

THE CHEMICAL COMPOSITION AND PYROLYSIS CHARACTERISTICS OF THERMAL BITUMEN DERIVED FROM PYROLYZING HUADIAN OIL SHALE, CHINA

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Abstract. Thermal bitumen is an important intermediate derived from kerogen decomposition during oil shale pyrolysis. In this study, thermal bitumen was obtained by extracting oil shale char generated from pyrolysis of Huadian oil shale at 360–530 °C. The chemical composition and pyrolysis characteristics of bitumen were investigated by ultimate analysis, liquid chromatography fractionation, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The decomposition of oxygen-containing structures at 420–450 °C decreased the oxygen content from 4.66 to 0.75 wt%. The intense cracking of aliphatic compounds or alkyl chains at 450–480 °C resulted in the selective concentration of aromatic compounds and the decrease of H/C ratio from 1.350 to 1.262. The pyrolysis of thermal bitumen could be tentatively divided into two stages – the evaporation of light components (150–410 °C) and the cracking of heavy components (410–550 °C), which corresponded respectively to a shoulder and an obvious peak in differential thermal gravimetry (DTG) curves. For pyrolysis of oil shale, the evaporation process dominated the pyrolysis of thermal bitumen at 420–450 °C, which decreased the content of light components. In a higher temperature range, 450–480 °C, the cracking of large molecules became more intense and, as a result, increased the content of light components and decreased that of heavy components.

Keywords: Huadian oil shale, thermal bitumen, chemical composition, pyrolysis characteristics.

1. Introduction

Oil shale is a fine-grained sedimentary rock containing insoluble complex macromolecular organic matter called kerogen, which can be converted into

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shale oil, combustible gases and shale char upon pyrolysis or retorting processes [1, 2]. Huge resources of oil shale are located in many countries, e.g. USA, Russia, China, Morocco, Brazil, Jordan and Estonia. According to the nationwide oil shale resources evaluation that was carried out from 2003 to 2006, China's oil shale reserves were estimated at approximately 720 billion tons [3]. These huge energy reserves have great significance for alleviating pressure on petroleum supplies.

Pyrolysis of oil shale to liberate shale oil involves a complex reaction network, which relates to the breaking of bonds with different activation energies within the organic matter and between the organic and mineral matter [4]. Nevertheless, the pyrolysis processes can still be divided into two steps apparently. The first step involves the depolymerization of macromolecular organic matter of kerogen into soluble extracts (i.e. thermal bitumen) at low temperatures, releasing some small molecules such as moisture, CO and CO₂. The second step involves the further decomposition of thermal bitumen into shale oil, gas and shale char as the temperature increases [5].

Thermal bitumen is not only the product of kerogen degradation but also the initial reactant that forms the final products. Thus, the formation characteristics and chemical structure features of this organic intermediate are highly important to clarify the mechanism of kerogen pyrolysis. Wang et al. [6] reported that during pyrolysis of Longkou oil shale, the yield of thermal bitumen increased to the maximum value at 430 °C and then decreased with temperature further increasing. Taking thermal bitumen as the intermediate material resulting from kerogen pyrolysis, various decomposition schemes have been proposed to model the kerogen degradation process [7–9]. Miknis et al. [10] compared the formation of thermal bitumen of Colorado and Kentucky oil shales and found that the amount of thermal bitumen was inversely proportional to the carbon aromaticity of kerogen. Li et al. [5] discovered that the aliphatic carbons were decreased while the aromatic carbon structures were well retained during the thermal decomposition from kerogen to the intermediate bitumen. So far, investigators mainly focused on the formation characteristics of thermal bitumen and the chemical structure transformation from kerogen to bitumen. There have been reported a few studies on the composition variation and chemical structure transformation of bitumen during its decomposition to oil, gas and carbon residue. This information is important to better understand the conversion pathway of thermal bitumen.

