.25 μm) was obtained from SUPELCO, INC. (Bellefonte, PA). Compounds were identified by comparison of sample component retention data with those of pure standards and by gas chromatography/mass spectrometry (GC/MS). Mass spectral data were collected with a Hewlett-Packard 5970 mass spectrometer system operated in the electron-impact mode at 70 eV with the ion source and analyzer temperature held at 250 and 280°C, respectively, with the scan speed set at 300 amu s^{-1}.

Results and Discussion

Given's et al.[22,23,25] reported that the yield of n-alkanes and n-alkyl aromatics released from coals by liquefaction in tetralin at 400-425°C was 6-10 times greater than the yield obtained by Soxhlet extraction. They found it difficult to conceive of such homologous series being released from the macromolecular network by thermal reactions, and inferred that the compounds were clathrated inside the network. It is, however, impossible to distinguish between the disruption of chemical bonds and physical bonds using their data. Since most of the organic matter of high-volatile bituminous coals could be extracted with THF after mildly heating in n-butylamine, n-alkanes and PAH were analyzed for the THF extracts from an original and n-butylamine heated coals to investigate physically trapped low-molecular-weight compounds. The THF extract from the n-butylamine heated coal was pyrolyzed using the Given's procedure as well as another different method to differentiate between breaking covalent bond and physical forces (Figure 1). Although the detailed solvation mechanism in n-butylamine is not clear, the differences of abundances of such compounds between Sample II and Sample III or IV are unequivocally due to degradation of chemical bonds. (See Figure 1)

The yield of Sample II from the Illinois No. 6 coal was approximately 85 wt %, which was normalized for the extract and the non-extract because of 18 wt % of the weight gain after heating in n-butylamine. Relative abundances of n-alkanes in the Samples were semi-quantitatively analyzed by GC. The results are shown in Table I relative to n-$C_{20}H_{42}$ in Sample I. It is obvious that the yields of these compounds in Samples III and IV are greater than 10 times of those in Samples I and II, while the yields of these compounds in Samples I

and II are almost comparable. From this result, it can be concluded that the increased compounds in Samples III and IV were mostly derived from the thermal pyrolysis of macromolecules, and were not released from clathrated compounds inside the network or immobile phase.

Figure 3 shows the gas chromatograms of the aliphatic fractions of Samples I, II, and IV. It is obvious that n-alkanes with carbon numbers 17 to 22 were relatively increased from Samples II to IV by the pyrolysis. Pentacyclic triterpanes are presumably thermally labile compared with n-alkanes, and their abundances decreased in the order of Samples I, II, and IV as expected. The relative abundances of the major PAH in Samples I - V are also shown in Table I relative to phenanthrene in Sample I. These compounds in Samples III - V were noticeably increased by thermal reactions similar to the n-alkanes. They are apparently important partial constituents of coal macromolecules, or derived from macromolecules during pyrolysis.

It can be interpreted that the great increase of n-alkanes in the product obtained by Given et al. was due to the degradation of coal macromolecules, because more than 10 times of n-alkanes originally present in Illinois No. 6 coal extracts were formed from n-butylamine extracts under their reaction conditions. It is proposed that n-alkyl groups are one of important constituents of Illinois No. 6 coal macromolecules, and most of the n-alkanes in coal-derived products were formed from high molecular weight compounds.

The Illinois No.6 THF extract and a dried mixture of fractions A-3 and A-4 were heated at 250 °C for 24 h and fractionated into chemical classes as shown in Figure 2. Since high-molecular-weight aromatic Compounds strongly adsorb on neutral alumina, they are not eluted by benzene but are found in the A-3 and A-4 fractions.[26] Figure 4 shows gas chromatograms of the A-2 (aromatics) fractions of these heat-treated samples as well as the A-2 fraction of the original coal extract. Significant amounts of material were found in fractions A-1 and A-2 after heating the extract fractions A-3 and A-4 to 250 °C for 24 h. Simply refractionation a mixture of A-3 and A-4 gave very little material in the A-1 and A-2 fractions, so it is clear that the origin of the new compounds is pyrolysis. Furthermore, many new peaks are found in the chromatograms of these fractions. Clearly new compounds are present. Their origin could only be pyrolysis reactions occurring in a coal extract at 250 °C. Among the new compounds are a number of low-molecular-weight aromatic compounds such as alkylbenzenes, alkylnaphthalenes, phenanthrene, and alkylhydroaromatic triterpanes, presumably formed by pyrolysis of the high-molecular-weight fractions. Both results, obtained by different experimental procedures, are clearly consistent.

There were two purposes for the reaction leading to Sample V. One was to confirm the identification of the hydroaromatics, because it is known most of the hydroaromatics are dehydrogenated by Pd on activated carbon at the low temperature used in this study. The second was to investigate the effect of aromatization by dehydrogenation during coal liquefaction.

Hydroaromatics such as hydroanthracenes, hydrophenanthrenes, and hydropyrenes were abundant in Sample IV compared to Sample III, while 4- and 5- ring PAH such as chrysene and benzopyrenes were abundant in Sample III (Table I). It is thought that the major reaction producing Sample IV from Sample II is a mild radical cracking while the major reaction involved in forming IV from Sample II is hydrocracking including thermal aromatizations at high temperature. Hydroaromatics, therefore, seem to be one of important constituents of coal macromolecules. Although aryl groups such as biphenyls

and phenylnaphthalenes are abundant in Samples III and IV, carbon linked aromatics were not found in these samples at a significant level. The abundances of the aliphatics and aromatics in Sample V are quite similar to other coal liquids such as the Solvent-Refined Coal II heavy distillate (SRC II HD),[27] although the feedstock was a different coal.

From above results, we can infer as the follows: coal components are quite uniform despite extracts or non-extracts. Most n-alkanes and PAH are not physically trapped inside networks. They are both free molecules and partial constituents of macromolecules or derived from macromolecules during pyrolysis, and can be thought as "preferred" constituents.[27] Most the neutral free low-molecular-weight compounds can be extracted under conventional conditions, such as a Soxhlet extraction.

Since the two phase model does not appear to be appropriate for Illinois No. 6 coal, the coal should be considered as a mono phase. Coal molecules contain "preferred" components such as n-alkanes and PAH studied in this paper. The preferred components are estimated for Illinois No. 6 coal. It also seems that aromatics linked with a couple of carbons are not so substantial in Illinois No. 6 coal as above "preferred" structures.

The mono phase model and its "preferred" structures contained in the Illinois No. 6 coal are essentially different from the two phase model. The "preferred" moieties are partial constituents of coal macromolecules regardless of molecular weight, and some exist as free molecules of low-molecular-weight.

Acknowledgments

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Table I. Approximate Relative Abundances of Selected Compounds in Each Sample

	Sample[b]				
	I	II	III	IV	V
n-$C_{17}H_{36}$	1	4	40	110	40
n-$C_{18}H_{38}$	2	5	40	70	70
n-$C_{19}H_{40}$	2	4	50	30	30
n-$C_{20}H_{42}$	1	3	40	20	20
n-$C_{21}h_{44}$	2	6	80	20	20
n-$C_{22}H_{42}$	0.3	0.5	30	10	10
naphthalene	a	a	3	4	10
fluorene	a	a	0.2	5	5
phenanthrene	1	1	3	10	20
anthracene	0.05	0.05	0.1	1	4
fluoranthene	a	a	2	4	5
pyrene	0.1	0.1	2	3	4
benzo[b]fluorene	a	a	0.4	0.5	0.05
benz[a]anthracene	a	a	2	0.03	0.06
chrysene	a	a	2	0.1	0.01

[a] <0.01

[b] Relative abundances are shown as n-$C_{20}H_{42}$=1 for aliphatics and phenanthrene=1 for aromatics.

Table II. Neutral Aromatics Identified in Original and Pyrolyzed Illinois No. 6 Samples

Peak No.	Molecular Mass and/or Major Fragments[a] m/z	Possible Structure
1	106, 120	C_2- and C_3-benzene
2	142	2-methylnaphthalene
3	142	1-methylnaphthalene
4	156	C_2-naphthalene
5	168	methylbiphenyl
6	182	C_2-biphenyl
7	355(100), 281(62.5), 221(44.5), 207(77.0)	unknown
8	180	methylfluorene
9	178	phenanthrene
10	178	anthracene
11	194	C_2-fluorene
12	198	methyldibenzothiophene
13	355(3.3), 281(5.3), 223(10.3), 207(22.1), 149(100)	unknown
14	192	methylphenanthrene
15	208	C_3-fluorene
16	202	pyrene
17	216	methylpyrene
18	228	benzo[a]anthracene
19	281(2.0), 259(3.3), 241(1.2), 207(8.7), 147(14.6), 129(100)	unknown
20	228	chrysene
21	279(9.5), 207(37.8), 167(30.1), 149(100)	unknown
22	412(12.0), 397(10.4), 384(6.1), 369(4.0), 281(21.9), 207(100)	alkyl pentacyclic hydroaromatics
23	440(2.0), 339(28.3), 281(22.1), 207(100)	alkyl pentacyclic hydroaromatics
24	429(3.4), 415(3.4), 289(30.6), 281(20.5), 207(100)	unknown

[a]Numbers in parentheses denote relative abundances of mass spectra.

