

## A TGA-MS INVESTIGATION OF THE EFFECT OF HEATING RATE AND MINERAL MATRIX ON THE PYROLYSIS OF KEROGEN IN OIL SHALE

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**Abstract.** *A demineralized Dachengzi oil shale sample, p-kerogen, is obtained through hydrochloric & hydrofluoric (HCl&HF) treatment. Thermogravimetric analysis combined with on-line mass spectrometry (TGA-MS) tests on original oil shale and p-kerogen were carried out at two heating rates, 5 °C/min and 15 °C/min, to study the effect of heating rate and mineral matrix on the pyrolysis of kerogen in oil shale. In the pyrolysis products, the amounts of both the organic and inorganic gases generated are significant with the evolution of oil in the temperature range of 370–570 °C. Increasing the heating rate from 5 °C/min to 15 °C/min leads to the decrease of most of the small molecule products of interest in this research, which indicates that in the oil shale pyrolysis the secondary cracking reactions may be inhibited by such increase. With increasing heating rate the thermogravimetric (TG) curves shift to a higher temperature region with an increase of about 10 °C due to the temperature difference between the surface and the center of the sample particles. The amount of alkenes generated is higher than that of alkanes and the alkene/alkane ratio increases with heating rate. At the same heating rate, the amounts of both the inorganic and organic compounds generated in the oil shale pyrolysis are higher than those produced in the p-kerogen pyrolysis, suggesting that mineral matrix has an obvious catalytic effect on the pyrolysis of kerogen. Hydrogen release is markedly strengthened in the oil evolution process because of the resultant effect of mineral matter which promotes the cracking reactions in the pyrolysis of kerogen. Compared with oil shale, the TG curves of p-kerogen shift to a lower temperature zone with a decrease of about 10 °C because the pore channels formed in the demineralization treatment intensify the heat and mass transfer in the sample particles.*

**Keywords:** *oil shale pyrolysis, TGA-MS, heating rate, mineral matrix.*

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## 1. Introduction

Oil shale is a natural fine-grained laminated black or brown sedimentary rock with organic matter called kerogen, its ash content is more than 33% [1, 2]. The conventional utilization of oil shale includes combustion and pyrolysis [3]. The combustion of oil shale generates electricity, while pyrolysis produces shale oil. With the decreasing availability of petroleum, pyrolysis of oil shale to get shale oil has become more and more significant. The oil shale resources are rich and widespread all over the world. China has an oil shale reserve of about 719.937 billion tons, which is equivalent to about 47.644 billion tons of shale oil, and this is very advantageous in terms of energy security [4].

To better control the oil shale pyrolysis and get more useful products, it is necessary to study the process even more thoroughly [5]. However, thermal events occurring during the pyrolysis and the product forming principles are not fully understood yet. Thermogravimetric analysis-mass spectrometry (TGA-MS) is a widely-used and simple tool to study the thermal characteristics of oil shale pyrolysis. TGA can provide information about the weight loss of oil shale with temperature, while MS can afford detailed data about the evolved products. The mass spectrometer has been widely applied to analyzing both the inorganic and organic compounds in the pyrolysis products [6–8]. In MS analysis, molecular ion fragments are the most widely used targets. Ojala et al. [9] used the mass spectrometer to study the variation trends of benzene ( $m/z = 78$ ), toluene ( $m/z = 92$ ), *o*-xylene ( $m/z = 106$ ) and 1,3,5-trimethylbenzene ( $m/z = 105$ ). Campbell et al. [10] used this instrument to investigate the release rates of  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and both  $\text{C}_2$  and  $\text{C}_3$  hydrocarbons during the pyrolysis of Colorado oil shale by tracing the molecular ion signals. Lv et al. [11] carried out analytical pyrolysis studies on the main organic products of corn stalk, including alcohols, aldehydes, acids, furans, ketones, phenols, and also other components of the plant, using TGA-MS to investigate their behavior during the process. Tiwari et al. [12] employed TGA-MS to study the pyrolysates of Green River oil shale, including hydrocarbons and aromatic compounds, at different heating rates and found that at higher heating rates the amount of alkenes generated was higher than that of alkanes. Marshall et al. [13] investigated the kinetics of generation of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  with TGA-MS during the pyrolysis of Australian oil shale. TGA-MS enables the pyrolysis products to be identified before the reactions between them take place. Thus, we can get an objective and detailed information on the generation mechanism of the products.

Heating rate is an important factor which affects the oil shale pyrolysis process and product distribution. Many researchers have studied the effect of heating rate on the product yields and compositions. Shen et al. [14] concluded that the entire mechanism of oil shale pyrolysis and composition of the derived oil were dependent on the heating rate and the decomposition

pathways of kerogen became more diverse at higher heating rates. Al-Harabsheh et al. [15] found that an increase of heating rate increased the content of aliphatic compounds and decreased the aromatic fraction in the liquid shale oil. Al-Ayed et al. [16, 17] studied the pyrolysis of oil shale in a fixed bed reactor and established that a decrease in oil yield and an increase in shale oil density occurred with increasing heating rate. It was also indicated that the maximum weight loss shifted to a higher temperature region with the increase of heating rate [18, 19].

