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INFLUENCE OF RETORTING CONDITIONS ON THE PYROLYSIS OF YAOJIE OIL SHALE

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Abstract. *Factors influencing the pyrolysis of Yaojie oil shale, such as pyrolysis temperature, residence time, heating rate and particle size, were investigated. Pyrolysate yield was influenced most of all by pyrolysis temperature and residence time, followed by heating rate and particle size. Pyrolysis temperature and residence time had a great effect on the composition of retorting gas, while the influence of heating rate and particle size was less significant, corresponding to a change of oil yield of only 0.6% and 0.5%, respectively. The oil and gas yields were less affected when the oil shale sample was pressed into balls. The oil shale ball with a bentonite content of 6% was optimal.*

Keywords: *oil shale, pyrolysis, influential factors, oil shale ball.*

1. Introduction

Several factors are considered to influence the process of oil shale pyrolysis, including categories and contents of minerals, properties of oil shale, heating rate, pyrolysis temperature, particle size and heating time [1]. While the effect of properties of oil shale and content and categories of minerals is generally low, other influences are investigated in the experiments. Several researches about influential factors of oil shale pyrolysis have been reported [2–5].

Pyrolysis temperature and residence time are two key factors affecting the retorting process and pyrolysates yield [6]. Wang and Liang [7] studied the influence of pyrolysis temperature on Huadian oil shale retorting. The yield of shale oil was maximal when the pyrolysis temperature reached 530 °C. When the temperature was higher than 530 °C, the yield of shale oil

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decreased, while the contents of H_2, CO, CO_2 and CH_4 in the retorting gas increased. Sun [8] evaluated characteristics of pyrolysis of Fushun oil shale. It was found that organics started to undergo pyrolysis at 400 °C. Much bound water and CO_2 were released at 500–550 °C for Fushun oil shale. Williams and Ahmad [9] observed that the optimal pyrolysis temperature was 500 °C. Han et al. [10] studied the pyrolysis of Huadian oil shale, showing that the yield of shale oil could be increased to 80% when prolonging the residence time to 69 min at 430 °C. However, increasing pyrolysis temperature was more efficient than prolonging residence time, to improve the yield of shale oil.

Heating rate is also one of the dominating influential factors for oil shale pyrolysis, besides pyrolysis temperature and residence time. Nazzal [4] showed that the yield of shale oil was enhanced with increasing heating rate in the range of 2–10 °C/min. The yield of shale oil decreased slightly at the heating rate of 30 °C/min. Li et al. [11] found that the initial and final pyrolysis temperature both rose when heating rate was enhanced. Al-Harahsheh et al. [12] discovered that the percentage of saturated hydrocarbons increased when increasing heating rate in the range of 0.2–6 °C/min.

Particle size plays a significant role in the pyrolysis process, too. Now all the companies in China use Fushun or modified Fushun retort with raw materials of 6–75 mm in particle size. Many researchers [13–15] demonstrated that the yield of shale oil increased with increasing particle size within the above limits. Nazzal [13] indicated that the more intensive production of retorting gas reduced enlarging the particle size of oil shale. In conclusion, enlarging the particle size of oil shale within the above limits, the yield of shale oil increased. For oil shales from different areas, the composition of retorting gas was different.

In this article, the oil shale sample from Yaojie of Gansu province was pyrolyzed in an aluminum or iron retort to investigate influential factors, such as pyrolysis temperature, heating rate, residence time and particle size. The composition of retorting gas was analyzed with an Agilent-6890 gas chromatograph.

2. Experimental

2.1. Materials

The investigated oil shale sample was from Yaojie mine in Gansu province of northwest China.

2.2. Pyrolysis reactors and experimental conditions

50 g of oil shale sample was heated in Fischer Assay when the final pyrolysis temperature was lower than 525 °C. Fischer Assay was carried out according to SH/T 0508-92. A steel retort similar to an aluminum one was used when the final temperature was higher than 525 °C.

The diameter of sample particles was limited to 0.2–3 mm when investigating the influence of pyrolysis temperature, residence time and heating rate. Sample particles with a diameter of 6–13 mm, 13–20 mm, 20–40 mm and 40–60 mm were used to analyze the effect of particle size. Different heating procedures were used to investigate the effect of different factors.

