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Quarterly Report

PROJECT TITLE: Organosulphur compounds in coals as determined by reaction with Raney Nickel and microscale pyrolysis techniques.

INVESTIGATORS: L. Stalker and P. Philp.

Work in Progress: Since the last report, we have concentrated on completing all the chemical degradation experimental work. This has involved the completion of a series of chemical degradation experiments using deuterium labelled sodium borohydride (NaBD_4) and deuterated methanol (CH_3OD). The products of these desulphurization experiments have, as usual, been fractionated into aliphatic and aromatic hydrocarbons and NSO compounds. The aliphatic hydrocarbon fractions of each desulphurization experiment are currently being analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS). The object of the deuterium labelling experiments is to determine the relative abundance of thioether, triolane, and thiophene organic sulphur units cleaved in the different coal fractions (i.e. pre-extracted coal matrix, asphaltene and free polars from the maltenes).

We are currently preparing data on the bulk products generated during the desulphurisation process as well as data on the abundance of individual compounds in the aliphatic fraction.

Bulk data for the total aliphatic and aromatic hydrocarbons cleaved from the pre-extracted coal matrix, asphaltene, and free polar fractions are shown in Tables 1 and 2. The data in each case have been presented as mg/g original coal. The numbers down the left hand side of Table 2 relate to the coal samples where 667B=Iowa coal ($S_{\text{org}}=5.91\%$); 1352=Illinois No. 6 ($S_{\text{org}}=3.20\%$); 515=Oklahoma coal ($S_{\text{org}}=1.25\%$); and 1495=Missouri coal ($S_{\text{org}}=3.37\%$); and MX=preextracted coal matrix; AS=asphaltenes; PO=free polars and any sample labelled D was an experiment performed with deuterium labelled reagents.

The data from Table 1 show how little total extract was removed from the crushed coals by washing repeatedly with methanol/toluen mixtures. The abundance of asphaltenes and free polars is similar for all but sample 667B. In Table 2 the weights recovered from the duplicate experiments are generally low for each sample and similar between samples. If we remember that we have used 500mg pre-extracted coal matrix, 300mg asphaltenes, and between 30-50mg free polars per experiment, and the abundance of these fractions in the total coal, the production of aliphatic and aromatic hydrocarbons is clearly the greatest per mg of free polar material. Whether this is a product of the solubility of the free polars or a genuine observation is currently being determined.

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Significance of deuterium studies: In the previous reports and more briefly above we have discussed the nature of the compounds that are released by the nickel borohydride desulphurisation reactions. However the information that is obtained from those experiments is to some extent rather general since a number of differently structured organosulphur precursors may be cleaved to produce hydrocarbons such as *n*-alkanes for example. In order to obtain more specific information on the nature of the precursors it is necessary to utilize reagents which are labelled with deuterium. As mentioned above the desulphurization reactions are performed using nickel chloride and sodium borohydride to form nickel borohydride in situ. Utilization of sodium borodeuteride permits formation of nickel borodeuteride such that any products formed as result of cleavage of a C-S bond will now contain deuterium atoms at the point of cleavage rather than hydrogen atoms. These deuterium labels may be traced and used to give some information on the structure of the precursor organosulphur compounds. Furthermore by monitoring the distribution of D atoms by GCMS it is possible to infer that a *n*-alkane containing one D atom was probably formed from a thioether compound, a *n*-alkane containing 2 D atoms was probably cleaved from a thiolane and a compound containing a thiophene unit may contain from 4-6 deuterium atoms in its structure as illustrated in Fig. 1.

Preliminary data obtained to date are encouraging and in Fig. 2 the mass spectrum of a C₃₅ hopane shows the characteristic fragment ion at *m/z* 191 and a molecular ion at *m/z* 484. This suggests that at least two deuterium atoms have been incorporated and possibly up to four deuteriums. Since it is known that the hopane precursor, namely the bacteriohopanetetrol, can be incorporated into the solid matrix via four thioether linkages in the side-chain it is proposed that a deuterium has been incorporated at each cleavage point. In addition the fact that these deuterium atoms are being incorporated support the concept that the products being examined are truly degradation products and not compounds that may have been trapped or difficult to remove by solvent extraction.

Whilst these are just two examples of the type of information that can be obtained from the deuterium experiments it demonstrates the value of using the labelled reagents. One of the overall objectives of this project is to evaluate the nature of the organosulphur compounds in coals as well as the ways in which they are bound into the coal structures. Whilst our initial experiments provided information on the wide range of compounds incorporated into the structures via sulphur linkages, it did not provide the information on how the precise nature of these linkages. The deuterium labelling experiments have the potential to do this although the analytical data will be somewhat more time consuming to interpret since one has to initially unravel the number of incorporated deuteriums and then determine in which part of the molecule they reside. However in the remaining time period of this project it is proposed to interpret as much of the deuterium labelling data as possible in order to determine the nature of the compounds incorporated into the coal structure and

also how these compounds are incorporated.

Future Work: In the near future, we will be preparing the DOE presentation for the Pittsburgh meeting, by adding new data, which we expect to obtain from the recent analyses of some of the deuterium labelling experiments. This will involve the identification of relevant compounds from the aliphatic fraction and optimizing the manner in which we can sensibly semi-quantify the relative abundance of non-deuterated versus 1D, 2D and 6D labelled species. Once we feel we have successfully developed an appropriate method for quantifying and presenting these data, we will analyse the remaining sets of experiments.

Table I. Yields of bulk fractions from different coals.

Fraction	667B	1352	516	1495
Pre-extracted coal matrix	804.4*	913.0	907.6	901.2
Asphaltenes	173.7	67.2	62.9	78.6
Free polars	15.8	6.9	9.1	6.0

* All values in mg/g of coal

	MX-1	MX-2	MX-D	AS-1	AS-2	AS-3	AS-D	PO-1	PO-2	PO-D
667B										
Alip(mg/ g coal)	0.63	0.32	0.59	0.38			0.48	0.21		.37
Aro. "	1.35	0.48	1.85	1.80			1.67	3.11		2.36
1352										
Alip(mg/ g coal)	0.44	0.88	1.15	0.53	1.13	0.62	0.11	0.07	0.02	0.11
Aro. "	0.55	1.77	1.33	1.24	0.73	0.30	0.83	0.62	0.46	0.61
516										
Alip(mg/ g coal)	0.65	0.04	0.34	0.41			0.36	0.27		0.24
Aro. "	0.94	0.53	2.50	3.02			?	2.10		1.48
1495										
Alip(mg/ g coal)	2.81		0.49	0.51			0.29	0.001		0.11
Aro. "	3.33		1.35	4.64			7.12	0.05		1.72

Table 2. Yields of various fractions from the different coal fractions used in the degradation experiments.

Fig. 1. Schematic representation showing the possible pathways for deuterium incorporation into different thio-compounds as a result of the cleavage reactions.

Deuterium Labelling of C-S Links

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Thioether

Thiolane

Thiophene

Fig. 2. Mass spectrum showing the C₃₅ extended hopane that had been cleaved by the deuterated reagent and during the cleavage had incorporated at least two deuteriums into the side chain of the hopane molecule. The fact that the deuteriums were incorporated into the side chain is demonstrated by the fact that the major fragment ion at m/z 191 is the same regardless of whether the deuterated reagent is used or not and corresponds to the A/B ring fragment.

C35 Hopane