STUDY ON THERMAL CONVERSION OF HUADIAN OIL SHALE UNDER N_2 AND CO_2 ATMOSPHERES

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Pyrolysis of Chinese Huadian oil shale using carrier gases N_2 and CO_2 was investigated by TG-FTIR method. The results show that carrier gas does not change weight loss or mechanism of pyrolysis, while decomposition of carbonates in the mineral part can be retarded by CO_2. This regulation was found to be in accordance with kinetic analytical results. The pyrolysis of oil shale in a fixed bed from room temperature to 500 °C at heating rate of 10-20 °C/min was also investigated. Hydrocarbons are the main components in shale oil, and hydrocarbon derivatives concentrate in the number of C_{16}-C_{23} by CO_2 retorting, the chains being longer than those of hydrocarbons obtained by N_2 retorting.

Introduction

China is in severe shortage of petroleum resource and thus the development of other substitute liquid fuels is quite necessary [1]. Oil shale, a solid fuel, can be used for shale oil production by thermal treatment. Shale oil has properties similar to petroleum. The oil shale resource is relatively abundant in China, so oil shale is recognized as an important energy source [2]. Fushun-type retort, a combined process of pyrolysis and gasification, has been the predominant oil shale retort technology for shale oil producing in China for a long time. Investigations on oil shale retorting are necessary to improve the present technology and to develop new ones.

Pyrolysis of oil shale or coal has been widely studied under the N_2 atmosphere, while the research under the CO_2 atmosphere is rather scare. Jamil [3] reported that the yield or the composition of tar from pyrolysis of brown coal in a wire-mesh reactor varies little from the atmosphere of He to CO_2 at heating rate of 0.5–1000 °C/s and holding at 500–900 °C for 0–120 s.

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However, Lee [4] reported that the carbon dioxide atmosphere can increase the oil yield by 7 to 25 percent compared with that under the nitrogen atmosphere. In Masri's study [5], it was also found that retorting of Jordan oil shale under CO_2 gave a slightly higher oil yield of 31.65 gal/ton than the yield of 30.8 gal/ton under N_2, with shorter-chain aliphatic hydrocarbons prevailing. Thermogravimetric analysis used by Jaber and Probert showed that CO_2 as carrier gas led to a slightly greater weight loss during the devolatization period than N_2 [6–8]. The differences in the results may be attributed to the differences in sample properties and experimental conditions.

Thermogravimetric analysis has been widely used to study the pyrolysis or gasification of oil shale. However, pyrolysis and gasification are both complex processes with many parallel reactions, hard to be characterized by a mere weight loss information. TG-FTIR can provide a continuous IR spectrum to monitor the composition of the volatile matter [9]. In this work, TG-FTIR was employed to study the pyrolysis and gasification of Chinese Huadian oil shale under the N_2 and CO_2 atmospheres. Oil shale was pyrolyzed in a fixed bed to get oil and gas products under the N_2 and CO_2 atmospheres, and the products were analyzed to give more detailed information on their compositions.

Experimental

Samples

Oil shale samples were from Huadian district, Jilin province, China. The samples used for TGA remained below 0.28 mm, and those for pyrolysis in fixed bed were 5–10 mm. The results of proximate and ultimate analysis of Huadian oil shale are as follows (%):
proximate analysis:

$$M_{ad} - 3.45, \ V_{ad} - 39.52, \ A_{ad} - 52.65, \ FC_{ad} - 4.39;$$

ultimate analysis:

$$C_{ad} - 29.83, \ H_{ad} - 3.92, \ O_{ad} - 8.62, \ N_{ad} - 0.62, \ S_{ad} - 0.92.$$

Proximate analysis was made according to the National Standard method of China for coal analysis (GB/T 212-2008), ultimate analysis was carried out by the element analyzer (CE440, EAI).

Experimental

In TG analysis, pyrolysis of oil shale from 30 °C to 1200 °C at heating rate of 20 °C/min was carried out by thermogravimetric analyzer (Nietzsche STA449) using carrier gas N_2 or CO_2 at constant flow rate of 80 mL/min. The mass of the sample was around 5 mg.