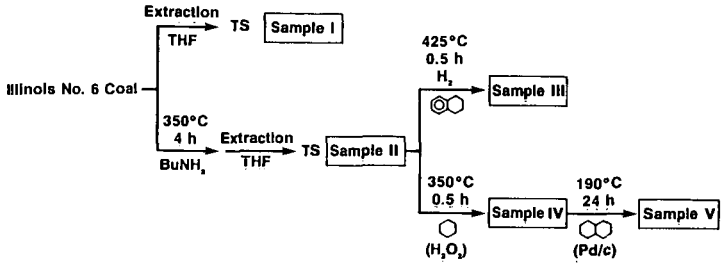

Figure 1. Solvent treatment and reaction scheme of Illinois No. 6 coal.

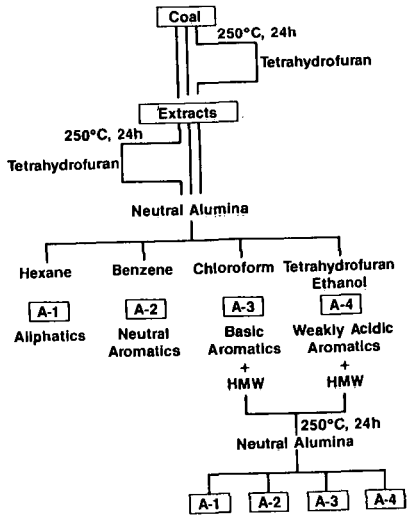

Figure 2. Fractionation and pyrolysis scheme. Key: HMW = high-molecular-weight compounds.

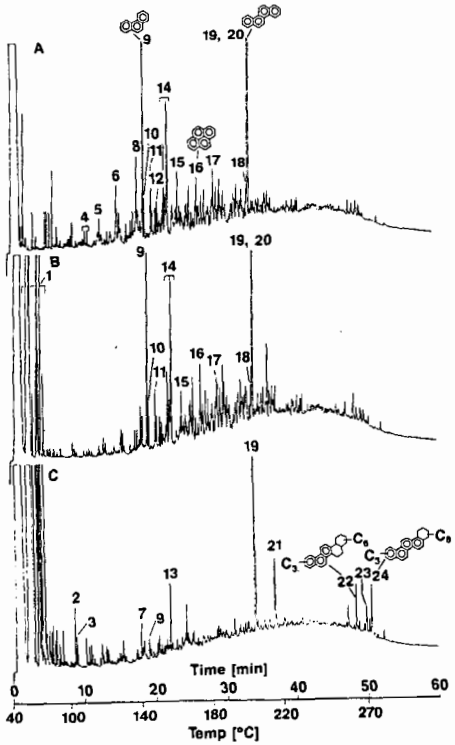

Figure 3. Gas chromatograms of aliphatic fractions of (A) Sample I, (B) Sample II, and (C) Sample IV.

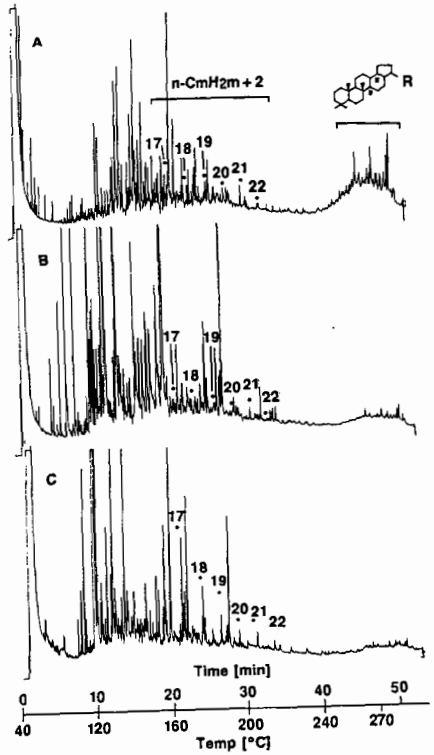

Figure 4. Gas chromatograms of the aromatic fractions (A-2) of the (A) original coal THF extract, (B) heat-treated THF extract, and (C) heat-treated A-3 and A-4 mixture for Illinois No. 6.

THE MOBILE PHASE IN COAL VIEWED FROM A MASS SPECTROMETRIC PERSPECTIVE

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INTRODUCTION

In recent years few topics have generated a more spirited discussion among coal scientists than the issue of the putative binary (mobile + network) phase nature of coals [1]. Initially based on NMR observations [2], the concept of a "mobile phase" in coal soon came to encompass a broad range of more or less readily extractable and/or distillable lower molecular weight (MW) components, variously referred to as "guest molecules" [3], "clathrates" [1,4] or simply, and perhaps most succinctly, "bitumen" [5].

None of these terms appears to be completely satisfactory. The concept of "mobility" in NMR spectroscopy is quite different from that in the field of separation science, where mobility generally requires a measurable degree of solubility and/or distillability in liquid or gaseous media, respectively. For example, polymethylene-like moieties, such as found in some coal components [6], are highly "mobile" in NMR terms [1], without necessarily being extractable by solvents or distillable by nondestructive heating.

The term "guest molecules", originally introduced to indicate specifically labeled marker molecules used in NMR studies of coal [7], is equally unsatisfactory for mobile phase components indigenous to the coal itself. Also, there appears to be insufficient evidence for the presence of sizeable quantities of true "clathrates" to rule out other possibilities, e.g., strong noncovalent bonding rather than physical entrapment.

Finally, completely equating the "mobile phase" with solvent (e.g. pyridine) extractable "bitumen" in coal ignores the potential presence of colloidal particulate matter in the pyridine extracts as well as possible solvent-induced scission of weak chemical bonds. Furthermore, the solvent-extractable fraction may well include macromolecular components, such as resinites.

Mass spectrometric observations have thus far played a rather limited role in the "mobile phase" discussions [1] but are starting to shed some light on the key question: is there conclusive evidence for the presence of a chemically and/or physically distinct "mobile phase", as opposed to a continuum of possible molecular sizes and structures?

In the context of the present discussion the term "mobile phase" will be used to describe those components which can be thermally extracted ("distilled", "desorbed") under vacuum at temperatures below the thermal degradation range of the coal. The residue, designated as the nonmobile ("network") phase, is

thermally degraded in the pyrolysis temperature range. Of course, the onset of pyrolysis may vary considerably, depending on heating rate, rank and coal type [8].

EXPERIMENTAL

Two samples of -100 mesh ANL-PCS (Argonne National Laboratory-Premium Coal Sample) coal, a Pittsburgh #8 seam (hvAb) and a Beulah Zap seam (lignite) sample, were analyzed by vacuum pyrolysis field ionization mass spectrometry (Py-FIMS) and Curie-point pyrolysis low voltage electron ionization mass spectrometry (Py-EIMS) in the time-resolved (TR) mode. In addition, a sample of fresh -60 mesh Hiawatha seam (hvBb) coal, obtained from an Emery County (Utah) mine was analyzed by TR Py-EIMS. Conventional characterization data on ANL-PCS coals can be found elsewhere [9].

For temperature-programmed pyrolysis in combination with TR-FIMS, about 100 ug samples were transferred into a quartz crucible and introduced into the high vacuum (10^{-3} Pa) of the ion source (200 C). The instrumental setup using a Finnigan MAT 731 double-focussing mass spectrometer, a combined EI/FI/FD/FAB ion source and a AMD Intectra direct introduction system has been previously described in detail [10]. The samples were heated linearly from 50 C to 750 C at a rate of 100 C/min. In general, 34 FI mass spectra were recorded in the m/z 50-900 mass range.

The Py-EIMS experiment was performed using an Extranuclear 5000-2 Curie-point Py-MS system. The coal sample was hand ground into a fine, uniform suspension in Spectrograde methanol (5 mg of sample per ml of methanol). A single 5 µl drop of the suspensions was coated on the ferromagnetic filament (Curie-point temperature of 610 C) and air-dried under continuous rotation for approximately 1 min, resulting in 25 µg of dry sample on the filament. The filament was inserted into a borosilicate glass reaction tube and introduced into the vacuum system of the mass spectrometer. Directly in front of the open, cross beam type electron ionization chamber the ferromagnetic wire was inductively heated for 0.4 s at a rate of approximately 1500 K/s to an equilibrium temperature of 610 C (as determined by the Curie-point temperature of the wire). The pyrolysis inlet was preheated at 200 C to reduce the condensation losses. Other MS conditions were as follows: electron impact energy 12 eV, mass range scanned 50-200 amu, number of scans 41, total scan time 15 s.

RESULTS AND DISCUSSION

Is there a chemically and/or physically distinct "mobile phase" in coal as opposed to a continuum of molecular sizes and structures? The temperature-resolved total ion intensity (TII) profile of a Pittsburgh #8 coal in Figure 1 obtained by temperature programmed Py-FIMS shows the presence of a low temperature "hump' which appears to explain 25-30% of the total integrated FI signal intensity in the mass range m/z 50-900. Previously, Chakravarty et al. [11] reported a similar profile for Pittsburgh #8 coal obtained by Curie-point pyrolysis in combination with time-resolved low voltage EIMS and were able to demonstrate that the low temperature hump consisted primarily of homologous series of alkylsubstituted aromatic (e.g., benzenes, naphthalenes, phenanthrenes) and hydroaromatic (e.g., tetralins) compounds. These compounds were interpreted to represent the thermally extractable ("vacuum distillable") fraction of the well known "bitumen" component of most high volatile bituminous coals.

