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Performance of PAHs emission from bituminous coal combustion*

YAN Jian-hua (严建华)†, YOU Xiao-fang (尤孝方), LI Xiao-dong (李晓东),
NI Ming-jiang (倪明江), YIN Xue-feng (尹雪峰), CEN Ke-fa (岑可法)
(*National Key Lab of MOE Clean Energy and Environmental Engineering, Zhejiang University, Hangzhou 310027, China*)
†E-mail: yanjh@cmee.zju.edu.cn

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Abstract: Carcinogenic and mutagenic polycyclic aromatic hydrocarbons (PAHs) generated in coal combustion have caused great environmental health concern. Seventeen PAHs (16 high priority PAHs recommended by USEPA plus Benzo[e]pyrene) present in five raw bituminous coals and released during bituminous coal combustion were studied. The effects of combustion temperature, gas atmosphere, and chlorine content of raw coal on PAHs formation were investigated. Two additives (copper and cupric oxide) were added when the coal was burned. The results indicated that significant quantities of PAHs were produced from incomplete combustion of coal pyrolysis products at high temperature, and that temperature is an important causative factor of PAHs formation. PAHs concentrations decrease with the increase of chlorine content in oxygen or in nitrogen atmosphere. Copper and cupric oxide additives can promote PAHs formation (especially the multi-ring PAHs) during coal combustion.

Key words: Polycyclic aromatic hydrocarbons (PAHs), Organic pollutants, Bituminous coal, Combustion
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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have caused great environmental health concern because of their carcinogenic and mutagenic characteristics, although the amounts of the organic PAHs pollutants emitted into the environment are lower than those of the inorganic pollutants such as SO_2, NO_x, and CO. PAHs may be formed during inefficient combustion of fossil fuels (petroleum, coal and so on), wood, paper, and tobacco that contain carbon and hydrogen, or produced during pyrolytic process. Usually, anthropogenic and industrial processes such as home heating, power generation, road transportation, and incineration are the major PAHs emission sources. Some PAHs indicators of different processes have been identified. Chrysene and benzo(k)fluoranthene are indicators of coal combustion, and pyrene and fluoranthene are associated with incineration. The most toxic PAHs, benzo(a)pyrene (BaP), emitted from boilers accounts for 51.6% of the total BaP emissions in the world (Sai, 1995).

Coal is mainly composed of a wide variety of organic structures such as aromatic clusters, aliphatic bridges and rings, side chains, and oxygen functional groups (Solomon *et al.*, 1988). Upon heating, coal structures undergo major physical and chemical changes and release volatile organic compounds. CO and CH_4 are also produced because of the rupture of the function groups in coal. Weaker bonds in aliphatic bridges and rings break

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up first, then the aromatic structures, resulting in more aromatic hydrocarbons produced in the products.

PAHs formation during coal combustion process may occur through complex pathways. There are two important factors influencing PAHs emission in coal combustion: (1) the unburned organic materials because of the poor combustion conditions (Mastral *et al.*, 1998a; 2000), and (2) the initial stage of pyrolysis process in the combustion (Mastral *et al.*, 1998b). PAHs emission from energy generation has been reviewed, including emission sources, sampling, extraction and measurement techniques, and the influences of the fuel and combustor type (automobile engines, domestic combustors, industrial stokers and fluidized bed combustors) on PAHs emission. Pyrolysis and pyrosynthesis are the two main PAHs formation mechanisms (Mastral and Callen, 2000; Ni *et al.*, 2003).

Although the influence of coal structure on PAHs emissions from coal combustion is not well understood, the other factors that influence PAHs emissions had been studied (Liu *et al.*, 2001; Li *et al.*, 2003). The influences of chlorine and sulfur contents in coal on PAHs emission had also been examined. They included the different influences of organic chlorine and inorganic chlorine on the distribution of PAHs in the gas phase and solid phase emission (Liu *et al.*, 2001).

Total PAHs emission depends mainly on the pyrolitic process and to a lesser degree on the combustion efficiency. A study conducted by US EPA (Miller, 1994) suggested that the efficient combustion conditions in the pulverized coal-fired boilers had very little potential for PAH emissions. Different types of free radicals, aromatic and alkyl structures undergo association through cyclization, can lead to PAHs formation. Once the coal combustion efficiency is optimized, the pyrosynthetic process has very important influence on PAHs formation. The effect of temperature on PAHs produced from the pyrolysis of a bituminous coal in a drop-tube reactor had been studied (Wornat *et al.*, 1987). Their results showed that PAHs products decreased as the pyrolysis temperature increased from 900 °C to 1000 °C. Another study showed increase of PAHs yields resulted from the pyrolysis of a coal with increasing temperature at about 600 °C (Ledesma *et al.*, 2000).

