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INVESTIGATION OF PYROLYSIS OF CHINESE COALS USING THERMAL ANALYSIS/MASS SPECTROMETRY

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Abstract

TA/MS (thermal analysis coupled with mass spectrometry) was applied to the pyrolysis of Chinese coals with different ranks. A total of 13 Chinese coals were investigated. The samples were deliberately chosen to represent the 13 types of Chinese coals according to the Chinese Coal Classification System. The experiments were carried out in an argon atmosphere with a flow rate of 150 mL min^{-1}. The samples were heated from 40 up to 1200°C with a constant heating rate of 10 K min^{-1}. The main evolved pyrolysis products were identified through the on-line recorded mass spectra. The thermal and evolution behavior was compared between the coals. The results showed a strong thermal and evaluation behavior dependence on the coal rank. Different aliphatic fragments and also some aromatic substances, which are of environmental concern (BTX, PAHs), were found to be released depending on the different types of coal.

Keywords: coal characterization, pyrolysis, thermal analysis/mass spectrometry

Introduction

China is the number one country worldwide producing and consuming coals. Besides being combusted as an energy resource, coal is also utilized as raw materials in coal conversion chemical engineering processes, e.g. coal hydrogenation, gasification, etc. Pyrolysis is an important step in all these thermal conversion processes.

Pyrolysis studies can be performed in various devices, such as the pyroprobe, the Curie-point reactor, fixed bed reactor, thermal analysis, etc. Combining these devices with different analytic techniques, e.g. mass spectrometry (MS), Fourier transform infrared spectrometry (FTIR) and gas chromatography (GC) or gas chromatog-

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raphy-mass spectrometry (GC-MS) etc., the volatile pyrolysis products can be investigated simultaneously or afterwards [1–9]. Friebel and Köpsel studied nitrogen release of the pyrolysis of a series of lignite from the main German mining districts. The pyrolysis experiments were carried out in a fixed bed annular reactor with a temperature range 673 to 1173 K and the pyrolysis gases were determinated by gas chromatography and NDIR gas analyser [5]. Bonfanti *et al.* investigated some coals with very different geographic origins by pyroprobe pyrolysis technique. The pyroprobe was coupled to a gas chromatograph and the products were detected using different systems: mass spectrometry (MS), nitrogen and phosphorus selective detector (NPD) or flame ionisation detector (FID). Different aliphatic hydrocarbons, monocyclic aromatic hydrocarbons, phenolics and polycyclic aromatic hydrocarbons (PAHs) evaluated at different pyrolysis temperatures (250, 400, 550, 700, 850, 1000°C) were identified and compared between different coals [9].

Thermal analysis (TA) is one of the most common techniques employed to study the pyrolysis behavior of coals [10–12]. Kök *et al.* investigated effect of particle size on coal pyrolysis through thermogravimetry [11] and Iordanidis *et al.* studied seven lignite samples from Amynteon lignite deposit, northern Greece by TG/DTG [12].

Simultaneous TA/MS is a coupled technique between thermal analysis and on-line mass spectrometry. The main advantage of this combination is that it permits the mass spectra to be recorded on-line, enabling the on-line monitoring of nearly all kinds of volatiles, especially the environmentally interesting ones (BTX, PAHs). Since it emerged in the 1980s, TA/MS has been employed to study and characterize the combustion and pyrolysis of coals by many authors [13–16]. TA/MS was applied for the first time in 1984 to analyze coal samples by Ohrbach *et al.* [16]. In that work, one anthracite was analyzed. The possibility to estimate the ash content, the volatile matter and moisture content in one experiment by using TA/MS was investigated and the volatile products released in different atmospheres were studied through the on-line recorded mass spectra. In 1999 five German coals were extensively investigated using TA/MS by Matuschek *et al.* [13]. They found different aliphatic and aromatic volatiles, which are of environmental interest, being released during the heating. Arenillas *et al.* analyzed four coals with different volatile matter using TA/MS [15]. The different compounds, which evolved during the pyrolysis process, were followed and correlated with the volatile matter content of the parent coals. The nitric oxide released during pyrolysis together with its precursor species were also analyzed in their experiments.