2.2.1. The heating procedure for pyrolysis temperature

The oil shale sample was first heated from room temperature to 350 °C within half an hour and then from 350 °C to the final temperatures of 375 °C, 400 °C, 425 °C, 450 °C, 475 °C, 500 °C, 525 °C and 550 °C at the heating rate of 2 °C/min. Each final temperature was held for 30 min. The heating procedure for the final temperature of 525 °C was taken as an example (see Table 1).

Table 1. The heating procedure for the final pyrolysis temperature of 525 °C

Heating time, min	Temperature, °C	Heating time, min	Temperature, °C
0	RT 10	25	450
10	150	25	500
10	250	12.5	525
10	350	30	CT 525
25	400		

RT – room temperature; CT – constant temperature.

2.2.2. The heating procedure for residence time

The oil shale sample was heated to 525 °C as indicated in Table 1 and was held at the final temperature for 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 min.

2.2.3. The heating procedure for heating rate

The oil shale sample was first heated from room temperature to 350 °C within half an hour, and then from 350 °C to 525 °C at the heating rate of 2 °C/min, 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, and was held at 525 °C for 30 min.

2.2.4. The heating procedure for particle size

The oil shale sample with different particle sizes was heated to 525 °C according to Table 1.

2.3. Retorting gas analysis

During the whole experiment the gas was collected using gas bags. The composition of retorting gas was analyzed with an Agilent-6890 gas chromatograph equipped with four valves and five columns. The oven temperature was maintained at 50 °C for 3 min, and then increased to 100 °C at 5 °C/min. The temperature continued increasing to 180 °C at the heating rate of 10 °C/min and was held at 180 °C for 3 min. The injection temperature was 25 °C and detector temperature was 250 °C.

2.4. Oil shale balls

2 kg oil shale particles were weighted. Some amount of bentonite was mixed with oil shale and the mixture was further mixed using some water. 10 minutes later the mixture was poured into the balls forming machine. So, 38 mm × 29 mm oil shale balls were obtained (Fig. 1).

Three different compositions of balls were obtained. The mass ratios of ingredients are shown in Table 2.

Fig. 1. Oil shale balls.

Table 2. Mass ratio of ingredients of oil shale balls

Sample	Bentonite, %	Water, %	Oil shale, %
2%	2	5	93
4%	4	8	88
6%	6	7.5	86.5

3. Results and discussion

3.1. Basic properties of Yaojie oil shale

Table 3 indicates that the yield of shale oil was more than 10% and that of retorting gas was about 3.4%.

Table 3. Standard retorting analysis of Yaojie oil shale

Oil, %	Moisture, %	Total water, %	Semicoke, %	Gas, %
10.47	1.00	2.58	83.55	3.40

3.2. Influential factors of retorting

3.2.1. Influence of pyrolysis temperature

Figure 2 shows the yields of oil, gas and water produced from Yaojie oil shale at the pyrolysis temperatures from 350 °C to 550 °C. The oil yield increased with increasing temperature and attained a maximum at 525 °C, while the maximal oil yield from Huadian oil shale was obtained at the pyrolysis temperature of 530 °C. When the temperature was higher than 530 °C, the yield of shale oil decreased [7]. The rate of decomposition was high at the temperatures between 400 °C and 525 °C, indicating degradation of much organics. When studying Lucogou oil shale, Tao et al. [16] reported that the hydrocarbon compound contents in retorting gas increased rapidly at 450–510 °C. The oil yield did not change significantly at the temperatures between 525 °C and 550 °C, indicating the end of conversion of high-molecular organic compounds to oil. The yield of retorting gas always increased from 350 °C to 550 °C, which was due to the desorption of

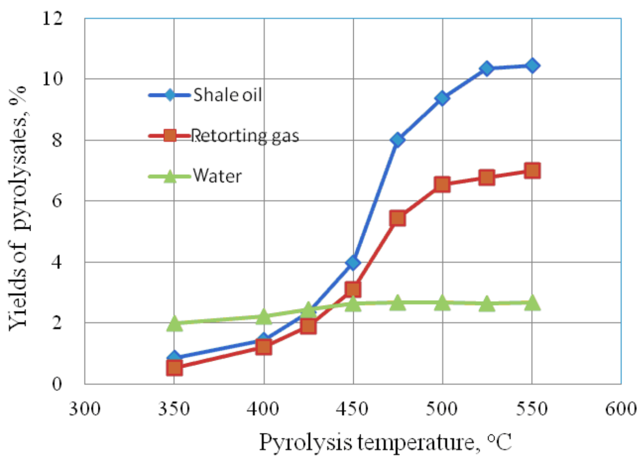

Fig. 2. Yields of pyrolysates at different pyrolysis temperatures.

adsorbed gas on the surface and in the micropores of oil shale sample, as well as to decarboxylation and decomposition of carbonate and organic compounds. Originating mainly from the aromatization and condensation of organic matter in spent shale, the content of H_2 was increased gradually.