The external influences of combustion temperature, excess air, and coal rank on PAHs emission from fluidized bed combustion had been studied (Mastral *et al.*, 1998a; 1998b; 1999; 2000; Mastral and Callen, 2000; Liu *et al.*, 2001; Yan *et al.*, 1996). Their results suggested that PAHs emission increased first and then decreased with increasing temperature. When the residence time increased, the total PAHs emission decreased (Liu *et al.*, 2001). There is a specific PAHs emission trend that follows the combustion temperature. PAHs in the gas phase are higher than those in the solid phase. The higher the percentage of excess air, the lower the total PAHs emitted. Lower percentage of excess air could favor the deposition of PAHs on the more stable particulate matters, while the higher percentage of excess air could favor the shift of PAHs to the gas phase. There will be a slugging regime at higher flows causing PAHs yields to increase (Mastral *et al.*, 1998a; 1999).

The effects of adding desulfurization agents to coal combustion on PAHs emission had been studied experimentally (Liu *et al.*, 2001; Mastral *et al.*, 2001a). Their results showed that more PAHs tended to concentrate on the solid phase when limestone was added to the reactor.

Metal additives have little influence on low molecular weight compound (C_1-C_4) formation. With decreasing flame temperature, iron (Fe) is released as a metal in gas phase, and manganese (Mn) is released as an oxide. They form active sites on particle surfaces and can catalyze PAHs and soot formation with the reaction of acetylene (Feitelberg *et al.*, 1993). The presence of chloride has distinctive influence on organic compound formation. Under oxygen deficient condition, the addition of a metal chloride can promote thermal decomposition of PE and form PAHs with the participation of benzene (Wey *et al.*, 2000).

Based on the above analysis, to gain understanding of PAHs formation from coal combustion process, PAHs contents in raw bituminous coals were analyzed and PAHs distribution from coal combustion was determined. Furthermore, the influences of chlorine and heavy metal on PAHs formation were studied. The results are reported in this paper.

EXPERIMENTS AND PROCEDURE

Analysis of PAHs content in raw coals

Five Chinese bituminous coals were analyzed for PAHs content. Proximate and ultimate analyses of the five coals are listed in Table 1.

Coal (5.0000 g) was mixed with quartz sand, extracted for 18 hours in a Soxhlet apparatus with dichloromethane as solvent. The solution was then concentrated to 2–3 ml in a rotary vapor. N-hexane was used to deposit pitch matter, silica gel and aluminum oxide were filled in a chromatograph column. N-hexane (20 ml in 4 times), dichloromethane/n-hexane (V/V: 2/1 15 ml in 3 times), anhydrous alcohol (10 ml) and chloroform (10 ml) were used to elute different organic compounds with increasing polarity of the compounds as aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds. The solvent of the eluted liquid was vaporized at 40 °C and the residue was kept in a vacuum oven for 30 minutes at a pressure of 5.33×10^4 Pa, then stored in desiccator for 30 minutes before the mass was weighed. The conditions for analyzing the extracts of these five coals using a gas chromatograph coupled with a mass spectrometer (GC/MS) are listed in Table 2.

Experimental procedure

All combustion experiments were carried out in a laboratory-scale tubular furnace shown in Fig.1. The furnace temperature was regulated to the set point (±20 °C) by the electric heating equipment.

Each time 0.5000 gram of coal (80–400 mesh)

Table 1 Analysis of bituminous coal

Coal	Proximate analysis					Ultimate analysis (%)				
	M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	FC_{ad} (%)	$Q_{net,ad}$ (MJ/kg)	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}
Datong	4.66	13.90	26.59	54.82	27.50	66.21	3.47	10.15	0.84	0.75
Zaozhuang	1.84	18.10	29.43	50.63	27.73	65.88	4.06	9.80	1.22	0.88
Yanzhou	1.82	19.69	30.46	48.02	25.75	63.45	4.06	9.00	1.27	0.70
Hongyan	0.79	22.70	19.08	57.43	29.14	66.64	4.44	0.89	1.38	3.16
Datun	2.21	38.24	22.48	37.07	18.67	46.94	3.23	7.96	0.94	0.48

Table 2 GC-MS analytical condition for aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds

Compound	Aliphatic hydrocarbons	Aromatic hydrocarbons	Polar compounds
Column	DB-5, 30 m×0.25 mm	DB-5, 30 m×0.25 mm	WAX-10, 30 m×0.25 mm
Initial temperature (°C)	70	60	60
Time hold (min)	0	3	0
Increasing rate I (°C/min)	8	3	10
Final temperature I (°C)	–	100	–
Increasing rate II (°C/min)	–	12	–
Final temperature II (°C)	270	270	240
Time hold (min)	20	6	25
Carburetor temperature (°C)	250	–	240
Diffluent rate	30:1	30:1	50:1
He (ml/min)	1	1	1
MS	EI, 70 eV	EI, 70 eV	EI, 70 eV, full scan
Scanning mass range (u)	40–500	40–500	35–300
Scanning time (s)	0.5	0.5	0.5

