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Molecular distribution of coal pyrolysis products of bituminous and anthracite from Huainan coalfield by vacuum pyrolysis furnace coupled with mass spectrometer under different electron ionization energies

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Abstract: Bituminous, anthracite and natural coke from Huainan coalfield were investigated by a vacuum pyrolysis furnace coupled with mass spectrometer (MS) directly under different electron ionization (EI) energies. Through total intensity of ions (TII), total number of ion species (TNI), number average molecular weight ($\overline{M}_n$), and weight average molecular weight ($\overline{M}_w$) of the three coals pyrolysis products, it can be obtained that TNI, $\overline{M}_n$ and $\overline{M}_w$ of bituminous pyrolysis products are similar to those of anthracite pyrolysis products, which indicates that the molecular distribution of the bituminous pyrolysis products is similar to anthracite pyrolysis products, but is much different to natural coke pyrolysis products. Through the ratios of specific mass fragment ions of $C_7H_7^+/C_6H_6^{\cdot+}$ and $C_4H_9^+/C_6H_6^{\cdot+}$ in the three coals pyrolysis products, it can be obtained that the ratios of $C_7H_7^+/C_6H_6^{\cdot+}$ in the three coals pyrolysis products are similar, but that of $C_4H_9^+/C_6H_6^{\cdot+}$ in natural coke pyrolysis products is more than the ratio of $C_4H_9^+/C_6H_6^{\cdot+}$ in the pyrolysis products of bituminous and anthracite, which indicates that the relative content of alkylbenzene to benzene in the three coals pyrolysis products is similar, and that the relative content of aliphatic compounds to benzene in natural coke pyrolysis products is more than that in bituminous and in anthracite. And through all MS data, the proper range of EI energy for coal pyrolysis is from 65 eV to 75 eV. The vacuum pyrolysis furnace coupled with mass spectrometer fleetly can be useful to the quick investigation of molecular distribution characteristics of coal pyrolysis products for coal non-fuel utilization.

Key words: online vacuum pyrolysis; molecular characteristics; coal pyrolysis

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尹浩,刘桂建,钮志远,等. 利用真空热解炉—质谱联用仪研究不同电子电离能量下淮南烟煤和无烟煤热解产物的分子组成分布特征[J]. 中国科学技术大学学报,2019,49(4):311-320.

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利用真空热解炉—质谱联用仪研究不同电子电离能量下淮南烟煤和无烟煤热解产物的分子组成分布特征

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摘要：采用真空热解炉—质谱联用仪研究了不同电子轰击能量下，来自淮南煤田的烟煤、无烟煤和天然焦的热解产物的分子组成分布特征. 结果表明，烟煤热解产物的离子种类数量（TNI）、数均分子量（$\overline{M}_n$）和重均分子量（$\overline{M}_w$）与无烟煤热解产物相似，与天然焦热解产物有很大不同，但是烟煤热解产物的总离子量（TII）多于无烟煤热解产物，这表明烟煤热解产物的分子组成分布与无烟煤热解产物是相似的，与天然焦热解产物有很大不同；在三种煤热解产物中，通过对代表烷基苯的特征碎片离子 $C_7H_7^+$ 的量与代表苯的分子离子 $C_6H_6^{\cdot +}$ 的量的比值 $C_7H_7^+/C_6H_6^{\cdot +}$，以及代表脂肪烃的特征碎片离子 $C_4H_9^+$ 的量与 $C_6H_6^{\cdot +}$ 的量的比值 $C_4H_9^+/C_6H_6^{\cdot +}$ 进行分析，得到三种煤热解产物中的 $C_7H_7^+/C_6H_6^{\cdot +}$ 的值比较接近，但是天然焦的 $C_4H_9^+/C_6H_6^{\cdot +}$ 值却大于无烟煤和天然焦，这表明三种煤热解产物中的烷基苯相对于苯的含量相似，但是天然焦热解产物中脂肪烃相对于苯的含量却比烟煤和无烟煤的相应含量高. 通过对不同电子电离能量下获得的三种煤热解产物质谱数据进行分析，得到适宜的电子电离能量范围是 65～75 eV. 研究显示，利用真空热解炉—质谱联用仪可以快速获得煤热解产物的分子组成分布信息，为煤的非燃料用途提供指导.

