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Effects of retorting factors on combustion properties of shale char

Part 4. Combustion characteristics

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Abstract For obtaining high shale oil yield as well as treating shale char efficiently and in an environmentally friendly way in a new comprehensive utilization system of oil shale, a series of fundamental experiments have been conducted for exploring the effects of retorting factors on shale oil yield and shale char characteristics. Based on these previous studies, in this article, combustion experiments of shale chars obtained under various retorting conditions were performed with a Q5000IR thermogravimetric analyzer and a Leitz II-A heatable stage microscope and the effects of retorting factors were discussed on the combustion characteristics of shale char. Among four studied retorting parameters, retorting temperature and residence time exert very significant influence on the combustion characteristics of shale char. Either elevating the retorting temperature from 430 to 520 °C or lengthening the residence time at a low retorting temperature will largely decrease residual organic matters within shale char, resulting in decreasing mass loss in the low-temperature stage of combustion process of shale char, an elevation of ignition temperature and a shift of ignition mechanism from homogeneous to heterogeneous. One set of retorting condition was also recommended as a reference for designing the comprehensive utilization system of oil shale studied in this work: retort temperature of 460–490 °C, residence time of 20–40 min, particle size of <3 mm, and low heating rate of <10 °C/min.

Keywords Oil shale · Shale char · Retorting factors · Combustion characteristics

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Introduction

Oil shale, a fine-grained sedimentary material with organic matter called kerogen, is rich and widespread in the world. According to the current data reported by Qian et al. [1], shale oil (converted from the in situ oil shale) accounts for about 400 billion tons, higher than that of crude oil (more than 300 billion tons). The uncertainty of petroleum prices, its growing worldwide consumption and limited availability have motivated more countries rich in oil shale resources to investigate means to produce and use shale oil as an alternative. Currently, total annual production of shale oil in the world accounts not more than one million tons, and it is predicted that till 2015, it may reach 3.5 million tons [1].

Shale char, formed in retort furnaces of oil shale, is a source of severe environmental pollution and is classified as a dangerous waste, containing several toxic compounds [2]. Provided that oil shale is to be exploited and retorted largely, it will become a serious issue how to treat shale char efficiently and in an environmentally friendly way. Some studies [3–5] have shown that shale char may be fired in circulating fluidized bed (CFB) furnaces, due to its fixed carbon and residual organics. Thus, a new comprehensive utilization system of oil shale was recently proposed for shale oil production, electricity generation, oil shale ash utilization, economical efficiency, and environmental protection [6, 7]. Compared with conventional retorting and burning technologies of oil shale, this comprehensive utilization technology has many advantages, for example: (1) higher utilization efficiency of oil shale resources; (2) diversified products, such as shale oil, fuel gas and electricity; (3) lower pollutants emission; and (4) successive use of the waste from one process as the input to another, which can decrease mass loss and energy loss. For obtaining shale oil with a high yield as well as treating shale char efficiently in this system of oil shale, a series of fundamental experiments have been conducted for systemically studying the effects of retorting factors on shale oil yield and shale char characteristics. Retorting experiments of oil shale were performed with an aluminum retort at low retorting temperatures ranging from 400 to 520 °C [8], showing that an increase in the retorting temperature, the residence time, and the heating time has positive significant effect on improving the yield of shale oil, and a middle particle size is helpful for increasing the oil yield as well [8]. The shale chars obtained in the retorting experiments were applied to the subsequent work [9–11] to explore the effects of retorting factors on the characteristics of shale char. The pyrolysis history of shale chars formed by retorting different oil shales at a retort temperature of 520 °C is very similar below the pyrolysis temperature of 660 °C, and above 660 °C there exist different mass losses attributing to large decomposition of carbonates and organic matters containing amide group. Either increasing retort temperature from 430 to 460 °C or prolonging residence time at a retort temperature of 430 °C can obviously decrease mass loss of shale char in the low-temperature stage of pyrolysis and, however, have little influence on the pyrolysis history of all the samples including oil shale in the high-temperature stage. Particle size and heating rate show little effect on the pyrolysis of shale char. Organic matters within shale chars were extracted and identified using a gas chromatography/mass spectrometry (GC/MS) method [10]. As a result, a retorting condition with a retorting temperature of 460–490 °C, residence time of <40 min, and a middle particle size was recommended for both keeping nitrogenous organic matters and aromatic hydrocarbons in shale char and improving the yield and quality of shale oil. In the reference [11], it was found that elevating retorting temperature can largely increase the pore volume and specific surface area of shale char. However, at higher retorting temperatures, the cracking and carbonization of residual organic matters within shale char become more intensive. Subsequently, the pores are easily blocked (especially micropores), and the specific surface area of char particles decreases slightly. In terms of the residence time of retorting at a temperature of 430 °C, increasing the residence time of retorting causes the pore structure parameters of shale char to undergo a complex change due to the resolidification and decomposition of organic matter. Particle size and low heating rate show a little effect on the surface area and pore volume of shale char. These studies mentioned above have laid an important experimental foundation for further studies of combustion characteristics of shale chars.