Mineral matter in oil shale may affect the pyrolysis of organic matter both physically and chemically [20, 21]. So it is necessary to investigate the possible catalytic effect of mineral matter on the pyrolysis process more thoroughly. Oil shale mineral matter mainly includes two major types of compounds – carbonates and silicates, while some other components like pyrite, etc., are of low content [22]. The conventional hydrochloric & hydrofluoric (HCl&HF) acid treatment can remove most of the carbonate, oxide, silicate and monosulfide minerals from sedimentary rocks [23], and has little effect, if any, on the macromolecular structure of coals, as reported by Larsen et al. [24]. Removal of pyrite without alteration of the organic composition has not been achieved yet [25]. Yan et al. [23] did researches on the effect of oil shale mineral matrix on the pyrolysis and combustion of kerogen by using TG-FTIR and concluded that the mineral matter in oil shale promoted the decomposition and release of organic matter in the sample during the pyrolysis. Lu et al. [26] reported that carbonate and aluminosilicate minerals can decrease the oil yield and increase the yield of gases in the oil shale pyrolysis. Joseph and Forrai [27] reported that alkali and alkaline earth metal cations may affect the reactivity of oil shales.

In this study, Dachengzi oil shale and its kerogen are studied to investigate the effect of heating rate and mineral matrix on the pyrolysis of oil shale by employing the combined TGA-MS technique. The pyrolysis temperature ranges from room temperature to 1000 °C. Hydrocarbons, aromatic compounds and inorganic gaseous compounds with a molecular weight lower than 200 atomic mass units are continuously formed in the process. Through analysis and comparison of the experimental results, the effect of heating rate and mineral matrix on the pyrolysis behavior of kerogen is investigated, to have information to be taken advantage of in the utilization of oil shale.

## 2. Materials and methods

### 2.1. Materials

The oil shale sample analyzed in this study was obtained from Dachengzi mine located in Huadian city, China. The sample was crushed, ground and sieved to the size of 0–0.25 mm according to the National Standards of China (GB 474-1996). Part of the oil shale sample was demineralized according to the method reported by Yürüm et al. [28]. Briefly, 400 ml of

6 mol/L HCl solution was added to 20 g of the prepared oil shale sample. The mixture was stirred in a nitrogen atmosphere for 24 h in a 70 °C water bath. This mixture was filtered and washed with triple-distilled water until the filtrate became neutral. Then the filter residue was dried at 110 °C under vacuum. Subsequently, 350 ml of 40 wt% HF was added to the HCl-treated oil shale in a Teflon container. After similar stirring, filtering, washing and drying procedures, the treated oil shale sample was ground to the size of 0–0.25 mm and then preserved in dark-colored airtight bottles and stored in a desiccator for further use. According to Yan et al. [23], the treated oil shale sample is free of most minerals, except for pyrite which has little effect on the macromolecular structure of kerogen, and might be called p-kerogen.

Table 1 shows the ultimate analysis data of oil shale and p-kerogen samples. Before each experiment, the original oil shale and p-kerogen samples were dried at 110 °C under vacuum to remove free water.

**Table 1. Ultimate analysis of oil shale and p-kerogen samples, wt%**

Sample	C <sup>daf</sup>	H <sup>daf</sup>	O <sup>daf</sup>	N <sup>daf</sup>	S <sup>daf</sup>	Ash <sup>d</sup>
Oil shale	67.95	8.93	19.61	1.42	2.09	53.59
p-kerogen	77.52	10.54	8.08	1.72	2.14	2.62

<sup>daf</sup> – on dry ash-free basis; <sup>d</sup> – on dry basis.  
O content was calculated from difference.

## 2.2. TGA-MS analysis

The TGA-MS analysis was performed on a TGA instrument (STA 409 PC, NETZSCH, Germany) coupled with a mass spectrometer (Omni Star 200, Balzers, Liechtenstein). In each test, about 8 mg of the sample was heated from ambient temperature up to 1000 °C in the TGA instrument in an Ar (99.999%) atmosphere with a flow rate of 60 ml/min at a pressure of 150 kPa, at heating rates of 5 °C/min and 15 °C/min, respectively. The evolved gas in the pyrolysis process was swept into the MS instrument and tested online over the entire temperature range. To avoid condensation during transportation, the TGA furnace chamber outlet was connected to the MS instrument inlet through a heated quartz capillary at 300 °C. The Omni Star 200 mass spectrometer (mass range 1 to 200 amu) was operated with an electron-impact ion source at 70 eV electron energy. The tests were conducted using the selected ion monitoring mode in which the ion current signal intensities of the selected ions were monitored. The intensities of selected ions should be normalized to the sample mass to compare the test results obtained for different samples at different conditions [29]. Because there are great differences in ash content between oil shale and p-kerogen samples, the MS data are compared on dry ash-free basis in order to more suitably reflect the emission differences of gaseous products [28].

Pyrolysis of oil shale is a complex process that produces a wide range of low molecular weight compounds. In this process, a number of different compounds are released at the same time, leading to the overlapping of many signals in the MS instrument. Hence, it is a big challenge to identify the pyrolysis products using the TGA-MS coupling. When the evolved volatile compounds pass through the MS instrument, they might be broken into fragments by the electron impact ionization. There are two kinds of fragments which are revealed in the mass spectrum in the form of a fragment ion peak and a molecular ion peak. The molecular ion is generated in the ionization process during which the molecule loses one electron. Ignoring the mass of the electron, the mass of the molecular ion is the same as that of the molecule. Normally, in the mass spectrum of one compound, the molecular ion peak has the strongest  $m/z$  signal. The fragment ions are formed due to the bond cleavages between the atoms of the molecular ion with a high energy electron impact. The masses of fragment ions are lower than the mass of the molecular ion and one fragment ion may come from different compounds. Though in the mass spectrum of one organic compound the intensities of part of the fragment ions are much higher than that of the molecular ion, we can track the intensity of the molecular ion online to obtain the release regularity of the compound in the pyrolysis process under the same ionization conditions. Raemarkers and Bart have proved that very low  $m/z$  values ( $< 200$ ) can be used for degradation studies employing TGA-MS [30]. The selected ions and their corresponding compounds in the MS analysis are listed in Table 2.