关键词：在线真空热解；分子特征；煤热解

0 Introduction

Pyrolysis is an attractive coal conversion technology to efficiently and economically produce clean coal[1-3]. Coal tar, a complex mixture and a product of coal pyrolysis, is abundant in olefins, polycyclic aromatic hydrocarbons (PAHs), phenols and heterocyclic compounds[4-7]. Thus, the characteristics of molecular distribution of coal pyrolysis products would be helpful with understanding the molecular distribution of coal for the further non-fuel utilization of coal[8-10]. Especially, it is important for more efficient utilization of Chinese lignite, because lignite is estimated to account for the most amount of Chinese coal reserves[11-15].

Gel permeation chromatography (GPC) and mass spectrometry (MS) have been known as the main technologies in the analysis of the molecular weight distribution. However, due to the incapability of GPC in both analyzing coal pyrolysis products online and capturing signals of small molecules, it is not appropriate to be applied in coal pyrolysis products which are mainly composed of small molecules[16-18]. Gas chromatography-mass spectrometry (GC-MS) has been used widely to analyze coal tar, but it is hard to detect the fractions of high-boiling points in coal pyrolysis products, due to the limit of inlet temperature[19-22]. And GC-MS is also unsuited for monitoring the molecular distribution of the process of coal pyrolysis in real time, because GC requires a long separating time to identify the chemicals of coal pyrolysis products.

However, although electron ionization (EI) is a hard ionization method to produce fragment ions for MS, the hydrocarbons, such as paraffin, olefins, aromatics and etc., are easier to be ionized by EI than other "soft" ionization methods, such as filed ionization (FI)[23-24], electrospray ionization (ESI)[25-26], and atmospheric pressure chemical ionization (APCI)[27-28]. Thus, EI can induce almost every ion of coal pyrolysis products and provide the whole information of molecular composition of coal pyrolysis products. Furthermore, to interpret the molecular distribution of coal pyrolysis products, a proper EI energy should be investigated, because all ions of coal pyrolysis products induced by EI, including the molecular ions, fragment ions and isotopic ions, would influence the analysis results of molecular distribution characteristics of coal.

Here, we utilized a vacuum pyrolysis furnace coupled with mass spectrometer (VPF-MS) and EI source to investigate the molecular distribution of coal pyrolysis products under different EI energies in real time. All coal samples are from Huainan coal field as well as bituminous, anthracite and natural coke. The aims of this study are to qualitatively interpret the molecular distribution of coal pyrolysis products, and to anchor the appropriate EI energy to investigate the molecular distribution for the further non-fuel utilization of coal.

1 Experiment and data

1.1 Coal analysis

Bituminous, anthracite and natural coke with gradual rank advance, from the Huainan coal field, Anhui province, China, were used. Raw coal samples were dried and crushed to the particle size more than 100 mesh. The proximate analysis and ultimate analysis of these coal samples were carried out according to GB/T 212-2008[29] and GB/T 476-2008[30] and were shown in Tab. 1.

Tab. 1 Proximate and ultimate analysis of studied coals

	Ultimate analysis(mass fraction)/%					Proximate analysis(mass fraction)/%			
	C_{daf}	H_{daf}	N_{daf}	S_{daf}	O_{daf}	M_{ad}	V_{ad}	A_{ad}	$F\text{-}C_{ad}$
Bituminous	82.21	6.19	1.21	0.48	9.91	1.26	24.64	14.51	59.59
Anthracite	88.11	4.01	1.33	0.56	5.99	2.31	11.78	13.14	72.77
Natural Coke	92.86	1.31	1.07	0.23	4.53	5.73	4.75	6.94	82.58

[Note] daf: dry ash free; ad: air dry.

1.2 Apparatus and procedures

Coal vacuum pyrolysis was performed by using a time of flight-mass spectrometer (TOF-MS) coupled with a vacuum pyrolysis furnace (VPF) (Fig. 1) under a pressure on 5.7×10^{-3} Pa. The whole system of VPF-TOF-MS was manufactured by Micromass Company, U. K. A heating cavity and thermocouple assembly were located in the end of the furnace and a quartz sample tube was located into the heating cavity with a thin strip of tungsten foil holding the sample tube firmly in position. The heating cavity closing to the ionization source of MS ensured the volatiles from the samples directly and fleetly entering the ionization source in real time and in vacuum. And the temperature control precision of VPF for heating samples with ±1℃ was a default by Micromass company[31].

