

# Identification and classification of aromatic hydrocarbons from fast pyrolysis of coal for the purpose of environment-pollution evaluation

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**Abstract.** Aromatic hydrocarbons are the main composition in coal tar from industrial coal processing process, which have long been recognized as the major environment pollutant. The biological toxicity of aromatic hydrocarbons are closely related to their structural configurations. In this work, detailed composition of aromatic species during fast pyrolysis of Shandong coal were identified and classified to evaluate their toxicities based on the specific structure features. In total, 83 kinds of aromatic hydrocarbons were identified and the most abundant aromatic hydrocarbons were toluene, p-xylene, 1-ethylidene-1H-Indene, and 1,2-dehydro-as-hydrindacene. Carbon number of aromatic hydrocarbons ranged from 6 for benzene to 16 for the alkyl-substituted phenanthrene and the content of C<sub>8</sub> aromatic hydrocarbons was largest. The ring of aromatic hydrocarbons is distributed from 1 to 4 and their contents decrease gradually with increasing of ring number.

## 1. Introduction

Coal currently is and will be one of the main energy resources in China. The dominant uses of coal in the past decade are in thermoelectricity generation and coke production industry in China [1]. With the development of society and national economy, utilization of coal in efficient and environment-friendly manner to meet custom regulations is urgent. Therefore, some new technologies are emerged to better process the coal such as, entrained flow gasification, fast pyrolysis, and direct coal liquefaction [2]. Pyrolysis occupies an exceptional position in the field of efficient utilization of coals because it is the basic process for obtaining value-added feedstocks and also serves as the initial and accompanying reaction during thermochemical process. Coal tar is a main product generated from the pyrolysis process and has not been effectively employed in the existing technology level. Entrained flow gasification and fixed bed pressured gasification processes generally produced large amounts of waste water containing coal tar. The main chemical composition of coal tar is aromatic hydrocarbons such as, BTEX (benzene, toluene, ethylbenzene and xylene) and polycyclic aromatic hydrocarbons (PAHs) [3]. The composition of coal tar pitch differs from process to process, mainly due to different coal types and treatment used during production. Coal tar is toxic for human and animals on the aspects of carcinogenesis, teratogenesis, and mutagenesis [4]. Because of its broad industry production, it has long been recognized as one of

the major environment pollutant in China.

The biological toxicity of aromatic hydrocarbons are closely related to their structural composition, such as molecular sizes and activation of the substituents [5]. However, so far little is known about the detailed molecular composition of aromatic hydrocarbons in coal pyrolysis tar, especially for fast pyrolysis tar. Furthermore, to best of our knowledge, the partition of aromatic hydrocarbons coal tar derived from fast pyrolysis according to their biological toxicity is rarely reported.

Therefore, in this work, a typical bituminous coal was fast pyrolyzed to direct trace the aromatic hydrocarbon product using on-line gas chromatography equipped with time of flight mass spectrometry. Detailed structural composition of the produced aromatic hydrocarbons were identified and the contents of each type of aromatic hydrocarbons (carbon number, ring number, substituted degree) according to the biological toxicity were also determined. The aim of this work is to identify and classify the aromatic hydrocarbons based on their biological toxicity to the environment, which should be benefit for understanding of the toxicities of aromatic hydrocarbons in the volatiles evolved from coal thermal processing industry.

## 2. Experimental section

### 2.1. Materials

Coal sample was obtained from a coal mine in Shandong province, China and denoted as SD. The lump coal was grounded to pass through the 200 mesh sieve, and the pulverized coal was vacuum-dried at 80 °C for 6 h prior to use.

### 2.2. Fast pyrolysis of SD

The SD coal was pyrolyzed in a fast pyrolyzer (CDS5200 HPR, CDS Analytical Inc., USA) with direct connection to a gas chromatography (Master GC, DANI, Italy) in split mode, equipped with time of flight mass spectrometry (Master TOF-MS, DANI, Italy). Detailed procedures are according to the relevant literature [6, 7].

## 3. Results and discussion

### 3.1. Identified aromatic hydrocarbons

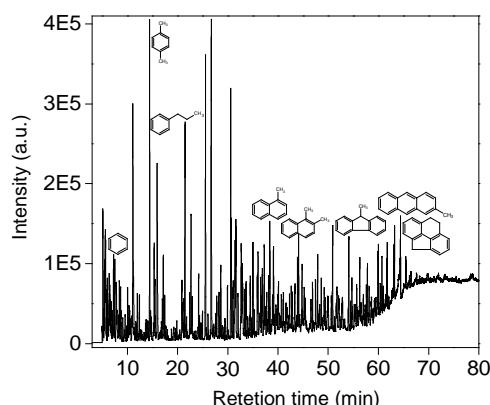


Fig. 1. Typical ion chromatograms from Py-GC/TOF-MS of SD coal.

As shown in Fig. 1, large numbers of compound peaks were generated during fast pyrolysis of SD coal. Among the volatile products, aromatic hydrocarbons were abundant and in total, 83 kinds of aromatic hydrocarbons were identified according to the different retention time of the compounds. As listed in Table 1, the most abundant aromatic hydrocarbons were toluene, p-xylene, 1-ethylidene-1H-Indene, and 1,2-dehydro-as-hydrindacene, during which each compound had the

content higher than 5%. It is believed that biological toxicity of aromatic hydrocarbons is dependent on their molecular structures, such as molecular weight, substituted degree of the alkyl side chains, and ring number [8]. Thereby, pyrolysis products of coal are composed of many different aromatic hydrocarbons with a specific molecular structure for each one, which presents different degree of biological toxicity. The clarification of the aromatic hydrocarbon according to their structural diversity were performed and discussed in the sections below.