In this work, TA/MS was applied to investigate 13 Chinese coal samples which were specially selected to represent the 13 coal types of the Chinese Coal Classification System. The aim of this study was to obtain an overall knowledge of the thermal behavior and emission characteristics of Chinese coals. This would be of interest and use for the Chinese coal industry and for the related environmental considerations.

Experimental

The coal samples were air dried and ground into fine powder and then passed through a 200-mesh screen. The powder was then stored in an airtight container.

Table 1 presents the proximate analysis of the 13 coal samples used in this study. The coal rank decreases as the sample code increases, beginning with sample 1 (anthracite) to sample 13 (lignite).

Table 1 Results of proximate analyses and total value of sulphur of 13 Chinese coals

Sample	Type	Name of mine	V_{da3f}/%	A_d/%	M_{ad}/%	$St3_d$/%
1	Anthracite	Jincheng	5.52	5.71	1.94	0.29
2	Meager coal	Changcun	14.68	10.24	0.94	0.28
3	Meager lean coal	Sanxipubai	12.88[a]	19.10[c]	0.88	1.42[d]
4	Lean coal	Shigejie	17.08	12.06	0.85	0.26
5	Primary coking coal	Shanxishetou	20.63	8.10	0.74	0.40
6	Fat coal	Shanxihuozhou	30.33	10.42	0.88	2.87
7	1/3 primary coking coal	Huozhousanjaohe	34.05	9.05	1.24	0.65
8	Gas-fat coal	Xinwen	43.10[b]	3.89	2.29	2.73
9	Gas coal	Yanzhou	46.23	14.60	1.92	4.00
10	Weakly caking coal	Datong	26.82[a]	15.64[c]	2.10	0.28[d]
11	Non-caking coal	Shenfu	36.84	7.02	10.56	0.42
12	Long flame coal	Yima	41.13	21.31	8.04	2.61
13	Lignite	Huolinhe	48.42	25.56	17.38	0.536

daf: dry ash-free basis, ad: air dried basis, d: dry basis; V_{daf}: volatile matter in dry ash-free basis, A_d: ash in dry basis, St_d: total sulphur in dry basis; [a]V_{ad}: volatile matter in air dried basis, [b]V_d: volatile matter in dry basis, [c]A_{ad}: ash in air dried basis, [d]St_{ad}: total sulphur in air dried basis

The experiments were carried out using a STA 429 simultaneous thermal analyzer (Netzsch) coupled with a QMS 420 quadrupole mass spectrometer (Balzers). Samples of about 100 mg were placed in a ceramic sample holder, heated from 40 up to 1200°C at a constant rate of 10 K min^{-1} in an argon atmosphere with a constant flow rate of 150 mL min^{-1}. The on-line registered mass spectra in the range of m/z 10 to 200 were taken every 30 K.

Results and discussion

Thermal behavior

The DTG curves of the 13 studied coal samples are shown in Fig. 1a. The DTG peaks around 100 and in the range of 300–900°C correspond to the evaporation of the physically bound water and to the actual pyrolysis of the samples, respectively. In general, more physically bound water was released from the low rank coals (sample 1 – anthracite – released a very small amount of water. The apparent big peak around 100°C for sample 1 is due to the relativation of the scale employed to plot the DTG curves). Pyrolysis occurs, for all the studied coals, in the temperature range of 300 to 900°C, in a two-step pattern. The first step is comprehended in the temperature range of 300–600°C, which corresponds to the primary pyrolysis step. The main mass loss occurs in this step. The second step takes place around the temperature range of 600–900°C. The mass loss of this step is rather small compared to that of the first step. The pyrolysis peaks of the second step for some coals such as primary coking coal, fat coal, 1/3 primary coking coal, gas-fat coal and gas coal are not very appreciable (Fig. 1a samples 5–10) because the relative scales were used for different coals (e.g. the scale of intensity of sample 1 is –0.4 mg min^{-1} while the scale of intensity of sample 8 is –4 mg min^{-1}). Figure 1b is the DTG curve of pyrolysis of the second step for gas-fat coal (sample 8) in small relative scale and the pyrolysis peak of the second step around 700°C is distinguishable. The pyrolysis peak for the highest rank coal, anthracite (sample 1), is rather broad and obviously comprises two peaks, indicating the overlapping of the two pyrolysis steps. The examination of Fig. 1a also reveals that the primary and second pyrolysis peaks shift to higher temperatures as the coal rank increases. This trend reflects that in the lower rank coals more thermal labile