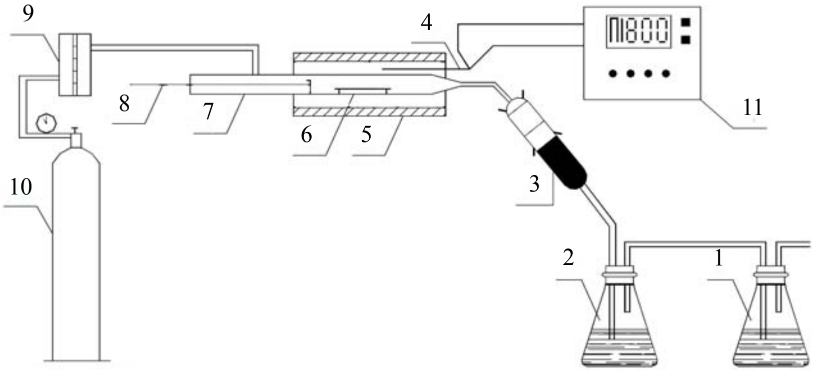


Fig.1 Schematic of the tubular furnace
1: distilled water, 2: dichloromethane, 3: XAD-2 adsorbent, 4: thermocouple, 5: heater, 6: ceramic boat, 7: quartz tube, 8: handspike, 9: flow meter, 10: gas container, 11: control panel

was weighed accurately in a ceramic boat. Bottle 3 was filled with XAD-2 adsorbent to absorb PAHs in flue gas. Conical flask 1 was filled with distilled water and conical flask 2 was filled with dichloromethane. After the combustion experiment was completed, the distilled water contained in flask 1 was extracted with dichloromethane as solvent. The extraction solution and the XAD-2 adsorbent contained in bottle 3 were both extracted for 20 hours in a Soxhlet apparatus and concentrated to 5 ml by a rotary evaporator at a temperature of 40 °C. The condensate was pretreated for separation before it was analyzed by using a gas chromatography (GC); it was considered as PAHs in flue gas. The rest of the materials in the ceramic boat after combustion was also extracted as above and considered as PAHs in residue.

GC analysis condition for coal combustion samples

GC analysis of the combustion products was performed using a ThermoQuest/Trace2000 system equipped with a flame-ionization detector (FID). A quartz capillary column DB-5 (30 m×0.25 mm× 0.25 μm) was used. Initial column temperature was 70 °C, heated up to the final temperature I of 180 °C at a rate of 3 °C/min. The rate was changed to 10 °C/min up to the final temperature II of 280 °C, and kept at this point for 20 minutes. The FID temperature was 280 °C. Boil off temperature was 250 °C, the flow rate of the helium (He) carrier gas was 1 ml/min, the mode of sample entrance was spitless. Flow rates of hydrogen (H_2), air, and nitrogen (N_2) were 35, 350, and 45 ml/min respectively. The injection volume to GC was 1 μl.

The seventeen PAHs to be analyzed are: Naphthalene (NaP, 50 pg), Acenaphthylene (AcPy, 10 pg), Acenaphthene (AcP, 10 pg), Fluorene (Flu, 10 pg), Phenanthrene (Phe, 10 pg), Anthracene (AnT, 10 pg), Fluoranthene (Fla, 5 pg), Pyrene (Pyr, 5 pg), Benzo[a]anthracene (BaA, 5 pg), Chrysene (Chr, 5 pg), Benzo[b]fluoranthene (BbF, 10 pg), Benzo[k]fluoranthene (BkF, 10 pg), Benzo[e]pyrene (BeP, 10 pg), Benzo[a]pyrene (BaP, 10 pg), Indeo[123-c,d]pyrene (IND, 50 pg), Dibenz[a,h]-anthracene (DBA, 50 pg), Benzo[g,h,i]perylene (BghiP, 50 pg). Figures in the brackets are the sensitivities of the GC for PAHs detection. Substance qualitative determination was performed based on retention times, substance quantitative determination was performed using the external standard method. A mixture of 17 PAHs standards was obtained from the Cambridge Isotope Laboratory (serial number: ES-8032, concentration: 100±10 μg/ml, solvent: toluene).

RESULTS AND DISCUSSION

PAHs content in five bituminous coals

The organic components of the five bituminous coals determined by the solvent extraction method (SY5119-86) are listed in Table 3. The results showed that the main components of the five bituminous coals tested were aromatic and polar structures. Aliphatic structures were the minor components in these coals (about 10%–20%).

PAHs distribution by ring number and the total TEQ value of the five coals tested are listed in Table 4. The most abundant PAHs were 5- and 6-rings PAHs. The total TEQs of the bituminous coals tested were very similar (1.3−1.6 μg/g) except for the Hongyan coal, which had much lower total TEQ 0.62 μg/g) than those of the other four coals. The PAHs content in the five bituminous coals tested was under10 μg/g.

