



Study on the source of polycyclic aromatic hydrocarbons (PAHs) during coal pyrolysis by PY–GC–MS

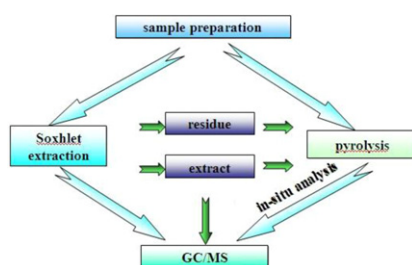
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HIGHLIGHTS

- ▶ A novel approach to obtain a more fundamental understanding of the PAHs production from the coal pyrolysis was reported.
- ▶ The relation between the amount of PAHs from the raw coal and that generated from coal pyrolysis were studied.
- ▶ PAHs generated from residue pyrolysis was also included.
- ▶ PAHs mainly came from complex chemical reactions of coal pyrolysis rather than from the free PAHs in the raw coals.

GRAPHICAL ABSTRACT



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ABSTRACT

Hazardous organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) generated during the course of coal pyrolysis are highly mutagenic and carcinogenic. The relation between the amount of PAHs from the raw coal and that generated from coal pyrolysis were studied. Firstly, three Chinese coals from Huolinhe, Ximeng and Fenxi were respectively extracted by dichloromethane, and then, online pyrolysis analysis of the raw coals, their extraction residues and extracts were carried out respectively by PY (Pyroprobe CDS 5250)–GC–MS. The experimental results showed that the PAHs generated from the Huolinhe, Ximeng and Fenxi coals in the course of their pyrolysis was 523, 327 and 1707 $\mu\text{g/g}$, respectively, which were much higher than the free PAHs extracted from their corresponding raw coals. The PAHs in the raw coals were dominated by 4,5-ring PAHs, while those generated from the coal pyrolysis were dominated by lower-ring (2,3-rings) PAHs. A lot of important information about the generation of PAHs from residue pyrolysis was also included in the paper which indicated that the PAHs were mainly from complex chemical reactions of the coal pyrolysis, and PAHs were more likely to be generated from the residue pyrolysis due to the increased pores that appeared on the coal surface during the course of extraction operation.

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1. Introduction

Generally speaking, polycyclic aromatic hydrocarbons (PAHs) mainly come from incomplete combustion of fossil fuels, refuse

burning, coking, and motor vehicle operation[1–4]. As PAHs have the property of teratogenicity, carcinogenicity and mutagenicity, lots of reports[5–16] indicated that the generation of PAHs during the coal utilization process including coal combustion, gasification and carbonization has received considerable attention of the people. During that process, the generation of PAHs could be classified into two different approaches, one is from complex chemical reactions and the other is from direct release of PAHs from coal which

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Table 1
Analytical values of the coals used in the study.

Sample	Proximate analysis w%			Ultimate analysis w%				
	M_{ad}^a	A_{ad}	V_{daf}^b	C_{daf}	H_{daf}	O_{daf}^c	N_{daf}	S_{daf}
HLH	8.9	19.62	49.76	67.17	5.96	24.44	0.88	1.55
HLHR	6.57	19.22	48.41	73.16	5.18	19.02	0.93	1.71
XM	16.14	7.77	45.69	62.96	2.9	30.1	1.01	3.03
XMR	12.23	8.25	47.28	70.06	4.71	22.01	0.68	2.54
FX	0.91	11.15	27.44	86.47	4.16	6.33	1.25	1.79
FXR	1.29	12.51	28.07	87.42	4.84	4.44	0.95	2.35

^a Air dried basis.

^b Dry and ash-free basis.

^c By difference.

is known as free PAH existing in macromolecule structure of coal [17]. Many researchers focus their attention on the relationship between the generation of PAHs and the pyrolysis conditions of the coal [18,19]. Yet, some lay their emphasis on the amount of PAHs that exist in the raw coals. Bhattacharyya [20] reported that the amount of PAHs obtained from coal extract decreased rapidly with the increase of the carbon content from 81% to 90%, and there was practically no PAH with the carbon content from 90% to 91%. Yan et al. [21] was of the opinion that the dichloromethane extract of bituminous and lean coals are rich in PAHs. Zhao et al. [22] studied the relationship between PAHs existing in the coal extracts and the coal properties when eight bituminous coals were extracted. Lauermann et al. [23] deemed that the distribution of 2–3 ring PAHs has nothing to do with coal origin. However, the relationship between the free PAHs in the raw coal and that generated from the pyrolysis of the raw coal has scarcely been reported.