Table 1. Several selected aromatic hydrocarbons from fast pyrolysis of SD coal.

RT*	Compounds	RA <sup>#</sup>	RT*	Compounds	RA <sup>#</sup>
7.737	Benzene	2.26	48.219	2,3,6-trimethyl-Naphthalene	0.15
11.078	Toluene	<b>10.31</b>	48.225	2-(1-methylethyl)- Naphthalene	0.07
15.49	Ethylbenzene	2.41	48.615	1,4,6-trimethyl- Naphthalene	1.71
15.927	p-Xylene	<b>10.98</b>	49.199	4,6,8-trimethyl- Azulene	1.81
21.022	1-ethyl-4-methyl- Benzene	0.94	50.894	1,2-Dehydro-as-hydrindacene	<b>5.24</b>
30.389	2,4-dimethyl-1(1-methylethyl)-Benzene	0.07	56.701	1,1-methylenebis[4-methyl-Benzene	0.13
38.365	1-ethylidene-1H-Indene	<b>5.32</b>	58.739	1,1-Biphenyl, 2,2,5,5-tetramethyl-	0.13
45.429	1,4-dimethyl-Naphthalene	1.06	64.017	3,10B-Dihydrofluoranthene	0.05
46.723	2,3-dimethyl-Naphthalene	0.30			

Note: RT\*: Retention time (min), RA<sup>#</sup>: Relative abundance (%).

### 3.2. Distribution of carbon number

Carbon number of aromatic hydrocarbons from fast pyrolysis of SD coal is shown in Fig. 2a. The carbon number ranged from 6 for benzene to 16 for the alkyl-substituted phenanthrene and the content of C<sub>8</sub> aromatic hydrocarbons was largest. Higher carbon numbers reflects the larger molecular weight and therein the higher biological toxicity of the compound. Except for the compounds with lowest and the highest carbon numbers, the relative abundance of others did not show apparent difference. Furthermore, contents of different carbon numbers for aromatic hydrocarbons were distributed in a nearly normal fashion.

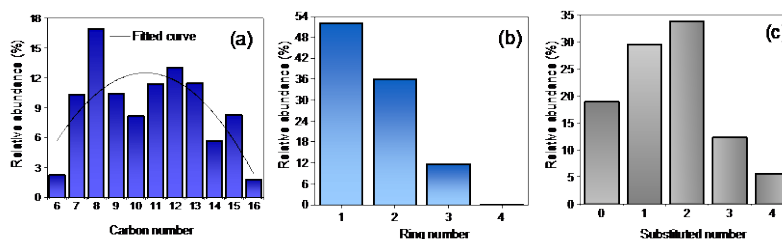


Fig. 2. Distribution of carbon numbers (a), (b) ring numbers and (c) substitute degree for aromatic hydrocarbons.

### 3.3. Distribution of ring number

As we known, aromatic hydrocarbons with more rings i.e., fused aromatics have higher toxicity due to their metabolic difficulties. The ring number distribution for aromatic hydrocarbons is depicted in Fig. 2b. It is found that the ring of aromatic hydrocarbons is distributed from 1 to 4 and their contents decrease gradually with increasing of ring number. Aromatic hydrocarbons with one and two rings are the most abundant species and account for near 88 % of total species. Therefore, toxicity of volatiles from fast pyrolysis of SD coal is governed by 1-2 ring aromatic hydrocarbons.

### 3.4. Distribution of substitute degree

It is well known that biological toxicity of benzene is much higher than that of toluene due to the benzene is lack of alkyl side chains. Therefore, substitutes on the aromatic hydrocarbons are the

important structure to affect their biological toxicity. The contents of aromatic hydrocarbons with different number of alkyl side chains from fast pyrolysis of SD coal were calculated and summarized in Fig. 2c. No alkyl substituted aromatic hydrocarbons were about 19 % and the contents of aromatic hydrocarbons with one and two alkyl side chains were 29% and 34%, respectively. However, amounts of aromatic hydrocarbons with three and four substituents were relatively low, which occupy only 10% and 5%, respectively. The above results may imply that aromatic hydrocarbon products from fast pyrolysis of SD are relatively toxic due to high level of less substituted aromatics.

#### 4. Conclusions

In total, 83 kinds of aromatic hydrocarbons were identified and the most abundant aromatic hydrocarbons were toluene, p-xylene, 1-ethylidene-1H-Indene, and 1,2-dehydro-as-hydrindacene. Carbon number of aromatic hydrocarbons ranged from 6 for benzene to 16 for the alkyl-substituted phenanthrene and the content of C<sub>8</sub> aromatic hydrocarbons was largest. The ring of aromatic hydrocarbons is distributed from 1 to 4 and their contents decrease gradually with increasing of ring number. Furthermore, volatile products cover a series of aromatic hydrocarbons with the substituents from zero to four and the most abundant aromatics are those with substituent less than two.

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