Correlations of PAHs in raw coal with different coal components are shown in Fig.2. Volatiles are the important sources for PAHs formation during combustion, with increasing volatiles in coal, PAHs content also increased to about 26%, then decreased slightly at higher volatile content. As was also true for the fixed carbon, PAHs content decreased with increasing $(H/C)_m$.

PAHs formation from coal combustion and comparision with PAHs in raw coal

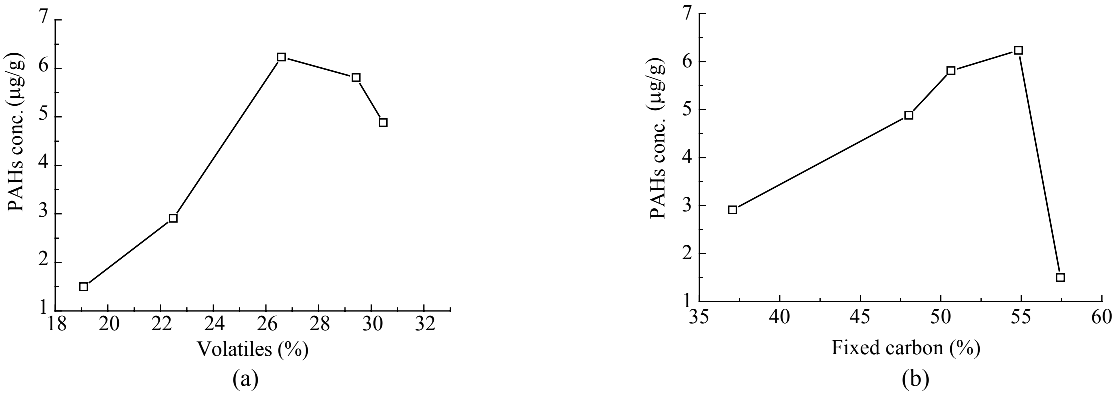
Datong and Yanzhou bituminous coal were burned in a tubular furnace (Fig.1) at a temperature of 800 °C with a residence time of 30 minutes. PAHs emissions from coal combustion were compared with those existing in the raw coal. Table 5 shows that total PAHs emission from combustion are much higher than those existing in the raw coal.

Table 3 Distribution of aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds in bituminous coal

Coal origin	Aliphatic hydrocarbons (%)	Aromatic hydrocarbons (%)	Polar compounds (%)
Datong	13.60	39.46	46.94
Zaozhuang	19.12	40.58	40.30
Yanzhou	7.09	40.69	52.22
Hongyan	28.04	30.88	41.08
Datun	11.35	45.39	43.26

Table 4 PAH TEQ and distribution by ring numbers of bituminous coal (μg/g)

Coal origin	Two-rings	Three-rings	Four-rings	Five-rings	Six-rings	Total TEQ
Datong	0.0023429	1.0500904	1.9333938	2.142396	1.102886	1.594978
Zaozhuang	0.0039785	1.2017492	0.9933058	1.9789069	1.6570118	1.639949
Yanzhou	0.0029211	0.7081887	0.9366154	1.6953002	1.543408	1.588046
Hongyan	0.0027862	0.2181811	0.0658004	0.6197251	0.5915693	0.62015
Datun	0.0046977	0.1823678	0.164392	1.3688066	1.1900291	1.312737



(a) (b)

Fig.2 Correlations of PAH in raw coal with different coal component

(a) PAHs concentration vs volatiles in coals; (b) PAHs concentrations vs fixed carbon in coals

PAHs contents in raw coal contribute little to PAHs emissions from coal combustion. These results also suggested that the coal structure had very little influence on PAHs emissions from coal combustion.

Effects of temperature on PAHs emission from Datong coal combustion

Temperature is an important parameter in coal combustion. Bituminous coal was burned at 100 °C interval from 600 °C to 1000 °C in our experiments. PAHs produced from coal combustion at different temperatures showed a single peak trend (Fig.3). The highest PAHs emission was at 800 °C, below which, most of the PAHs were formed from the pyrolytic process.

Condensed aromatic and hydroaromatic units in bituminous coals are connected by either short alkyl bridges, or ether linkages. Coal contains 80% of the carbon as vitrinite (Berkowitz, 1985). Upon heating, weaker C-C bonds in the virtinite macerals begin to break. At low temperatures, the most abundant PAHs released are the multi-ring PAHs (six-ring PAHs especially) are the most abundant, whereas two-ring PAHs are the least abundant at combustion temperature of 600 °C, above which, relatively more three- and four-ring PAHs are formed because of the breaking up of the C-C bonds in the large aromatic hydrocarbons that produce relatively smaller fragments. PAHs in the residue and those in the flue gas, increased with increasing combustion temperature. At higher temperatures, PAHs formed through the reactions of synthesis and polymerization of small molecules, while the total PAHs produced from combustion decreased because of more effective combustion. Two competitive reactions occur during combustion, PAHs formation and PAHs oxidation. Therefore, the amounts of PAHs formed decrease when the temperature increases above 800 °C. Fig.4 shows that two- and three-ring PAHs increase from 600 °C to 800 °C because decomposition of multi-ring matter produces PAHs with fewer rings. From 800 °C to 1000 °C they both decrease, because they are destroyed through more effective combustion.