As seen from Figure 3, the pyrolysis temperature was from 400 °C to 500 °C. Some gas can be collected in gas bags below 400 °C and above 500 °C. Figure 3 demonstrates that the content of CH compounds first increased with increasing temperature. The content of CH compounds, from the cracking of macromolecules, or some side chains, was maximized at 475 °C. The reason is that the organics in oil shale were greatly decomposed. When the temperature was higher than 475 °C, the rate of increase of other gases content was higher than that of CH compounds, leading to a decrease in the content of the latter. When the temperature continued rising, the content of CO_2 sourced mainly from decarboxylation of organics in the temperature range of 400–450 °C decreased. At the same time, the content of H_2 generated from condensation and aromatization reactions progressively increased with increasing temperature. The content of CO changed little.

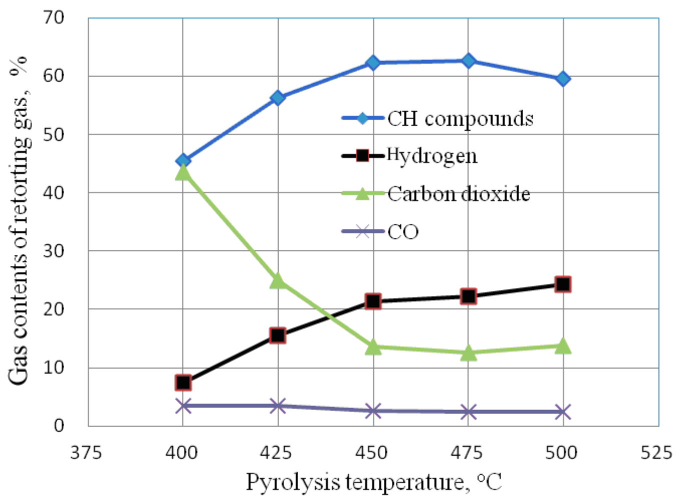

Fig. 3. The composition of retorting gas at different pyrolysis temperatures.

3.2.2. Influence of residence time

The degree of decomposition of organic matter in oil shale depends not only on pyrolysis temperature, but also on residence time. At the lower pyrolysis temperature, the yield of shale oil increases with extending residence time. When the heating temperature was increased, the time necessary for decomposition of organics was shortened. The influence of residence time on the yield of pyrolysates and gas compounds contents of retorting gas is shown in Figures 4 and 5, respectively.

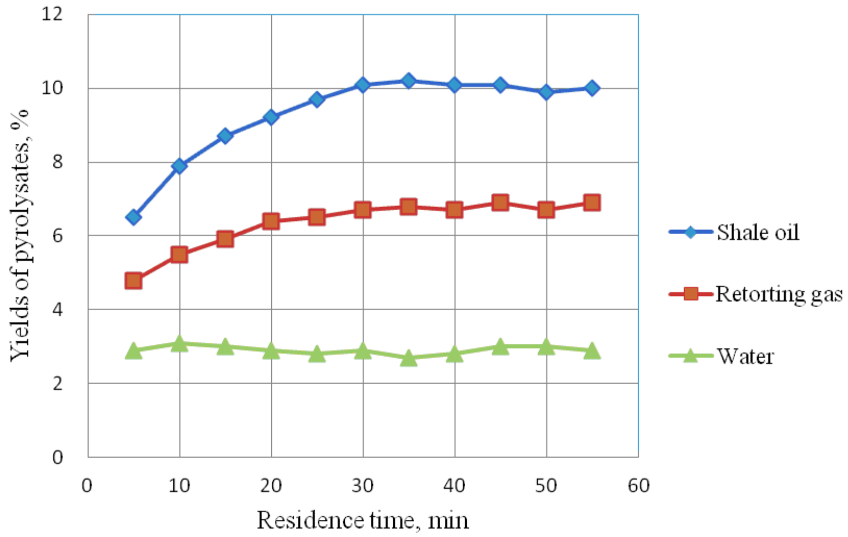

Fig. 4. Influence of residence time on pyrolysates yield.