Each of the 0.5 mg coal samples covered with quartz fiber was held in VPF. Coals were pyrolyzed at the same heating rate under different EI energies from 5 eV to 100 eV at an interval of 5 eV. The

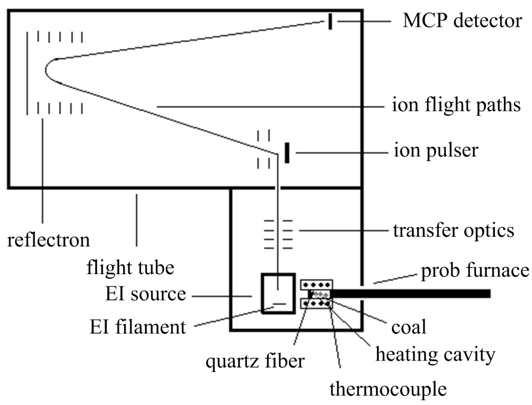


Fig. 1 The vacuum pyrolysis furnace coupled with TOF-MS

initial temperature of heating rate was set at 30 ℃ and held for 2 min, and then a rate ramp of 150 ℃/min was used until the temperature reached 600 ℃ (holding for 5 min). The ion source temperature was set at 250 ℃ to prevent the condensation of coal tar volatile fractions. The trap current was set at 100 μA, which was necessary to maintain a constant ionizing current[32].

1.3 Mass calibration and data conversion

The TOF-MS (GCT, Micromass Company,

U. K.) was tuned and calibrated by using heptacosafluorotributylamine (Sigma-Aldrich, USA), for mass resolution of 8000 (FWHM) and a mass accuracy below 3×10^{-6} [33]. A single point lock mass at m/z 128.0626 u (napthaline $C_{10}H_8$, a coal pyrolysis product compound) was applied as internal reference to compensate the instrument drift. The mass range was set between m/z 50 u and m/z 800 u, to avoid detector saturation by high abundance chemical species below m/z 50 u. Mass peaks were selected above 20:1 (S/N). OpenLynx software within MassLynx (Micromass Company, U. K.) was used for data acquisition and analysis. The mass spectrometric data were generated and recorded every second.

Although the profile of total ion chromatogram (TIC) (Fig. 2) presents a bimodal distribution representing the consecutive evolution of thermally extractable "bitumen" components and "bulk pyrolysis" components[23], respectively, both humps as the molecular distribution of one analyte are interpreted in the whole vacuum pyrolysis.

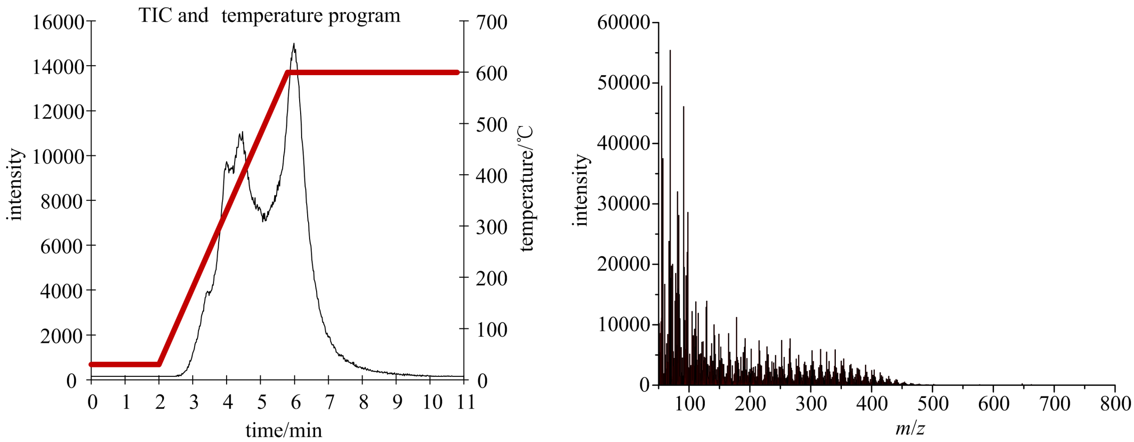


Fig. 2 The bituminous diagram of the total ion chromatogram (TIC) with the profile of setting temperature program (left) and mass spectrogram (right) at 70eV EI energy