Formation of four- and five-ring PAHs changed greatly with increasing combustion temperature. Four- and five-ring PAHs can be burned

Table 5 Ratios of PAHs from combustion with PAHs in raw coal

Coal origin		2-rings	3-rings	4-rings	5-rings	6-rings	total
Datong	Flue gas	57.6	26.6	119.9	24.7	10.2	38.7
	Residue	51.3	1.1	35.4	1.7	0	7.5
	Total	108.9	27.7	155.3	26.4	10.2	46.2
Yanzhou	Flue gas	2474.7	24.4	9.7	27.5	11.2	19.5
	Residue	2462.5	26.4	12.2	20.9	0	16.3
	Total	4937.2	50.8	21.9	48.4	11.2	35.8

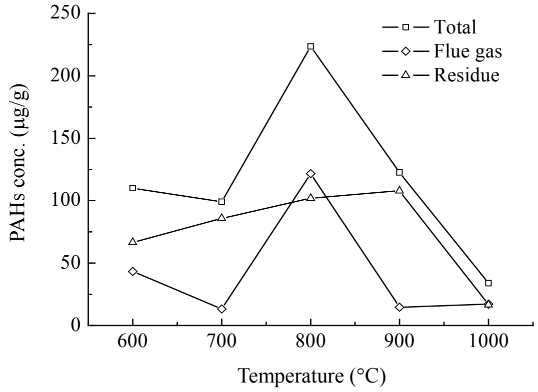


Fig.3 Effect of the combustion temperature on the total PAHs emission

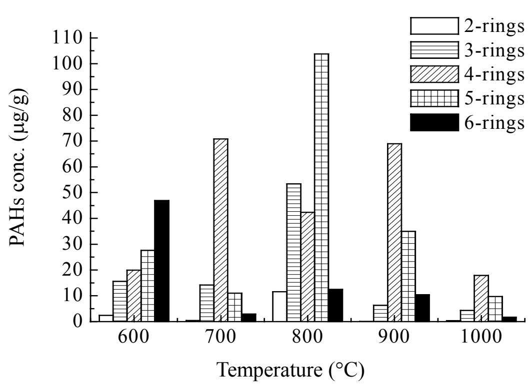


Fig.4 Distributions of the total PAHs by ring number at the different combustion temperatures

or decomposed to compounds with lower number rings; and the deep pyrolysis of coal and the decomposition of higher ring number compounds can produce more PAHs. Six-ring PAHs decrease as combustion temperatures increases from 600 °C to 1000 °C. In addition, decrease of PAHs formation above 900 °C is due to the condition of pyrolysis reaching maximum, when the products of pyrolysis can be completely combusted to CO_2 and H_2O. Therefore, when the temperature is over 900 °C, the combustion is almost completed.

Fig.5 of the distributions of PAHs in flue gas and in residue shows that at 600 °C, concentration of two-ring PAHs in flue gas is much higher than that in the residue. The distribution of the three-ring PAHs is nearly the same as that of the two-ring PAHs. With increasing temperature, the two- and three-ring PAHs decrease in flue gas, while they increase in residue in the deep pyrolysis process of coal, so that the ratio of PAHs in flue gas to PAHs in residue decreases. Most of the six-ring PAHs are in residue at low temperature. With increasing temperature, six-ring PAHs in the flue gas increase because of the synthesis reaction.

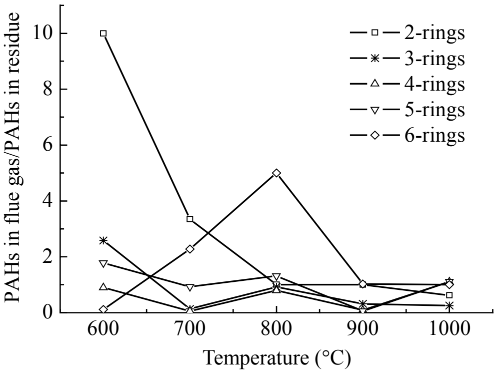


Fig.5 Distributions of PAHs in flue gas and residue at different combustion temperatures

Effect of chlorine content in coal on PAHs emission

Three kinds of bituminous coals with different chlorine contents were tested in the present study. Chloride in coal begins to release as hydrogen chloride (HCl) at temperature of 200 °C, with about 80% of the total chloride released at 400 °C as HCl. And the reaction atmosphere has little influence on chloride emission. The combustion rates of chlorinated hydrocarbons are slower than those of the non-chlorinated hydrocarbons, and as the sooting tendency is also high, there will be two flame zones because of the C-Cl bond is weaker than the C-C bond (Bose *et al.*, 1983).