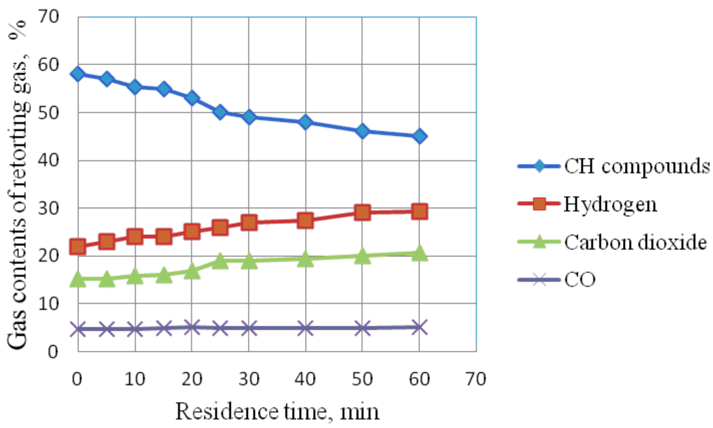

Fig. 5. Influence of residence time on the composition of retorting gas.

Figure 4 demonstrates that the yield of shale oil increased more quickly within the first 30 minutes. From the 30th minute onwards, the yield of shale oil changed insignificantly, in the range of 9.8–10.2%, indicating that the suitable pyrolysis time was 30–35 min. However, the oil yield of Huadian oil shale could be increased to 80% when prolonging the residence time to 69 min at 430 °C [7]. The yield of retorting gas rose when the residence time was prolonged. Due to the simultaneous generation of retorting gas and shale oil, the changes in the respective yields showed similar trends within the first 30 minutes. The condensation and aromatization reactions took place all the time, the retorting gas yield continued increasing from the 30th minute onwards. Water yield did not change significantly when the residence time was prolonged. All in all, the residence time of 30–35 min was reasonable.

Figure 5 demonstrates that with prolonging residence time, the percentage of CH compounds decreased significantly. The increase of H_2 content indicated that condensation and aromatization of organics took place all the time. The content of CO did not change much, implying that decarboxylation was in progress.

3.2.3. Influence of heating rate

The changes of pyrolysate yields and gas contents of retorting gas are illustrated in Figures 6 and 7, respectively.

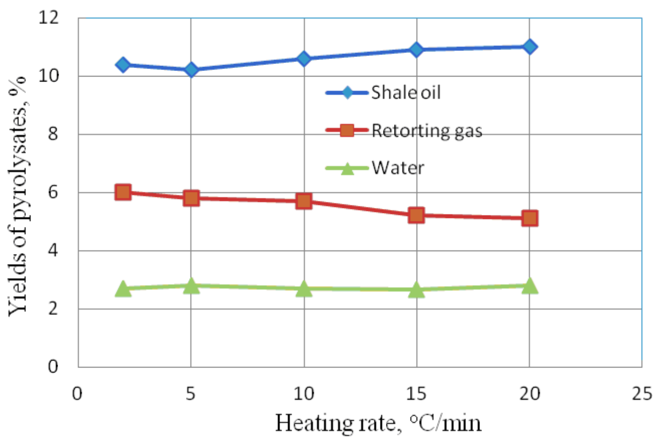

Fig. 6. Influence of heating rate on pyrolysates yield.

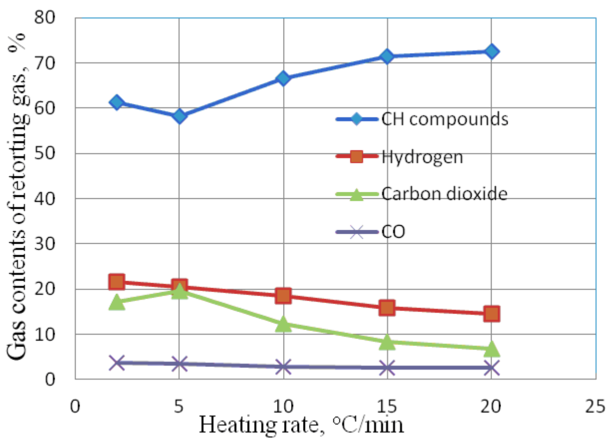

Fig. 7. Influence of heating rate on the composition of retorting gas.

