CURIE-POINT PYROLYSIS MASS SPECTROMETRY OF SHANXI COALS

Huaying Huai, Alec F. Gaines+ and Peter J.J. Tromp++
Center for Micro Analysis and Reaction Chemistry, University of Utah,
Salt Lake City, Utah 84112
+ Middle East Technical University, Institute of Marine Science, P.O. Box 28,
33731 Erdemli - ICEL, TURKEY
++ Institute of Chemical Engineering, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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ABSTRACT

Seven Shanxi (PRC) coals, having carbon contents from 80.5% to 94.2%wt (daf), have been studied by the Curie-point pyrolysis mass spectrometry technique. Markham Main (British) coal, 83.5 %C and Bulli (Australian) coal, 89.3 %C, have been used as references. As reported by other workers [1,2] studying very different depositions, three major groups of compounds, aliphatic hydrocarbons (e.g. alkenes), aromatic hydrocarbons (e.g. alkylbenzenes, alkylnaphthalenes, alkylpolyaromatics) and oxygen containing aromatics (e.g. alkylphenols, dihydroxylbenzenes), were prominent amongst the pyrolysis products. The relative proportions of oxygen containing compounds and aromatic hydrocarbons, illustrated by the ratio of the intensities of the m/z 156/108 peaks, change with rank. The spectra are consistent with the low liptinite content and the moderately low sulfur contents of Shanxi coals.

INTRODUCTION

Pyrolysis-mass spectrometry (Py-MS) was first introduced as a promising technique for the study of polymers in 1948 [3,4]. In 1973, Meuzelaar et al. [5] designed a Py-MS system in which products from a Curie-point pyrolyzer were ionized by low energy electrons so that molecular, rather than fragment, ions were formed and passed directly into a quadrupole mass spectrometer. Since then many studies of solid fuels have been reported [1,6,7,12-18]. These studies have shown coal pyrograms to be dominated by series of ions representing several groups of aromatic and aliphatic hydrocarbons as well as heteroaromatic compounds. Differences between the spectra were shown to correlate with rank (maturity) [1,3], maceral composition [12,14] and reactivity towards liquefaction [10,11].

Thus, the method gives detailed, and at least semiquantitative information about the structures of the complex but volatile products obtained from the pyrolysis of solid fuels at rather fast rates of heating. Moreover, there is a sufficient bank of existing data in the literature that the nature of the products from any individual coal can be related to such parameters as its maceral group composition, its deposition and its rank.

The North China Block (tectonic plate), approximately coincident with Shanxi Province, gives rise to about one third of China's current production of coal. As part of a study to delineate the organic geochemistry of Shanxi coals and to relate the chemistry of these coals to their present and potential use, seven Shanxi bituminous coals, covering a range of rank from 80.5 to 94.2 %C (daf) have been studied by means of Curie-point Py-MS. The results have been compared with those from well characterized coal deposited in Euramerica (Markham Main coal, Britain) and another deposited in Gondwanaland (Bulli coal, New South Wales, Australia).

EXPERIMENTAL

Sample Preparation

Nine coals were sampled for this study. Seven of these were mined from six coalfields of Shanxi Province, PRC [19]. Markham Main and Bulli coals were mined in Yorkshire (Britain) and in New South Wales (Australia), respectively. The elemental composition of the coals is given in table 1. The samples were ground in a nitrogen - filled glove box to a particle size smaller than 63 μm, dried in a vacuum oven at 70 C for 3 hours, sealed under nitrogen and kept in a deep freeze until needed. The samples for each experiment were taken from a coal/water slurry, prepared by impregnation of the ground coal sample with deionized water until the pore volume was filled. Aliquots (~50 μm) from these slurries were applied with a spatula to ferromagnetic pyrolysis wires on which they were air-dried.

Pyrolysis Mass Spectrometry Analysis

The Curie-point Py-MS technique has been described elsewhere [2]. Within 1 hour of coating, the wire samples were pyrolyzed at a Curie-point temperature of 770 K (pure iron wires), previously found to be optimal for the pyrolysis of coal samples. The pyrolysis conditions were: vacuum, ~ 10^{-4} Pa; heating time, 0.1 sec; and heating rate, ~ 7000 C/sec. The mass spectrometer conditions were: temperature of the expansion chamber, 200 C; electron energy, 15 eV; mass range scanned, m/z 25-225; scan speed, 10 scans/sec; and total number of spectra averaged, 200. Each coal slurry was analyzed in triplicate.