Thermogravimetric (TG) analysis has extensively been used as an effective means of studying combustion and pyrolysis characteristics of oil shale [12–18]. Although extrapolation to other devices at larger scale cannot be performed directly, thermogravimetric analysis is very useful from a fundamental viewpoint, and for comparison between samples [19–21]. Non-isothermal thermogravimetric experiments can be used not only for providing information about the combustion process itself but also as a fast and simple ranking method of solid fuels with respect to their reactivity. Thus, it can be said that thermogravimetric analysis gives relevant information about combustion, not in absolute terms (i.e., temperature values) but in giving reliable combustion trends. For optimizing the comprehensive utilization system of oil shale and developing a new industrial CFB boiler with shale char as fuel, combustion characteristics of shale chars obtained under different retorting conditions were studied with a Q5000IR thermogravimetric analyzer and a Leitz II-A heatable stage microscope in this article. In another article, combustion characteristics of a lab-scale CFB of shale char will be described in detail.

Experimental

Samples

A representative oil shale sample used in this work was obtained from Dachengzi mine located in Huadian city, China. Its analytical data are given in Table 1. According to the national standards of China, the samples were ground as received, sieved to the desired mesh, and dried at 45–50 °C to constant weight, and then stored in a desiccator for use.

An experimental retorting system of oil shale was constructed for preparing shale chars under retorting conditions, about which the reference [8] has given a detailed description. Table 2 gives the proximate analysis of shale chars obtained under different retorting conditions.

Ignition experiments

Ignition phenomenon of oil shale and its shale chars was observed and photographed using a Leitz II-A heatable stage microscope with high definition video camera. The experimental conditions were: (1) sample mass of ~28 mg;

Table 1 Proximate and ultimate analysis of Dachengzi oil shales

Proximate analysis[a]		Ultimate analysis[a]/mass%	
Moisture/mass%	11.54	C	27.33
Volatile matter/mass%	36.21	H	3.59
Ash/mass%	48.24	O[b]	7.89
Fixed carbon/mass%	4.01	N	0.57
Net calorific value/kJ kg^{-1}	11076.07	S	0.84

[a] As received basis; [b] O content was calculated by difference

Table 2 Proximate analysis of shale chars obtained under different retorting conditions

Shale char	Retorting conditions				Proximate analysis/mass%			
	Particle size/mm	Average heating rates/°C min^{-1}	Residence time/min	Retorting temperature/°C	Moisture	Ash	Volatile matter	Fixed carbon
1#	<0.60	7.33	6	430	0.82	59.02	33.48	6.68
2#	<0.60	7.33	20	430	0.89	62.71	27.78	8.61
3#	<0.60	7.33	40	430	0.91	67.39	22.51	9.19
4#	<0.60	7.33	60	430	0.88	68.39	21.50	9.23
5#	<0.60	7.33	40	460	0.88	72.29	16.92	9.92
6#	<0.60	7.33	40	490	1.01	73.67	15.58	9.74
7#	<0.60	7.33	20/40	520	0.21	74.65	16.25	8.89
8#	<0.28	7.33	20	520	0.91	73.97	15.34	9.77
9#	<1.20	7.33	20	520	1.18	74.90	14.61	9.31
10#	<0.60	9.57	20	520	0.90	73.38	15.17	10.56
11#	<0.60	3.67	20	520	0.43	74.83	14.94	9.81

(2) sample size of 3 × 3 × 3 mm^3; and (3) 99.9999 vol.% O_2 concentration with a flow rate of 250–260 mL/min.