Fig.6 shows that PAHs emission decrease as chlorine content in coal increases for both pyrolysis and combustion cases, and that some PAHs are converted into chlorinated aromatic compounds during the pyrolysis and combustion processes. There may be significant influence of oxygen on PAHs formation when coal is burned in air. In addition, when the coal chlorine content changes, the amounts of the three-, four- and five-ring PAHs vary significantly, while the amounts of two- and six-ring PAHs show very little variation. As the high reactivities of the three-, four- and five-ring PAHs, these PAHs may be more easily substituted by chlorine to form chlorinated compounds. TEQs of the PAHs produced from coal combustion and from pyrolysis are shown in Fig.7. Similar to PAHs emission, the TEQ values of PAHs from pyrolysis are higher than those from combustion. TEQ value decreases with increasing coal chlorine content in the combustion case, and there is no specific trend in TEQ value in the pyrolysis case. It can be seen from Fig.8 and Fig.9 that in inert atmosphere, PAHs formation in the flue gas is much higher than that in the residue. More free radicals are formed from pyrolysis, and as a result, PAHs formation in flue gas increases.

PAHs emission from the combustion of Datong coal with copper added

Copper was mixed with Datong coal and then the mixture was burned in a tubular furnace. The mass ratio of $(Cu/Coal)_m$ was 1:100. Coal combustion tests were conducted at 600–1200 °C. Table 6 and Fig.10 show the results of the PAHs emission tests. Fig.10 shows two formation peaks with increasing temperature. The first maximum peak is at 800 °C, which is also the temperature point of maximum PAHs formation without the addition of

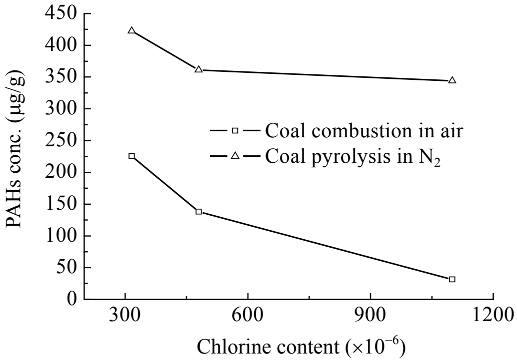


Fig.6 Influence of chlorine content on PAHs emission from coal pyrolysis and combustion

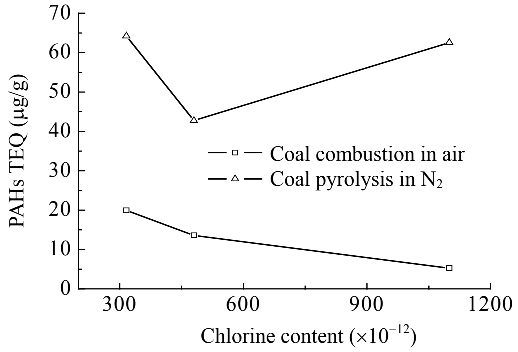


Fig.7 PAHs TEQ from coal pyrolysis and combustion

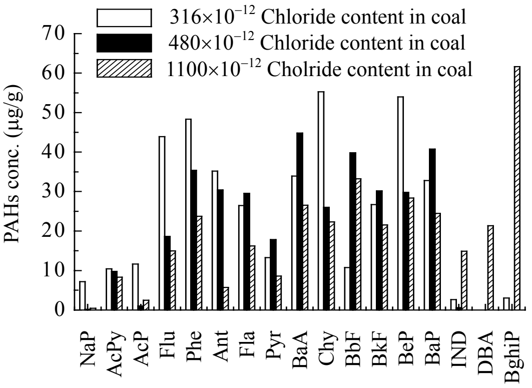


Fig.8 PAHs distribution in flue gas of coal pyrolysis in N$_2$

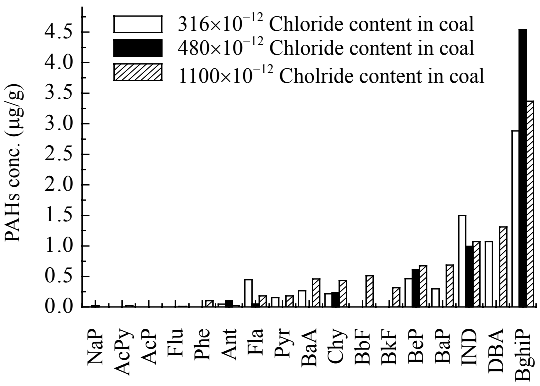


Fig.9 PAHs distribution in residue of coal pyrolysis in N$_2$

Table 6 PAHs emission from combustion of coal with addition of copper (μg/g)