In TG-FTIR analysis, the volatiles released from the TG oven were transferred to a gas cell in length of 10 cm for simultaneous FTIR analysis

(Bruker Equinox55). The temperature of the gas cell and the transferring line between the TG oven and the gas cell was kept constant at 220 °C.

The fixed bed for pyrolysis is composed of a quartz tube (inner diameter of 22 mm and length of 900 mm) and a quartz basket placed in the middle part of the tube reactor for sample containing. A sample of about 20 g in the basket was put into the tube and heated from room temperature to 500 °C at heating rate of about 10–20 °C/min using carrier gas N_2 or CO_2 at flow rate of 100 ml/min. The liquid was trapped by two conical flasks in an ice-water bath for analysis. The composition of shale oil was analyzed by GC-MS (HP6890/5972).

Results and discussions

TG-DTG analysis

The two TG curves in Fig. 1 represent oil shale pyrolytic behavior under the N_2 and CO_2 atmospheres. The two curves overlap before 500 °C. Thereafter the curve under the CO_2 atmosphere shows a slightly greater loss between 500 °C and 680 °C. The curve under N_2 gives more weight loss between 680 °C and 760 °C. After 760 °C the curve under CO_2 shows a much greater weight loss.
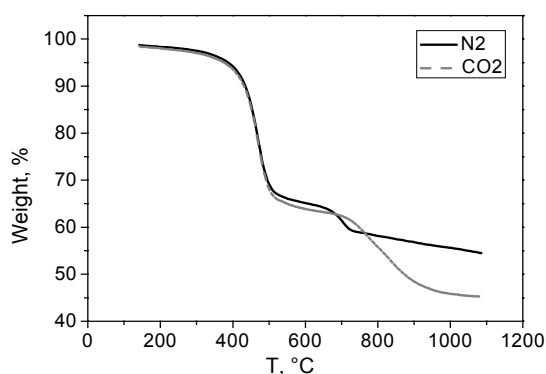

Fig. 1. TG curves of oil shale pyrolysis under N_2 and CO_2.

The stage from 400 °C to 500 °C, where two curves almost overlap, represents pyrolysis of organics. At the stage above 600 °C, a deep decomposition or a gasification of the residue proceeds. The continued weight loss under N_2 above 600 °C can be attributed to decomposition of carbonates in the mineral ash and further pyrolysis of organics forming the residual carbon. Under the CO_2 atmosphere, the residual carbon further reacts with CO_2 forming CO, contributing to a further weight loss.

The widely accepted mechanism of pyrolysis is that kerogen, the insoluble organic matter in oil shale, is converted into soluble bitumen, which further decomposes into oil and gas. It can be described as follows [6–11]:
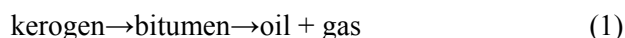
$$kerogen \rightarrow bitumen \rightarrow oil + gas \qquad (1)$$

Figure 2 shows the DTG curves under the N_2 and CO_2 atmospheres. The N_2 curve shows two peaks. In the CO_2 curve, three peaks can be identified. The first peak is overlapped by that of N_2 curve between 400-500 °C. The second peak appears later than the N_2 one, which can both be attributed to decomposition of carbonates in the mineral matter. The later appearance of the second peak can be interpreted by fact that CO_2 may retard the decomposition reaction of the mineral matter. The third peak at 840 °C represents the reaction between the residual carbon and CO_2 [12, 13].
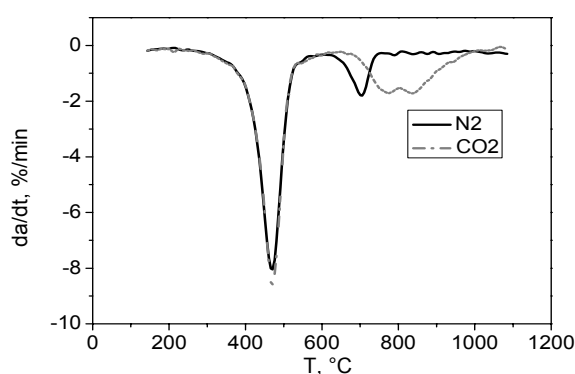

Fig. 2. DTG curves of oil shale pyrolysis under N_2 and CO_2.

