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Soluble polycyclic aromatic hydrocarbons in raw coals

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are considered to be a group of compounds that pose potential health hazards since some PAHs are known carcinogens. During coal utilization processes, such as coal combustion and pyrolysis, PAHs released may be divided into two categories according to their formation pathways. One category is derived from complex chemical reactions and the other is from free PAHs transferred from the original coals. PAHs released from complex chemical reactions during combustion and pyrolysis have received considerable attention in recent years. However, free PAHs contained in raw coals have not been seriously considered as a source of these materials to be released during the utilization of coal. The goal of this study was to observe the relation between the content of PAHs in different coals and the elemental composition of the coals. In this study, eight bituminous coals with dry, ash-free carbon values varying from 65% to 90% were selected. Each coal was extracted with dichloromethane in a Soxhlet extractor for 6 h. The extracts were quantitatively analyzed with a gas chromatograph/mass spectrometer (GC-MS). More than 20 kinds of PAHs were identified. The total amount of PAHs determined varied from 1.2 to 28.3 mg/kg from the various coal types. The maximum total PAHs extracted was reached when the carbon content exceeded 84% by weight. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PAHs; Bituminous coals; GC-MS analysis; Priority pollutants; Aromatic ring size

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1. Introduction

The study of PAHs has been an interesting subject since a study of the incidence of skin cancer on coke production workers was conducted at the beginning of the century [1]. It has been found that some PAHs have mutagenic or carcinogenic properties and are a group of compounds considered to be potential health hazards. It has been reported in several sources [2–5] that PAHs have been widely researched in coal utilization processes including coal combustion and coal pyrolysis. However, it is well known that low molecular weight PAHs with two or three rings (such as naphthalene, acenaphthene and anthracene) can evaporate from the solid phase and be emitted into the environment at atmospheric temperature [6]. As a consequence, PAHs in raw coal may be released to the surrounding air during transportation or preparation processes. However, data about the content and varieties of PAHs in different types of coals are still scarce.

Coals are derived from plant materials such as cellulose, lignin, resins, spores, leaves, stems and roots. The nature of the swamp producing the coal-forming materials, the burial process, heat, pressure, time, the coalification process, and several other factors, all lead to very complex coal structures. The predominant type of structure in coal is aromatic. The formation of aromatic ring compounds follows two general pathways during the coalification of the original plant material. One pathway forms macromolecules that are thought to be grouped together in cohesive units of varying size. These units are connected to each other by aliphatic carbon chains. The other pathway is to form low molecular weight polycyclic aromatic hydrocarbons that exist as solids and liquids in the coal matrix.

Coals may be divided into four major types: lignitic, subbituminous, bituminous and anthracitic, according to some elemental and other properties [7] such as carbon, hydrogen, oxygen, volatile matter calorific value. Anthracitic coal is the highest in metamorphic rank and has a brilliant luster. Bituminous coal contains higher volatile matter contents of 15–40% by weight, and is the most abundant type of coal. Subbituminous coal is not as high in metamorphic rank as bituminous coal and lignite is lowest on the scale.

Typically, the amount of aromatic materials in coals increases as the rank varies from lignite to anthracite, while the side units appending or connecting the main macromolecular network decrease. Bhattacharyya [8] reported that the amount of extract obtainable decreases rapidly with an increase in carbon content for coal with more than 81% carbon, and essentially no extract is obtained from coals with more than 90–91% carbon.

Solvent extraction processes of coals have been observed to involve several stages, including colloidal dispersions and, finally, true solutions. First, the solvent diffuses into the coal, which will disrupt hydrogen bonds between molecules associated with the coal. The components extracted from coal depend on the particular coal/solvent system and extraction conditions used. The extracts of coal using benzene as a solvent were found to contain alkylbenzenes, alkyl-naphthalenes and alkylphenanthrenes, as well as derivatives of anthracene, alkylchrysene and picene. Dichloromethane is an excellent solvent for PAHs [9]. The yield of extract varies directly with extraction temperature at temperatures below those normally required for the thermal decomposition of coal. At tempera-

tures below 350°C, the solvent power of the extracting liquid appears to be determined by the ability of the solvent to alter the coal physically (by swelling) prior to the onset of the degradation process. At temperatures in excess of 350°C, the coal undergoes decomposition.