RESULTS AND DISCUSSION

The pyrolysis mass spectra of the coals, including the Markham Main and Bulli coals, are shown in Figure 1 in order of increasing rank of coal. The spectra include peak sequences apparently representing suites of limited numbers of homologous compounds. The chemical structures and corresponding mass numbers of the most important species are given in table 2.

The differences between the spectra in Figure 1 appear to be related primarily to rank. In agreement with the known effects of rank on the chemical composition of coals, the relative intensities of aromatic compounds which do not contain oxygen functional groups, such as alkylbenzenes (m/z: 78, 92,106, etc.), alkylnaphthalenes (m/z: 128, 142, 156, etc.), and alkylphenanthrenes/anthracenes (m/z: 178, 192, 206, etc.) increase with rank, whereas the intensities of such oxygen containing aromatic hydrocarbons as alkylphenols (m/z: 94, 108, 122, etc.) decrease. Since relatively few samples were used in this study, factor and/or discriminant analysis were not applied. However, the ratio of the relative intensities of the m/z 156 (C2-naphthalenes) and the m/z 108 (C1-phenols) peaks as functions of the carbon content and the atomic ratio of oxygen/carbon (Figure 2 and 3, respectively) illustrates the rank dependence. Due to very low absolute amounts of ions generated, the results from the anthracite, Fenghuang Shan coal, are not included in the Figures 2 and 3. It is to be noted that the results from Bulli coal differ from those of Shanxi coals of similar rank. Bulli coal contained 74.5% of inertinite with a rather large amount of fusinite [19]. Consequently, the spectra of Bulli coal, containing prominent alkylbenzenes, resemble the fusinite spectra obtained by Larter [6]. Other features of the mass spectra derived from Shanxi coals are: (1) low H_2S formation (m/z 34) consistent with the moderately low sulfur content indicated by the elemental analyses (Table 1), and (2) low formation of alkanes (m/z: 58, 72, 86, etc.) consistent with the low liptinite content of these coals [19].

Finally, the coherence of the pyrolysis mass spectra of coals from depositions on different tectonic plates and in different climatic conditions is part of the evidence that the whole coal family, which may now be taken to include the Shanxi coals, shares a common system of structural chemistry [2]. Differences in pyrolysis mass spectra are caused by variations in the rank of the coal (that is, by differences in the geochemical temperatures to which the coals were subjected [20]) and, to a lesser extent, by differences in their maceral group composition (that is, by variations in the original flora and the degree to which it was preserved by the deposition). That being written, it should be understood that the volatile products examined by Py-MS may have structures which are the result of secondary, retrogressive reactions as well as of the structures in the original coals. Relatively few of the mass spectra generated by the Shanxi coals contained hydroaromatic structures characteristic of vitrinite [21] and the presence of alkanes is direct evidence of cracking.

CONCLUSIONS

Curie-point pyrolysis of seven coals from the North China Block generated volatiles in which alkenes, alkylaromatics, alkylphenols and dihydroxylbenzenes were prominent. The ratio of the C2-naphthalenes to the C1-phenols produced by the pyrolyses increased with the rank of the coals. The pyrolysis products, though they may have suffered retrogressive, secondary reactions, are nevertheless consistent with the coals from the North China Block having the structures expected of liptinite poor, bituminous coals.