On the other hand, thermogravimetric analysis (TGA) has been widely used to determine the pyrolysis characteristics of oil shale and kerogen [11–16]. Wang et al. [11] performed the non-isothermal pyrolysis of Huadian oil shale. The researchers established that the pyrolysis process of oil shale involved three stages, of which the mass loss in the second stage (200–600 °C) was attributed to the decomposition of kerogen. Jaber and Probert [12] investigated the decomposition kinetics of two Jordanian oil

shales and found that the decomposition rate changed significantly at a critical temperature of 305 ± 15 °C. Chang et al. [13] studied the effect of transitional metal salts on oil shale pyrolysis by TGA, showing that $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ could cause a greater mass loss than raw oil shale. By comparing the TG curves of oil shale and kerogen, Yan et al. [14] demonstrated that the mineral matrix promoted the decomposition and release of organic matter in oil shale during pyrolysis. A lot of information about the pyrolysis characteristics of oil shale and kerogen has been obtained by TGA to date. However, very little information is available on the pyrolysis of thermal bitumen, which is a crucial step to yield shale oil.

Therefore, in the present study, the pyrolysis of oil shale was carried out in a fixed bed retort in the temperature range of 360–530 °C. The shale char samples were subjected to Soxhlet extraction to obtain thermal bitumen derived at different temperatures. Ultimate analysis, liquid column chromatography and Fourier transform infrared (FTIR) spectroscopy were used to characterize the composition variation and structure transformation of bitumen during pyrolysis of oil shale. TGA was applied to analyze the pyrolysis characteristics of thermal bitumen fractions. The objective of this work was to throw some light on the complex mechanisms of kerogen decomposition and shale oil formation.

2. Experimental section

2.1. Materials

Oil shale samples investigated in this study were obtained from the 4th layer of Dachengzi mine located in Huadian city, China. Proximate and Fischer assay analyses of oil shale were conducted as per Chinese National Standards GB/T 212-2008 and SH/T 0508-92, respectively. The contents of C, H, N and S were determined by the vario MACRO cube CHNS elemental analyzer, the results are presented in Table 1. Representative samples of Huadian oil shale were ground to less than 0.18 mm before pyrolysis and stored in sealed containers until used.

Table 1. Proximate, ultimate and Fischer assay analyses of Huadian oil shale

Proximate analysis, wt%, ad		Ultimate analysis, wt%, ad		Fischer assay, wt%, ad	
Moisture	2.92	C	19.87	Shale oil	9.57
Volatile matter	25.03	H	2.84	Gas + Loss	3.50
Ash	70.45	N	4.82	Water	7.95
Fixed carbon	1.60	S	0.41	Residue	78.98

Note: ad – air-dried.

2.2. Pyrolysis of oil shale

A detailed configuration of the fixed bed pyrolysis apparatus employed in oil shale pyrolysis experiments is described elsewhere [13]. The retort was constructed from aluminum according to the National Standard of China SH/T 0508-92. In addition, a stainless steel pipe was added to the cover of the retort for the carrier gas inlet. Briefly, 50 g oil shale was placed inside the pyrolyzer and electrically heated from ambient temperature to 360, 390, 420, 435, 450, 465, 480, 495, 510 or 530 °C at 3 °C /min with no holding at a final temperature. Nitrogen gas at 50 mL/min was introduced to the retort to sweep the generated products toward the outlet of the retort. The formed shale oil, steam and gases were directed into a conical flask which was immersed in a tank filled with water and ice. The gases were collected in a plexiglass cylinder by using the water displacement method. The product yield was calculated by dividing the product mass by the dry mass of oil shale. Detailed information can be found in our previous work [13].

2.3. Thermal bitumen extraction

A 24 h Soxhlet extraction was performed on 20 g shale char to recover thermal bitumen derived from kerogen pyrolysis. Chloroform was used as a solvent for its good solubility in thermal bitumen [5]. Evaporation of chloroform from bitumen solutions took place at about 40 °C at slightly reduced pressure to recover the bitumen samples, which were in turn weighed to calculate the bitumen yield and reserved for subsequent analyses. In addition, the Soxhlet extraction was also conducted on raw oil shale to determine its content of inherent bitumen, which was composed of solvent-soluble organic compounds present in oil shale.