Thermogravimetric analysis

In this present work, combustion process of oil shale and its shale chars was investigated and compared using a Q5000IR thermogravimetric analyzer (TA Instruments, USA). Samples of 3–10 mg for each experiment were taken and heated at a constant heating rate of 20 °C/min in a pure oxygen from 40 °C up to a final temperature of 900 °C. The thermogravimetric analyzer provided for the continuous measurement of sample mass as a function of temperature, and the rate of mass loss, namely derivative thermogravimetric (DTG) curve, was thus obtained as well.

The Q5000IR thermogravimetric analyzer with ±0.1% mass accuracy and <0.1 µg sensitivity has high automation level, and its temperature and mass accuracy are calibrated periodically using Curie temperature and standard material, respectively. Therefore, the experimental results are representative, and repeatable experiments would not be performed unless the regularity of the effects of retorting factors on combustion characteristics of shale char was unexpected or relatively disorderly.

Results and discussion

Retorting temperature

Combustion characteristics

Figure 1 gives combustion TG and DTG curves of Dachengzi oil shale and its shale chars 3# and 5#–7# prepared at different retorting temperatures. According to the change of TG curves, the whole combustion process may be divided into two stages: low-temperature stage from 185 to 550 °C for oil shale and from 250 to 550 °C for shale chars, and high-temperature stage from 550 to 735 °C. After 735 °C, all the TG curves are closely level, showing that mass loss ceases. In the low-temperature stage, mass loss decreases largely with increasing retorting temperature to 490 °C, and then decreases slightly with increasing retorting temperature from 490 to 520 °C. In the high-temperature stage, similar TG and DTG curves between oil shale and its shale chars show that retorting temperature has no effect on the combustion process of the high-temperature stage. Figure 2 shows the ignition phenomena of oil shale and its shale chars, from which the ignition temperature T_i was obtained as well.

From Fig. 1, mass loss of combustion TG curve of Dachengzi oil shale begins at 200–250 °C far lower than its pyrolysis temperature (~400 °C) [9], attributed to volatile release advanced in O_2 atmosphere. Usually, there exist many active sites on the surface of fuels [22]. These active sites will physico-chemically absorb O_2 of ambient gas to form complex, releasing a certain heat energy that will accumulate within oil shale particles. Once total heat value of ambient heat plus the heat released by physico-chemical reactions exceeds the pyrolytic heat value of oil shale volatile, a great deal of volatile will sharply erupt out from solid particles though the real ambient temperature is still lower than the pyrolysis temperature of the volatile, followed by the instant ignition of the volatile. From Fig. 2a, a light flame enwraps the solid particles so that it is very difficult for ambient gases to contact the surface of solid particles, showing that the ignition of the volatile is very intense and concentrated. Therefore, in the beginning stage of the combustion process of oil shale, burning matter is volatile and combustion mechanism is homogeneous. With

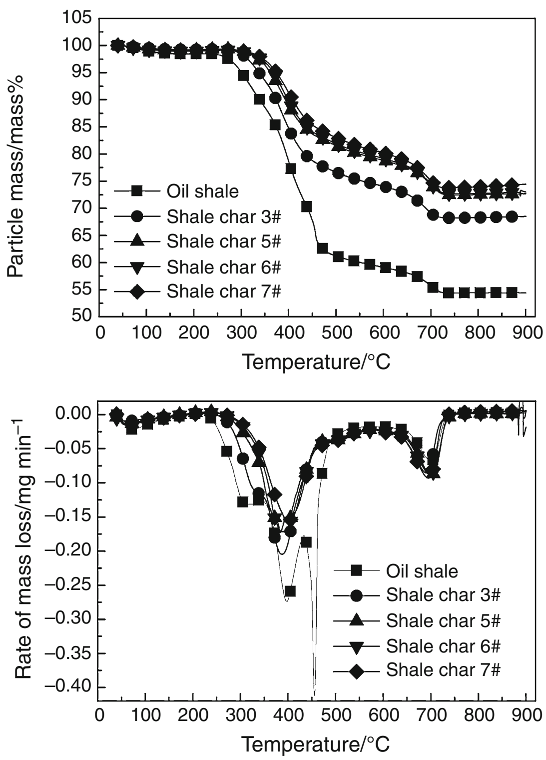

Fig. 1 Effects of retorting temperature on combustion TG and DTG curves of shale chars