FTIR analysis of the pyrolysates

Table 1 shows the band assignments of some species. Figure 3 gives the infrared spectrum of oil shale pyrolysates under the N_2 atmosphere at different times, including gas, water and light oil. In Fig. 3, the highest peak at 2928 cm^{-1}, representing C–H bond, indicates that aliphatic hydrocarbons are the main components in the light oil formed at oil shale pyrolysis. The other distinct peak at the wavenumber of 2355 cm^{-1} indicates that CO_2 is a major component in gaseous products.

Infrared (IR) absorbance of light oil (C-H), CO_2, and CO at different temperature under the N_2 atmosphere is shown in Fig. 4. The figure shows that the generation of light oil starts at 350 °C, reaches the maximum at 470 °C, and generally ends at 530 °C. The IR curve of light oil is in accordance with that of the DTG curve before 600 °C as shown in Fig. 2.

Table 1. **Infrared absorption band assignment for pyrolysates of oil shale**

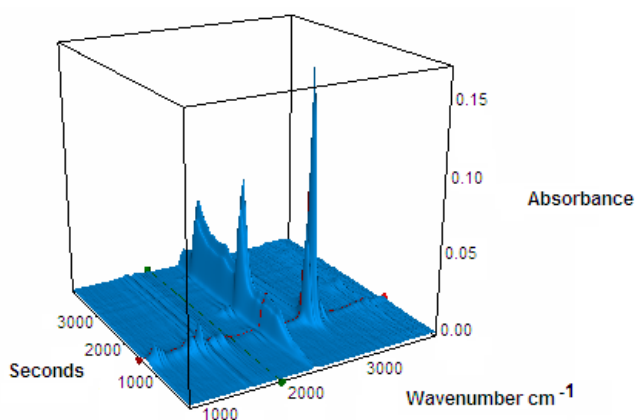| wavenumber, cm^{-1}	assignment of functional groups
2928	aliphatic hydrocarbon (C-H)
2355	CO_2
2187	CO

Fig. 3. Infrared spectra of the pyrolysates of oil shale under N_2.

It indicates that C-H compounds are the major products. The release of CO_2 starts at 200 °C and proceeds at a constant rate till 600 °C. The CO_2 peak in the IR curve is in accordance with the second peak in DTG curve, indicating that the weight loss above 600 °C can be attributed to decomposition of carbonates in the mineral ash.
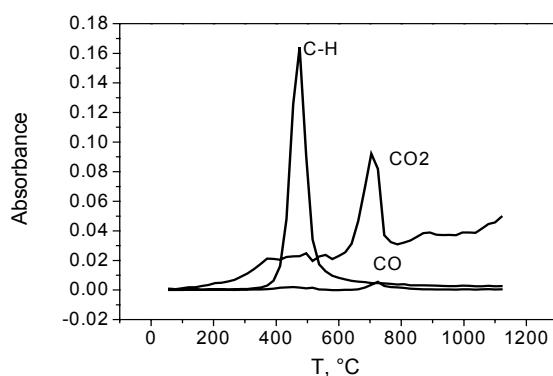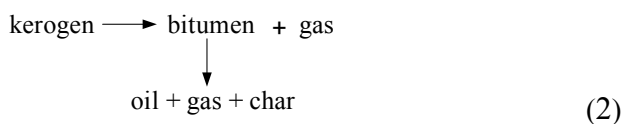

Fig. 4. Infrared absorbance of some main components at different temperatures under the N_2 atmosphere.

So we proposed that the traditional pyrolysis mechanism of the oil shale (Eq. 1) can be described in more detail as follows:

$$kerogen \longrightarrow bitumen + gas$$
$$\downarrow$$
$$oil + gas + char \tag{2}$$

Gas can be generated at the early stage of pyrolysis. In this stage kerogen is converted to bitumen; when above 350 °C, the bitumen further decomposes to more oil, gas, and char.

CO, compared to CO_2, does not contribute much to the gas composition. The first peak in the CO curve weakly appears at about 450 °C, when the oil is mainly released. The second peak appears at about 720 °C, when CO_2 is largely produced, indicating a weak reaction between CO_2 and the carbon residue.