2.4. Thermal bitumen characterization

2.4.1. Ultimate analysis

The contents of C, H, N and S of thermal bitumen were determined with the vario MACRO cube CHNS elemental analyzer, and the O content was calculated by difference.

2.4.2. Chemical class composition

The chemical class composition of thermal bitumen was analyzed according to the Chinese Petroleum Industrial Standard SY/T 5119-2008. Bitumen was fractionated into aliphatic, aromatic, resin and asphaltene (SARA) fractions by using a glass column packed with silica gel and neutral alumina [17, 18].

2.4.3. FTIR analysis

FTIR analyses for the asphaltene fractions of thermal bitumen were performed on a Nicolet 6700 spectrometer. For preparing pellets, the asphaltene sample (1 mg) was mixed with KBr (200 mg) and then ground to powder

with a size smaller than 200 mesh. A sample presser was used to press the resulting mixtures to discs of 10 mm diameter at 15 MPa for 3 min. FTIR spectra were obtained with a spectral range of 4000–400 cm^{-1} , a scanning frequency of 32 and a resolution of 4 cm^{-1} .

2.4.4. Thermogravimetric analysis

Thermogravimetric analysis of thermal bitumen samples was carried out in a Mettler-Toledo TGA/DSC 1 analyzer. During the experiment, about 10 mg bitumen sample was placed in a ceramic crucible and heated from 30 to 600 °C under 50 mL/min N_2 atmosphere with a heating rate of 10 °C/min. The sample mass and rate of mass loss were recorded by a computer.

3. Results and discussion

3.1. Product yields

Figure 1 shows the yields of shale char, shale oil, water and non-condensable gas as a function of pyrolysis temperature. Generally, as the pyrolysis temperature increases from 360 to 530 °C, the shale char yield decreases while the yields of shale oil, water and non-condensable gas increase. This is expected as the pyrolysis of kerogen becomes more active at high temperature and large amounts of kerogen are converted into volatile products. This is also because the oil shale used contains a considerable amount of mineral matter (81.5 wt%), including quartz, calcite, pyrite and clay minerals [18]. The chemical reactions that mineral matter undergoes also contribute to the formation of pyrolytic products. For example, clay minerals lose their structural water via dehydroxylation reactions over a wide range of

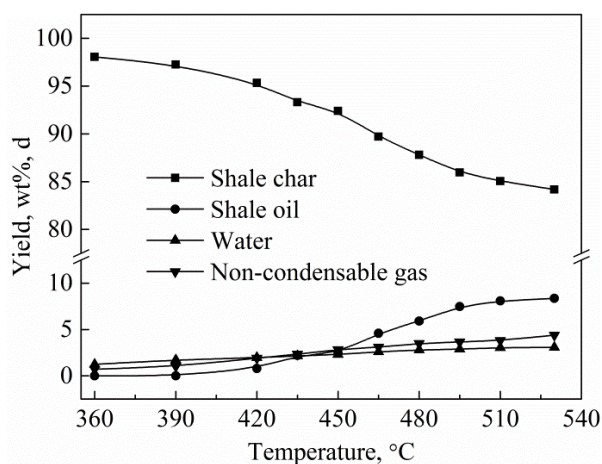


Fig. 1. Influence of pyrolysis temperature on product yields by pyrolysis of Huadian oil shale.

temperatures up to about 550 °C, and the decomposition of calcite occurs to release carbon dioxide with the assistance of silicate minerals present in oil shale or organic acids resulting from kerogen breakdown [19, 20].

