



# Release behavior and formation mechanism of polycyclic aromatic hydrocarbons during coal pyrolysis



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## HIGHLIGHTS

- Emissions of 16 PAHs during pyrolysis of different coals were studied by PY-GC/MS.
- Types of carbon atoms present in different coals were determined by CP/MAS <sup>13</sup>C NMR.
- Release amounts and species of PAHs depend on coal rank and pyrolysis temperature.
- Formation mechanism of PAHs during coal pyrolysis was revealed.

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are major environmental pollutants. They have attracted considerable attention due to their severe potential carcinogenic, mutagenic and genotoxic effects on human health. In this study, five different rank coals from China were pyrolyzed using pyro-probe CDS 5250 and the release behavior of 16 PAHs under different pyrolysis conditions were studied by Gas Chromatography-Mass Spectrometer (GC-MS). The structural characteristics of the five coals were determined by Cross-Polarization/Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (CP/MAS <sup>13</sup>C NMR) spectroscopy, and then the factors influencing the formation of PAHs during coal pyrolysis were discussed together with the coal structural data. It was shown that the amount of PAHs generated during coal pyrolysis was largely related to coal rank and followed the order of medium metamorphic coal > low metamorphic coal > high metamorphic coal. The amount of total PAHs varied as the temperature was increased from 400 °C to 1200 °C, which showed a trend of first increasing and then decreasing, with the maximum value at 800 °C. Moreover, the species of PAHs released varied with pyrolysis temperatures. When the temperature was lower than 800 °C, the small ring PAHs were the most abundant, while the proportion of heavy rings increased at higher temperature. The results indicate that the formation of PAHs during coal pyrolysis depends on the structure of the coal. The species and amounts of PAHs generated during coal pyrolysis are closely related to the contents of protonated aromatic carbons and bridging ring junction aromatic carbons present in the coal structure.

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## 1. Introduction

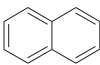
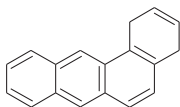
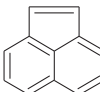
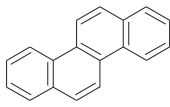
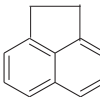
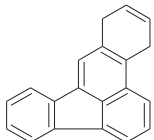
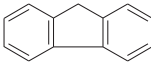
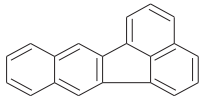
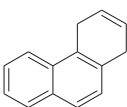
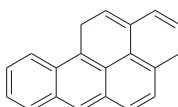
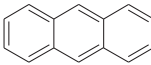
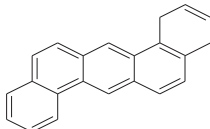
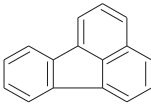
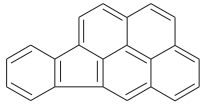
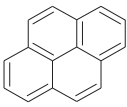
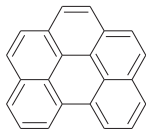
Polycyclic aromatic hydrocarbons (PAHs) are serious environmental contaminants produced by the combustion of fossil fuels in heat and power generation and refuse burning applications (Lima et al., 2005; Achten and Hofmann, 2009). The US Environmental Protection Agency (US EPA) has prioritized 16 PAHs compounds as

hazardous air pollutants since 1979 due to their severe carcinogenic, mutagenic and genotoxic effects on human health (Boström et al., 2002; Pieterse et al., 2013; Mugica-Alvarez et al., 2015). These compounds include naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PhA), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (In [1,2,3-cd]P), dibenz[a,h]anthracene (DBahA), and benzo[g,h,i]perylene (BghiP). The chemical structures and number of aromatic rings of these compounds are shown in Table 1. Up to now, PAHs

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**Table 1**  
Chemical structure and number of aromatic rings of 16 PAHs

PAH name	Structural formula	Aromatic rings	PAH name	Structural formula	Aromatic rings
Naphthalene (Nap)		2	Benz[a]anthracene (BaA)		4
Acenaphthylene (AcPy)		3	Chrysene (Chr)		4
Acenaphthene (AcP)		3	Benzo[b]fluoranthene (BbF)		5
Fluorene (Flu)		3	Benzo[k]fluoranthene (BkF)		5
Phenanthrene (PhA)		3	Benzo[a]pyrene (BaP)		5
(Anthracene) AnT		3	Dibenz[a,h]anthracene (DBaA)		5
Fluoranthene (FluA)		4	Indeno[1,2,3-cd]pyrene (In[1,2,3-cd]P)		6
(Pyrene) Pyr		4	Benzo[g,h,i]perylene (BgHiP)		6

have attracted increasing attention because they can cause lung cancer and increase the cardiopulmonary mortality (Pozzi et al., 2005; Luo et al., 2015; Wang et al., 2015a). Furthermore, they are easily trapped in particulate matter (PM<sub>2.5</sub>) which is considered as the main cause of atmospheric haze. With the development of clean coal technology and the increasing global demand of contaminant emission reduction, it is imperative to study the release behavior and formation mechanism of PAHs during coal pyrolysis because coal pyrolysis is one of the important parts of the comprehensive use of coal and it occurs almost in all major coal thermal conversion processes.

Several studies have been reported on the PAHs generated during coal pyrolysis (Wornat et al., 1987; Nelson and Tyler, 1988; Hayashi et al., 1993; Yu et al., 1998) and the PAHs extracted from coals (Dong et al. 2012). However, these studies have just focused on the release characteristics of PAHs during coal pyrolysis. Sharma and Hajaligol (2003) used a two zones reactor to investigate the effect of pyrolysis condition on the formation of PAHs under inert atmosphere. Their results showed that larger PAHs having more than 3 rings were favored at higher temperature. Dong et al. (2013) studied the emission of 16 PAHs during coal pyrolysis using a CDS-5250 pyroprobe. The release behavior of the PAHs was found to

depend on the temperature and heating rate during pyrolysis. Emsbo-Mattingly and Stout (2011) analyzed PAHs which were extracted from different rank coals as per the EPA Method 8270D by GC/MS. It was found that PAHs with 2–3 rings were the dominant species contained in lignite and bituminous coals. Moreover, the concentration of the PAHs increased markedly going from lignite to highly-volatile bituminous coal but decreased going from highly-volatile bituminous coal to anthracite coal. However, there is still limited information on the formation mechanism of PAHs and the relationship between the emission of PAHs and the structure of coal. As is well-known, the structure of coal varies significantly depending on the different ranks of coal. It is highly likely that the differences in the structure of coal lead to different pathways for formation of PAHs. As an important technique that can get direct information of carbon atoms in coal structure, CP/MAS <sup>13</sup>C NMR spectroscopy has been applied in the studies of coal structure by some researchers (Solum et al., 1989; Liu and Peng, 2008; Liu et al., 2015; Wang et al., 2015b).

In this study, a series of coals of different ranks were subjected to pyrolysis at different temperatures to study the corresponding PAHs emissions. An analytical pyrolyzer, which is directly coupled with the inlet of a gas chromatograph (GC) and a mass

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