CHARACTERIZATION OF COALS, OTHER KEROGENS, AND THEIR EXTRACTS BY THERMAL MASS SPECTROMETRY

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INTRODUCTION

The objective of this study is to elucidate the nature of the medium size molecules derived from coals by a succession of stronger extraction conditions. The Argonne Premium Coals have been extracted with pyridine, binary solvents and with KOH/ethylene glycol at 250 °C. Thermal desorption and pyrolysis mass spectrometry were the major approachs chosen to provide detailed information on structure and heteroatom composition. Soft ionization techniques including desorption chemical ionization (DCI) and fast atom bombardment (FAB) were combined with high resolution and tandem MS techniques. This paper will focus on the comparison of the nature of the unextracted coals, the pyridine extract and the extracted coal residue. With this approach the desorption-pyrolysis yields of the extracts and residues combined were greater than the yields from the starting material. Although molecule weight distributions had a minor dependence on rank, the nature of molecules with the same nominal mass varied greatly with rank.

Pyrolysis combined with a variety of mass spectometric techniques has been used extensively to study coals and separated coal macerals. High resolution mass spectrometry elucidated the distribution of heteroatoms in vacuum pyrolysis products resulting in the discovery of a large number of products containing multiple heteroatoms.[1] The more volatile pyrolysis products have been examined by PyGCMS and PyMS methods. Thermogravimetric MS techniques yield quantitative data with rather slow heating rates.[2] Field ionization MS (FIMS) is a technique widely used to provide molecular weight distributions of volatile tars.[3] Data are available for all eight of the Argonne Premium coals[4,5] and will be compared to the results by other MS techniques. In addition, Meuzelaar, Schulten and co-workers have compared the results of PyFIMS, low voltage PyMS and TGAMS and discovered similar patterns in the low mass regions.[6] Recently, FABMS has been applied to the characterization of coal vacuum pyrolysis products yielding data similar to FIMS.[7] Initial results using the DCIMS approach on demineralized and extracted Argonne coals have been presented[8], and this paper will extend this study to include the pyridine extracts. Also, tandem MS is used to elucidate the structure of larger molecules. The problem of secondary reactions occurring due to the pyrolysis step is reduced by focussing on extracts.

EXPERIMENTAL

A complete discussion of the characteristics of the coals used in this study has been reported.[9] Selected elemental analysis values and results from vacuum pyrolysis, and extractions are given in Table 1. Details on how the coals were treated are shown on the flow diagram in Scheme 1. A complete description of the KOH in ethylene glycol treatment has been reported.[10]

The DCIMS studies have been performed on a Kratos MS 50 triple analyzer with isobutane as the reagent gas. The solids and extracts were heated directly in the source of the mass spectrometer on a small platinum wire coil. The wire was heated from 200° C to 700° C at 100° C/min with the source body kept at 200° C.

In addition to the three-sector MS 50, tandem MS data have been obtained on a four-sector instrument located at the University of Manchester, Institute of Science and Technology (UMIST). The spectrometer is a combination of two Kratos Concept-H's, each with a 10,000 mass range. The sensitivity in MS-2 where the daughter spectra are obtained is enhanced by using an array detector.

