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 quarterly report was submitted to you on October 14th we have continued with the detailed analyses of the coal degradation products by gas chromatography-mass spectrometry (GCMS). This is a very time consuming process since the degradation products are very complex, even though they have been separated into saturate and aromatic fractions. Most of our efforts are centering on the saturate fractions at this time. Furthermore it is necessary to make detailed comparisons between the deuterated and non-deuterated samples in order to ascertain where, if anywhere, deuterium atoms have been incorporated into the degradation products. Table I which was also included in previous reports summarizes the samples that we have available for analyses. Since we have been looking at four coals, and from each coal we have a coal matrix, asphaltene and polar fraction that has been degraded with both deuterated and non-deuterated reagents, that gives a total of 24 saturate fractions that need to be analysed in detail by GCMS. Fortunately it would appear that there are a certain number of similarities in the products being produced from these degradation reactions, which will be extremely helpful during the data processing. I have attached two examples of data obtained from these analyses which illustrates these similarities. For each sample I have attached the total ion current chromatogram plus a number a single ion current chromatograms illustrating the distributions of individual compounds classes. These two samples sets are derived from the degradation of the asphaltenes and the coal matrix isolated from coal sample 1495. This is the Missouri coal we are using with a sulphur content of 3.37%. As can be seen both chromatograms are dominated by the n-alkanes, maximizing around C. These are more clearly shown in the single ion plot of m/z 71. The second main group of compounds are those between scan 1000 and 1400. At this point we do not know the exact identification and structures of these compounds. However from the second set of figures where we have plotted the single ion chromatograms at m/z 132; 229; and 253 for both samples a simple comparison of these chromatograms shows that the major components are identical in each sample. Similarly if we look at the same single ion chromatograms from sample 516, an Oklahoma coal with a sulphur content of 1.5%, we see again that there is a similar distribution for these compounds in that sample. Hence working in this way we can see that all three samples have certain similarities in the distributions of their major components, hence reducing the total number of compounds that need to be examined and identified in detail.

Now for our purposes it is not always necessary to

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

What we are really interested in are the compounds containing the deuterium atoms. To date we have observed that in several of the fractions the C₃₅ extended hopanes contain varying numbers of deuterium and also some of the C₂₉ steranes. In both cases this suggests that these compounds are bound into the insoluble matrix via sulphur linkages. Surprisingly enough we have not found any of the smaller and more volatile compounds which contain deuterium atoms. At this stage the significance of this observation is somewhat unclear.

Future Work: As mentioned in the previous report all of our efforts continue to be directed towards completion of the final report and finishing analyses of all the samples by GCMS. The complexity of the data is such that it will take some time to complete the processing. However when complete it should provide us with a more precise picture of the nature of the sulphur compounds present in coal structures as well as the nature of the linkages by which these compounds are bound into the coal matrix.

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

Table 1. Yields of various fractions from the different coal fractions used in the degradation experiments.

Fig. 1. A comparison between the total ion current chromatograms for the degradation products produced from the asphaltene and coal matrix from the Missouri coal using the deuterated reagents.

CHRO: rpp8122
 Samp: 1495 ASPHALTENES DEUTERATED 12-DEC-96 00:36:00.0 887
 Comm: GC=gc95 ICL=FS ALIPHATIC Start : 07:28:32 3993
 Mode: EI +Q3MS LMR UP LR
 Oper:
 Peak: 1000.00 mmu Label wndw: 1 > 3993 Inlet : GC
 Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
 Label : 0, 40.00

CHRO: rpp8121 11-DEC-96 Elapse: 00:35:59.6 887
Samp: 1495 MATRIX DEUTERATED ALIPHATICS Start : 19:37:15 3994
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1 > 3994 Inlet : GC
Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
Label : 0, 40.00

Fig. 2. A comparison between the m/z 71 chromatograms showing the n-alkane distributions for the degradation products produced from the asphaltenes and coal matrix from the Missouri coal using the deuterated reagents.

CHRO: rpp8122 12-DEC-96 Elapse: 00:42:18 1249
Samp: 1495 ASPHALTENES DEUTERATED ALIPHATIC Start : 07:28:32 3993
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1 > 3993 Inlet : GC
Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
Label : 0, 40.00

CHRO: rpp8121 11-DEC-96 Elapse: 00:42:17 1249
Samp: 1495 MATRIX DEUTERATED ALIPHATICS Start : 19:37:15 3994
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1 > 3994 Inlet : GC
Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
Label : 0, 40.00

CHRO: rpp8117
 Samp: 516 MATRIX DEUTERATED ALIPHATICS
 Comm: gc=gc95 ICL=FS
 Mode: EI +Q3MS LMR UP LR
 Oper:
 Peak: 1000.00 mmu Label wndw: 1 > 3989
 Area: 0, 4.00 Baseline : 0, 3

06-DEC-96 Elapse: 00:42:21 1249
 Start : 13:43:44 3989

Inlet : GC
 Masses: 50 > 550
 Label : 0, 40.00

Fig. 3. A comparison between the m/z 132;229 and 253 chromatograms for the degradation products produced from the asphaltenes and coal matrix from the Missouri coal using the deuterated reagents. The products from the Oklahoma coal matrix are also included for comparison purposes.

CHRO: rpp8117
Samp: 516 MATRIX DEUTERATED ALIPHATICS
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1000 > 1500
Area: 0, 4.00 Baseline : 0, 3

06-DEC-96

Elapse: 00:59:20 2225

Start : 13:43:44 3989

Inlet : GC

Masses: 50 > 550

Label : 0, 40.00

CHRO: rpp8122 12-DEC-96 Elapse: 00:38:11 1013
Samp: 1495 ASPHALTENES DEUTERATED ALIPHATIC Start : 07:28:32 3993
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1000 > 1500 Inlet : GC
Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
Label : 0, 40.00

CHRO: rpp8121 11-DEC-96 Elapse: 00:43:27 1316
Samp: 1495 MATRIX DEUTERATED ALIPHATICS Start : 19:37:15 3994
Comm: gc=gc95 ICL =FS
Mode: EI +Q3MS LMR UP LR
Oper:
Peak: 1000.00 mmu Label wndw: 1000 > 1500 Inlet : GC
Area: 0, 4.00 Baseline : 0, 3 Masses: 50 > 550
Label : 0, 40.00