More recently, Yun et al. [12] confirmed the presence of this low temperature hump in vacuum thermogravimetry (TG)/MS studies of ANL PCS coals using low voltage EIMS. An important aspect of the latter study was that the mass spectra obtained for the thermally extractable components as well as for the main pyrolysis event were found to be virtually indistinguishable from those observed by Chakravarty et al. using Curie-point Py-EIMS, notwithstanding a 5 orders of magnitude lower heating rate (3.3×10^{-2} C/s vs. 1.5×10^{3} C/s) and 3 orders of magnitude larger sample (50 mg vs. 25 μg).

Furthermore, with proper preheating of the transfer zone between pyrolysis and ionization regions, the low voltage EI mass spectra of Pittsburgh #8 coal were shown to be highly similar to the corresponding FI mass spectra in the m/z 50-300 mass range when allowing for known differences in ion transmissivity between the different types of mass spectrometers used [13]. In other words, time-resolved TII profiles similar to those shown in Figure 1 as well as to the corresponding mass spectra in Figure 2a have been observed (up till m/z 300) by means of 3 separate Py-MS methods, together covering a broad range of different pyrolysis, ionization and mass spectrometric detection techniques.

The advantages of the FIMS data shown here are that little or no fragmentation of molecular ions occurs during the ionization process and that FI response factors for aromatic and hydroaromatic compounds tend to show relatively little variation [14]. In combination with the large mass range and nearly constant ion transmissivity of the magnetic sector instrument used, the FI ion profiles and FI spectra shown in Figures 1 and 2, respectively, are suited for making reliable semiquantitative estimates with regard to relative the yield and molecular weight distribution of coal tar fractions consisting primarily of aromatic and hydroaromatic or alicyclic compounds. Unfortunately, FI response factors for aliphatic compounds show a great deal more variation [15]. Consequently, for the purpose of this discussion no attempt will be made to quantitate the contributions or molecular weight distributions of aliphatic components in spite of their well recognized role in coal pyrolysis processes.

Comparison of the low temperature component ("mobile phase") and high temperature component ("bulk pyrolyzate") spectra in Figures 2b and 2c, respectively, reveals roughly similar average molecular weights (M_n~350) but rather different MW distributions. Moreover, there are pronounced differences in relative FI signal intensities, especially in the mass range up to m/z 400.

Figure 3 shows the relationships between the temperatures and molecular weight distributions for 6 successive regions of the TII profile in Figure 1. Interestingly, regions a, b and c, primarily representing the low temperature components, show relatively narrow MW distributions around M_n values which markedly increase with temperature. This is consistent with the proposed interpretation of the low temperature "hump" as a vacuum desorption and distillation process rather than as a pyrolytic process. By contrast, regions d, e and f, representing the major TII maximum in Figure 1, exhibit much broader MW distributions characterized by a gradually decreasing average molecular weight of the pyrolyzate. This would seem to be consistent with the proposed interpretation of the major TII peak as the "bulk pyrolysis" event [11].

The transition between c and d is rather abrupt, suggesting that we may indeed be witnessing contributions from two more or less discrete populations of molecules with regard to molecular size distributions. However, in view of the extremely complex interplay between intramolecular and intermolecular, as well

as intraparticle and extraparticle, parameters in the experiments described here, the possible presence of a continuum of molecular sizes can certainly not be ruled out at this point.

More informative, perhaps, are the marked differences in relative FI signal intensities between the mass spectra shown in Figures 2b and 2c. In agreement with the previously mentioned results reported by Chakravarty et al. [11] and Yun et al. [12], the mass spectrum of the low temperature component (Figure 2b) appears to be dominated by homologous series of aromatic and hydroaromatic compounds. Chemical identification of many of the compounds up to MW 350 has been accomplished by high resolution GC/MS [16,17], although precise identification of the many possible isomeric structures involved will have to await the availability of suitable reference compounds.

The spectrum of the bulk pyrolysis event in Figure 2c appears to be dominated by hydroxy aromatic compounds, e.g., alkylsubstituted phenols and naphthols. Positive identification of these compounds is much less straightforward, although a surprisingly high degree of correspondence can be found with Py-GC/MS data on Pittsburgh #8 coal [18]. Moreover, Chakravarty et al. have demonstrated that the main pyrolysis event can be deconvoluted into at least three overlapping events involving vitrinitic moieties in addition to alginite/cutinite-like and sporinite-like components [11].

In Curie-point Py-MS studies of maceral concentrates [19], vitrinitic moieties were shown to be the main source of the hydroxy aromatic components. Consequently, the hydroxy aromatic signals observed in Figure 2c appear to be primarily derived from vitrinite-like components by means of pyrolytic processes. Presumably, therefore, the "nonmobile phase", rather than the "mobile phase", is the main source of the phenols observed in TG/MS and Py-MS studies of Pittsburgh #8 coal. Further support for this conjecture comes from the observation that phenolic products are also observed in Py-MS analysis of pyridine extracts of Pittsburgh #8 coal known to contain colloidal matter whereas the corresponding tetrahydrofuran extracts, free of colloidal material, produced no phenols [18].

In low rank coals, such as lignites, vitrinitic components have been shown to produce abundant (alkyl) dihydroxy benzene and methoxy hydroxy benzene compounds of a structural type which can be traced back to fossil lignin moieties [20]. In agreement with these earlier studies, the high temperature component spectrum of a Beulah Zap lignite (Figure 4c) exhibits dominant (alkyl) dihydroxy benzene signals at m/z 110, 124, and 138. The low abundance of FI signals above m/z 200 can be attributed to the more highly crosslinked nature of the macromolecular network phase in lignites.

As shown in Figure 4b, the low temperature fraction of Beulah Zap lignite reveals a completely different type of mass spectrum. From previous studies on soil organic matter by Hempfling et al. [21], the FIMS signals in Figure 4b are known to represent various plant-derived compounds such as n-fatty acids or monomeric esters (m/z 368, 396, 424, 452, 480) and aromatic diesters (m/z 544). Apparently, we are dealing with thermally extractable "biomarker" compounds which have not yet been linked into the macromolecular network phase of the lignite.

The above observations point to the importance of <u>rank</u> and <u>depositional environment</u> in defining the molecular characteristics of the "mobile phase" as

well as the "network phase" of coals. To complicate matters further, post-depositional factors, such as "weathering" during storage or transportation, also strongly effect the composition of both phases, as reported by Jakab et al. [22]. Figures 5 and 6 illustrate the effects of mild oxidation of a Hiawatha hvb coal for 100 hours at 100 C under controlled laboratory conditions, as measured by time-resolved Curie-point Py-MS. Both the low temperature hump as well as the bulk pyrolysis event are markedly reduced. Moreover, the composition and nature of the low temperature components have undergone a dramatic change (Figure 5b). The alkyl substituted naphthalenes and tetralins dominating the spectrum of fresh coal (Figure 5a) are nearly completely gone. Instead, we now find low MW, oxygen-containing mass signals apparently representing aliphatic carboxylic and carbonylic functionalities, e.g., liberated by low temperature pyrolysis of weak oxygen bonds [22]. These observations would seem to indicate that it is pointless to study "mobile phase"/"network phase" phenomena in coal samples of uncertain weathering status.

CONCLUSIONS

Temperature-programmed vacuum pyrolysis in combination with time-resolved soft ionization mass spectrometry allows principally to distinguish between two devolatilization steps of coal which are related to the "mobile" and "non-mobile" phase, respectively. The mass spectrometric detection of almost exclusively molecular ions of the thermally extracted or degraded coal products enables to study the change of molecular weight distribution as a function of devolatilization temperature. Moreover, major coal components can be identified which are released at distinct temperature intervals.

When limiting our analysis and discussion of mobile phase components to the thermally extractable fraction, we may conclude that the yields and compositions of these products (estimated to constitute 5-15% of dmmf coal weight) are strongly dependent on rank, coal type and weathering status. In coals of hvb and higher rank the nature of the thermally extractable bitumen fraction is consistent with that of a natural pyrolyzate formed by catagenetic processes during the "oil formation window" stage of maturation with subsequent loss of the more reactive oxygen containing moieties. Not surprisingly, in low rank coals various types of relatively little altered "biomarkers" molecules appear to be important constituents.

Furthermore, artificial "weathering" of coal under carefully controlled conditions in the laboratory, reveals a rapid loss of thermally extractable mobile phase components (possibly by "grafting" to the network phase [23]) accompanied by a decrease in total pyrolysis yields. This points out that in future discussions of "mobile phase" phenomena only results obtained on coals of known weathering status, e.g., ANL-PCS coals, should be used.

With regard to the central question whether there exists a chemically and/or physically distinct "mobile phase" in coals, mass spectrometric data on ANL-PCS coals (only 2 of 8 are presented here) strongly support the presence of a thermally extractable, bitumen-like fraction which is chemically distinct from the remaining coal components.

ACKNOWLEDGEMENT

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phases of the coal studies leading to the experiments reported in this paper. The work described here is financially supported by the Advanced Combustion Engineering Research Center (funded by NSF, the State of Utah, 23 industrial participants, and US DOE).

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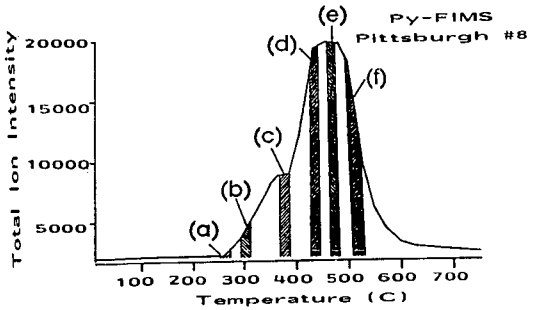


Figure 1. Thermogram of a Pittsburgh #8 coal sample showing a distinct low temperature release of mobile phase components. Crosshatched intervals a-f correspond to molecular weight profiles of FI ions in Figs. 3a-f, respectively.