Figure 6 shows the influence of heating rate on the yields of pyrolysates. The influence of heating rate on the yield of shale oil was low, corresponding to oil yield in the range of 10.4–11%. Oil yield decreased at first and then increased; the decrease may result from the aeolotropism of oil shale. This oil yield-heating rate relationship was similar to that established by Al-Ayed et al. [17]. Under similar operating conditions, i.e. the same reactor, pressure and operations, with increasing heating rate, the decomposition rate of organics was accelerated and reaction time shortened. So the cracking and coking reactions of shale oil became less intensive and oil yield was increased. The experiments were carried out in Fischer Assay retorts. However, there are four reasons which may make applying high heating rate in the actual production process difficult. Firstly, it would be difficult to control pyrolysis reactions of organics. Secondly, coking would occur in some phase of the retort and, at the same time, the temperature would not be high enough for pyrolysis in other phases. Thirdly, when the heating rate is too high and oil and gas yields high, there may be difficulties in condensing oil and gas. Finally, the temperature of the retort would be difficult to control. Considering the above, the heating rate of 2–5 ^{o}C/min was suggested to be applied in practice.

From Figure 7 it is obvious that the percentage of CH compounds increased with rising heating rate. The slight decline in the CH compounds curve may result from the anisotropism of oil shale samples. High heating rate shortened the heating time from room temperature to final temperature and suppressed the condensation and aromatization of organic matter, so the contents of H_2 and CO_2 were both decreased. The trend of H_2 percentage change with heating time is consistent with the results obtained by Campbell et al. [18]. The rate of generating of CH compounds was lower than that of H_2 and CO_2, leading to an increase in the content of CH compounds.

3.2.4. Influence of oil shale particle size

The influence of oil shale particle size on pyrolysates yield and composition of retorting gas is shown in Figures 8 and 9, respectively.

It is obvious from Figure 8 that the yield of shale oil was decreased slowly with increasing particle size. The possible reasons can be summed up as follows. Firstly, mass transfer and heat transfer by oil shale of larger particle size influenced the process. Secondly, the route of diffusion of shale oil from the inside to the exterior of oil shale sample was extended and the second cracking of shale oil became more difficult. Finally, organics were not completely pyrolyzed due to the poor heat conductivity of oil shale of larger particle size. The influence of particle size on the yield of shale oil was low, corresponding to oil yield in the range of 10–10.5%. Gas yield increased with enlarging particle size.

From Figure 9 it can be seen that the content of CH compounds rose with increasing particle size of oil shale. When the particle was larger, the route of diffusion of oil and gas from the inside to the exterior of oil shale sample

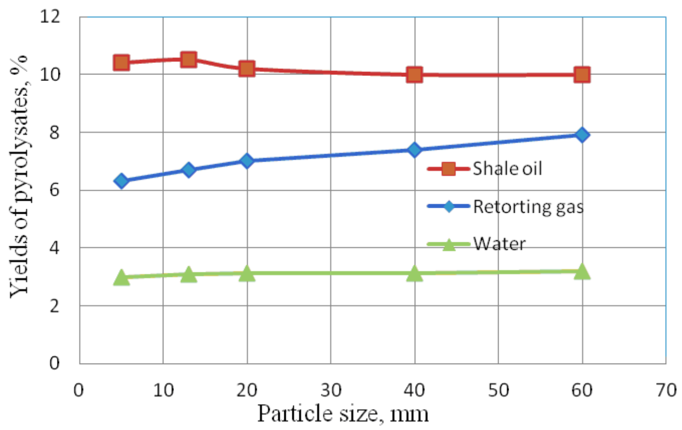

Fig. 8. Influence of particle size on pyrolysates yield.

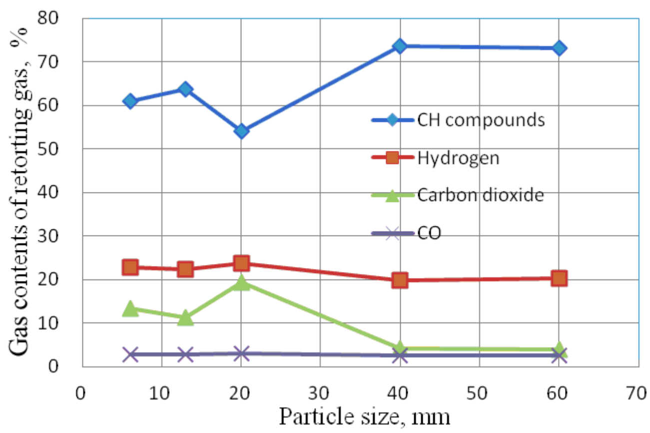

Fig. 9. Influence of particle size on the composition of retorting gas.

was extended and, at the same time, the second cracking of shale oil became more difficult. The percentage of CO_2 and H_2 in retorting gas was decreased. The reason was that due to the great difference in temperature between the exterior and inside of oil shale sample, the condensation and aromatorization reactions, as well as decomposition of some minerals with carbanion were suppressed. The content of CO was less affected by particle size.