To study the effect of heating rate and mineral matrix on the release of pyrolysis products, the oil shale and p-kerogen samples were analyzed using the same experimental method at 5 °C/min and 15 °C/min, respectively.

**Table 2. Targeted compounds in TGA-MS analyses**

Compound	Molecular formula	Targeted $m/z$	Compound	Molecular formula	Targeted $m/z$
<b>Inorganic gas</b>			<b>Alkene</b>		
Hydrogen	H <sub>2</sub>	2	Propene	C <sub>3</sub> H <sub>6</sub>	42
Water	H <sub>2</sub> O	18	Butene	C <sub>4</sub> H <sub>8</sub>	56
Carbon monoxide/ethylene	CO/C <sub>2</sub> H <sub>4</sub>	28	Pentene	C <sub>5</sub> H <sub>10</sub>	70
Carbon dioxide/propane	CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	44	Hexene	C <sub>6</sub> H <sub>12</sub>	84
			Heptene	C <sub>7</sub> H <sub>14</sub>	98
<b>Alkane</b>			<b>Aromatic compound</b>		
Methane	CH <sub>4</sub>	16	Benzene	C <sub>6</sub> H <sub>6</sub>	78
Ethane	C <sub>2</sub> H <sub>6</sub>	30	Toluene	C <sub>7</sub> H <sub>8</sub>	92
Butane	C <sub>4</sub> H <sub>10</sub>	58	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106
Pentane	C <sub>5</sub> H <sub>12</sub>	72	Propylbenzene	C <sub>9</sub> H <sub>12</sub>	120
Hexane	C <sub>6</sub> H <sub>14</sub>	86	Butylbenzene	C <sub>10</sub> H <sub>14</sub>	134
			Phenol	C <sub>6</sub> H <sub>5</sub> OH	94

### 3. Results and discussion

The demineralization effect of the HCl&HF method on the Dachengzi oil shale has been studied by Yan et al. [23] using XRD spectrum. In our work, the dominant mineral phases identified in the original oil shale sample were quartz and calcite. Besides, some other minerals, including muscovite, kaolinite, pyrite and some varieties of zeolite, also existed in small amounts. After demineralization, only pyrite was identified in the XRD spectrum of p-kerogen. It means that most of the minerals except for pyrite were removed by the HCl&HF treatment.

#### 3.1. TG/DTG analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of oil shale and p-kerogen on dry ash-free basis at heating rates of 5 °C/min and 15 °C/min are presented in Figure 1. Due to desiccation of the samples at 110 °C before each test, the evaporation of the free moisture was insignificant. The DTG curves show that the pyrolysis of oil shale is a two-stage process while that of p-kerogen consists of one stage. The first stage of oil shale and p-kerogen pyrolysis is mainly the decomposition of the kerogen macromolecule which is insoluble in the samples. The second stage of oil shale pyrolysis is the decomposition of carbonate minerals which generally occurs between 600 and 700 °C. In this research, to more reasonably compare the pyrolysis processes of oil shale and p-kerogen, mass percentages are all on ash-free basis. So the first stages of oil shale and p-kerogen pyrolysis show quite similar variation trends of curves, while in the second stage of oil shale pyrolysis its TG curves are lower than those of p-kerogen owing to the decomposition of minerals. Below 300 °C, the mass losses are small. However, above 300 °C the mass loss rates increase rapidly because of the cracking reactions of organic compounds in the samples.

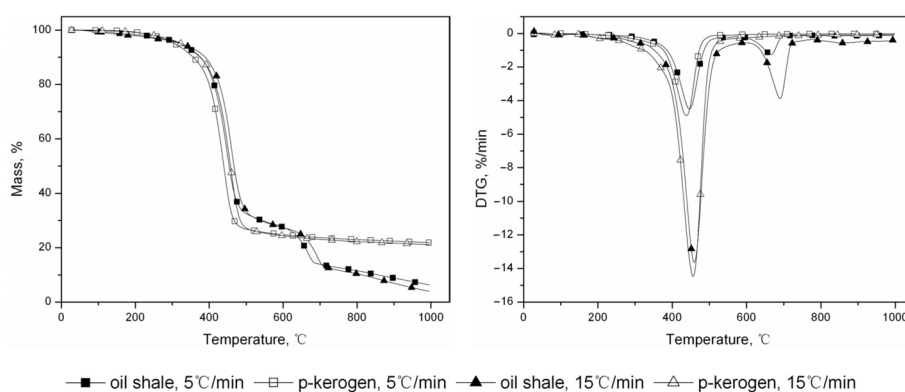


Fig. 1. TG and DTG curves for oil shale and p-kerogen at different heating rates<sup>daf</sup> (<sup>daf</sup> = on dry ash-free basis).

Above 500 °C, the cracking reactions of organic matter come to an end. During pyrolysis, heating rate affects the mass loss of both the oil shale and p-kerogen samples. The TG curves shift to higher temperatures when the heating rate varies from 5 °C/min to 15 °C/min. This is because the higher heating rate increases the temperature difference between the surface and the center of the sample particles, which affects the inner temperature distribution and thus also the pyrolysis of the inner part of the particles. This makes the maximum weight loss rate shift to a higher temperature region (see Fig. 1).