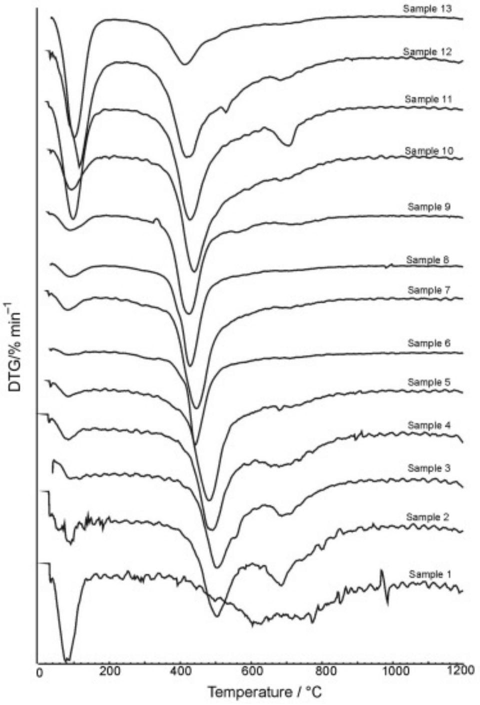

Fig. 1a DTG curves of the 13 Chinese coals by heating sample from 40 to 1200°C at a constant heating rate of 10 K min^{-1} in an Ar atmosphere (* Scales of intensities change for different samples)

groups are present and these groups can be decomposed and release volatile matter at lower temperature. With rank increase, maturation and carbonization reactions in coals remove these thermal labile groups or change them into more stable structure which need higher temperature to decompose, resulting pyrolysis peaks shift to higher temperature.

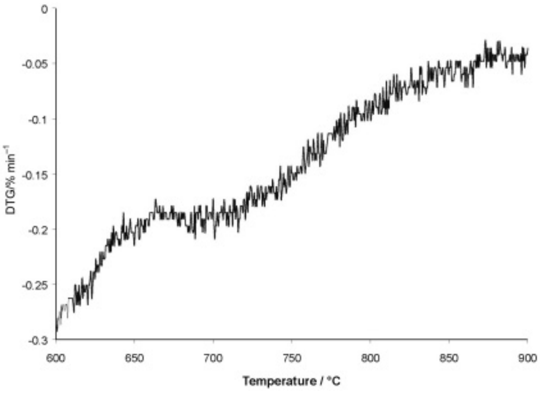

Fig. 1b The DTG curve of pyrolysis of the second step for gas-fat coal (sample 8) in small relative scale

Table 2 Temperatures of maximum mass losing rate and initial thermal decomposition

Sample code	1	2	3	4	5	6	7	8	9	10	11	12	13
DTG_p/°C	600	500	500	490	490	440	440	430	420	440	420	400	400
T_i/°C	440	400	420	400	360	360	380	360	360	330	320	320	320

DTG_p: temperature of maximum mass loss rate
T_i: temperature of initial thermal decomposition

Table 3 Total mass losses of 13 coal samples heated up to 1200°C

Sample code	1	2	3	4	5	6	7
Total mass loss/%	7.2	13.1	12.5	12.9	16.8	26.4	26.5
Sample code	8	9	10	11	12	13	
Total mass loss/%	36.2	40.5	33.6	26.4	35.6	35.8	

From the DTG-curves, two important characteristic parameters, which depend on the sample properties, can be obtained: the temperature of maximum rate of mass loss, DTG_p and the initial thermal decomposition temperature, T_i. As the pyrolysis peaks shift gradually to higher temperatures with coal rank increasing as mentioned above, DTG_p shifts from 400 for lignite to 600°C for anthracite while T_i shifts from 320 to 440°C. The values of DTG_p and T_i for the examined coals are listed in Table 2. The total mass losses of the examined coals are listed in Table 3.