In coal, the three-dimensional network composed of condensed aromatic and hydro-aromatic units are connected by either short alkyl bridges, ether linkages, or thioether linkages. In general circumstances, unless solvolysis is involved, organic solvents dissolve little of the basic framework and usually extract only the material that is occluded within the coal matrix. It was once thought that the manner in which volatile and low molecular weight material could be recovered was consistent with the notion that it resided in micropores of the coal matrix. This suggested the waxy matter in coals is in part metamorphically degraded to terpenoids, which are then dehydrogenated and aromatized during progressive coalification. The relationship among dehydrogenation, aromatization of waxy matter and coal rank needs to be further studied. The objective of this study is to observe the relationship among PAHs in coal extracts, coal types, and other coal properties.

2. Experimental

Eight bituminous coals supplied by the Western Kentucky University Coal and Fuel Laboratory were selected for this study. To minimize the possible loss of low molecular weight PAHs from the coals, these samples were crushed to –8 mesh (2.4 mm), sealed, and stored in a freezer with a temperature below 0°C after they were obtained from various sources. This a common practice in the Coal and Fuel Laboratory for all coals crushed to –8 mesh or smaller. The coals were then pulverized to –60 mesh (250 μm) before being used in this study. The analytical values for the eight coals used in this study are listed in Table 1. These coals are a combination of high volatile A, B and C bituminous (hvb) and low volatile bituminous (lvb) coals [6]. In each run, 15 g of the –60 mesh (250 μm) coal were placed in the extraction thimble with the

Table 1
Analytical values for the coals used in the study^a

Coal	% C	% H	% N	% S	% O (diff)	% Vol Mat	% Ash	H/C (daf)	O/C (daf)
hvCb-1	77.93	5.58	1.42	6.74	8.26	44.95	39.39	0.853	0.0796
hvCb-2	78.03	5.59	1.46	5.55	9.24	45.03	18.50	0.854	0.0888
hvCb-3	80.34	5.16	1.59	4.54	8.32	42.35	11.32	0.765	0.0777
hvBb-1	80.51	5.17	1.48	1.16	11.63	39.63	7.14	0.764	0.1083
hvBb-2	81.38	5.40	1.73	2.67	8.49	41.70	10.78	0.790	0.0782
hvAb-1	85.56	5.73	1.75	0.72	6.13	43.08	7.22	0.798	0.0537
hvAb-2	83.88	5.56	1.83	3.43	5.05	40.72	10.97	0.791	0.0452
lvb	90.42	4.61	1.39	0.46	3.09	21.67	9.42	0.607	0.0256

^aAll values, except ash, are given as percent by weight on a dry, ash-free (daf) basis. Ash is given on a dry basis.

Table 2
The operating conditions for the gas chromatograph

Item	Condition
Detector	Quadrupole MS
Detector temperature	330°C
Liquid sample volume	2.0 μ l
Sample injection temperature	260°C
Column	60 m/0.32 mm i.d. fused silica capillary column, CBJ1-S60-100
Carrier gas flow	Helium, 24.2 ml/min
Initial temperature	100°C held for 1 min
Final temperature	300°C held for 7 min
Split ratio	Splitless

dichloromethane. A Tecator Soxtec 1045 extraction system was heated to 120°C to extract materials from the coal for 1 h. Then the thimble and coal were removed from the apparatus and the extract was heated with the refluxing dichloromethane (80 ml) for another 5 h. The extracted solution was condensed and transferred to a 5-ml volumetric flask. A 2- μ l portion of condensed solution was analyzed quantitatively with a Shimadzu QP5000 Gas Chromatograph/Mass Spectrometer. The PAH compounds were identified using the 60,000 compound National Institute of Science and Technology (NIST) library search program, and the sixteen US EPA specified PAHs were confirmed using the retention times obtained from the standard PAH compounds. The gas chromatograph operating conditions are given in Table 2.