At the same heating rate, the oil shale sample needs higher temperature than the p-kerogen sample to achieve the same mass loss. This is illustrated in Figure 1 where oil shale pyrolysis curves are on the right from p-kerogen curves on both TG and DTG diagrams. Compared with the pyrolysis of p-kerogen, that of oil shale has a delay of about 10 °C. This is because the acid treatment removes most of the minerals and widens the pores and channels inside the particles, which promotes the heat and mass transfer in the reaction process. As a result, the temperature difference between the surface and the center of the particles gets smaller and the gaseous products can be released much easier in a shorter time.

### 3.2. Effect of heating rate and mineral matrix on product emissions

#### 3.2.1. Effect of heating rate and mineral matrix on the release of inorganic gases

The release of inorganic gases is shown in Figure 2. Because of the same molecular weight, the diagram of  $m/z = 28$  represents CO and C<sub>2</sub>H<sub>4</sub>, while that of  $m/z = 44$  represents CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>. From the diagrams it can be seen that the inorganic gases begin to form at about 400 °C. Heating rate influences the generating rates and temperatures corresponding to the maximum formation rates of gases. For the oil shale sample, at the heating rate of 5 °C/min, the formation and evolution of H<sub>2</sub> and H<sub>2</sub>O attain maximum at 450 °C. But at 15 °C/min, the maximum values are both achieved at 483 °C. The temperature of the maximum evolution rate is raised by 33 °C with the increase of heating rate. A similar phenomenon is observed in the generating processes of  $m/z = 28$  (CO and C<sub>2</sub>H<sub>4</sub>) and  $m/z = 44$  (CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>). The peaks of the oil shale sample appear at higher temperatures than those of the p-kerogen sample owing to the porous structure of p-kerogen particles. The inorganic matrix in the oil shale samples inhibits the release of gaseous products. At the same time, the evolution curves of oil shale samples are above the curves of p-kerogen samples at the same heating rate. This indicates that mineral matrix promotes the bitumen pyrolysis process generating H<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>. Generally speaking, mineral matrix may promote the pyrolysis of kerogen to generate more gases, but, at the same time, prevent the release of the generated gases.

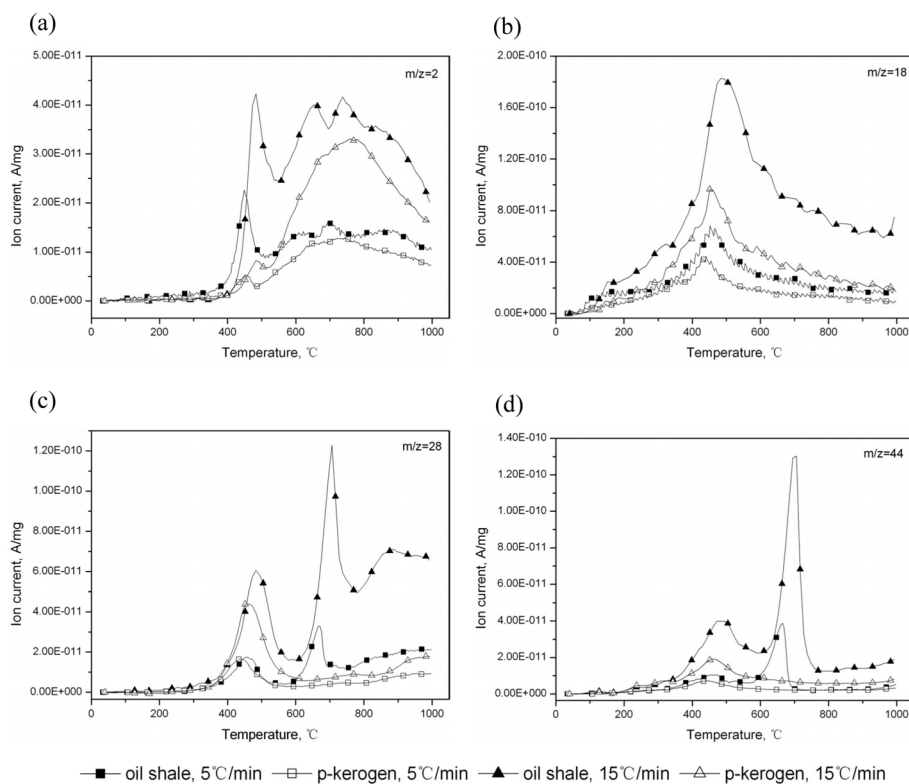


Fig. 2. Evolution signals of inorganic gases<sup>daf</sup>: (a) H<sub>2</sub>; (b) H<sub>2</sub>O; (c) CO and C<sub>2</sub>H<sub>4</sub>; (d) CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> (<sup>daf</sup> = on dry ash-free basis).

For the oil shale sample, there is a high peak below 500 °C signifying the evolution of hydrogen (see Fig. 2a), while the corresponding peak of the p-kerogen sample is much lower. The release of H<sub>2</sub> in this temperature region is associated with the bitumen-to-oil pyrolysis reaction. It indicates that minerals in oil shale have a catalytic effect on the pyrolysis of kerogen and promote the generation of H<sub>2</sub>. At about 500 °C, there occurs an obvious release of H<sub>2</sub> from both the oil shale and p-kerogen samples. This accords with the results obtained in other researches on different oil shales [10, 31]. The release of H<sub>2</sub> in this temperature region is associated with the pyrolysis reactions of carbon residues remaining after the primary bitumen decomposition, which contain a series of chemically nonequivalent sites [10].