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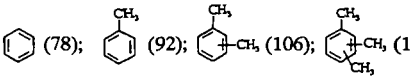
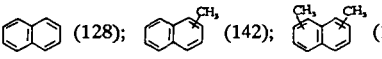
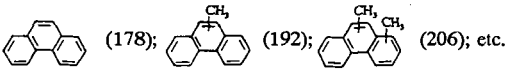
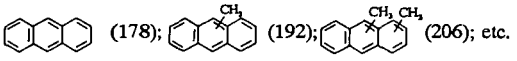
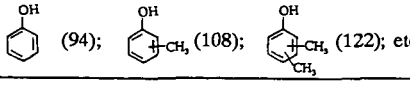
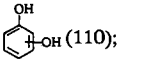
Table 1. Elemental Composition of Coal Samples

	Weight % daf					
Sample	C	H	N	S	O(diff)	O/C
Pinglu Erpu coal	80.5	4.9	1.3	0.6	12.7	0.118
Markham Main coal	83.5	5.1	1.4	1.0	9.0	0.081
Datong Jueqiang Buxiang coal	83.9	5.2	0.9	0.9	9.1	0.083
Xuangang Jiaojia Zhai coal	86.2	5.2	1.7	1.8	5.1	0.044
Xishan Gujiao coal	86.9	5.0	1.6	1.4	5.1	0.044
Fenxi coal	89.9	5.1	1.5	0.5	3.0	0.025
Bulli coal	89.3	4.9	1.7	0.5	3.6	0.030
Jishuigou coal	89.6	4.8	1.2	1.2	3.2	0.027
Fenghuang Shan coal	94.2	2.9	0.9	0.9	1.1	0.009

Table 2. Chemical Structures and Corresponding Mass Numbers
of the Most Important Compounds and Groups of Homologous Compounds,
Present in the Mass Spectra of the Coals

Groups of homologous compounds	Chemical Structures with corresponding mass numbers
Alkenes	C_2H_4(28); C_3H_6(42); C_4H_8(56); C_5H_{10}(70); etc.
Benzenes	 (78); (92); (106); (120); etc.
Naphthalenes	 (128); (142); (156); etc.
Phenanthrenes & Anthracenes	 (178); (192); (206); etc.
	 (178); (192); (206); etc.
Phenols	 (94); (108); (122); etc.
dihydroxylbenzenes	 (110);
Sulfur compounds	H_2S(34); CH_3SH(48);