Figures 5 and 6 represent the IR spectra of volatiles obtained at pyrolysis of oil shale under the CO_2 atmosphere. The light oil (C-H) profile shows a tall and narrow peak, like that under the N_2 atmosphere. The profile of CO shows a more distinct and wider peak than the profile of CO under N_2. This wide peak between about 700 °C and 1000 °C is in accordance with the third peak in DTG curve as shown in Fig. 2, representing the gasification reaction between the residual carbon and CO_2.
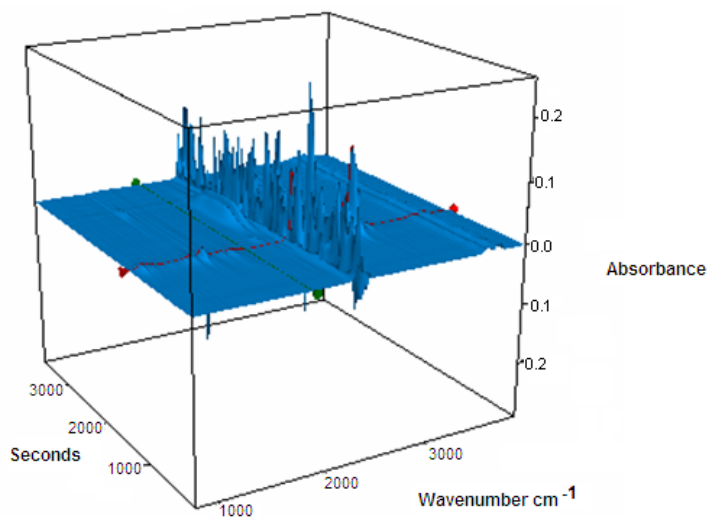

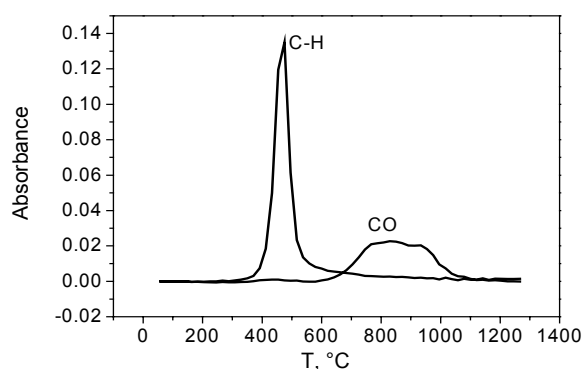*Fig. 5*. Infrared spectra of the pyrolysates of oil shale under CO_2.

Fig. 6. Infrared absorbance of some main components at different temperatures under the CO_2 atmosphere.

Kinetic analysis

Based on the thermogravimetric analytical results, kinetic analysis was carried out to make a comparison between the N_2 and CO_2 atmospheres. Herein, the Doyle first-order simplified integral formula model was used to describe the kinetic behavior:

$$-\ln(1-\alpha) = \frac{AE}{\beta R} e^{-53308 - 1.0516E/RT}.$$ (3)

Eq. (3) can be transformed into the form of Eq. (4), and the kinetic parameters can be obtained by linear regression of Eq. (4).

$$Y = a + bX,$$ (4)

where:

$$Y = -\ln(-\ln(1-\alpha))$$ (5)

$$a = -\ln\frac{AE}{\beta R} + 53308,$$ (6)

$$b = 1.0516\frac{E}{R},$$ (7)

and

$$X = \frac{1}{T}$$ (8)

E – activation energy (kJ/mol); A – pre-exponential factor (s^{-1}); T – temperature (K); β – heating rate (K/min); α – conversion (%).