Figure 2 displays the yield of thermal bitumen as a function of temperature varying from 360 to 530 °C. For the purpose of comparison, the shale oil yield and inherent bitumen content are also plotted in the graph. At a low temperature, 360 °C, no shale oil is produced and the thermal bitumen yield is equal to the inherent bitumen content, suggesting that kerogen is not decomposed at this temperature. The yield of the obtained thermal bitumen actually equals the inherent bitumen content of oil shale. As the temperature increases from 360 to 390 °C, the thermal bitumen yield exceeds the inherent bitumen content, which indicates that chloroform-soluble organic materials were derived through partial depolymerization of kerogen together with the reduction of macromolecules to smaller molecules [9]. And then, with temperature further rising, the thermal bitumen first increases and then decreases and attains the maximum value (3.37 wt%) at 450 °C. Being a critical intermediate of kerogen pyrolysis, the formation and decomposition of thermal bitumen occur at the same time. Therefore, the formation rate of thermal bitumen is higher than its decomposition rate at 390–450 °C while the case is vice versa at 450–540 °C. Wang et al. [6] and Shi et al. [21, 22] also indicated that the thermal bitumen yield first increased and then decreased with increasing pyrolysis temperature. The investigators emphasized the transient nature of thermal bitumen during decomposition of oil shales.

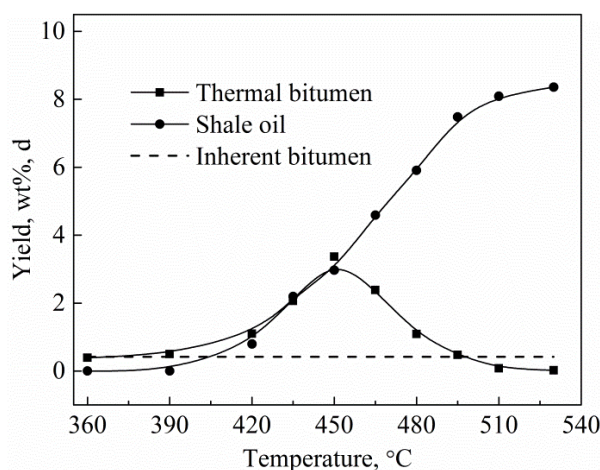


Fig. 2. The effect of pyrolysis temperature on the thermal bitumen yield.

3.2. Thermal bitumen analysis

Analyses of the chemical properties of bitumen were limited by the small amounts of bitumen extracted from the 20 g shale char. This was especially

true for the shale char samples produced at lower or higher temperatures at which little bitumen was derived or remained. As the bitumen yield varied dramatically at 420–480 °C, samples of the thermal bitumen produced in this temperature range were chosen to characterize its chemical composition and structural properties. Analysis revealed that thermal bitumen underwent compositional and structural variations during pyrolysis.

3.2.1. Ultimate analysis

The results of ultimate analysis of the thermal bitumen derived from oil shale pyrolysis are presented in Table 2. The bitumen produced at 420 °C contains obviously more oxygen (4.66 wt%) than other bitumen samples, which means that this sample contains a large amount of oxygen-containing compounds. As the C=O groups can decrease the dissociation energy of the adjacent C–C bonds [23], the C–O bond is weaker than other bonds [24, 25]. The oxygen-containing structures such as carboxyl groups and ether bridges act as active reaction sites during kerogen decomposition. Therefore, the oxygenated compounds are mainly produced in the initial stage of kerogen pyrolysis and are present in the 420 °C thermal bitumen. As bitumen accumulates at temperatures from 420 to 450 °C, the oxygen content is decreased from 4.66 to 0.75 wt%, owing to the rupture of oxygen functional groups, and the dilution effect. In addition, the atomic H/C ratio first increases and then decreases in this range. It may be because the production of aliphatic and aromatic compounds is more dominant at 420–435 °C and 435–450 °C, respectively. Tiwari and Deo [26] reported that aliphatic compounds were produced at slightly lower temperatures than aromatic compounds during oil shale pyrolysis. With temperature further increasing from 450 to 480 °C, the atomic H/C ratio decreases from 1.350 to 1.262. It implies that bitumen becomes more aromatic by nature. The plausible reason is that aliphatic compounds are decomposed or vaporized to form oil, which results in the selective concentration of aromatic compounds. Since the nitrogen of Huadian oil shale kerogen is mainly contained in aromatic molecules [27], its content increases significantly, from 1.39 to 1.57 wt% at 465–480 °C.