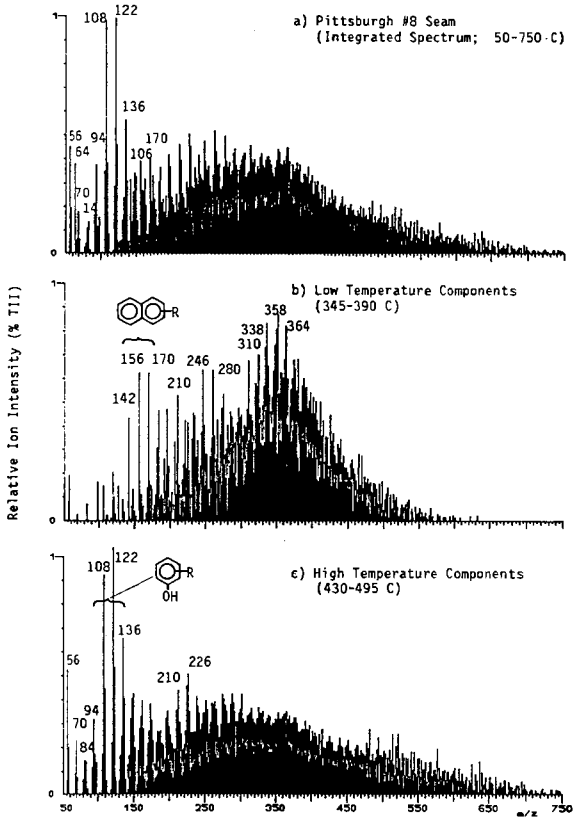


Figure 2. Comparison of Pittsburgh #8 (hvb) coal Py-FI mass spectra recorded over different temperature intervals. Note marked differences between low temperature components in (b), thought to represent primarily vacuum distillable "mobile phase" constituents, and high temperature components in (c), thought to represent mainly pyrolysis products derived from the macromolecular "network phase".

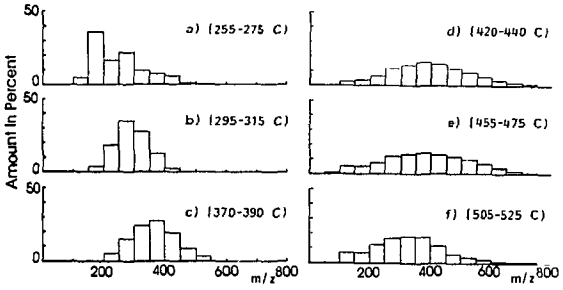


Figure 3. Molecular weight distributions of pyrolyzates in six successive temperature intervals during Py-FIMS analysis of Pittsburgh #8 coal. Each interval corresponds to a cross-hatched region in Figure 1. The FI signal intensities were added in arbitrarily chosen mass classes of 50 daltons.

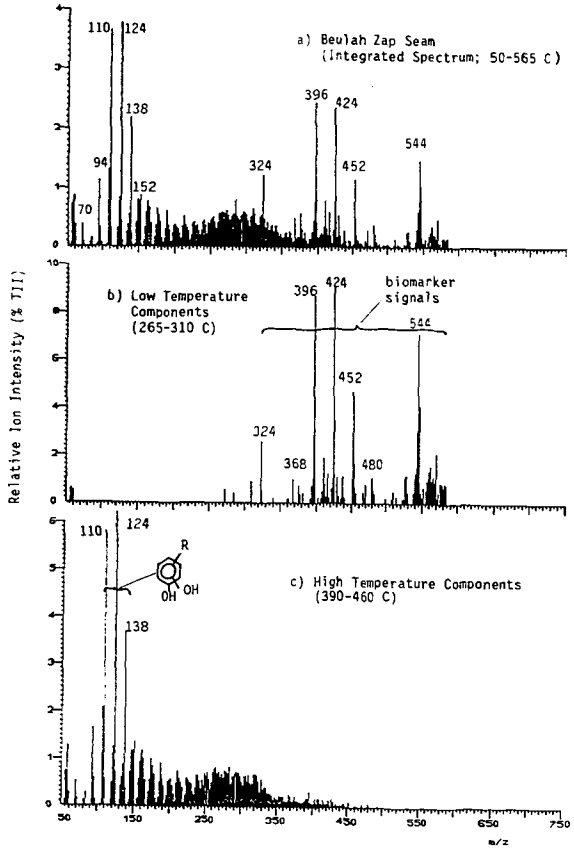
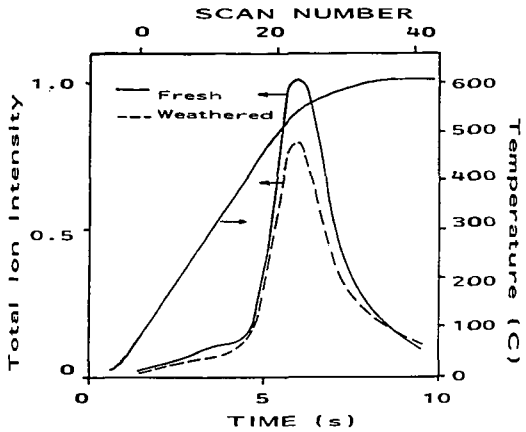


Figure 4. As Figure 2 but representing Beulah Zap seam lignite. Note biomarker pattern of vacuum distillable low temperature component in (b). Further note marked difference with Pittsburgh #8 in Figure 2.

Figure 5. Time-resolved TII profiles of a Hiawatha seam (hvBb) coal obtained by Curie-point pyrolysis in combination with low voltage EIMS. Note effect of artificial "weathering" compare with Figure 6.



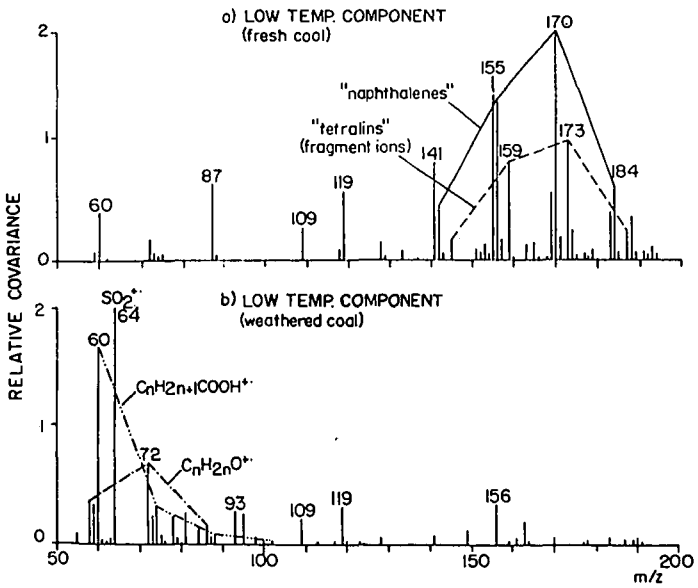


Figure 6. Comparison between low temperature component spectra obtained by low voltage EIMS. Note pronounced effect of mild artificial "weathering". Compare with Fig. 5.

MOLECULAR STRUCTURE AND CONFORMATIONAL STABILITY OF COALS

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ABSTRACT

Factors which influence the molecular conformation and stability of the organic fractions of coals are discussed. Data for an extensive suite of Australian coals from experiments using nuclear magnetic resonance techniques to measure the effects of heating and exposure to pyridine on the stability of coal molecular structures are presented. Two types of fusible material are identified and how these materials and their fusibility vary with coal rank are evaluated. Also the rank and maceral dependence of the destabilizing effects of pyridine are catalogued.

Key Words: Coal fusibility, NMR, macerals, molecular structure.

INTRODUCTION

The Molecular Properties of Coals

Dry coals are essentially organic solids at ambient temperature and, except for a degree of molecular mobility associated with aliphatic structures apparent from nuclear magnetic resonance measurements (1), they can be considered to be rigid molecular lattices. Although the molecular structures of organic substances profoundly affect their solid state properties, the molecular structure of coals has been little studied compared to their chemical composition and functionality. Studies of coal structure at any level are difficult because of the complex heterogeneity of any particular coal and the great variability of coal types that occur.

Broadly speaking three main concepts are used to model the molecular structure of coals:

i) Coals as macromolecular three-dimensional crosslinked viscoelastic glassy solids (2,3).

ii) Coals as macromolecular/molecular two-phase systems - the host/guest or 'rigid' and 'mobile' phase model (4-6).

iii) Coals as paracrystalline substances depicted as having amorphous and ordered micellar regions (7).

The major limitation to the usefulness of each of these concepts (and, no doubt, the necessity for all three) stems from the great variability of coal types. Also, these concepts have mostly been applied only to the vitrinite macerals.

Conformational stability and the molecular structure of organic solids are determined both by the nature of the molecular network (how discrete molecular units are connected by covalent crosslinks) and by the nature and distribution of the various non-covalent interactions amongst these units. The non-covalent interactions include localized (e.g. hydrogen bonds) and non-localized electrostatic interactions and the short-range non-polar interactions between molecular units due to the ubiquitous and weak van der Waals induction and London dispersion forces (8).

Thus in the case of the aromatic-rich (i.e. vitrinite and inertinite) macerals of coals, if the molecular units are considered to be condensed aromatic and hydroaromatic ring structures, the molecular conformation and stability of the

macerals is determined by the density of covalent crosslinks, the degree of polar functionality and the size and geometry of the condensed ring units.