As seen from Figure 2c, there are two peaks of evolution of CO and C<sub>2</sub>H<sub>4</sub> detected in the pyrolysis of oil shale samples, while only one peak is observed in that of p-kerogen. Taking the pyrolysis at 5 °C/min as an example, the release of CO and C<sub>2</sub>H<sub>4</sub> has two emission stages at 370–500 °C and 600–700 °C, respectively, for oil shale, while there is only one peak at 350–500 °C for p-kerogen. The second peak of the oil shale sample is



mainly due to the generation of CO. The main source of CO below 600 °C may be ether links or carbonyl groups, while the CO<sub>2</sub> released below 600 °C is mainly due to the decomposition of certain functional groups like carboxylic acids and esters [10]. As shown in Figure 2d, there is a second obvious peak indicating the evolution CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> at about 700 °C in the pyrolysis of oil shale caused by the decomposition of minerals, especially carbonates.

Figure 3 shows the concentrations of hydrogen and water which are calculated from integrating the ion currents over time. It provides an approximate quantification of the pyrolysis products to enable obtaining information about product yields. It can be noticed that as the response factors are not necessarily linear or well known, the areas cannot be directly related to the compound concentrations in the mass spectrometer [12]. It can also be observed that the concentrations of hydrogen and water decrease with increasing heating rate in the pyrolysis of both oil shale and p-kerogen. Also, the hydrogen and water concentrations in the p-kerogen pyrolysis products are lower than those in the oil shale sample due to the catalytic effect of its mineral matrix. Compared with the p-kerogen sample, the water content in the oil shale pyrolysis products is much higher and the decrease caused by heating rate is not that obvious. This may be partly caused by the water-gas shift reaction occurring in the oil shale sample [10].



In the pyrolysis of oil shale above 600 °C, a large amount of CO<sub>2</sub> is released because of the decomposition of minerals, during which some H<sub>2</sub> is converted to H<sub>2</sub>O. This could be proved by the higher ion current intensities of m/z=18 and m/z=28 in the high temperature region in Figures 2b–c.

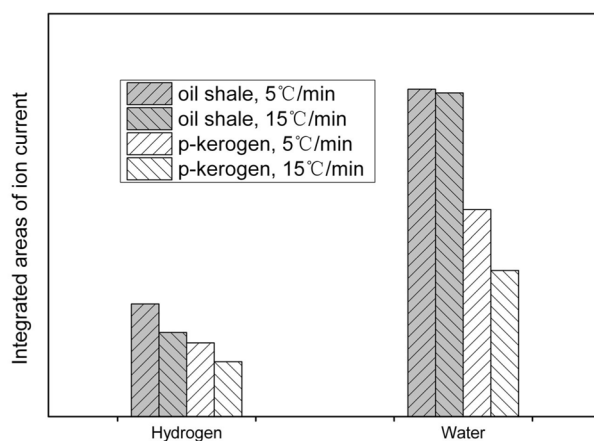


Fig. 3. Concentrations of inorganic gases as calculated from areas of peaks<sup>daf</sup> (<sup>daf</sup> = on dry ash-free basis).

### 3.2.2. Effect of heating rate and mineral matrix on the release of aliphatic hydrocarbons

The release of alkanes and alkenes is shown in Figures 4 and 5. It can be seen that the temperature of maximum generating rates of aliphatic hydrocarbons at 15 °C/min is higher than that at 5 °C/min, which accords with the release of inorganic gases.