Table 2. Ultimate analysis of thermal bitumen derived from oil shale pyrolysis

Element/Sample	B-420	B-435	B-450	B-465	B-480
C, wt%	84.40	86.37	87.43	87.88	87.74
H, wt%	9.04	10.01	9.84	9.52	9.23
N, wt%	0.98	1.24	1.40	1.39	1.57
S, wt%	0.92	0.70	0.58	0.49	0.50
O, wt%	4.66	1.67	0.75	0.71	0.96
H/C	1.285	1.391	1.350	1.300	1.262

Note: B-420, etc., signify samples of bitumen produced at respective temperatures.

3.2.2. Chemical class fractionation

Figure 3 shows the weight percentages of SARA fractions of bitumen as a function of temperature. Resins are the major components of thermal bitumen, accounting for about one half of the bitumen sample. For comparison, the contents of saturates are much lower and fluctuate around 15 wt% in the temperature range of 420–480 °C. Wang et al. [17] reported that saturates constituted 50–70 wt% of Huadian shale oil. It can be concluded that most of the saturates constituents have low boiling point and they can leave the shale matrix once they are produced from kerogen pyrolysis. The oxygen-containing molecules of bitumen should mainly be present in the resin fraction. In the temperature range of 420–450 °C, the decrease of the resin fraction leads to the decrease of the oxygen content of bitumen samples. The continuously increasing temperature from 450 to 480 °C increases the aromatics content and decreases the saturates content at the same time, which is consistent with the decrease of atomic H/C ratio to a certain extent.

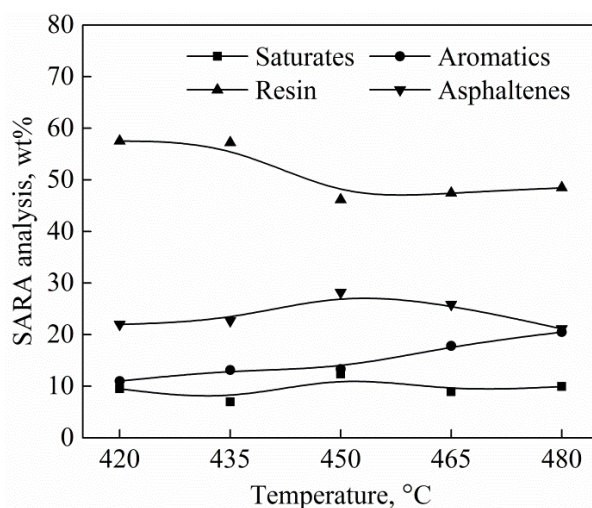


Fig. 3. The SARA composition of thermal bitumen at different temperatures.

3.2.3. FTIR analysis

Figure 4 shows the FTIR spectra of asphaltene fractions that are composed of highly polar compounds with high molecular weights. Based on the reported FTIR absorption bands of thermal bitumen [21, 22] and kerogen [27, 28], a summary of the characteristic bands of some functional groups in asphaltenes is presented in Table 3.

Figure 4 shows that as pyrolysis temperature increases from 420 to 450 °C, the intensity of the band at 1711 cm^{-1} decreases while the band at

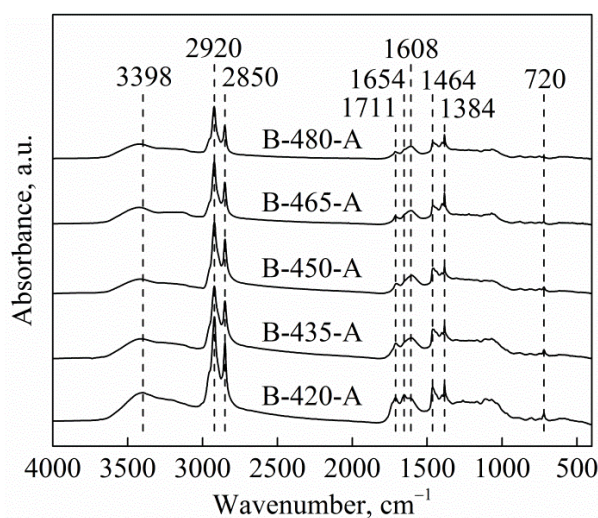


Fig. 4. FTIR spectra of asphaltene fractions of thermal bitumen at different temperatures.