The aliphatic-rich liptinite macerals are comprised of a variety of structures including long-chain alkanes, polymerized alicyclic structures and hydroaromatic units (9). Their conformation is determined largely by covalent crosslinks and probably only to a minor extent by polar interactions.

One means of investigating molecular structures is to determine the extent to which a solid can be destabilized by heat prior to its pyrolytic decomposition.

Significant molecular mobility activated in brown coals at temperatures between 300 and 600 K has been related to the fusion of the extractable, aliphatic-rich fraction of the coals (10). Thermal destabilization of the molecular lattice of aromatic-rich macerals in bituminous coals at temperatures above ~600 K is associated with their characteristic thermoplasticity (11). The relationship between the extent of this fusion and the molecular properties of the vitrinite and inertinite macerals, however, is not well understood.

The interaction between solvents such as pyridine and coal can also be interpreted in terms of the structural features discussed above. How small nucleophilic molecules disrupt inter- and intra-molecular non-covalent interactions thereby 'relaxing' the structural matrix and allowing further solvent penetration has been extensively discussed by Peppas (12), Larsen (2,13) and Marzec (14,15) and their colleagues. Indeed the extent to which exposure to a solvent such as pyridine destabilizes a material's molecular structure is a measure of the extent to which the stability of the material depends on non-covalent and in particular polar interactions. Solvent destabilization of the molecular structure of organic materials can be quantified by simple NMR measurements at ambient temperatures. Such measurements have shown that up to ~60% of a coal's molecular structure can be destabilized by pyridine and, by the same token, that at least ~ 40% is impervious to pyridine (15-17).

Recently Quinga and Larsen (18) have considered the role of non-polar interactions in coals. In particular, they pointed out the likely importance of London dispersion forces between planar aromatic units and that the effect of these short-range interactions on the stability of a lattice would increase with increasing size of the molecular units. Thus the greater concentration and growth in average size of these units with increasing rank for bituminous coals lead to enhancement of the role of the London dispersion interaction in the stabilization of the molecular lattice of these coals. This process no doubt leads to the formation of the ordered graphite-like structures detectable by X-ray diffraction (e.g. ref. 7) and apparently not disrupted by exposure of the coals to pyridine and their resultant swelling (19). Also the microscopic conformal and reversible nature of the swelling of coals by pyridine established by Brenner (2) points to these ordered structures existing in microdomains of dimension less than ~ 10^{-6}m.

Strong evidence of the dominant influence of molecular structure on the properties of coals is implicit in the several data sets which show an extremum in the measured property when plotted against carbon rank. Examples are the extrema which occur in the solid state properties of mass density (20) and proton spin-lattice relaxation rate (21) as well as in solvent swelling and extractability (2).

Nuclear Magnetic Resonance Techniques

Proton nuclear magnetic resonance (^{1}H NMR) measurements can distinguish hydrogen in rigid molecular structures of coals, i.e. structures that do not undergo appreciable reorientation and/or translation during time intervals $<\sim 10^{-5}$ s, from hydrogen in mobile structures which possess more rapid molecular motions characteristic of fused or rubbery materials. The data provided by these measurements are presented in this paper in terms of a parameter M_{2T} that measures

the extent and degree of molecular mobility. M_{2T} is an empirical second moment of the frequency spectrum of the NMR signal (22), truncated here at 16 kHz, and is inversely related to the average molecular mobility of the specimen. Thus the relative decrease in M_{2T} is a sensitive measure of the extent and degree of mobility acquired by rigid molecular structures as a result of their destabilization by thermal or solvent treatment.

The technique of ^1H NMR thermal analysis yields data in the form of M_{2T} pyrograms (typical examples are shown in Figures 1 and 2). The fusibility of a coal can be ranked by the minimum value of M_{2T} (M_{2T}(min)) attained during the experiment.

Because the extensive property of a specimen measured by ^1H NMR is the hydrogen content, in the data analyses described below maceral contents which are determined on a volume basis (denoted by vol%) have been converted to a wt% hydrogen basis (denoted by H-wt%) by the method of Lynch et al. (23). In practice, the changes produced in the maceral content values are small except for the coals richest in liptinite.

EXPERIMENTAL

Data have been obtained for an extensive suite of well characterized Australian coals by ^1H NMR experiments which probe separately the effects of heat and the effects of exposure to the nucleophilic solvent pyridine on the molecular stability of the coals.

The coals and coal fractions which have been examined by ^1H NMR thermal analysis are subdivided into two sets as follows:

a) 95 Australian bituminous coals (both whole coals and maceral concentrates including 10 pairs of vitrinite and inertinite concentrates obtained by density separation) with carbon contents of 80 - 89% (daf) and hydrogen contents between 4.1 and 6% (daf);

b) 25 sub-bituminous and brown coals with carbon contents of less than 80% (daf).

The vitrinite and inertinite (predominantly semifusinite and inertodetrinite) contents of these coals are in the ranges 10 - 98 and 5 - 80 vol% (mmf) repectively. The liptinite content never exceeds 22 vol% and is <=10 vol% in most coals.

Pyridine swelling experiments involved a suite of 46 bituminous whole coals and maceral concentrates selected from set (a) above.

All coals were ground to <500 μm and acid-washed to remove HCl-soluble iron (24). The resulting specimens were stored at 255 K under nitrogen until they were dried overnight under nitrogen at 378 K immediately prior to thermal analysis or addition of pyridine.

The thermal analysis experiments involved the collection of ^1H NMR data while coal samples were being heated at 4 K/min to 875 K under non-oxidizing conditions.

In the solvent swelling study each coal was soaked in excess deuterated pyridine in a sealed glass ampoule for approximately two months before NMR measurements were made at room temperature.

DATA ANALYSES AND RESULTS

Thermal Analysis Data

In Figures 1 and 2 the M_{2T} pyrograms for seven representative coal specimens are plotted. Analytical data for these materials are listed in Table 1.

The M_{2T} pyrogram of a typical brown coal (a) reveals the significant thermally activated molecular mobility which occurs on heating from room temperature to ~ 600 K. This has been shown to be the result of fusion of the extractable component of these coals (10). The reduction in molecular mobility (increase in M_{2T}) above 600 K results mostly from volatile loss of this 'guest' material. The M_{2T} pyrogram of the extracted residue of a brown coal (b) which constitutes usually >80% of the total coal exhibits only a low level of thermally activated molecular mobility. The shallow minimum which does occur in this pyrogram is probably due to fusion of residual 'guest' material. Thus the extract residue or 'host' component of brown coals (considered to be lignin-derived) has no significant fusion event on heating to pyrolysis temperatures at 4 K/min. This is consistent with it being a highly crosslinked macromolecular solid.

The M_{2T} pyrograms of two nominally sub-bituminous coals are recorded in Figure 1. The thermal behaviour of the lower rank Collie specimen (74.4% C) (c) is similar to that of a brown coal containing little extractable 'guest' material but its fusion is shifted to higher temperatures than that of the brown coals. The higher rank Amberley specimen (80.2% C) (d) clearly shows two fusion transitions. The first parallels that of the Collie coal until the second sharp transition occurs above 600 K. This coal has a high liptinite content (18 vol%) and a correspondingly high hydrogen content. Its high volatile matter value (47.3% daf) ranks it as a sub-bituminous coal but its carbon rank (80.2% C daf) is indicative of a lower rank bituminous coal. The second fusion transition is characteristic of lower rank thermoplastic bituminous coals but this coal has a crucible swelling number of only 2.

The high-volatile Liddell bituminous coal (Figure 2(e)) shows little indication of thermally activated molecular mobility below 500 K. There is some fusion between 500 and 600 K followed by a major fusion transition above 600 K which appears very similar to the high temperature transition of the Amberley coal. This Liddell coal, however, has only 6% liptinite, has a crucible swelling number of 6.5 and exhibits considerable Gieseler fluidity. We therefore identify this high temperature fusion event with the aromatic-rich macerals of the coal and associate it with the thermoplastic phenomenon. Hence, by implication, a stage has been reached in the coalification processes whereby aromatic-rich material becomes fusible.

The medium-volatile bituminous Bulli coal which contains no liptinite and has significant thermoplastic properties has a M_{2T} pyrogram (f) showing only one fusion transition which is lesser in extent and shifted to higher temperatures than that of the Liddell coal. This transition is, of course, attributed to aromatic-rich macerals.

The M_{2T} pyrogram for the Baralaba low-volatile semianthracite (89.7% C) (g) shows this material to be totally infusible on heating to pyrolysis temperatures.

Statistical analyses were applied to the M_{2T} data for the 120 coals in sets (a) and (b) and for those swollen with pyridine to estimate values of this parameter for 'pure average' vitrinite, inertinite and liptinite maceral groups. It was assumed that interactive effects between macerals can be neglected and hence that M_{2T} varies linearly with maceral composition, i.e.

$$M_{2T} = a * \text{vitrinite content} + b * \text{liptinite content} + c. \qquad 1)$$

The regression coefficients a, b and c provide calculated M_{2T} values for 'pure' vitrinite (= 100 * a + c), 'pure' inertinite (=c) and 'pure' liptinite (= 100 * b + c). Because the liptinite contents span a limited range of values, extrapolations to 100% liptinite are much less reliable than those to 100% vitrinite or inertinite.