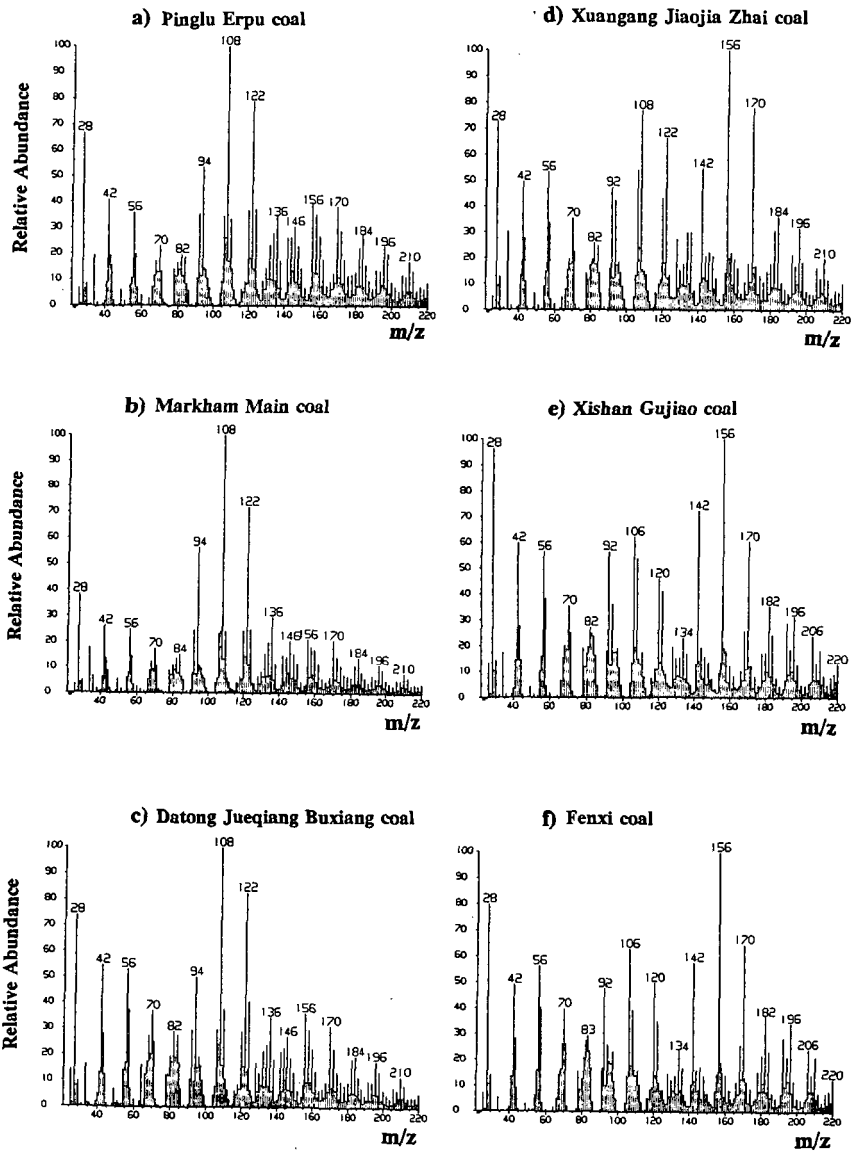


Figure 1. Average mass spectra of coals.

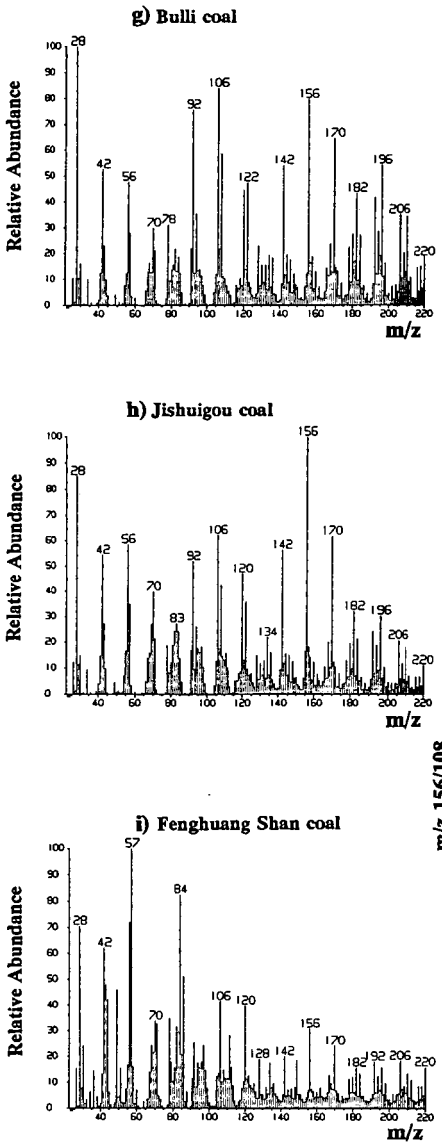


Figure 1. (continued).

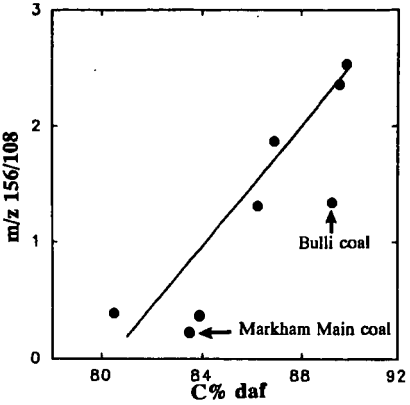


Figure 2. Variation of the ratio of m/z 156/108 from Py-MS with carbon content of coals.

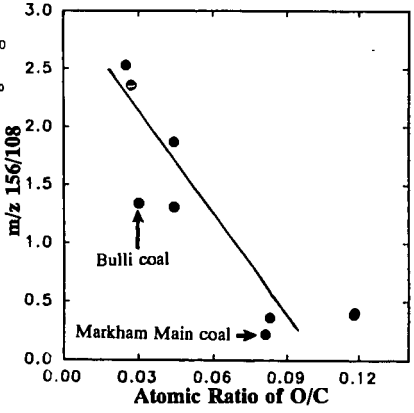


Figure 3. Variation of the ratio of m/z 156/108 from Py-MS with atomic ratio of O/C of coals.