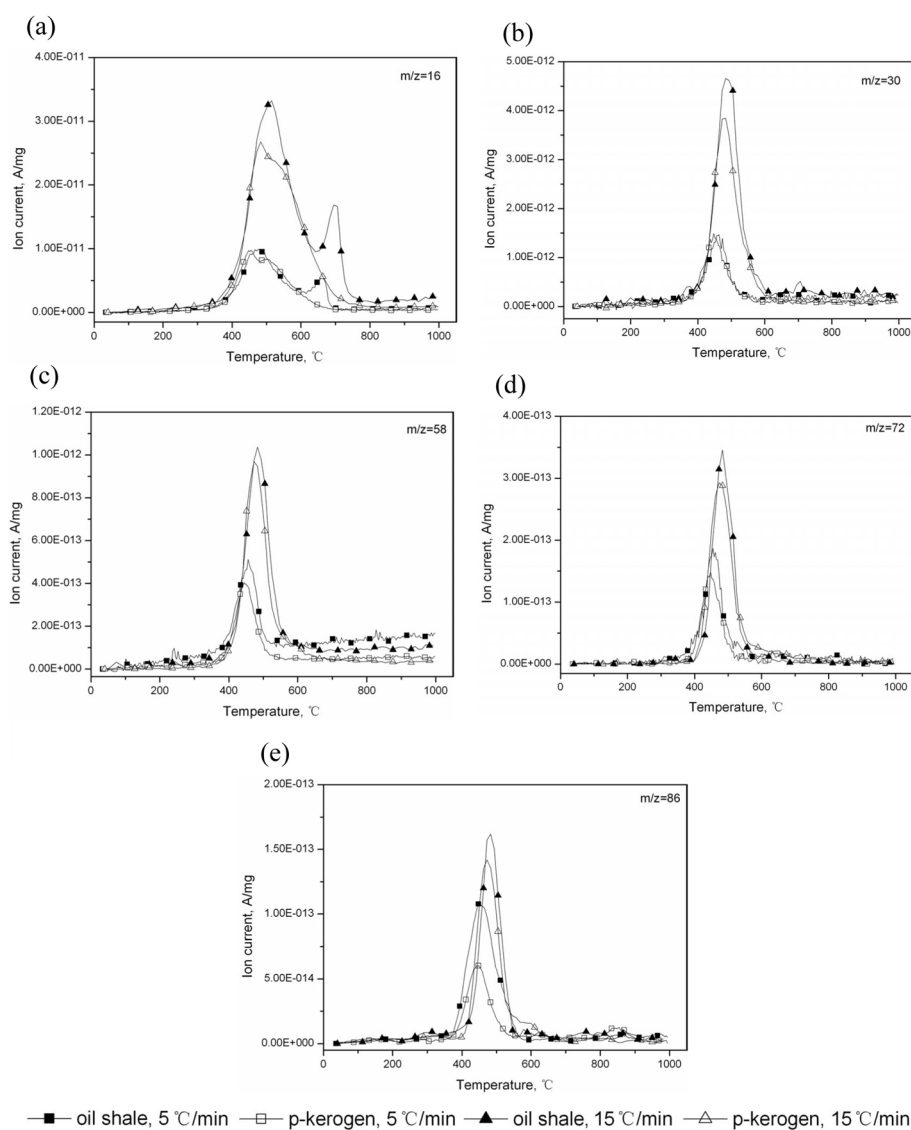


Fig. 4. Evolution signals of alkanes<sup>daf</sup>. (a) CH<sub>4</sub>; (b) C<sub>2</sub>H<sub>6</sub>; (c) C<sub>4</sub>H<sub>10</sub>; (d) C<sub>5</sub>H<sub>12</sub>; (e) C<sub>6</sub>H<sub>14</sub> (<sup>daf</sup> = on dry ash-free basis).

Figure 4a reveals that the generation of  $\text{CH}_4$  in the oil shale sample is different from that in the p-kerogen sample. The generation of  $\text{CH}_4$  has two obvious peaks in the oil shale sample while only one peak exists in the p-kerogen sample. The first peak is associated with oil evolution. The second peak of  $\text{CH}_4$  in the oil shale sample appears at about  $700\text{ }^\circ\text{C}$ , which is consistent with the evolution of  $\text{CO}_2$  due to the decomposition of minerals. The  $\text{CH}_4$  generated in this temperature region is mainly released during the char pyrolysis process which primarily includes the cleavage of methyl and methoxyl groups attached to aromatic structures, and possibly the cleavage of methylene bridges between aromatic rings [10]. The generation of  $\text{CH}_4$  in the second peak illustrates that the decomposition of minerals of oil shale promotes the char pyrolysis and thus increase the amount of  $\text{CH}_4$ . At temperatures from  $640\text{ }^\circ\text{C}$  to  $750\text{ }^\circ\text{C}$ , the decomposition of inorganic constituents like carbonates and some clay types, etc., is the main reaction in the oil shale sample [32]. In the decomposition of minerals, large amounts of (metallic)oxides like  $\text{CaO}$ ,  $\text{MgO}$ , etc., are generated which have been proved to have a catalytic effect on the pyrolysis reactions of oil shale [33, 34].

The evolution of  $\text{C}_3\text{H}_6$  (Fig. 5a) is distinct in that there is an intense generating process above  $600\text{ }^\circ\text{C}$  observed in the oil shale sample at  $15\text{ }^\circ\text{C}/\text{min}$  while this phenomenon does not exist at  $5\text{ }^\circ\text{C}/\text{min}$ , or in the p-kerogen sample. This is probably because of the secondary cracking reactions of the products remained in the particles with a catalytic effect of the metal cations. At high heating rates, large amounts of gaseous products are generated in a short time, but it is not easy for them to leave the inner of oil shale particles because of the mineral matrix, which promotes the secondary cracking reactions.

From Figures 4 and 5 it is clear that the acid treatment of samples promotes the release of products so that the emission of most of them is shifted to a lower temperature region with a decrease of about  $10\text{ }^\circ\text{C}$ .

The concentrations of alkanes and alkenes are shown in Figure 6. Similarly to the variation trends of inorganic gases emission, increasing the heating rate leads to the decrease of the amounts of alkanes and alkenes except for  $\text{CH}_4$ . The concentrations of alkanes decrease with increasing carbon numbers, and so do the concentrations of alkenes. Because of the existence of mineral matrix, the concentrations of alkanes and alkenes in the oil shale products are a little higher than those in the p-kerogen products. The listed alkanes and alkenes are all light compounds which to some extent are partly produced in the secondary cracking reactions. Their decrease with increasing heating rate reveals that the secondary cracking reactions may be effectively inhibited by increasing heating rate and thus the gaseous products amount may be reduced. This has been proved to favor the increase of oil yield [35]. Although the amounts of alkanes and alkenes decrease with increasing heating rate, the alkene/alkane ratios increase as shown in Table 3. The amount of alkenes released is greater than that of alkanes, which is consistent with the results obtained by Tiwari and Deo [12].