By applying this analysis at discrete 10 K temperature intervals to the NMR thermal analysis data for the 120 coals in sets (a) and (b) (subdivided into sub-bituminous and brown coals (<80% C), lower rank (80-85% C) and higher rank (85-89% C) bituminous coals), regression coefficients as functions of temperature and hence statistical M_{2T} pyrograms representative of the three maceral groups were generated (Figures 3-5). Because these pyrograms are derived statistically from data on coals with a range of thermal properties and whose petrographic specifications are subject to considerable experimental uncertainty (25), they are quantitatively imprecise and can be interpreted only in a broad qualitative manner.

The 'pure' vitrinites representative of both bituminous coal subsets remain thermally stable before the onset of fusion at temperatures above 600 K and have approximately the same maximum extent of fusion (minimum M_{2T}) (Figures 4 and 5). The region of greatest fusion is shifted to higher temperatures for the higher rank bituminous coal subset, consistent with the expected rank dependence of coal thermoplasticity (e.g. refs. 26 and 27). (This is better demonstrated by the plot of the temperature of maximum fusion (i.e. minimum M_{2T} value) versus mean maximum vitrinite reflectance $R_v$max for the individual coals of the set (Figure 6)).

The M_{2T} pyrograms for the 'pure' inertinites representative of the two lower rank coal subsets (Figures 3 and 4) indicate little molecular mobility in the temperature region of coal thermoplasticity (i.e. >~ 700 K). However, the well defined minimum in the corresponding pyrogram for the higher rank bituminous coal subset reveals a degree of fusibility of inertinites in these coals.

The much greater fusibility of the liptinite macerals compared to the aromatic macerals for all ranks is clearly demonstrated by the results shown in Figures 3-5. The low temperature fusion of the sub-bituminous liptinites is similar in profile to that of the brown coal (Figure 1(a)), consistent with these liptinites containing the 'guest' materials extractable from brown and other low rank coals (28). The greater thermal stability indicated by the much higher fusion temperatures of the bituminous liptinites can be explained in terms of these materials having a more highly crosslinked macromolecular structure than the liptinites in the brown coals.

Because liptinites comprise only a small fraction of most Australian bituminous coals, their contribution to the fusibility of the whole coals is expected to be minor. Thus the M_{2T} pyrograms for typical bituminous whole coals (Figure 2(e) and (f)) closely reflect the thermal behaviour of the aromatic-rich macerals.

Solvent Destabilization Data

The destabilization of bituminous coal structures due to exposure to pyridine is measured by the percentage change (decrease) in the value of M_{2T} (ΔMpyr) for the coal after two months soak. In interpreting the results for ΔMpyr we seek to isolate the separate influences of rank and maceral composition. When ΔMpyr for all the coals is plotted against vitrinite content (Figure 7), there is wide scatter and no recognizable trend. However, if the coals are separated into high (>86% C) and low (80-86% C) rank bituminous subsets (Figure 7), a strong dependence on vitrinite content for the lower rank subset becomes apparent - the greater the vitrinite content the greater the pyridine destabilization. The implication that vitrinite macerals are destablized by pyridine to a greater extent than the other maceral types is confirmed by statistical extrapolation of the ΔMpyr values to 'pure' macerals by means of a linear regression analogous to that given by Equation 1 (results not presented here).

From Figure 7 it is also apparent that within the bituminous range the lower rank coals are destabilized by exposure to pyridine much more readily than the higher rank coals. Indeed, some higher rank specimens containing ~80 H-wt% vitrinite are little influenced by prolonged exposure (Figure 7). This rank

effect becomes clear when ΔMpyr is plotted against $R_v$max for the vitrinite-rich specimens (>=60 H-wt% vitrinite) (Figure 8). Above $R_v$max ~ 1.0 the vitrinites become increasingly impervious to pyridine destabilization and it is only a minor effect when $R_v$max >~ 1.5.

Comparison of Thermal and Pyridine Destabilization

The relationship between the extent of thermal destabilization of the molecular structures of vitrinite-rich bituminous coals on the one hand and pyridine solvent destabilization on the other is illustrated in Figure 9 in which the ratio of the decrease in M_{2T} during heating to the temperature of maximum extent of fusion to the pyridine-induced decrease ΔMpyr is plotted versus $R_v$max. For coals with $R_v$max < 1 this ratio is independent of rank and its value of 1.5 - 2 (except for certain coals with relatively high liptinite contents which therefore enhance their overall fusibility) suggests (but does not require - see below) an appreciable commonality between the parts of the coal structure that are destabilized by solvent and by thermal treatment respectively. At higher rank the ratio tends to increase with $R_v$max, reflecting the reduced ability of pyridine to penetrate and destabilize molecular structures which are, however, thermally destabilized at high temperatures.

SUMMARY DISCUSSION

Two distinct types of fusible materials occur in coals. One type is aliphatic-rich and associated with the liptinite macerals and the other is contained in the aromatic-rich macerals and particularly the vitrinites of bituminous coals.

In the case of low rank brown coals the aliphatic-rich extractable material fuses at temperatures well below 600 K. With increasing coalification rank the thermal stability of this liptinite material increases and the temperature range of its fusion transition approaches that of the thermoplastic phenomenon of bituminous coals. The enhanced stability with increasing rank is attributed to progressive covalent crosslinking which also would make the material non-extractable. In the fused state it would remain a crosslinked 'rubbery' material resistant to solvent swelling and shear-induced flow.

Fusion in the aromatic-rich macerals is the basis of coal thermoplasticity and its occurrence in effect defines the bituminous range. Fusion within the aromatic-rich structures of low-rank sub-bituminous coals is inhibited by their high covalent crosslink density. With further coalification these crosslinks are degraded and there is loss of other functional side groups. A consequence of these processes is the consolidation of the aromatic units into microdomains or micelles (7) with increasing graphite-like order. These microdomains, stabilized by London forces, are initially small and poorly ordered. With increasing rank they become larger, more ordered and increasingly stable so that their fusion temperature rises. Thermoplasticity ceases in anthracites when these physically stabilized structures achieve a degree of stability which inhibits their fusion below their temperature of pyrolytic decomposition. This stabilization process is greatly accelerated by the rapid condensation and growth in size of the aromatic units forming the ordered domains at carbon rank > 87% (29).

Of the aromatic-rich macerals the behaviour described above is most characteristic of the vitrinites. Inertinites are in general more oxygenated and aromatic than their corresponding vitrinites. Their much greater thermal stability and resistance to pyridine destabilization must relate to greater covalent crosslink density at all stages of coalification and this would also inhibit the development of the ordered microdomains in inertinites compared to that in the vitrinites.

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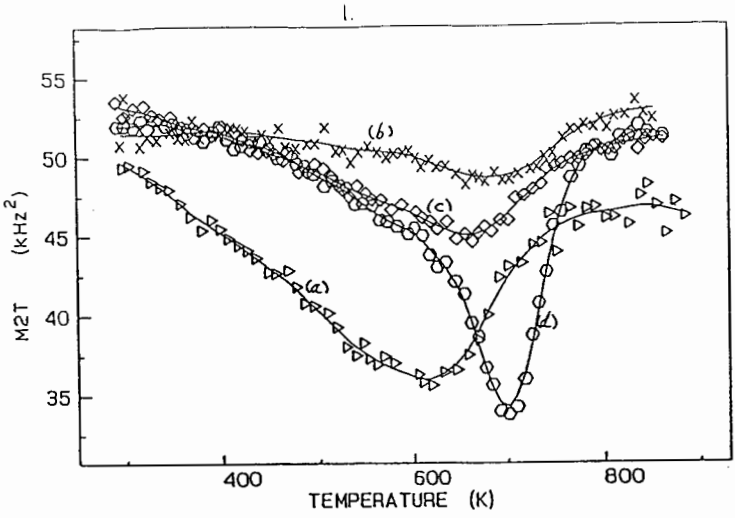
TABLE 1 Analytical data for representative coals

Coal description	moist. (%ad)	ash(%db)	VM(%daf)	C	H	N	S
					(% daf)		
R30, Vic.	-	0.3	50.7	69.5	5.14	0.57	0.38
Collie, WA	11.9	8.1	39.4	74.4	4.31	1.32	0.91
Amberley, Qld	4.3	12.2	47.3	80.2	6.22	1.60	0.82
Liddell seam, NSW	2.8	5.8	39.5	83.4	5.63	2.19	0.41
Bulli seam, NSW	1.2	8.9	22.4	89.2	4.86	1.62	0.46
Baralaba, Qld	1.4	8.4	12.0	89.7	4.12	1.88	1.18

	$R_v$max (%)	Vit. (%mmf)	Lipt. (%mmf)	CSN	Gieseler log (max fluidity, ddpm)
R30, Vic.	-	-	-	-	-
Collie WA	0.45	51	6	0	-
Amberley, Qld	0.59	80	18	2	-
Liddell seam, NSW	0.78	83	6	6.5	2.26
Bulli Seam, NSW	1.30	46	0	7.5	1.90
Baralaba, Qld	2.14	63	0	0.5	nd

nd = no detectable movement



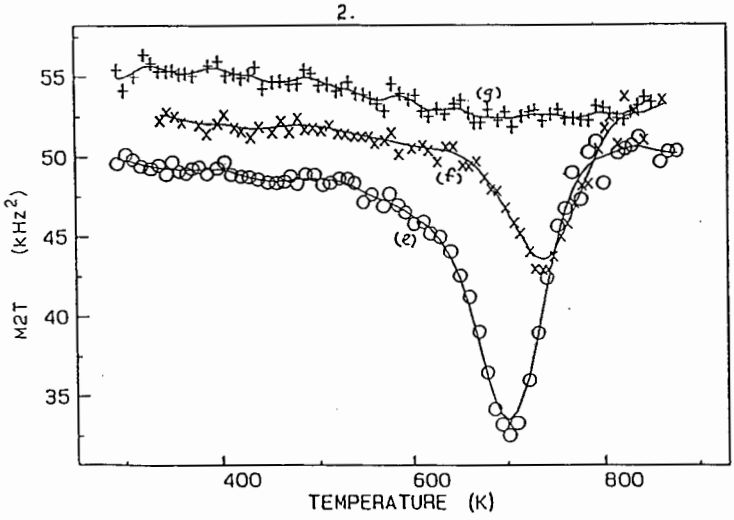


Fig. 1 M_{2T} pyrograms of a brown coal (R30) (a), its extracted residue (b), and a sample of Collie (c) and Amberley (d) subbituminous coal. Analytical data in Table 1.