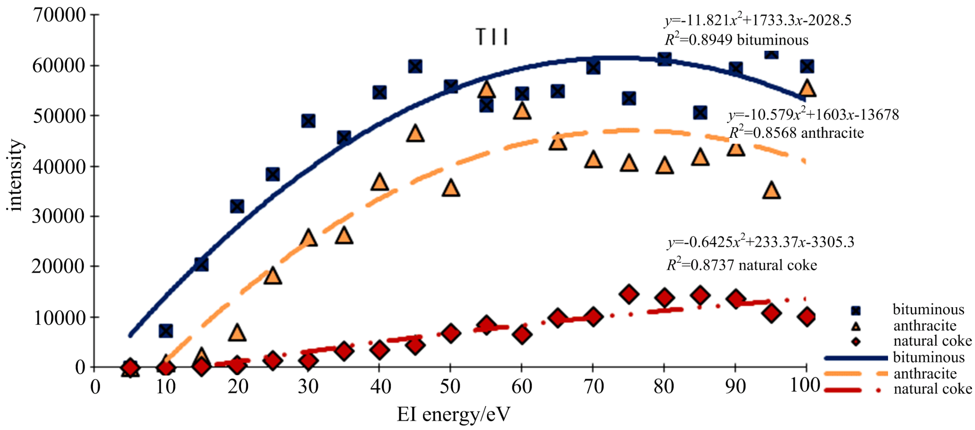


Fig. 3 TII of three coals pyrolysis productsunder different EI energies

3 Results and discussion

2.1 Molecular distribution

2.1.1 Total intensityof ions (TII) at different EI energies

The binomial fitting curves of bituminous and anthracite (Fig. 3) show that the strongest total intensity of ions (TII) of the three coals appear at about 70 eV EI energy, while TII of natural coke pyrolysis products increase continuously with the EI energy within the range of 10~100 eV. And the empirical equations of the binomial fitting curves of TII also are fitted and shown in Fig. 3. The TIIs objectify the quantity of all ions of coal pyrolysis products induced by EI energy, which include molecular ions, fragment ions and isotopic ions. In

Fig. 3, the TIIs of the pyrolysis products of bituminous and anthracite have a relatively stable intensity under the EI energy from 45 eV to 100 eV.

2.1.2 Total number of ion species(TNI) at different EI energies

The total number of ion species (TNI) is the summation of the number of all ion species, which depend on the resolving power of MS. The empirical equations of the binomial fitting curves of TNI for the three coals pyrolysis products are also fitted in Fig. 4. The binomial fitting curves of the bituminous and anthracite (Fig. 4) show that both the pyrolysis products of bituminous and anthracite have a similar TIN under EI energies from 25 eV to 95 eV, which indicates that bituminous and anthracite have similar ion species of pyrolysis products as well as similar molecular distribution of pyrolysis products, for the reason that TNI has a strong relationship with molecular composition. Furthermore, TNI of natural coke pyrolysis products is quite different from both TNIs of bituminous and anthracite just as the molecular distribution of natural coke pyrolysis products is quite different from the molecular distribution of the pyrolysis products of bituminous and anthracite.

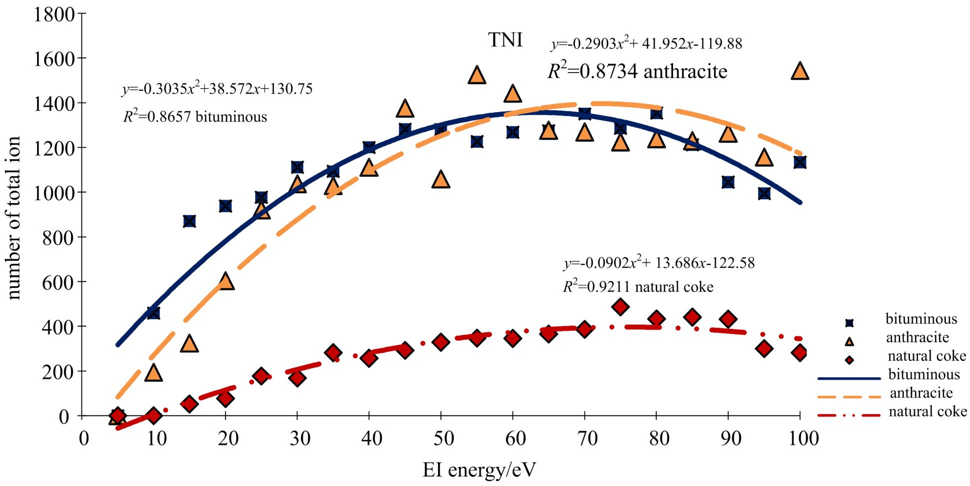


Fig. 4 TNI of three coals pyrolysis products under different EI energies

2.1.3 Number average molecular weight ($\overline{M}_n$) at different EI energies

The number average molecular weight ($\overline{M}_n$) has already been discussed by Lansing and Kraemer[34-35]. Furthermore, $\overline{M}_n$ can interpret the average of the molecular masses of the individual molecules for mixture and can be defined by

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i},$$

where N_i is the number of molecules of molecular mass M_i.