3. Results and discussion

The analytical results for extracts from the different coals are presented in Table 3. No PAHs with boiling points higher than 490°C (Benzo[*b*]fluoranthene) were identified. The PAH components in the extracts were mainly naphthalene, acenaphthalene, phenanthrene, anthracene, pyrene and benzo[*b*]fluoranthene, as well as their alkyl derivatives, especially methyl derivatives. These results suggest that 2–5 aromatic ring compounds are the major soluble PAHs present in the raw coal. The larger molecular weight PAHs might associate with the aromatic structure of coal by bonds such as in a three dimensional network connected by ether or thioether linkages and short alkyl bridges. The higher molecular weight materials are more difficult to extract. The concentration of the 16 PAHs identified as priority pollutants by the United States Environmental Protection Agency (USEPA) in the different coals are presented in Table 4. The data in Tables 3 and 4 shows that these PAHs make up less than 40% of the total PAHs extracted from the coals. Coal hvAb-2 contains the highest free PAHs (6.38 mg/kg) followed by Coal hvAb-1 (5.4 mg/kg), whereas Coal lvb has the lowest value (0.28 mg/kg). The relationship between the carbon content of the coals and the percent of the PAHs in the total PAHs extracted from the coals is shown in Fig. 1. For the coals studied the percentage of PAHs increases from 6% to 40% with an increase in coal rank.

Table 3
Amounts of PAHs extracted from coals

PAH	Coals and amounts (mg/kg) of PAHs extracted							
	hvCb-1	hvCb-2	hvCb-3	hvBb-1	hvBb-2	hvAb-1	hvAb-2	Ivb
Naphthalene			0.11	0.08	1.96		2.78	0.09
Methylnaphthalene	1.91	0.66	0.43	0.23	3.31	1.09	7.69	0.36
Acenaphthene							1.36	
Ethyl-naphthalene			0.08		1.30		1.84	
Dimethylnaphthalene	2.07	1.10	1.17	0.21	3.52		5.72	0.26
Trimethylnaphthalene	2.19	0.79	0.36	0.38	1.85		4.62	
7-ethyl-1,4-dimethylazulene	0.48	0.16	0.19	0.11	0.17		1.06	
Phenanthrene	0.51	0.09	0.22	0.14	0.34	1.89	1.46	0.19
Anthracene		0.19		0.06		2.22		
Methylphenanthrene				0.07	0.27		0.64	0.31
Methylanthracene	0.83			0.30				
Dimethylanthracene				0.06		3.67		
Dimethylphenanthrene				0.05		1.39		
Pyrene		0.12						
Methylpyrene		0.22						
9-ethylanthracene		0.11						
Trimethylphenanthrene						1.24		
Tetramethylphenanthrene		0.08				0.92	0.72	
Benzo[<i>b</i>]fluoranthene				0.05	0.10	1.29	0.78	
Total PAH	7.99	3.52	2.56	1.74	12.82	13.80	28.26	1.21

PAHs with four or more aromatic rings were not extracted from these coals. The porosity of the coals decreases almost linearly with an increase in rank in the 50–85% carbon range [10] and may be one reason why PAHs with more than three rings can not be extracted from the high carbon coals.