Abbr. (°C)	600	700	800	900	1000	1100	1200
NaP	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
AcPy	N.D.	0.014	N.D.	N.D.	0.005	N.D.	N.D.
AcP	0.116	N.D.	0.154	N.D.	N.D.	N.D.	N.D.
Flu	0.967	0.119	5.365	N.D.	N.D.	0.035	N.D.
Phe	4.997	4.499	13.710	N.D.	0.307	3.156	0.455
AnT	2.058	0.150	6.232	0.014	0.128	1.541	0.276
Fla	2.147	9.221	15.049	0.292	2.081	10.000	2.003
Pyr	2.063	5.064	7.583	0.062	0.833	6.008	1.940
BaA	1.708	1.962	19.597	0.175	2.574	6.387	1.779
Chr	1.615	6.501	15.144	0.296	2.048	1.815	0.337
BbF	0.296	2.508	16.821	0.846	2.716	5.698	1.928
BkF	0.015	0.134	0.096	1.452	3.267	4.502	0.555
BeP	2.943	3.743	15.137	0.082	1.775	2.250	0.871
BaP	1.598	1.855	21.668	0.763	4.002	8.631	2.147
IND	N.D.	N.D.	N.D.	3.297	N.D.	0.301	N.D.
DBA	N.D.	N.D.	N.D.	0.684	N.D.	N.D.	N.D.
BghiP	N.D.	N.D.	N.D.	N.D.	N.D.	0.620	N.D.
Total	20.524	35.771	136.555	7.963	19.736	50.943	12.290

N.D.–not detected

copper in the coal. The second maximum peak is at 1100 °C, which is higher than the boiling point of copper. As discussed earlier, there are two suggested main mechanisms for PAHs formation. The initial ring formation can occur through: hydrogen abstraction, C_2H_2 addition, and then ring closure; or C_2H_2 addition on an existing ring. There is also a possibility of the reaction of two C_5H_5 radicals to form two fused rings. It is the temperature that decides which mechanism is the dominant pathway. Metal can act as an active center and promote PAHs formation. It can be seen from Fig.11 that the 4- and 5-rings PAHs occur at highest concentrations in the emissions. At low temperature of 600 °C, Phe, a three-ring PAH occurs at the highest concentration. With increasing temperature, the concentration of the PAHs with more rings increase. It can be suggested that copper may promote PAHs formation at high temperatures, especially the multi-ring PAHs.

It can be seen from Table 7 and Table 8 that the 1:100 ratio of $(Cu/Coal)_m$ results in least PAHs formation at the two combustion temperatures. Except for some PAHs with low number of rings, individual PAHs concentration is somewhat high. Cupric oxide was mixed with coal and then the mixture was burned. The highest PAHs emission was observed at a combustion temperature of 1000 °C (Fig.12). Fig.13 shows that the four-ring PAHs are much higher in concentration than those of other PAHs at 1000 °C. The concentrations of other PAHs with more or fewer rings are peaked at 900 °C. Table 9 shows Fla and Pyr are the two PAHs with the highest concentrations.

Generally, PAHs formation from coal combustion with the addition of copper is lower than that from the case of addition of cupric oxide.

The TEQs of PAHs from coal combustion with the additions of copper and cupric oxide are listed in Table 9. The TEQs from coal combustion with the addition of copper are of the same magnitude as those with the addition of cupric oxide.

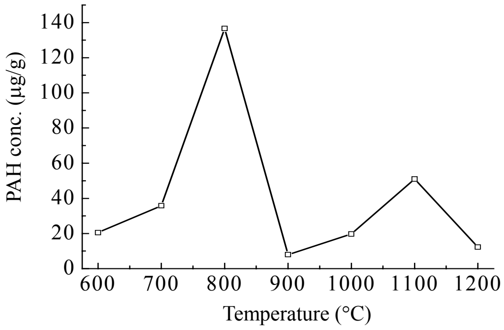


Fig.10 The influence of temperature on PAHs emissions from combustion of coal with addition of copper in coal

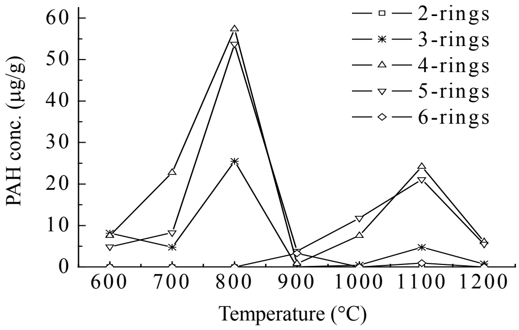


Fig.11 PAHs distributions by ring number from combustion of coal with addition of copper in coal

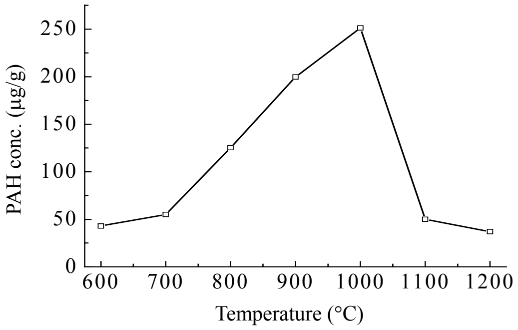


Fig.12 The influence of combustion temperature on PAHs emission from combustion of coal with addition of cupric oxide