In Fig. 5, the number average molecular weight ($\overline{M}_n$) of pyrolysis products of bituminous and anthracite are greater than m/z 200 u under low EI energies from 10 eV to 20 eV, and then maintain about m/z 170 u under EI energies from 65 eV to 75 eV. Both the $\overline{M}_n$ of the pyrolysis products of bituminous and anthracite have similar value under the same EI energies, which indicates that the pyrolysis products of bituminous and anthracite have a similar molecular distribution. The $\overline{M}_n$ of natural coke pyrolysis products is kept at m/z 95 u under EI energies from 15 eV to 100 eV.

2.1.4 Weight average molecular weight ($\overline{M}_w$) at different EI energies

Lansing and Kraemer[34-35] also have discussed weight average molecular weight ($\overline{M}_w$) which was amenable to physical measurement. Some properties of mixture are dependent on molecular size, therefore a larger molecule might have a larger contribution than a smaller molecule, which would need $\overline{M}_w$ to differ from $\overline{M}_n$. $\overline{M}_w$ is

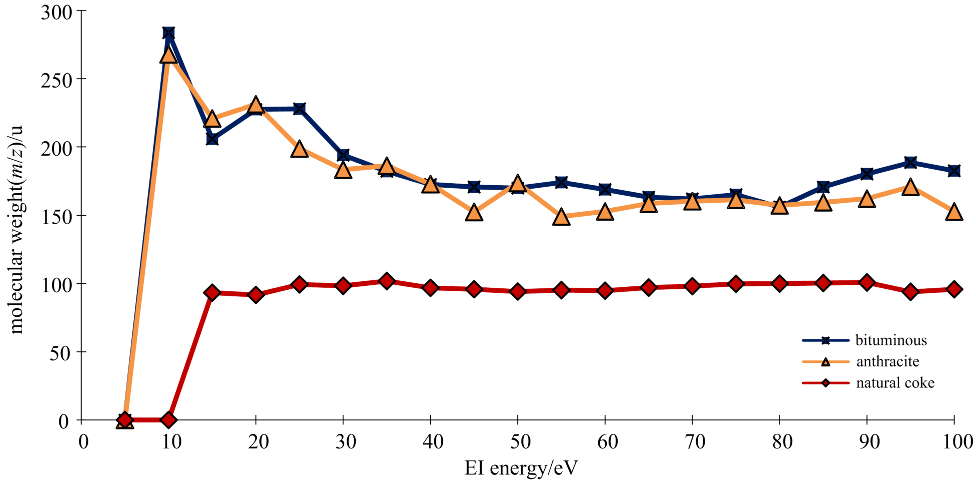


Fig. 5 $\overline{M}_n$ **under different EI energies**

defined by

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i},$$

where N_i is the number of molecules of molecular mass M_i.

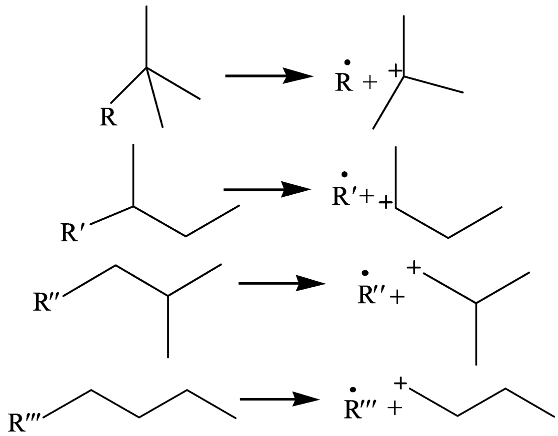
In Fig. 6, both the average molecular weight ($\overline{M}_w$) of the pyrolysis products of bituminous and anthracite also have similar values under the same EI energies, and maintain about m/z 235 u under EI energies from 65 eV to 75 eV. The $\overline{M}_w$ of natural coke pyrolysis products is kept at m/z 115 u under EI energies from 15 eV to 100 eV and is lower than both the $\overline{M}_w$ of the pyrolysis products of both bituminous and anthracite.

According to the above results, the bituminous and anthracite from Huainan coalfield have a similar molecular distribution of pyrolysis products, as observed by TNI, $\overline{M}_n$ and $\overline{M}_w$ under different EI energies. However, the quantity of bituminous pyrolysis products is greater than that of anthracite pyrolysis products observed from TII under different EI energies. And the molecular distribution of natural coke pyrolysis products is much different from that of bituminous and anthracite. Through TII, TNI, $\overline{M}_n$ and $\overline{M}_w$, the proper EI energy for molecular distribution of coal pyrolysis products are from 65 eV to 75 eV, including 70 eV as a traditional and frequently-used EI energy.