The relationship between the carbon content in the coals and the total amount of PAHs extracted is illustrated in Fig. 2. The total amount of PAHs extracted decreases

Table 4
Amounts of US EPA specified PAHs extracted from coals

PAH	Coals and amounts (mg/kg) of PAHs extracted							
	hvCb-1	hvCb-2	hvCb-3	hvBb-1	hvBb-2	hvAb-1	hvAb-2	Ivb
Naphthalene			0.11	0.08	1.96		2.78	0.09
Acenaphthene							1.36	
Phenanthrene	0.51	0.09	0.22	0.14	0.34	1.89	1.46	0.19
Anthracene		0.19		0.06		2.22		
Pyrene		0.12						
Benzo[<i>b</i>]fluoranthene				0.05	0.10	1.29	0.78	
Total PAH	0.51	0.40	0.33	0.33	2.40	5.40	6.38	0.28

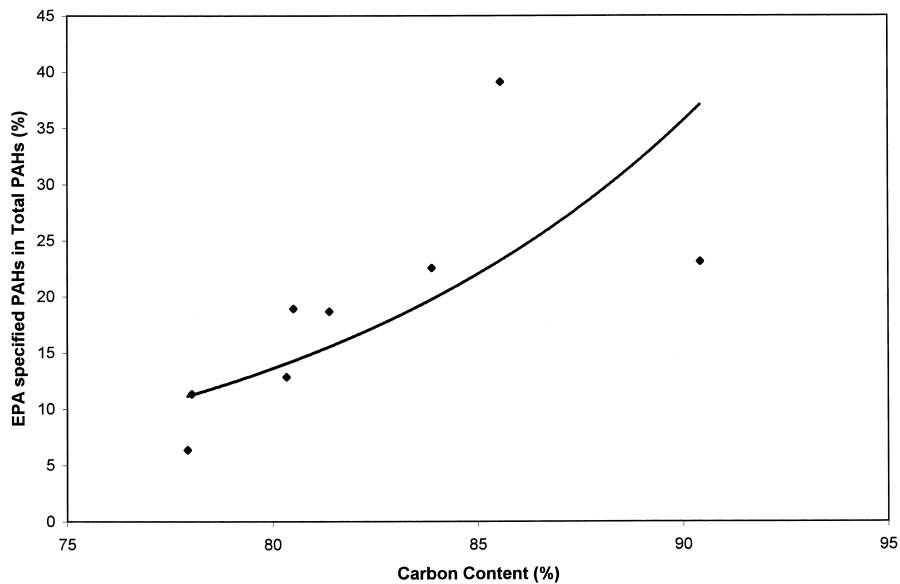


Fig. 1. Relationship between percent PAHs specified by EPA in total PAHs extracted from coals and the carbon content.

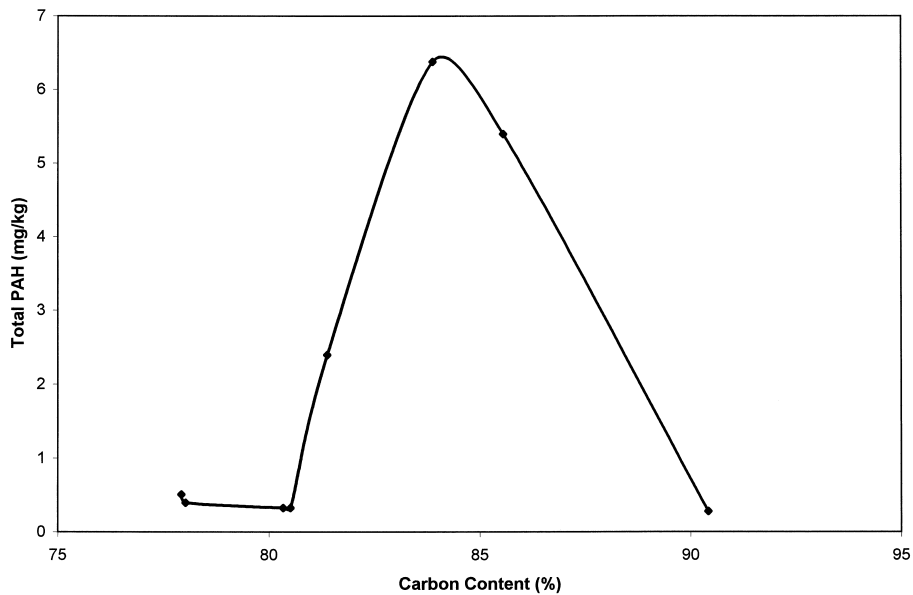


Fig. 2. Relationship between the total PAHs specified by EPA extracted from coals and the carbon content.