Figure 7 illustrates the variation of Y with X under the N_2 and CO_2 atmospheres. It can be seen from Fig. 7 that the whole process is hard to be
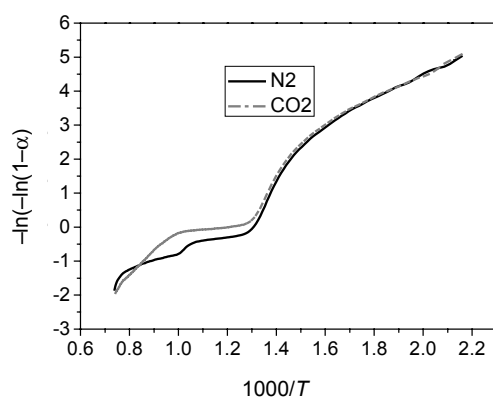

Fig. 7. Variation of $-\ln(-\ln(1-\alpha))$ with $1/T$ under N_2 and CO_2 atmospheres.

regressed by a single line, since different periods have different thermal characteristics, so a temperature region is necessary. The whole process is divided into three main stages, and each stage is described by the Doyle first-order model. The kinetic parameters are listed in Table 2.

Table 2. **Kinetic parameters under N_2 and CO_2 atmospheres**

	Temperature range, °C	E_a, kJ/mol	A, s^{-1}	Correlation coefficient
N_2	390–520	189.6	2.554×10^{14}	0.9934
	600–735	273.1	5.898×10^{15}	0.9930
	735–1000	151.0	4.946×10^{7}	0.9765
CO_2	390–520	189.8	2.588×10^{14}	0.9934
	665–800	313.4	6.806×10^{16}	0.9928
	800–1000	210.6	2.133×10^{10}	0.9601

It can be seen from Table 2 that in the temperature range 390–520 °C, representing the main pyrolysis of oil shale, there is almost no difference in the activation energy value (E_a) between N_2 and CO_2 atmospheres, which indicates the similarity of pyrolytic behavior under the two atmospheres as shown before. The linear regression region, mainly representing decomposition of mineral carbonates mixed with further pyrolysis of organics under the CO_2 atmosphere appears in 665–800 °C, obviously over the range of 600–735 °C under the N_2 atmosphere, which proves the retarding effect of CO_2 on decomposition of carbonates. In fact, the conversion above 700 °C is very complex, different thermal conversions proceed simultaneously, and thus no certain range can be nominated as a pure converting stage, and accordingly the correlation coefficient declines in some degree. Generally, the occurrence of the gasification reaction under the CO_2 atmosphere makes the activation energy value higher than that under the N_2 atmosphere.