Table 3. Characteristic FTIR bands of some functional groups in asphaltene fractions

Wavenumber, cm^{-1}	Band assignments
3398	–OH stretching of phenols and carboxylic acids
2920, 2850	Asymmetrical and symmetrical stretching of alkyl CH_2 groups
1711	C=O stretching of carboxyl or carbonyl groups
1654	Carbonyl C=O stretching highly conjugated with aromatic rings
1608	C=C stretching of aromatic rings
1464	Asymmetric bending of CH_3 and CH_2 groups
1384	Symmetric bending of CH_3 groups
720	Skeletal vibration of straight chains containing more than four CH_2 groups

1654 cm^{-1} almost disappears, indicating that a considerable amount of C=O groups is decomposed at 420–450 °C. Meanwhile, the intensity of the bands attributed to aliphatic carbons (2920 cm^{-1} , 2850 cm^{-1} , 1464 cm^{-1} , 1384 cm^{-1} and 720 cm^{-1}) decreases to varying extents between 420 and 450 °C. Ru et al. [23] calculated the bond order of chemical bonds in oil shale kerogen and reported that C=O groups could decrease the dissociation energy of the adjacent C–C bonds. The breaking of weak chemical bonds at the sites attached to the carbonyl carbon atoms occur in this stage, which should lead to the cleavage of the lateral alkyl chains of aromatic compounds and the decrease of aliphatic carbons. When the temperature rises from 450 to 480 °C, the bands of aliphatic carbons decrease obviously while those of C=O remain nearly unchanged. It is because the cracking of C–C bonds can occur at most sites in the aliphatic chains at high temperatures. Lots of alkyl

free radicals are generated and released in this stage, which should contribute to the decrease of the atomic H/C ratio of thermal bitumen at 450–480 °C.

3.3. Pyrolysis characteristics of thermal bitumen

Figure 5 shows the TG and DTG curves of thermal bitumen samples. From Figure 5b it can be seen that there is almost no mass loss below 150 °C. The rate of mass loss increases gradually with increasing temperature and a shoulder peak appears at 150–410 °C, stemming mainly from the evaporation of compounds with relatively low boiling point. The bitumen samples are composed of chemical compounds that remained in the shale matrix after

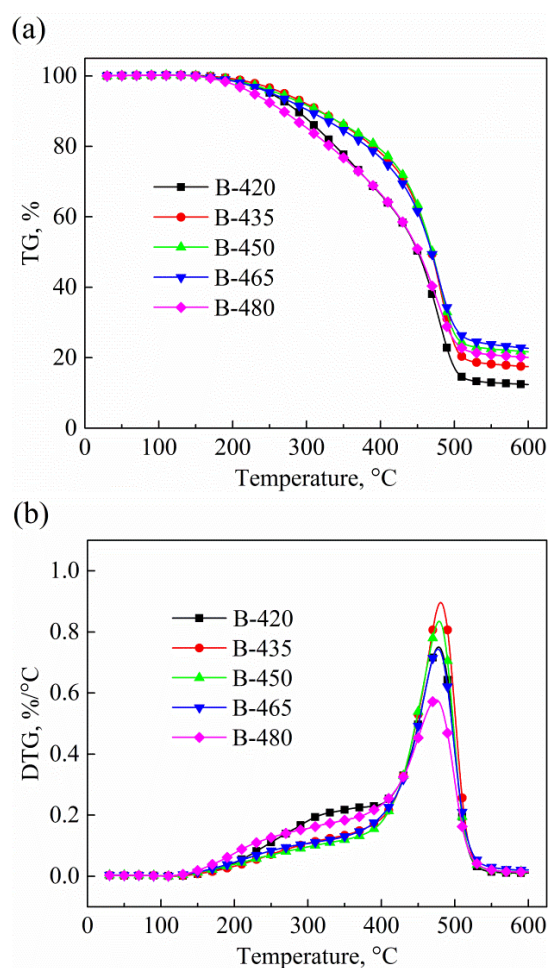


Fig. 5. Thermogravimetric analysis of thermal bitumen samples: (a) TG curves; (b) DTG curves.