gradually with an increase in carbon content in the range of 65–80%. This may be attributed to the process of coalification in which some PAHs containing oxygen, nitrogen and sulfur groups may undergo condensation reactions and bond with the macromolecular structures as the rank increases. The total amount of PAHs extracted increases sharply with an increase in the carbon content from 81% to 85%. This may be due to the cleavages of aromatic systems from the macromolecular structures in the 81–85% carbon content coals. After the carbon content reaches more than 85%, the total amount of PAHs decreases rapidly. As a consequence, the total amount of PAHs extracted is the least (1.21 mg/kg) for the coal with 90% carbon in this study.

The H/C and O/C molar ratios are two important factors to consider in the utilization of coals. Low H/C ratios usually represents a high degree of cyclization in the coal structure, meaning more aromatic compounds exist in the coal matrix. Meanwhile, a high O/C molar ratio means a low coalification degree in the coal formation process, and more aliphatic compounds are in the coal matrix. The relationship between the H/C and O/C molar ratios and the total PAHs specified by EPA are illustrated in Figs. 3 and 4, respectively.

More PAHs were extracted from the coals with O/C ratios between 0.04 and 0.08. At a low O/C ratio (lvb coal with the highest carbon content of all samples) the majority of organic compounds in the coal are probably high molecular weight aromatic compounds due to a high degree of coalification. These large molecules have higher physical and chemical stability than the smaller PAHs. At high O/C ratios, more aliphatic, and less aromatic compounds, are found in the coals.

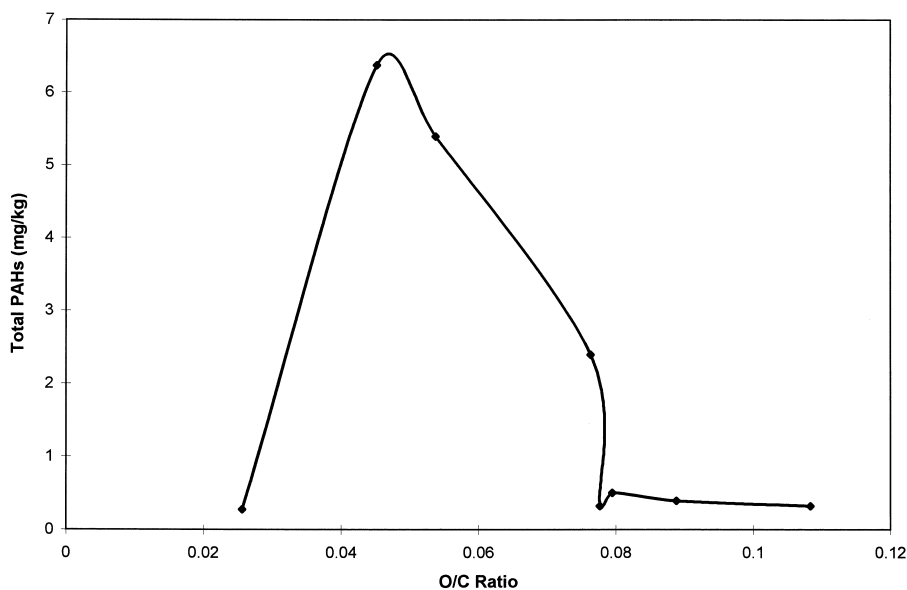


Fig. 3. Relationship between the total PAHs specified by EPA extracted from coals and the O/C ratio.