Pyrolysis of oil shale under the N_2 and CO_2 atmospheres in a fixed bed

Oil shale was pyrolyzed in a fixed bed under the N_2 and CO_2 atmospheres from room temperature to 500 °C at heating rate of 10–20 °C/min. The obtained shale oil was collected for qualitative analysis by GC-MS. The total ion chromatograms (TIC) of the two shale oils are shown in Figures 8 and 9. Distinct differences can be identified when comparing the two figures. The shale oil under either of N_2 or CO_2 atmosphere is rich in hydrocarbons. Comparatively, the generated hydrocarbon derivatives by CO_2 retorting mainly concentrate in the carbon number of C_{16}-C_{23}, the chains being longer than those of hydrocarbons obtained under the N_2 atmosphere. This composition difference may be attributed to a second further pyrolysis of shale oil formed firstly. The condition in the fixed bed is far different from that in the thermogravimetric analyzer, *i.e.* the retention time of the volatiles in the fixed bed is much longer than that in the analyzer. It seems that CO_2 can retard the release of some oxygen-containing groups from the organics and thereby further retards the cracking of the longer-chain hydrocarbon derivatives.
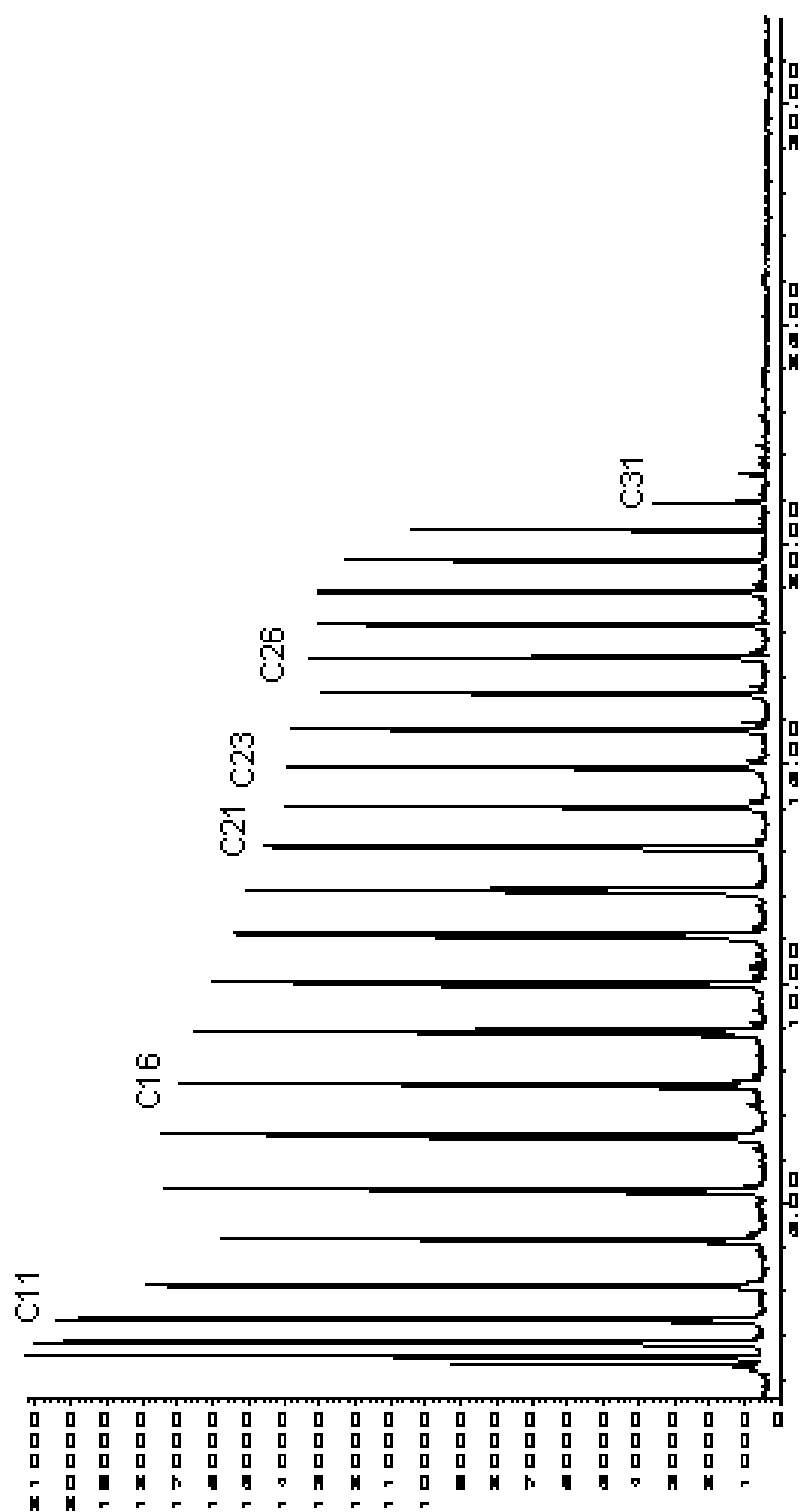
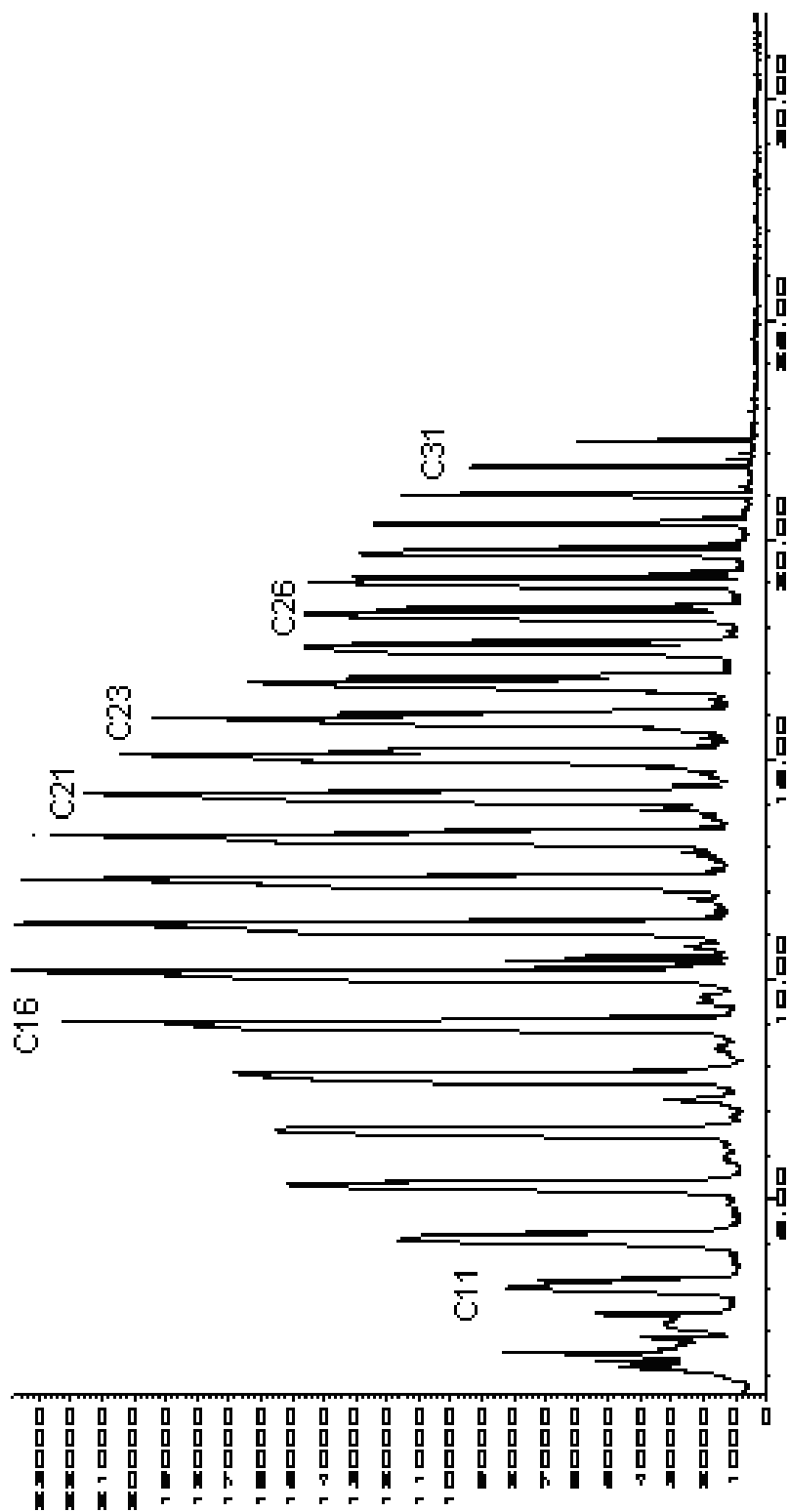*Fig. 8.* TIC of the shale oil obtained by N₂ retorting.

Fig. 9. TIC of the shale oil obtained by CO_2 retorting.

Conclusions

1. Pyrolysis of Chinese Huadian oil shale from 30 °C to 1200 °C at heating rate 20 °C/min under carrier gas N_2 or CO_2 were investigated by thermo-balance coupled with FTIR (TG-FTIR). The results show that different carrier gases do not change weight loss or pyrolysis mechanism at lower temperatures, while decomposition of carbonates in the minerals can be retarded by CO_2, and a gasification reaction occurs between CO_2 and residual carbon at higher temperatures.
2. The results of kinetic analysis show a quite similar value of pyrolysis activation energy under both N_2 and CO_2 atmospheres and illustrate an obvious delay in decomposition of mineral carbonates and a higher activation energy value above 800 °C due to the occurrence of gasification process under the CO_2 atmosphere.
3. Pyrolysis of oil shale in a fixed bed was investigated. The results show that up to 500 °C at heating rate of 10–20 °C/min, hydrocarbons are the main components in shale oil, and they concentrate in the number of C_{16}-C_{23} by CO_2 retorting, the chains being longer than those of the hydrocarbons obtained by N_2 retorting.

Acknowledgments

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