pyrolysis of oil shale above 420 °C. The contribution of cracking reactions is negligible in the 150–410 °C range. Once the temperature increases above 410 °C, the mass loss of thermal bitumen intensifies dramatically up to 550 °C. The dominant mass loss occurring in this range is due to the decomposition of heavy components. The rates of mass loss level off above 550 °C, which is attributable to the coking of aromatic compounds. After the TG experiment some carbon residue is left in the ceramic crucible.

The mass loss percentages at 30–410 °C and 410–600 °C represent the contents of light components and heavy components, respectively, while the mass percentage at 600 °C denotes the carbon residue content. Based on the TG curves, the composition of thermal bitumen produced at different temperatures was determined (Fig. 6).

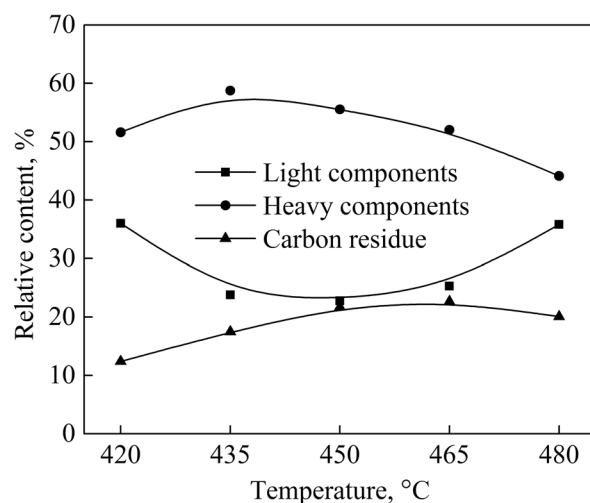


Fig. 6. The composition of thermal bitumen derived at different pyrolysis temperatures.

From Figure 6 it can be seen that the content of light components decreases with temperature increasing from 420 to 450 °C. This outcome is expected as the evaporation of light components results in the selective concentration of heavy components. However, the light components increase in the temperature range of 450–480 °C. The reasonable explanation is that the cracking of large molecules becomes more active above 450 °C, which will transform heavy molecules into light molecules. The formation rate is higher than the evaporation rate, leading to the increase of light components.

4. Conclusions

In this study, the chemical composition and pyrolysis characteristics of thermal bitumen derived from Huadian oil shale pyrolysis were investigated. Based on the results obtained, the following conclusions were drawn:

1. In the temperature range of 360–540 °C, the yield of thermal bitumen first increased and then decreased and reached its maximal value (3.37 wt%) at 450 °C. By comparing the thermal bitumen yield and inherent bitumen content, the depolymerization of kerogen occurred evidently above 390 °C to yield thermal bitumen.
2. With temperature increasing from 420 to 450 °C, the decomposition of oxygen-containing structures (e.g. carboxyl and carbonyl groups) decreased the oxygen content from 4.66 to 0.75 wt%. The cracking of aliphatic compounds and alkyl chains became more intense at 450–480 °C, which resulted in the selective concentration of aromatic compounds and the decrease of H/C ratio from 1.350 to 1.262.
3. The pyrolysis of thermal bitumen could be tentatively divided into two stages – the evaporation of light components and the cracking of heavy components, which corresponded respectively to a shoulder (150–410 °C) and an obvious peak (410–550 °C) in DTG curves.
4. In the temperature range of 420–450 °C, the evaporation of light components decreased their contents. The active cracking of large molecules at 450–480 °C could convert heavy components into light components. The formation rate was higher than the evaporation rate, which increased the content of light components and decreased that of heavy components.

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