Characterization of the evolution of the volatile products

Figure 2 shows the representative on-line registered mass spectra around DTG_p of the first pyrolysis step for the studied coals. For coals, the labile bridges and chains are progressively removed during the maturation, leading to higher rank coals, which are more stable. So for the low and mid rank coals, from lignite (sample 13) to fat coal (sample 6), many aliphatic and aromatic fragments in the *m/z* ranges of 12–18, 24–39, 42–59, 64–73, 77–86, 90–96, 105–109, 115–122, 128–146 were observed. The relatively high abundance of these fragments reflects an ample presence of the aliphatic chains and bridges among the macro-coal-molecules of the mid and low rank coals. The most fragments

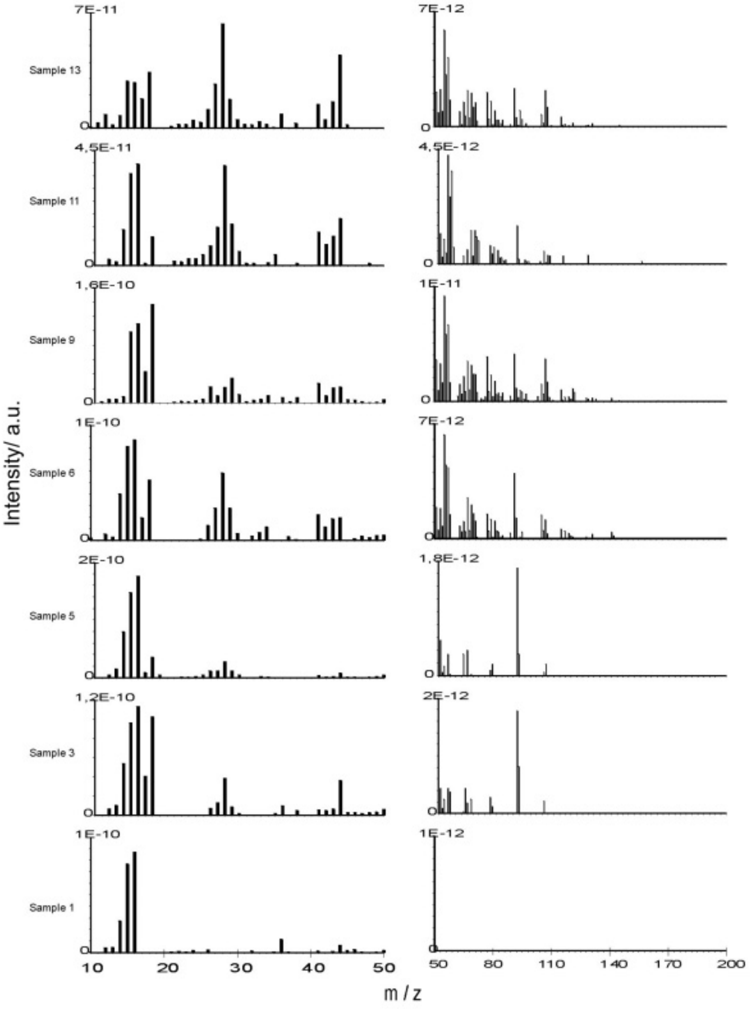

Fig. 2 The representative on-line registered mass spectra of *m/z* 10–200 at DTG_p of the studied Chinese coals

were observed in gas-fat coal (sample 8) and gas coal (sample 9). With increasing coal ranks, from primary coking coal (sample 5) to anthracite (sample 1), the evolved fragments reduced dramatically, indicating the high aromacity of these high rank coals. In the case of anthracite only the masses *m/z* 12–16 could be detected.