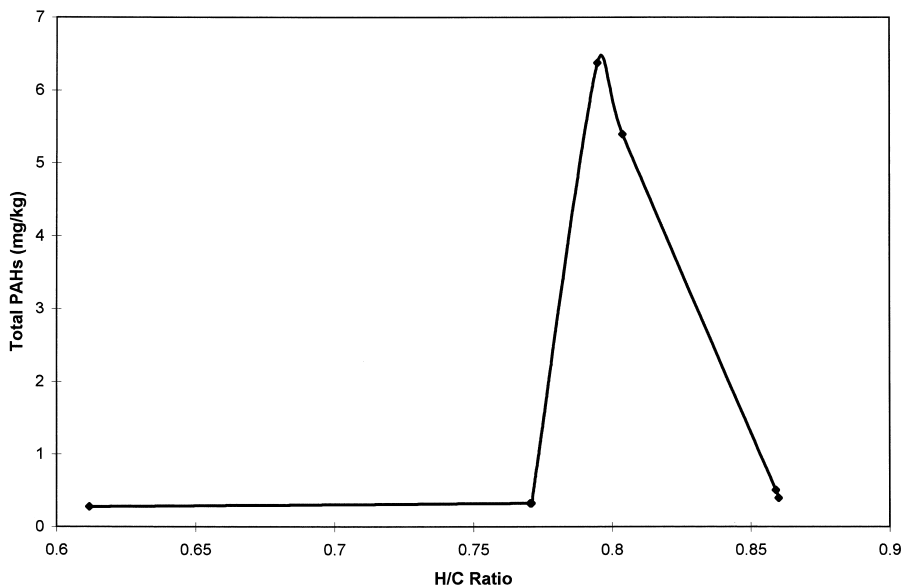


Fig. 4. Relationship between the total PAHs specified by EPA extracted from coals and the H/C ratio.

The trend for the total PAHs extracted with respect to the H/C ratio, as illustrated in Fig. 3, is similar to that for the carbon content, as shown in Fig. 1. The maximum was achieved for a H/C ratio around 0.79 (coals hvAb-1 and hvAb-2).

Table 5 lists the distribution of the EPA PAHs extracted from coals. More than 70% of the total PAHs for hvC series coals were low molecular weight PAHs with two aromatic rings. The other ranks of coals showed a variation with respect to the amount of two-ring systems extracted. For the hvB and hvA series, the distribution of two-ring compounds seems to depend on the ash content in the coals. A higher fraction of PAHs with two rings accompanies a higher ash content in the coals. A possible explanation for this could be the higher ash content coals are more friable and therefore may produce smaller particle sizes and more surface area for extraction. However the percentages of PAHs existing as three-ring compounds in the low ash coals is 3–6 times that in the high ash coals. This would lead one to conclude that the mineral matter content (ash) may influence the type of PAHs formed in the coals.

Table 5

Amounts of US EPA specified PAHs grouped by ring size extracted from coals

PAH	Coals and amounts (mg/kg) of PAHs extracted							
	hvCb-1	hvCb-2	hvCb-3	hvBb-1	hvBb-2	hvAb-1	hvAb-2	lvb
Two rings	73.96	72.44	83.98	51.72	93.14	46.34	81.41	58.68
Three rings	26.04	12.50	16.02	45.40	6.08	38.99	12.61	41.32
Four or more rings	0	15.06	0	2.80	70.8	14.67	5.98	0

4. Conclusions

PAHs determined in the extracts of original coals were mainly less than five-ring PAHs and their methyl derivatives. Smaller (less than three rings) PAHs were found in the lowest carbon content (hvCb-1) coal and the highest carbon content (lvb) coal. In general, the relationship between the number of fused aromatic rings and coal rank showed little agreement. The total amount of PAHs extracted from coals decreased as the carbon content increased in the range of 65–80%, and then increased sharply with an increase in carbon content in the range of 81–85%. The total amount of PAHs extracted decreased when the carbon content in the coals was higher than 85%. Since this study showed that more two- and three-ring PAHs specified by EPA are extracted from the hvAb series coals, these coals are more likely to release these PAHs into the environment during preparation and transportation processes.

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