The fact is that the EI energy of approximately 10 eV could be enough to ionize most organic molecules, and the excess energy over 10 eV can lead to extensive fragmentation, and higher EI energy would induce more fragment ions and smaller fragment ions[36], thus resulting in $\overline{M}_n$ and $\overline{M}_w$ under 10 eV EI energy being higher than those under EI energies from 65 eV to 75 eV, and TII and TNI under 10 eV being lower than those under EI energies from 65 eV to 75 eV.

2.2 Group analysis of aliphatic and aromatic compounds

Aliphatic and aromatic compounds are important components from coal pyrolysis. Furthermore, according to Stevenson's rule, the most aliphatic compounds can easily induce a specific fragment ion of $C_4H_9^+$ with m/z 57.0704 u under EI energy, accompanied by corresponding lower ionization energy neutral radical compared to other parts of long carbon chains in EI[36]:



The aromatic compounds with branched chain, such as alkylbenzene, can easily induce a

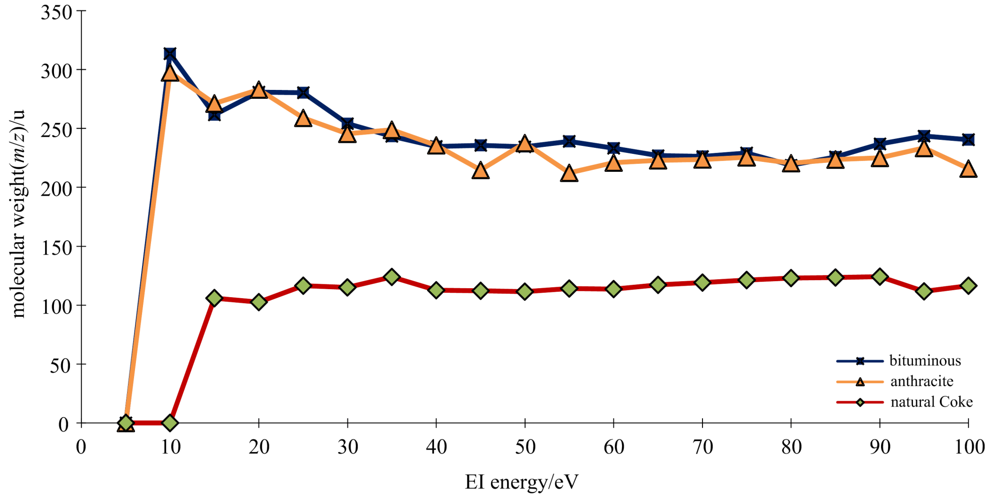
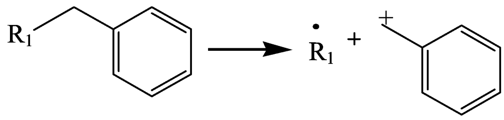


Fig. 6　$\overline{M}_w$ under different EI energies

specific fragment ion of $C_7H_7^+$ with m/z 91.0548 u[36]:



Benzene is a stable aromatic compound and always induces a characteristic molecular ion of $C_6H_6^{\cdot +}$ with m/z 78.0470 u[36].

In Fig. 7, the specific fragment ions of $C_4H_9^+$ and $C_7H_7^+$ are not observed below 10 eV EI energy, thus, the intensity of $C_4H_9^+$, $C_7H_7^+$ and $C_6H_6^{\cdot +}$ are recorded under 15 eV in Fig. 7.

Vacuum pyrolysis can provide an ideal condition, in which organic material can decrease its boiling point and fleetly break away from the macromolecule to avoid adverse secondary chemical reactions[23]. Although the content of benzene is different in the pyrolysis products of the three coals, as a stable aromatic compound in coal pyrolysis products under EI, benzene can be an internal reference to interpret the relative content of fragment ions of $C_4H_9^+$ and $C_7H_7^+$.

In Fig. 8, all ratios of $C_7H_7^+/C_6H_6^{\cdot +}$ in three coals pyrolysis products have a similar value maintaining a relative stable value of 3 from 35 eV to 70 eV EI energy. However, the ratio of $C_4H_9^+/C_6H_6^{\cdot +}$ in natural coke pyrolysis products is greater than those of $C_4H_9^+/C_6H_6^{\cdot +}$ in the pyrolysis products of bituminous and anthracite under different EI energies. The fact is that the pyrolysis products of natural coke are composed of small molecular compounds which are adsorbed in coal macromolecular networks, not decomposed from coal macromolecular networks, as is the case of the pyrolysis products of bituminous and anthracite. Therefore, although the content of aliphatic compounds in natural coke pyrolysis products is lower than that in bituminous and in anthracite (Fig. 7), the ratio of $C_4H_9^+/C_6H_6^{\cdot +}$ in natural coke pyrolysis products is higher than that in pyrolysis products of bituminous and in anthracite (Fig. 8), which indicates that the relative content of aliphatic compounds to benzene in natural coke pyrolysis products is higher than that in bituminous pyrolysis products and in anthracite pyrolysis products. The relative contents of alkylbenzenes to benzene in the products from the pyrolysis of the three coals are similar to each other.