Fig. 2 M_{2T} pyrograms of a high-volatile bituminous coal (e), a low-volatile bituminous coal (f) and a semi-anthracite (g). Analytical data in Table 1.

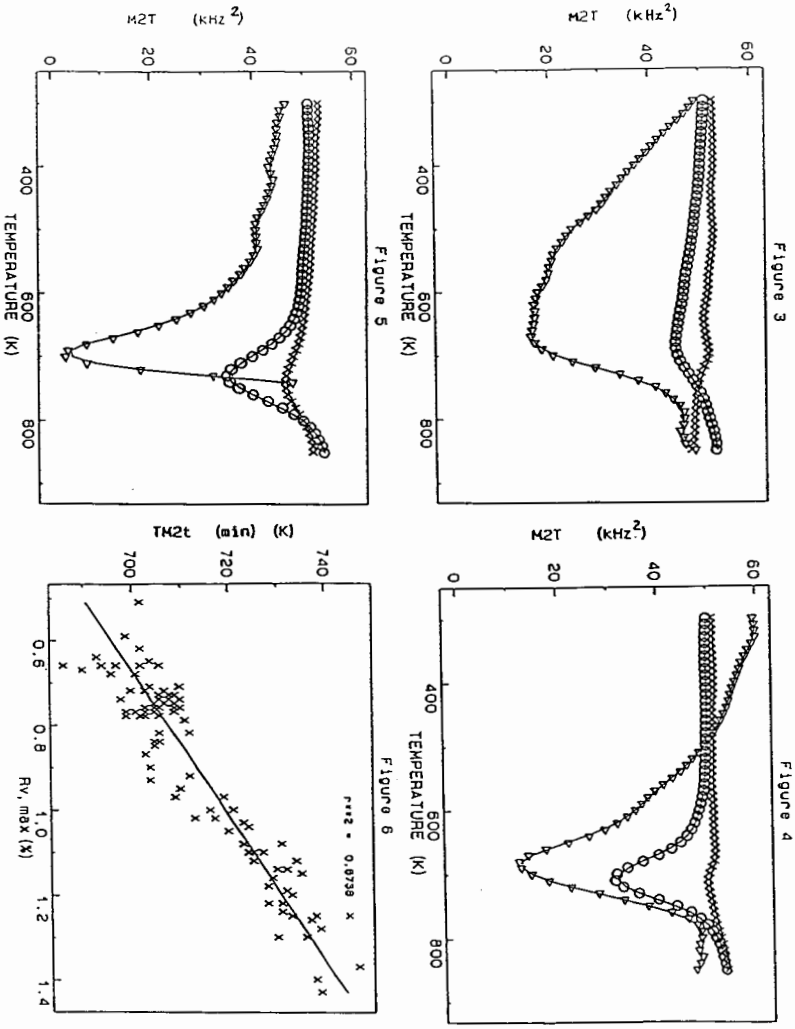
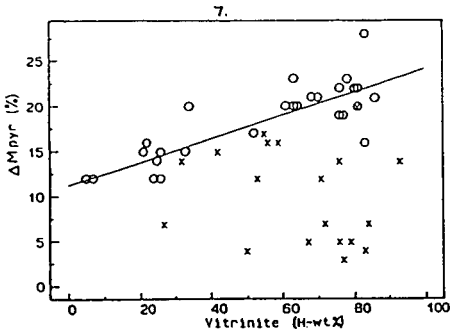


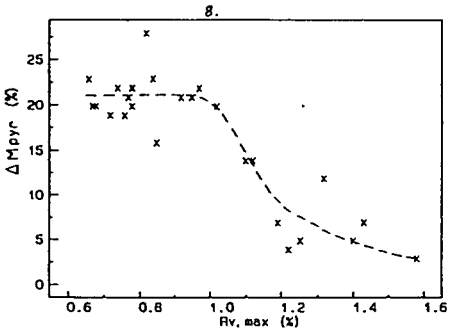
Fig. 3 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with < 80% carbon (daf).

Fig. 4 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with 80-85% carbon (daf).

Fig. 5 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with 85-89% carbon (daf).

Fig. 6 Plot of the temperature of maximum degree of fusion (TM2t(min)) against reflectance ($R_v$max) for bituminous coals.





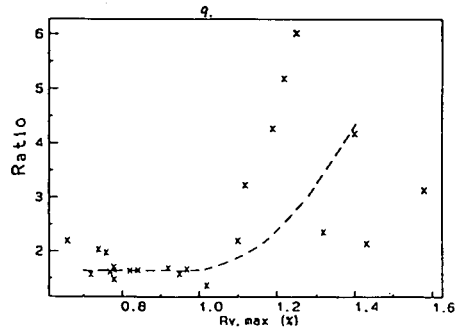


Fig. 7 Plot of ΔMpyr against vitrinite content (on a wt% hydrogen basis) for bituminous coals with 80-86% C (o) and >86% C (x). The line of best fit to these data for the lower rank subset is shown.

Fig. 8 Plot of ΔMpyr against $R_v$max for vitrinite-rich (>60 H-wt% vitrinite) bituminous coals.

Fig. 9 Plot of the ratio of the decreases in M_{2T} due to heating and to exposure to pyridine against $R_v$max for vitrinite-rich (> 60 H-wt% vitrinite) bituminous coals.

SPIN DIFFUSION AND SELECTIVE EXCITATION NMR TECHNIQUES FOR COAL STRUCTURE STUDIES

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ABSTRACT

The use of selective excitation NMR technique using DANTE pulse sequence is presented as a method to obtain higher resolution in the CP/MAS spectrum of coals. This technique is shown to work very well in isolating narrow individual resonance lines from otherwise broad NMR bands usually obtained for coals. Study of carbon spin diffusion is also discussed as a means of obtaining structural information on coals. The feasibility of observing carbon spin diffusion in coals with spin labelling and matching of magic angle spinning frequency with the chemical shift difference is discussed. This method is suggested as a possible means to derive aromatic-aliphatic carbon connectivity information.

INTRODUCTION

Solid state ^{13}C NMR is widely accepted as an important analytical technique for coal characterization. The extent of structural information available from solid state NMR experiments on coals is, however, limited. A typical cross-polarization/magic angle spinning (CP/MAS) spectrum of coals shows two broad lines, often without much fine structure, attributed to unsaturated and saturated carbons. It is well known that the nature of NMR line broadening in coals is mainly inhomogenous, i.e., extensive overlap of resonance lines occurs due to a distribution of slightly different carbon structure types (1). It is often desirable to determine the number of unique lines that comprise the broad band as an important step for elucidating the structural features of these materials. Due to inhomogeneous nature of line-broadening, not much gain in resolution is expected by obtaining the spectrum at higher magnetic field strength. An approach to achieving higher resolution is proposed here with the use of selective excitation pulse techniques (2). A series of experiments are performed to resolve the broad band into unique resonance lines. A set of such experiments can be used to reveal extended information previously obscured by overlap.

Another experiment which can provide useful information on coal structure is the study of carbon spin diffusion. Several studies reported previously have used carbon and proton spin diffusion under favorable circumstances to obtain information on the domain size in heterogenous solids (3), intimacy of mixing in polymer blends(4) and carbon-carbon connectivities in amino acids(5). Spin diffusion between spectrally resolved carbons (also refered to as spectral spin

diffusion) is induced largely via the homonuclear dipolar coupling. The diffusion rate is thus dependent upon the internuclear distance through the strength of their dipole-dipole coupling. Observing carbon spin diffusion in coals, however, is extremely difficult due to the statistical distribution of C-12 and C-13 isotopes which renders average dipole-dipole coupling to be 10-15 Hz and thus spin diffusion rate is very slow (.1 to .01 s^{-1}). Spin diffusion rate is further reduced by magic angle spinning and coupling of carbons with the protons. Therefore, to observe carbon spin diffusion in coals very long mixing time (1-100 s) with proton decoupling field kept on is required. This places an excessive demand on the instrument performance, but more importantly the spin lattice relaxation times can compete with spin diffusion rate, making the experiment impossible. In this paper we show that it is feasible to observe carbon spin diffusion in coals by a combination of spin labelling and adjusting the rotor spinning frequency to be equal to the chemical shift difference (in Hz) of two resonance lines. This work is primarily inspired by recent articles on rotation enhanced spin diffusion in dilute spin systems by Ernst and co-workers(6) and Veeman and co-workers(7). They have shown that under the conditions of rotary resonance, spin diffusion rate can be enhanced by an order of magnitude. With this condition fullfilled spin diffusion between aromatic and aliphatic carbons in coals can be observed in as short a time as 80ms.