Scheme 1

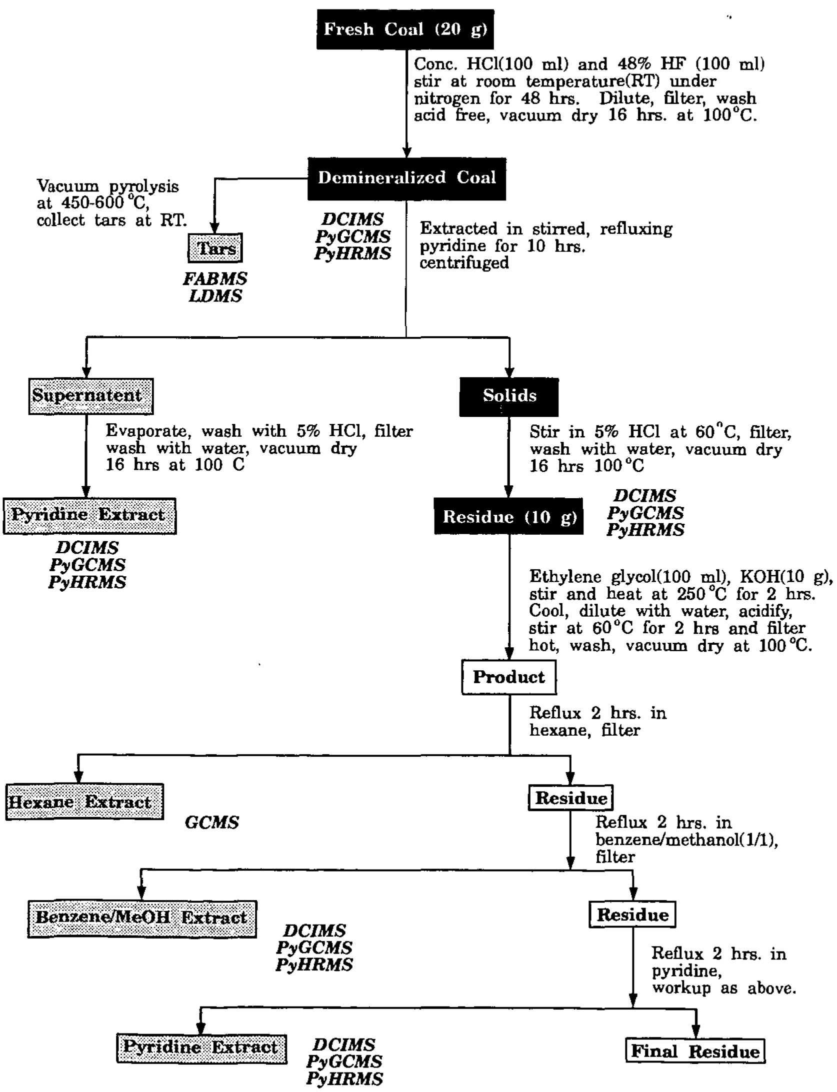
Fresh Coal (20 g)
Conc. HCl(100 ml) and 48% HF (100 ml) stir at room temperature(RT) under nitrogen for 48 hrs. Dilute, filter, wash acid free, vacuum dry 16 hrs. at 100°C.
Demineralized Coal
Vacuum pyrolysis at 450-600 °C, collect tars at RT.
Tars
FABMS
LDMS
DCIMS
PyGCMS
PyHRMS
Extracted in stirred, refluxing pyridine for 10 hrs. centrifuged
Supernatent
Solids
Evaporate, wash with 5% HCl, filter wash with water, vacuum dry 16 hrs at 100 C
Stir in 5% HCl at 60°C, filter, wash with water, vacuum dry 16 hrs 100°C
Pyridine Extract
DCIMS
PyGCMS
PyHRMS
Residue (10 g)
DCIMS
PyGCMS
PyHRMS
Ethylene glycol(100 ml), KOH(10 g), stir and heat at 250°C for 2 hrs. Cool, dilute with water, acidify, stir at 60°C for 2 hrs and filter hot, wash, vacuum dry at 100°C.
Product
Reflux 2 hrs. in hexane, filter
Hexane Extract
GCMS
Residue
Reflux 2 hrs. in benzene/methanol(1/1), filter
Benzene/MeOH Extract
DCIMS
PyGCMS
PyHRMS
Residue
Reflux 2 hrs. in pyridine, workup as above.
Pyridine Extract
DCIMS
PyGCMS
PyHRMS
Final Residue

Table 1. Elemental Analysis and Yields for the Coal Samples, Ordered by Carbon Content.

Sample	Name	%C dmmf*	Per 100 Carbons H	Per 100 Carbons O	Yields (Wt%, dmmf*) Pyrolysis	Yields (Wt%, dmmf*) Pyridine Extract	Yields (Wt%, dmmf*) KOH/Glycol Solubles
8	Beulah-Zap Lignite	74.1	79.5	20.9	23.6	17.9	84.1
2	Wyodak-Anderson SubB	76.0	85.6	18.0	39.3	29.3	79.0
3	Illinois No. 6	80.7	77.2	13.0	36.8	29.0	71.1
6	Blind Canyon hvBB	81.3	85.7	10.8	50.2	25.0	
4	Pittsburgh hvAB	85.0	76.7	7.96	16.2	24.4	
7	Lewiston-Stockton hvAB	85.5	76.3	8.93	22.9	16.9	
1	Upper Freeport mvB	88.1	66.0	6.59	14.3	3.6	
5	Pocahontas lvB	91.8	58.5	2.04	12.1	2.6	