3　Conclusion

The non-fuel utilization of coal depends on the investigation of molecular distribution characteristics of coal. A vacuum pyrolysis furnace coupled with mass spectrometer directly was used to investigate the molecular distribution of coal pyrolysis products of bituminous, anthracite and natural coke from Huainan coalfield, and the conclusions are:

(Ⅰ) Through TNI, $\overline{M}_n$ and $\overline{M}_w$ of coal pyrolysis products of bituminous, anthracite and

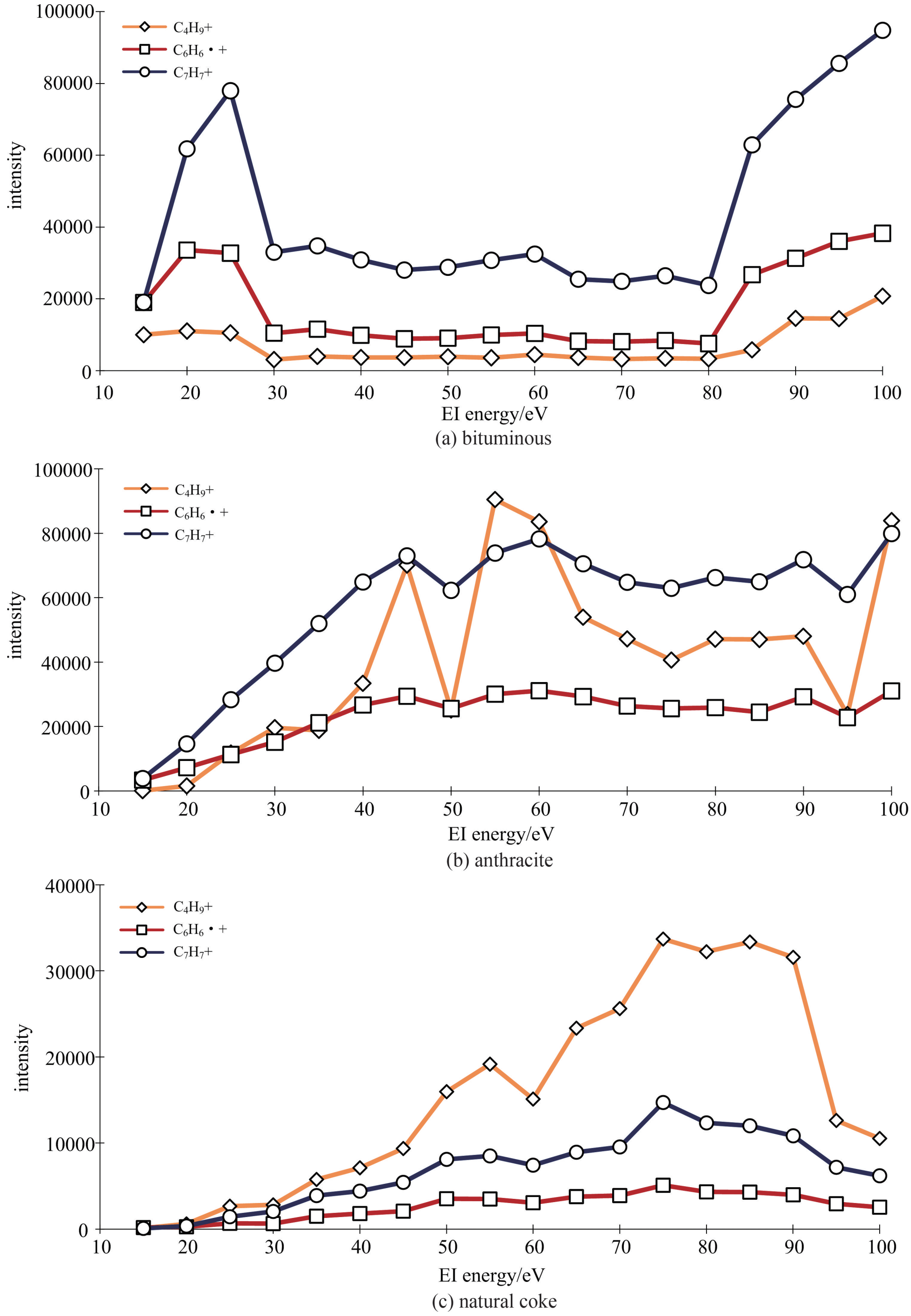


Fig. 7 The intensity of $C_4H_9^+$, $C_7H_7^+$ and $C_6H_6^{\cdot +}$ of the pyrolysis products of bituminous(a), anthracite(b) and natural coke(c) under different EI energies