Figure 3 illustrates the on-line registered mass spectrum of the second pyrolysis peak of Meager lean coal (sample 3). The main fragments are *m/z* 15 (CH_3^+), 16 (CH_4^+ or O^+), 17 (OH^+), 18 (H_2O^+), 28 (CO^+ or $C_2H_4^+$), 44 (CO_2^+, $C_3H_8^+$ or $C_2H_4O^+$) and nothing could be detected in the higher *m/z* range of 50–200. The fragments 36 and 38 are residue of background subtraction of Ar since Ar has isotopes at *m/z* 36, 38, 40. The oxygen containing fragments, OH^+, H_2O^+, CO^+ and CO_2^+ in this step come probably from the decomposition of O-containing heterocyclic ring clusters and inorganic carbonates. The other coals exhibit a similar behavior for their second pyrolysis peak as Meager lean coal.

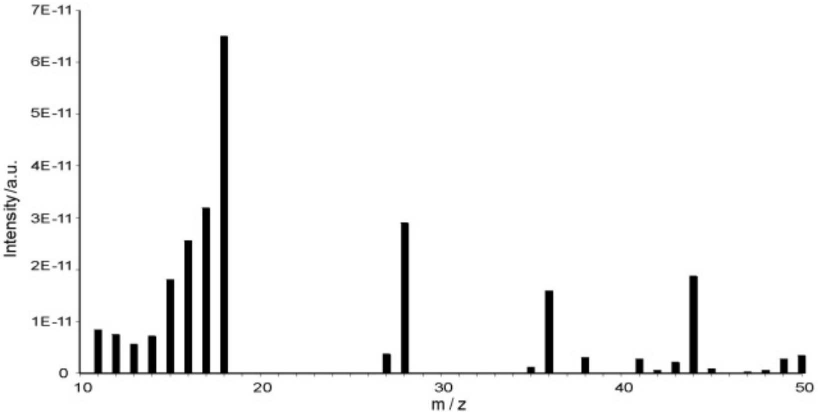

Fig. 3 On-line registered mass spectra of *m/z* 10–50 at temperature of the second pyrolysis peak of meager lean coal (sample 3)

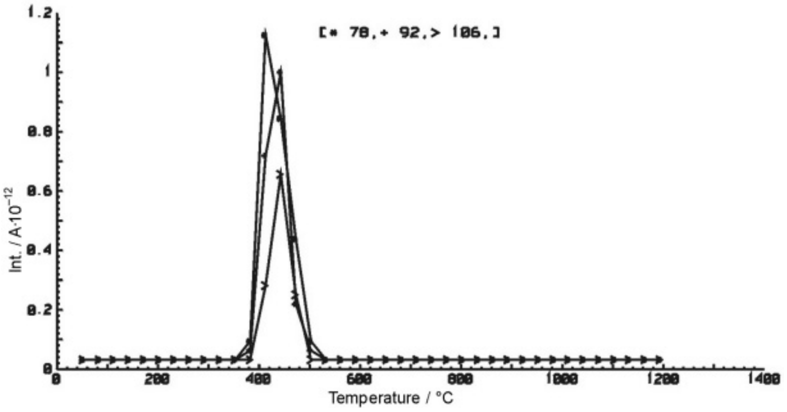

Fig. 4 Temperature dependence of benzene (*m/z* 78), toluene (*m/z* 92), xylene (*m/z* 106) evolved from gas coal (sample 9)

All coals, except anthracite, released benzene (*m/z* 78), toluene (*m/z* 91, 92) and xylenes (*m/z* 105, 106) aromatic fragments during 360 to 560°C in a one-step pattern. Figure 4 shows the temperature dependence of these fragments for gas coal. The emission profiles for the other coals are similar.

In the temperature range of 360–500°C, the fragment *m/z* 128 (naphthalene) was found to be released from the mid rank coals (fat coal, gas-fat coal, gas coal) and the higher PAHs fragments *m/z* 141 ($C_{10}H_7N^+$), 142 (methylnaphthalene), 152 (acenaphthalene) were also detected for gas coal (Fig. 5).