The objective of this study is to probe into the relationship between the amount of the PAHs in the raw coal and the amount of PAHs generated in the course of the coal pyrolysis. Three Chinese coals were extracted by dichloromethane in the Gerhardt Soxtherm macro 414, and then the 16 priority controlled PAHs specified by US EPA in the coal extracts were analyzed by GC–MS. After that, three raw coals, extracts and residues (residues with their free PAHs being extracted out during the course of extraction) were pyrolyzed by CDS 5250 respectively. In the end, 16 PAHs, namely: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), chrysene (Chy), benz[a]anthracene (BaA), benz[b]fluoranthene (Bbf), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,h]anthracene (DaA) and benzo[g, h, i]perylene (BgP) were measured by on-line GC-MS which was connected with CDS 5250.

2. Experiment

2.1. Chemicals and reagents for the experiment

The mixture standard of the 16 PAHs was supplied by Accustandard Inc (concentration: 200 µg/mL; solvent, a mixture of methanol and dichloromethane, v:v = 1:1); dichloromethane (ABSOLV TEDIA Company) was used as spike solvent.

2.2. Coal samples

Three Chinese coals include HLH (Huolinhe lignite from Inner Mongolia, XM (Ximeng lignite from Inner Mongolia), FX (Fenxi bituminous/coking coal from Shanxi) were selected for this study. The samples were collected according to coal sampling procedure GBT 19494-2-2004. To minimize possible loss of low molecular weight PAHs from the coals, these samples were milled to 60–100 mesh particles, sealed, and stored in a freezer with a

temperature below 0 °C after they were obtained. Three coals were extracted, the extraction of condensed solution containing 16 PAHs was respectively named as HLHE, XME, FXE, and the relevant residues whose free PAHs had been extracted out was named as HLHR, XMR, FXR. The Proximate analytical values of the three coals from China and their residues used in this study were analyzed by ISO11722:1999 (for moisture), ISO1171:1997 (for ash) and ISO562:1998 (for volatile). The ultimate analytical values were analyzed by ISO625-1996 (for C, H) and ISO333-1996 (for N), The analytical values were listed in Table 1.

2.3. Soxhlet extraction

The Soxhlet extraction process by Gerhardt Soxtherm macro 414 was performed in 5 steps to ensure complete extraction of the coal samples. In each run, 2 g of the 60–100 mesh coal was placed in the extraction thimble with 120 mL dichloromethane. The first step was hot extraction, and during this stage, the sample was submerged into the boiling solvent and the extractable matter was released from the sample. This process was carried out at 150 °C for 4 h. The second step was evaporation A, in which the excessive solvent was collected in the rear solvent recovery tank, as a result the solvent level was lower than that of the extraction thimble. The third step was rinsing, and during this process, the PAHs, still not yet lixiviated, could be extracted by the clean solvent of the reflux, and the PAHs thus extracted was collected in the solvent at the bottom of the thimble, and this step took 1.5 h. The fourth step was evaporation B, in which a large amount of solvent was distilled into the rear recovery tank to be reused. The fifth step was evaporation C, in which the extraction beaker was lifted from the hot plate automatically. Part of the remaining solvent was blown away by hot air, and in the end, the extract was concentrated to 10 mL by nitrogen purge, and that could be used for analysis.

2.4. Pyrolysis facilities

A CDS Analytical Pyro-probe 5250 was used for the pyrolysis. It contained a 1 cm quartz tube which could be heated up by a 2–3 mm diameter platinum filament, and that enables a temperature increase up to 1200 °C at a heating rate of 20 °C/ms. Every sample could be analyzed in multi-steps temperature and GC runs automatically under each temperature step. The average weight charged into the pyrolyzer (PY) was 1 mg and that occupied about 1–1.5 mm of the quartz tube. Quartz wool was properly packed at the top and bottom to avoid possible leakage, or the sample being blown out. Helium as the carrier gas for the GC/MS was used to purge off the air from the sample before pyrolysis, and send the gas generated during the course of pyrolysis to the GC for testing.

The pyrolyzer was connected to the FOCUS gas chromatograph and the DSQII mass spectrometer (Thermo Fisher, USA). With the pyroprobe/gas chromatograph/mass-spectrometer (PY-GC-MS)

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