natural coke from Huainan coalfield, it can be concluded that both bituminous and anthracite have a similar molecular distribution of pyrolysis products and are much different from natural coke. Through TII of the three coal pyrolysis products, it can be confirmed that the quantity of bituminous pyrolysis products is greater than the quantity of pyrolysis products of anthracite and natural coke.

(Ⅱ) Through the ratios of $C_7H_7^+/C_6H_6^{\cdot +}$ and $C_4H_9^+/C_6H_6^{\cdot +}$ in the three coal pyrolysis products, it is indicated that the relative content of alkylbenzene to benzene in the three coal pyrolysis products are similar, and the relative content of aliphatic compounds to benzene in natural coke

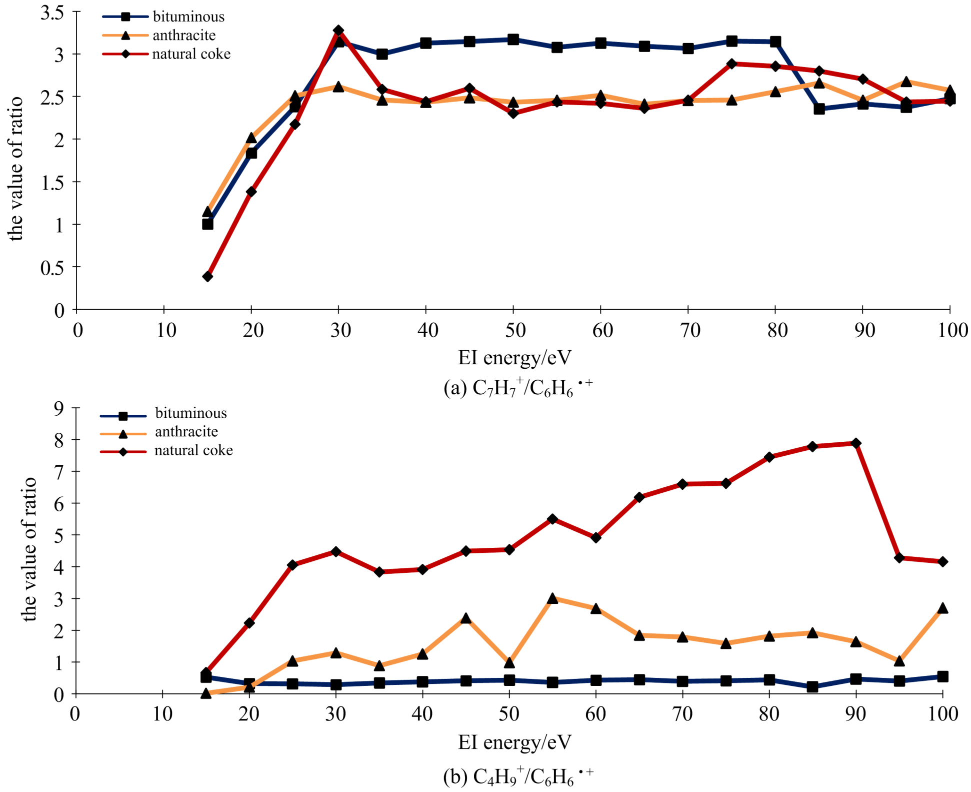


Fig. 8　The ratio of $C_7H_7^+/C_6H_6^{\cdot+}$ (a) and $C_4H_9^+/C_6H_6^{\cdot+}$ (b) of the three coals under the different EI energies

pyrolysis products is more than that in pyrolysis products of bituminous and anthracite.

(Ⅲ) To investigate molecular distribution of coal pyrolysis products, the proper range of EI energy is from 65 eV to 75 eV, including 70 eV as a traditional and frequently-used EI energy.

Furthermore, the vacuum pyrolysis furnace coupled with mass spectrometer could realize online coal pyrolysis under the ideal condition to observe the coal pyrolysis process in real time for the investigation of molecular characteristics of coal pyrolysis products.

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