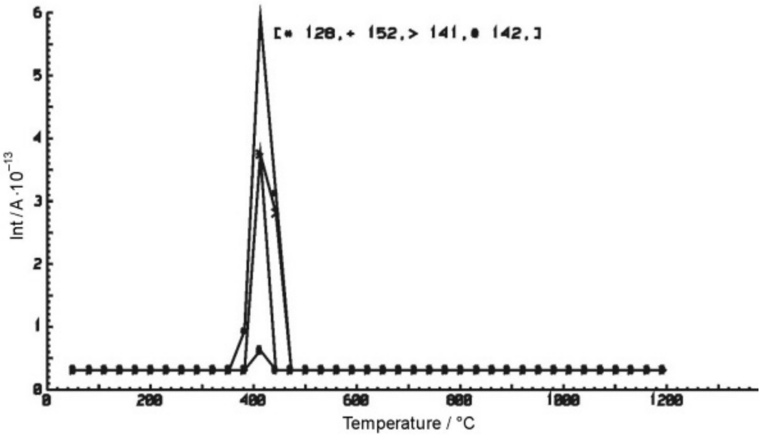

Fig. 5 Temperature dependence of naphthalene (*m/z* 128), acenaphthylene (*m/z* 152), methylnaphthalene (*m/z* 142), $C_{10}H_7N$ (*m/z* 141) of gas coal (sample 9)

Except for methane (*m/z* 15, 16), the evolution profiles of the other aliphatic and aromatic volatiles in different *m/z* ranges are similar to those discussed above, being released at about 360 to 500°C during the first pyrolysis step in a one-step pattern, suggesting that these fragments come from the cleavage of the aliphatic chains and bridges, which can be broken at lower temperatures because of the lower bond energies.

Methane fragments were released in a broader temperature range (360 to 800°C). Figure 6 shows a typical evolution profile for the *m/z* 16.

Figure 7 shows the representative evolution profiles of water from the studied coals. Physically bound water was released around 100°C by all coals. Water, which evolved above 300°C, is produced by decomposition of various oxygen-containing groups, mainly OH-groups, leading to the formation of this pyrolysis water in a rather broad temperature range [15]. Another source of water in this temperature range is the release of the crystal water from the inorganic components. The release temperature of chemically bound or formed water ranges from 300 to 800°C, shifting to lower temperatures as the coal rank decreases. For anthracite, chemically bound or formed water was released at 700–800°C. From meager coal to fat coal water was released at two different temperature ranges: from 300 to 600°C and from 600 to 800°C in a two-step pattern. For the coals with ranks lower than 1/3 primary coking coal, chemically bound or formed water was released only at 400 to 600°C in a single-step pattern. This trend also reflects the presence of more labile compounds or functional groups in the lower rank coals.

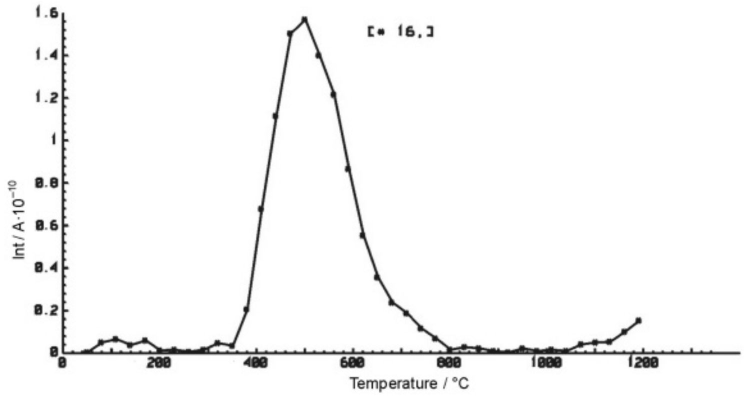

Fig. 6 Temperature dependence of methane (*m/z* 16) of gas coal. All other coals show similar evolution profiles