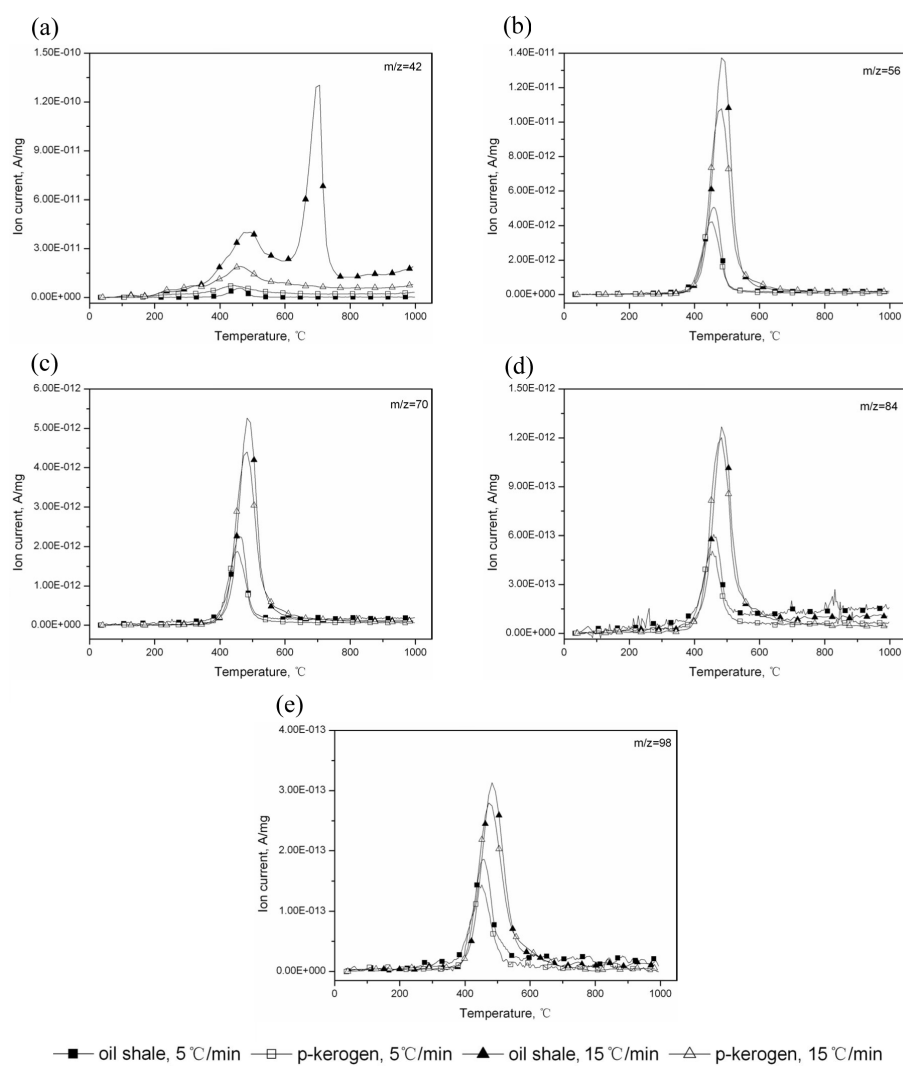


Fig. 5. Evolution signals of alkenes<sup>daf</sup>: (a) C<sub>3</sub>H<sub>6</sub>; (b) C<sub>4</sub>H<sub>8</sub>; (c) C<sub>5</sub>H<sub>10</sub>; (d) C<sub>6</sub>H<sub>12</sub>; (e) C<sub>7</sub>H<sub>14</sub> (<sup>daf</sup> = on dry ash-free basis).

**Table 3. Alkenes/alkanes ratios (ion current response area)<sup>daf</sup>**

	Oil shale, 5 °C/min	Oil shale, 15 °C/min	p-kerogen, 5 °C/min	p-kerogen, 15 °C/min
Butene/butane	3.62	7.68	5.70	9.34
Penene/pentane	9.70	17.81	12.35	14.11
Hexene/hexane	9.79	14.41	10.28	11.66

<sup>daf</sup> – on dry ash-free basis.

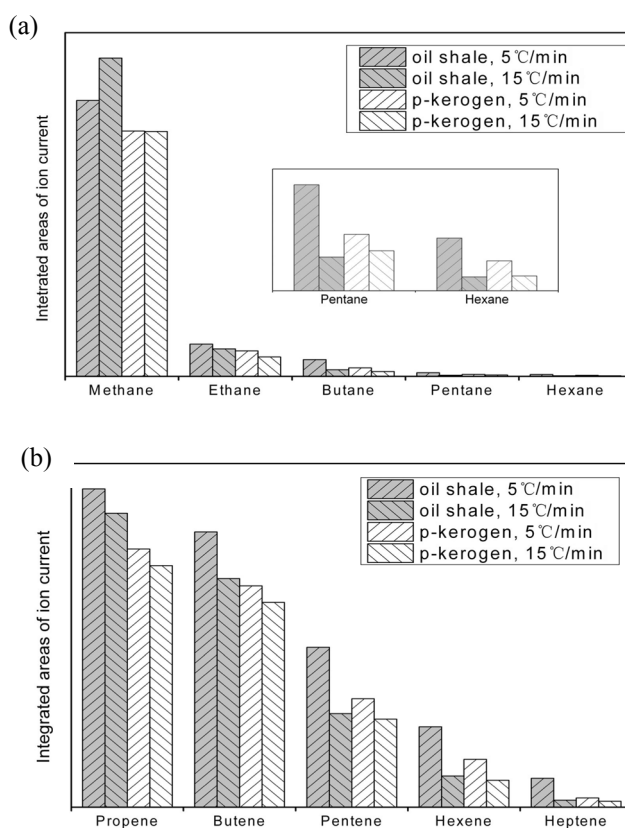


Fig. 6. Concentrations of alkanes and alkenes<sup>daf</sup>: (a) alkanes; (b) alkenes (<sup>daf</sup> = on dry ash-free basis).