EXPERIMENTAL

The experiments were performed on a Chem-Magnetics M-100 spectrometer operating at carbon frequency of 25.11 MHz. Normal spectrum acquisation employed cross-polarization contact time of 1ms with magic angle spinning. The spinning rate could be monitored with a tachometer during the experiment. The spinning rates were stable within 5Hz.

Selective excitation experiment proceeds as follows: cross-polarization is used to produce transverse carbon magnetization. A non-selective 90° pulse then restores the magnetization along the external magnetic field direction. DANTE (2) (delays alternating with nutation for selective excitation) pulse sequence is then used to selectively convert a single resonance line back to the transverse plane which is then detected under high power proton decoupling. DANTE pulse sequence was a series of 20 pulses of 0.3 microsec. long (corresponding to a 90° degree non-selective pulse of 6.5 microsec. duration). 100 - 200 microsec. delays were inserted between the pulses to perform chemical shift selectivity. An approximate analysis indicated that 85% of the original intensity could be detected. Interference of DANTE pulse sequence with magic angle spinning did not present any severe problems.

Spin diffusion experiment employed the spin-exchange pulse sequence described in detail by Maciel and co-workers(8). High power proton decoupling was applied during the entire experiment. A sequence of spectra obtained for 2D analysis were transfered to a VAX computer. The 2D data was processed in a standard way. The results are presented as a 2D contour plot.

RESULTS AND DISCUSSION

Application of selective excitation and rotation enhanced spin diffusion are illustrated here with a sample of Ill#6 coal which has been lebelled with C-13 enriched methyl groups at various reactive sites. Figure 1A shows the CP/MAS spectra of this sample. Two intense peaks in the aliphatic region of the spectrum correspond to the enriched methyl groups. These have been labelled as O-CH_3 and C-CH_3 indicating methyl groups which are bonded to oxygen and carbon respectively. Figure 1B-G shows the application of DANTE pulse sequence in isolating unique methyl resonance lines. The spacing between the pulses in DANTE sequence was adjusted in successive experiments in small increments to cover the full chemical shift range. Peaks representing unique chemical shifts were then selected to indicate the number of distinct methyl groups comprising the broad line. With this procedure only two unique resonance lines could be identified for the O-CH_3 groups occuring at 55 and 57 ppm whereas seven distint peaks were isolated for the C-CH_3 groups ranging from 16 ppm to 33 ppm (not all peaks are shown in the figure). As an example of the resolution, notice in figure 1D that three lines which are within 5 ppm can be distinguished. Such fine structure would otherwise have been obscured by overlap.

The width of the narrow lines obtained with the use of DANTE sequence approach the values that are typicaly obtained for resolved resonance lines from a polycrystalline pure compound in a CP/MAS experiment. Line-widths of the individual lines are in the range of 1-2 ppm, which is, therefore, the limit of chemical shift resolution that can be achieved.

The ability to isolate single narrow lines affords the possibility of applying other NMR techniques to identify the chemical nature of carbons giving rise to these lines. For example, use of proton multiple pulse instead of high power decoupling during detection of single lines would result in a spectra that is indictive of the number of protons attached to the carbon (J-spectroscopy)(9). Analysis of such dipolar spectra can establish the identity of each chemical shift as from methyl, methylene, methine or quaternary carbon.

Figure 2 shows a 2D contour plot for the spin exchange experiment on the same Ill#6 coal. The purpose of the experiment depicted here was to acertain the feasibility of observing carbon spin diffusion in coals. The off-diagonal ridges in the 2D plot indicate the chemical shifts that have participated in the spin exchange process during the mixing time. For the spin exchange to occur between two carbon atoms, they must neccessrarily be in close proximity to each other. Since it was unknown prior to the experiments which pair of resonance lines would satisfy such conditions, the spinning speed was set to 2630 Hz which corresponds to the chemical shift difference (in Hz) of the highest point of the C-CH_3 band and the highest point of the aromatic band. This was done with the assumption that the C-13 enriched methyl groups directly attached to the aromatic ring structure would have the greatest probability of undergoing spin exchange with the aromatic carbons.

Spin diffusion is enhanced for those carbon spins whose chemical shift differences are matched by the spinning frequency(6,7). To derive structural parameters from such experiments, a series of 2D experiments would have to be performed covering full shift range of aromatic and aliphatic carbon band

widths. This would be very time-consuming. Alternatively it is possible to derive the same information in less time by 1D NMR with the use of DANTE sequence as demonstrated by Ernst and co-workers(6) for pure model compound.

The study of spin diffusion is an extremely promising technique for obtaining structural information about spatial positions of carbon atoms in solids(10). In particular, rotation enhanced spin diffusion appears to be a well suited technique to study the aromatic-aliphatic carbon connectivities in coals. With an appropriate choice of mixing time, it should be possible to discriminate between pairs of carbon atoms as directly bonded or two or more bonds away, i.e., aliphatic carbons alpha to the aromatic ring versus others.

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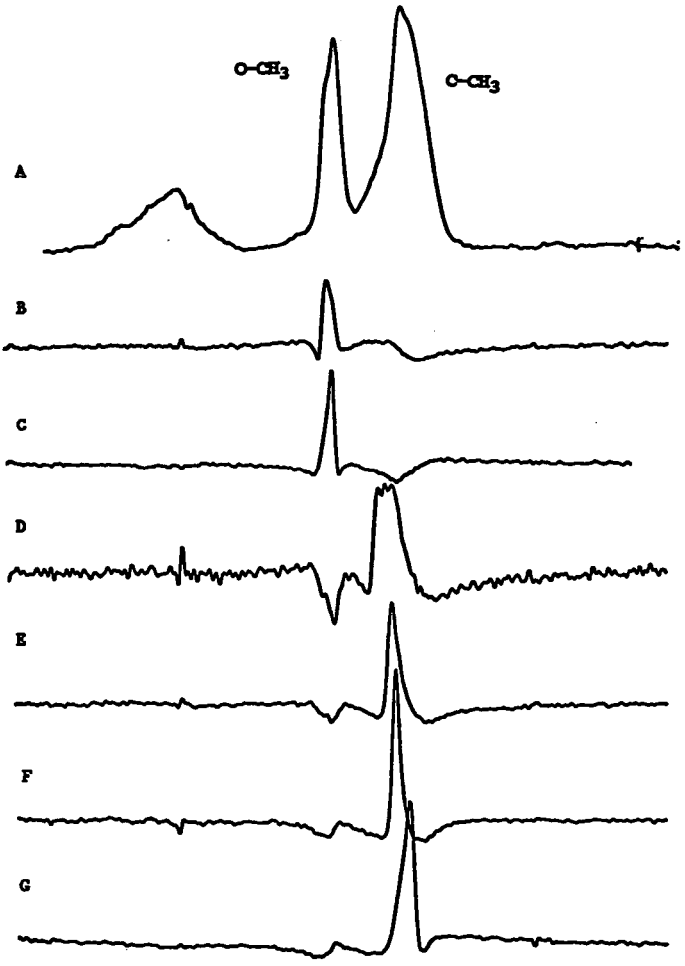

Figure 1: Application of DANTE pulse sequence to isolate invidual components of the C-13 enriched O-CH_3 and C-CH_3 groups. See text for details.

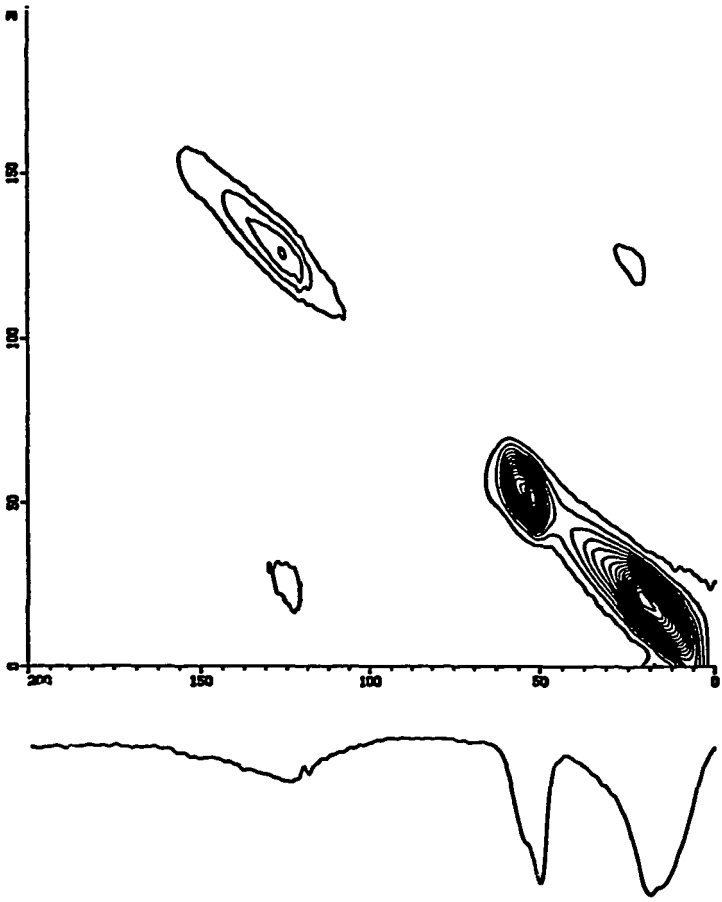

Figure 2: Absolute mode two dimensional contour plot for spin exchange with 80 ms mixing time for labelled Ill#6 coal. Spinning frequency = 2630 Hz. Markings on the axis are in ppm. See text for details.