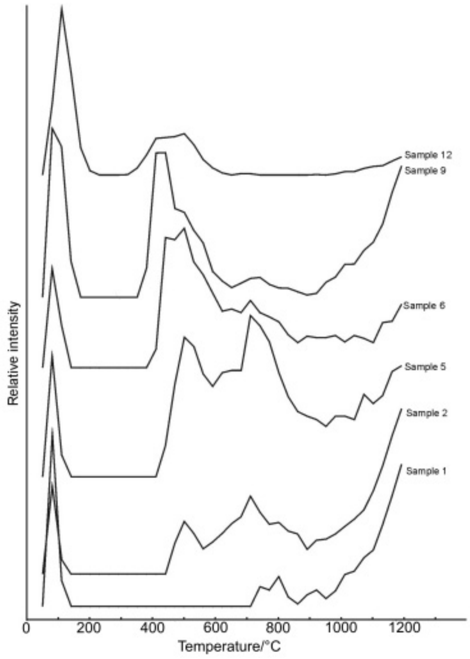

Fig. 7 The representative evolution profiles of H_2O (*m/z* 18) of the studied Chinese coals

Figure 8 is the representative evolution profiles of *m/z* 28 (CO^+ or $C_2H_4^+$) for the studied coals. It can be seen that its emission can be found in rather broad temperature range (except for anthracite and lean coal which only emit *m/z* 28 around 100°C). Mass spectrometry cannot distinguish different ions which have the same *m/z* value.

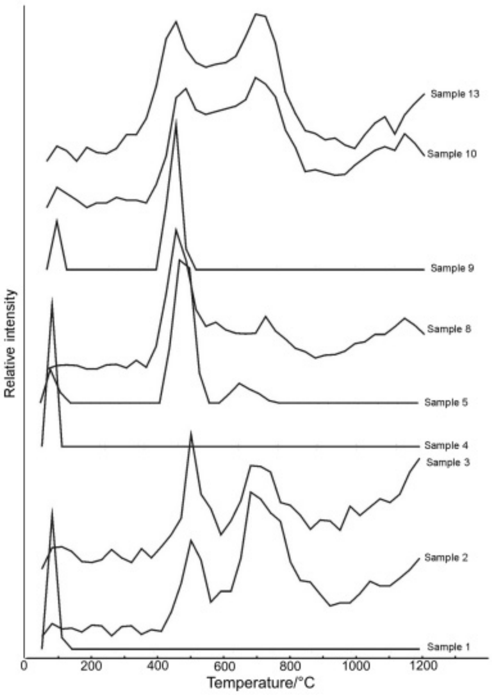

Fig. 8 The representative evolution profiles of *m/z* 28 of the studied coals

Comparing the temperature position and the shape of peaks at 400 to 600°C in Fig. 8 to the evolution profiles of other aliphatic peaks, the similarity between them suggests this peak should be constituted mainly by the aliphatic fragment $C_2H_4^+$. The emission peaks in the other temperature ranges can be considered to come from the CO emission.

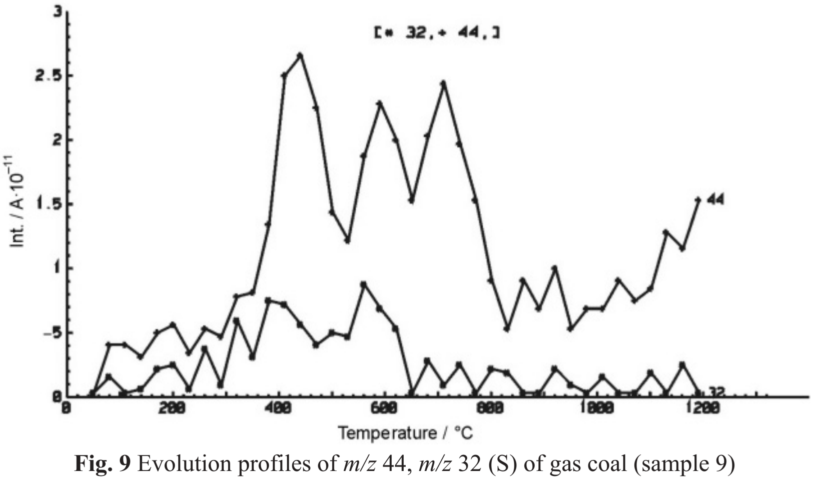

Fig. 9 Evolution profiles of *m/z* 44, *m/z* 32 (S) of gas coal (sample 9)