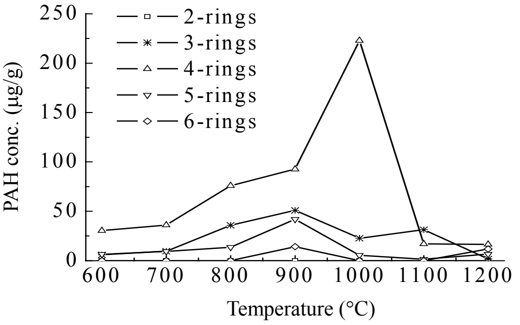


Fig.13 PAHs distribution by ring number from combustion of coal with addition of cupric oxide

Table 7 PAHs emission from combustion of coal with addition of different ratio of copper (μg/g)

Temperature (°C)	800		1200	
$(Cu/Coal)_m$	1:50	1:200	1:50	1:200
NaP	N.D.	N.D.	N.D.	N.D.
AcPy	N.D.	N.D.	N.D.	N.D.
AcP	N.D.	N.D.	N.D.	N.D.
Flu	0.009	1.054	3.538	N.D.
Phe	16.337	16.510	0.010	N.D.
AnT	0.006	17.466	0.008	0.019
Fla	20.957	54.616	11.786	15.698
Pyr	16.391	21.539	26.615	31.209
BaA	7.271	18.778	4.504	8.111
Chr	7.734	17.466	1.471	2.2041
BbF	0.520	13.564	0.125	0.955
BkF	6.310	0.170	0.359	0.287
BeP	5.643	13.141	3.528	4.854
BaP	7.970	13.354	5.076	5.1559
IND	7.185	N.D.	12.524	N.D.
DBA	2.247	1.342	N.D.	N.D.
BghiP	28.967	11.0778	0.404	10.195
Total	127.544	200.077	69.950	78.687

N.D. –not detected

Table 8 PAHs emission from combustion of coal with addition of cupric oxide (μg/g)

Abbr. (°C)	600	700	800	900	1000	1100	1200
NaP	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.034
AcPy	N.D.	N.D.	N.D.	N.D.	11.526	1.055	0.012
AcP	N.D.	N.D.	N.D.	N.D.	0.254	N.D.	N.D.
Flu	N.D.	0.046	1.679	5.714	10.433	3.742	0.036
Phe	4.684	8.134	22.673	24.784	0.312	1.049	1.492
AnT	1.187	1.470	11.394	20.406	0.236	25.528	0.171
Fla	20.397	17.044	39.546	41.745	118.765	0.579	5.156
Pyr	4.362	8.607	21.102	30.150	44.910	0.362	6.978
BaA	2.639	5.511	6.960	10.284	51.064	14.955	3.466
Chr	3.167	4.968	8.381	10.426	8.236	1.179	1.027
BbF	0.994	2.432	3.751	11.642	0.827	0.145	1.559
BkF	0.243	0.566	0.328	10.972	0.554	0.326	0.967
BeP	3.829	3.588	5.960	7.101	3.608	0.458	1.506
BaP	1.492	2.675	3.517	10.245	0.461	0.534	2.644
IND	N.D.	N.D.	N.D.	7.081	N.D.	N.D.	3.905
DBA	N.D.	N.D.	N.D.	1.891	N.D.	N.D.	0.033
BghiP	N.D.	N.D.	N.D.	7.173	N.D.	N.D.	8.004
Total	42.994	55.041	125.291	199.614	251.185	49.912	36.989

N.D. –not detected

Table 9 PAHs TEQ from combustion of coal with addition of copper and cupric oxide

Temperature (°C)	Coal+Cu (μg/g)	Coal+CuO (μg/g)
600	1.847	1.952
700	2.401	3.624
800	25.575	4.904
900	2.027	16.617
1000	4.882	5.976
1100	10.379	2.351
1200	3.239	0.830

CONCLUSION

PAHs formation in early stage of pyrolysis is more important in the whole coal combustion process. The combustion temperature has great influence on PAHs emission. PAHs formation process can be divided into two stages: low temperature stage and high temperature stage. At temperature of 800 °C, PAHs concentrations reach their maximum. In the low temperature stage, PAHs formation is from coal pyrolysis, but in the high temperature stage, PAHs formation is due to the synthesis of small hydrocarbons. As chlorine content of coal increases, the amounts of PAHs produced from combustion of coal in air and from pyrolysis of coal in N_2 decrease, probably because of the formation of chlorinated aromatic compounds. Copper and cupric oxide additives promote PAHs formation during coal combustion, especially the multi-ring PAHs.

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