3.2.5. Oil shale balls

Table 4 shows that the oil contents of oil shale ball and particle are quite similar. It can be concluded that the oil and gas yields were less affected when the oil shale sample was pressed into balls. It is known that in the Fushun retort, oil shale with a particle size larger than 10 mm can be retorted, but in the experiments the size of almost half the oil shale particles was less than 10 mm. So, oil shale with small particle size should first be pressed into balls and then the balls can be retorted in the Fushun retort.

Figure 10 demonstrates that the strength of shale balls was first increased and then decreased with increasing temperature, according to the percentage of complete for oil shale ball. The strength of a 6% oil shale ball is the highest. So, the oil shale ball with a bentonite content of 6% is optimal, its strength being similar to Fushun oil shale.

Table 4. Fisher Assay results for Yaojie oil shale particles and shale balls

Sample	Oil, %	Water, %	Gas, %
Oil shale particle	12.23	2.84	3.74
Oil shale ball	12.06	2.94	3.85

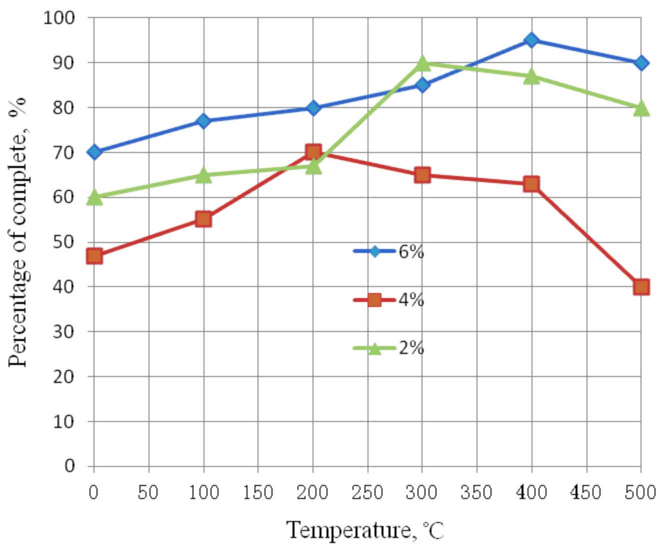

Fig. 10. The strength of shale balls at different temperatures when made fall from the height of 2 m.

4. Conclusions

1. Pyrolysis temperature and residence time were the most important factors influencing retorting process, while the effects of heating rate and particle size were less significant, corresponding to a change of oil yield of only 0.6% and 0.5%, respectively.
2. With increasing temperature, the oil yield of Yaojie oil shale was maximal at 525 °C. The yield of retorting gas increased all the time, while that of water did not change much. Higher pyrolysis temperature

led to an increase in CH compounds and H_2 contents, a decrease in that of CO_2 and a small change of CO content.

3. Residence time had a great influence on the yield of pyrolysates of Yaojie oil shale. The yield of shale oil first increased and then remained unchanged, indicating that the reasonable pyrolysis time is 30–35 min. However, increasing pyrolysis temperature was more efficient than prolonging residence time, to improve the yield of shale oil. When prolonging the residence time for Yaojie oil shale, the yield of retorting gas was increased and that of water did not change much. The percentage of CH compounds in the retorting gas was decreased, content of H_2 increased and that of CO remained unchanged.
4. The influence of heating rate on the yield of shale oil was low, corresponding to oil yield in the range of 10.4–11%. With the acceleration of heating rate, the oil yield somewhat increased, while the gas yield decreased slightly. The percentage of CH compounds increased with rising heating rate, while the contents of both H_2 and CO_2 were decreased.
5. Compared to other influential factors, the influence of particle size was slighter. Its influence on the yield of shale oil was low, corresponding to oil yield in the range of 10–10.5%. When enlarging particle size, the content of CH compounds in the retorting gas rose and the percentage of CO_2 and H_2 decreased, besides the minor change of CO content.
6. The oil and retorting gas yields were less affected when oil shale was pressed into balls. The oil shale ball with a bentonite content of 6% was found to be optimal.

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