### 3.2.3. Effect of heating rate and mineral matrix on the release of aromatic compounds

Through tracing the ion current intensities of the aromatic compounds listed in Table 2, it was found that the molecular ion signals of propylbenzene and butylbenzene were almost not detected in the pyrolysis products. Figure 7 shows the evolution signals of benzene, toluene, phenol and ethylbenzene. There is only one peak in each curve associated with oil generation. The mineral matrix in the oil shale sample hinders the release of gaseous aromatic compounds, as well as of inorganic gases and aliphatic hydrocarbons. The effect of heating rate and mineral matrix on the total amounts of aromatic products is shown in Figure 8. At the same heating rate, the total amounts of the aromatic products generated by oil shale pyrolysis are obviously larger than those produced from the p-kerogen pyrolysis. This indicates that the minerals have a catalytic effect on the cracking reactions, which leads to the increase of small molecule aromatic compounds. For both

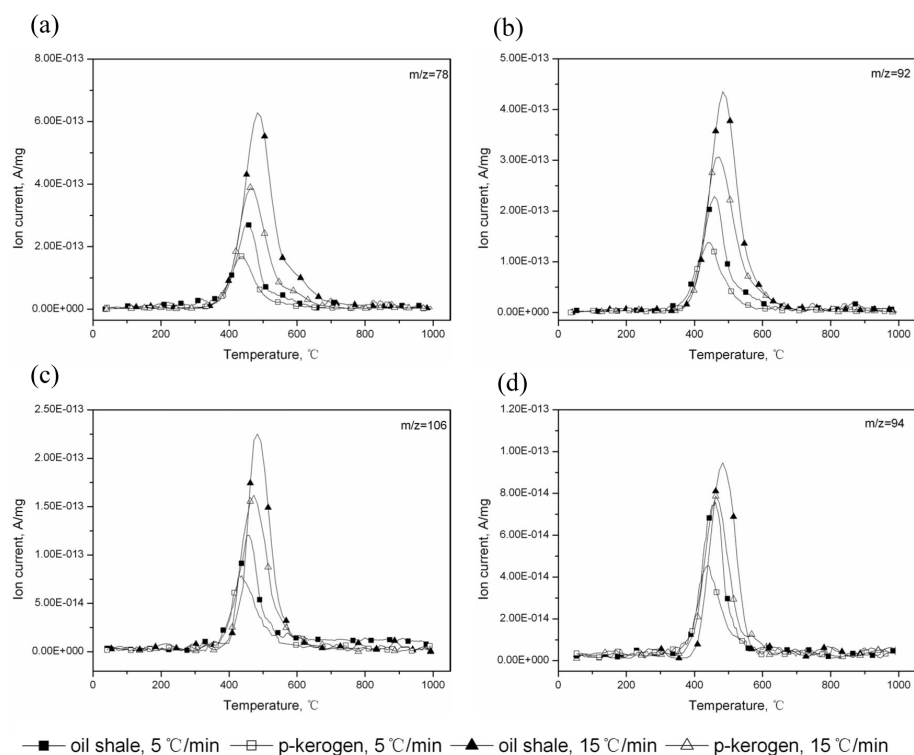


Fig. 7. Evolution signals of aromatic compounds<sup>daf</sup>: (a)  $C_6H_6$ ; (b)  $C_7H_8$ ; (c)  $C_8H_{10}$ ; (d)  $C_6H_5OH$  (<sup>daf</sup> = on dry ash-free basis).

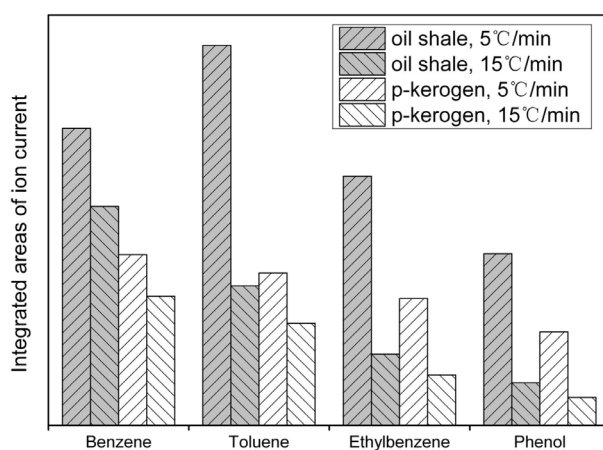


Fig. 8. Concentrations of aromatic compounds<sup>daf</sup> (<sup>daf</sup> = on dry ash-free basis).

oil shale and p-kerogen, increasing heating rate leads to the decrease of the total amounts of aromatic compounds. For oil shale, the integrated ion current areas of benzene, toluene, ethylbenzene and phenol have decreases of 26.3%, 63.3%, 71.4% and 75.3%, respectively. For p-kerogen, the respective figures are 24.3%, 33.1%, 60.3% and 70.0%. It is probably due to that at higher heating rates, the secondary cracking reactions are diminished to a large extent, so, fewer aromatic groups are separated from larger molecules, which results in the decrease of small molecule aromatic compounds.

#### 4. Conclusions

In this work, the effect of heating rate and mineral matrix on the yield and fractional composition of oil shale pyrolysis products was investigated using the TGA-MS method. Different heating rates and mineral contents lead to differences in the thermal behavior of products. At the same time, there may be observed similar variation trends with temperature.

The compounds analyzed in this research are mostly small molecule composites. The fractions of most compounds decrease with increasing heating rate, which indicates that this increase may also inhibit the secondary cracking reactions. Increasing the heating rate from 5 °C/min to 15 °C/min makes the TG curves of both oil shale and p-kerogen shift to the higher temperature region with an increase of about 10 °C because of its effect on the heat transfer in the sample particles.

Oil shale mineral matrix has an obvious catalytic effect on the pyrolysis of kerogen. As a result, the fractions of the targeted compounds produced in the oil shale pyrolysis are significantly larger than those generated in the p-kerogen pyrolysis. Mineral matrix markedly intensifies the hydrogen release in the temperature range from about 350 °C to 500 °C, which indicates that minerals in oil shale promote the cracking reactions in the pyrolysis of kerogen. In addition, mineral matrix inhibits the evolution of products and thus makes the TG curves shift to higher temperatures with an increase of about 10 °C.

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