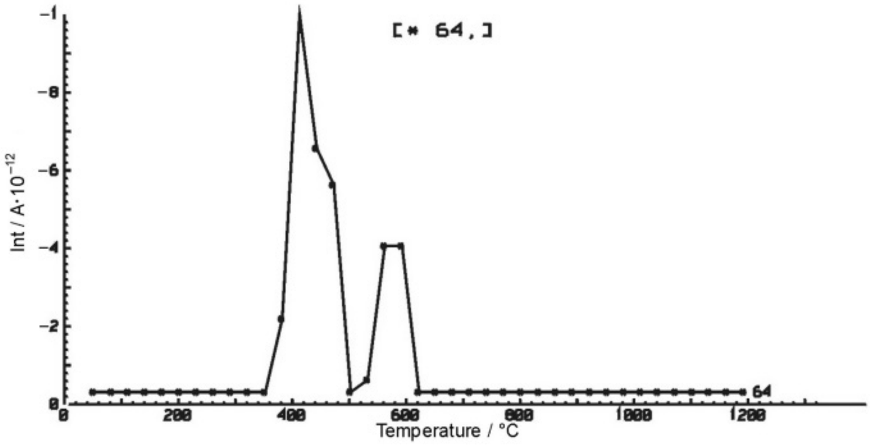

Fig. 10 Evolution profile of *m/z* 64 (SO_2) of gas coal (sample 9)

The emissions of *m/z* 44 (CH_2^+, $C_3H_8^+$ or $C_2H_4O^+$) also cover a broad range of temperature. Figure 9 gives the evolution profile of *m/z* 44 for gas coal. The largest part of CO_2 was produced in the range of 300 to 1000°C due to the decomposition of O-containing organic functionalities and inorganic carbonates. The peak at 350 to 550°C might be a mixture of CO_2^+, $C_3H_8^+$ and $C_2H_4O^+$.

The fragments *m/z* 32, 33, 34 were observed for the high sulphur-containing coals, meager lean coal, fat coal, gas-fat coal, gas coal and long flame coal, in the temperature range of 300 to 650°C. These fragments were identified as S^+ (*m/z* 32), HS^+ (*m/z* 33) and H_2S^+ (*m/z* 34) since these fragments were not found in other low HS^+ (*m/z* 33) and H_2S^+ (*m/z* 34) since there fragments weren't found in other low sulphur-containing coals. SO_2^+ (*m/z* 64) could also be detected at 400–600°C in these coals. Figures 9 and 10 show the temperature dependence of these fragments for gas coal.

Conclusions

The pyrolysis of the studied coals occurs at 300 to 900°C in a two-step pattern. With coal rank increasing, the pyrolysis peaks shift gradually to higher temperatures. DTG_p shifts from 400°C for lignite to 600°C for anthracite, indicating the increasing stability of the basic structure of the coals as the coal ranks increase.

The evolution of volatiles can be broadly divided into three steps: lower than 300°C; from 300 to 600 and from 600 to 900°C. Only physically bound water and a small amount of CO and CO_2 were released by temperatures lower than 300°C. 300–600°C is the temperature range in which primary pyrolysis occurs. In addition to H_2O, CO, CO_2, all the aliphatic and aromatic volatiles were released at this temperature range, indicating the breaking of the aliphatic bridges and chains. Abundant aliphatic and aromatic fragments were evolved from the coals with ranks lower than lean coal, reflecting the abundant presence of the aliphatic bridges and chains in the mid and low coals. The most fragments were found in gas-fat coal and gas coal. In the temperature range of 600 to 900°C (the second pyrolysis step), only H_2O, CO, CO_2 and methane were detected. All aliphatic and aromatic volatiles exhibit a one-step release at 300 to 600°C (for methane 400–800°C). H_2O, CO and CO_2 evolved stepwise due to the decomposition of different compounds or functional groups with different bond energies during nearly the whole heating procedure.

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