*dry mineral matter free

RESULTS AND DISCUSSION

From examination of Table 1 it is apparent that the batch pyrolysis yields and the pyridine extract yields parallel each other, except for the Blind Canyon coal (APCS 6). This coal is rich in liptinites which may account for the greater pyrolysis yield. However, the yields of products observed in the DCIMS experiments as a function of time and temperature for the coal and the extract differed significantly. This is shown for the Blind Canyon coal in Figure 1. The extract exhibits a much more bimodal character with a significant yield of volatiles at the lower temperature. In addition, the high temperature peak is shifted to higher temperatures for the extract compared to both the unextracted and extracted coal. This is a general phenomena for all the coals but becomes more pronounced with the higher rank coals. These data suggest that the thermally extractable material as discussed by Meuzelaar, et al.,[6] may be a subset of the potentially extractable material. In addition, the extracts appear to be more thermally stable compared to the solids. This may be due to a transport problem of moving the volatiles through the pore structure where secondary reactions can occur. Also, it may be that there is more donatable hydrogen available in the extracts.[11]

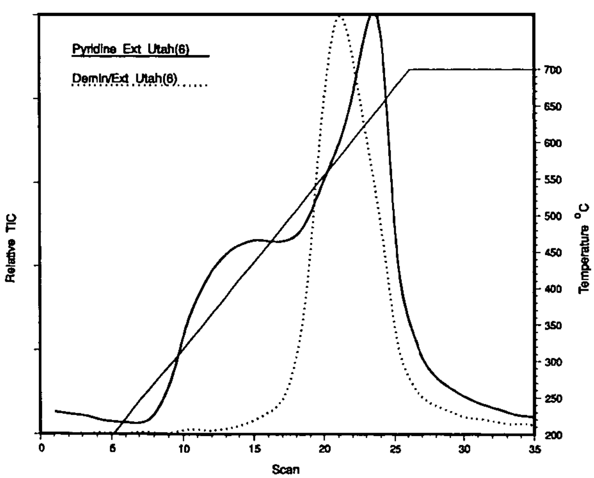

Figure 1. Total ion pyrograms from DCIMS of Blind Canyon (APCS 6) pyridine extract and demineralized and extracted residue.

In some cases the extracts yielded higher molecular weight products and a different set of compounds compared to the whole coal. Figure 2 shows an example of this result for the Lewiston-Stockton coal

(APCS 7). Note that the whole coal spectrum shows well defined series at m/z <250 while the extract contains two sets of series of peaks at m/z=250-400 and m/z=500-600. The high mass set is expanded in Figure 2b. There are pairs of peaks separated by two mass units and repeating every 14 units (methylene). What is even more interesting is that these products appear across the whole temperature range as is shown in Figure 3. Initially, it was thought that these peaks could be a series of M+1 ions

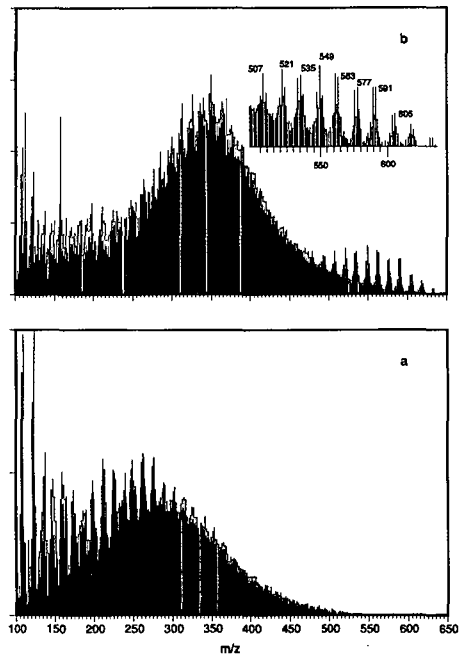

Figure 2. Averaged DCI mass spectra for (a) demineralized Lewiston-Stockton coal (APCS 7) and (b) pyridine extract of the same coal.

resulting from porphyrins. Because of the unusual nature of these ions, we felt it was worth further investigation by tandem MS. The daughter spectrum of m/z=535 is shown in Figure 4. It is a fairly complicated spectrum with a large number of aliphatic fragments. It is not a porphyrin or a very large ring number polycyclic aromatic compound. There is the possibility that it could be an aromatized terpenoid with the partial structure shown in Figure 4 for the fragment at m/z=255. A very different daughter spectrum is observed for parent ion m/z=533, demonstrating that these pairs of peaks are apparently not related.

The thermal stability of the extracts is seen also in the average molecular weight of the volatiles. An example is shown in Table 2 for the Lewiston-Stockton coal (APCS 7). The average molecular weight did not vary over a large temperature range for the coal while for the extract varied significantly. It started out high with the release of the large non-polar molecules, decreased at the start of the pyrolysis, and then increased with temperature.

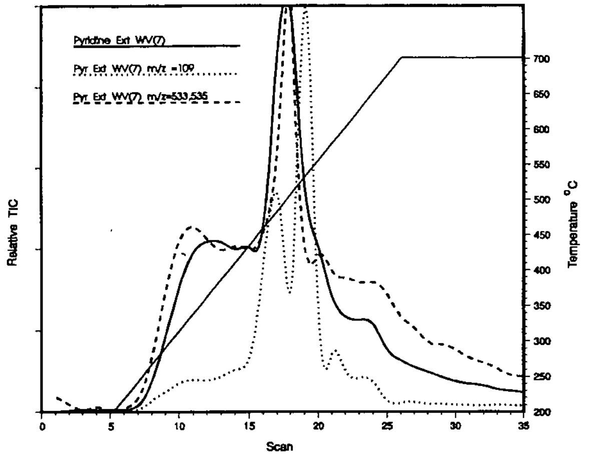

Figure 3. Total and selected ion pyrograms for DCI MS of pyridine extract of Lewiston-Stockton coal (APCS 7): solid - total ion, dotted - m/z = 109 and dashed - sum of m/z = 533, 535.

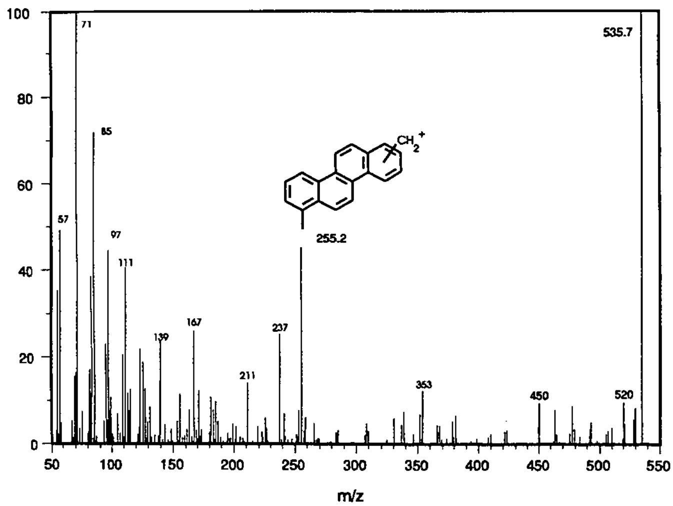

Figure 4. Daughter spectrum from parent m/z = 535 from CIMS of pyridine extract from Lewiston-Stockton coal (APCS 7) taken on UMIST four-sector instrument.

Table 2. Average Molecular Weights for Lewiston-Stockton (APCS 7) from DCIMS.

Sample	Temperature (°C)	M_n	M_w
Demineralized	475	240	283
	650	253	290
Pyridine Extract	375	316	345
	500	298	334
	650	319	356
	700	342	374

M_n= number average molecular weight; M_w= weight average molecular weight

Another interesting result is the suggestion from the extract data that large molecules derived from lignin sources are soluble in pyridine. In Figure 3, it is shown the selected ion (m/z=109) curve which would represent alkylphenol fragments. There is very little yield at the lower temperatures, but as soon as high temperature pyrolysis begins these fragments are observed. From some initial experiments with the base solubilized material, it is interesting to note that the most abundant products in the low rank coals are C_2 and C_3 alkylphenols derived from lignin. This helps to demonstrate the concept that coals are not a simple two phase system; however, they are more likely a continuum of increasing molecular weight species.

CONCLUSIONS

This work demonstrates that future work should place emphasis on the extracts and mild degradation products. Thermally extractable molecules and solvent extractable molecules are likely to be different with the former possibly a subset of the latter. Large lignin-derived fragments exist in the pyridine extractables which suggest that these extracts may be quite representative of the whole coal (vitrinite).

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