combustion progressing, decreasing volatile release from oil shale particles makes oxygen molecules of ambient gases gradually diffuse to the surface of oil shale particles and react with fixed carbon. Accordingly, the combustion behavior shifts to heterogeneous. In the high-temperature stage of TG curve, higher ambient temperature will make a portion of inorganic matters within particles begin to decompose, forming the mass loss of high-temperature stage together with the combustion of residual combustibles.

Shale char 3# was prepared by retorting Dachengzi oil shale at the retorting temperature of 430 °C for the residence time of 40 min. Major organic matters remaining within shale char 3# were those with the boiling point and pyrolysis temperature more than 430 °C. In addition, a small quantity of organic matters with the boiling point and pyrolysis temperature less than 430 °C were adsorbed on the surface of solid particles. When heating shale char 3# in the O_2, these residual organic matters can react with O_2 to release heat. However, the content and components of these organic matters within shale char 3# are far less than those of organic matters within oil shale, resulting in a slow accumulation of heat energy in the solid particles and corresponding ascent of both ignition temperature and starting temperature of mass loss. From Fig. 2, it is seen that the ignition of shale char 3# occurs on the surface of solid particles, showing that its ignition mechanism is heterogeneous. Since content and components of residual organic matters within shale chars 5#–7# are less than those of shale char 3#, their ignition temperatures are elevated further and ignition mechanism is heterogeneous as well, just as shown in Fig. 2. In the high-temperature stage of combustion TG curves, most organic matters have burnt out in the low-temperature stage and residual organic matters within solid particles is small and similar for oil shale and four shale char samples. The combustion of these organic matters resulted in a similar combustion process of high-temperature stage together with the decomposition of inorganic matters within particles.

Combustion kinetic analysis

When the sample size is small and with an excess air supply, the process of the combustion reaction is independent of the concentration of oxygen. Therefore, the oxidation can be described by the Arrhenius method [23, 24], and the combustion reaction rate equation may be expressed as follows:

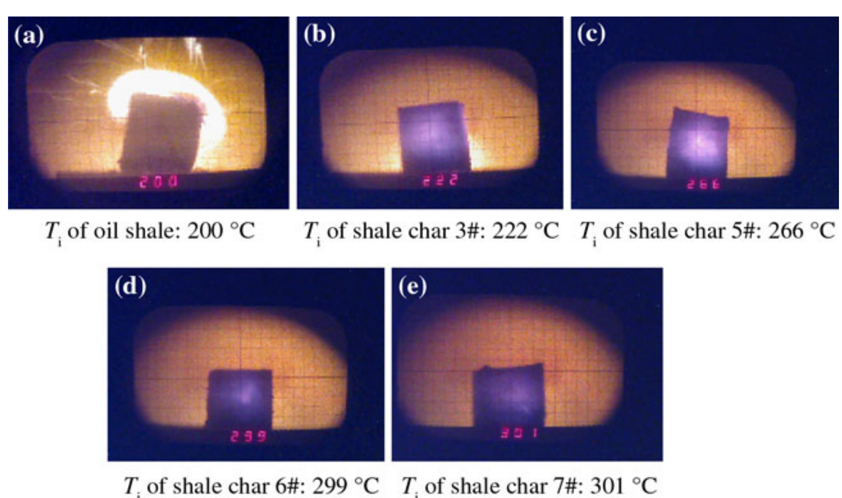

Fig. 2 Effects of retorting temperature on ignition temperature and mechanism of shale chars

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT}(1-\alpha)^n \quad (1)$$

where: A—pre-exponential factor, min^{-1}; E—activation energy, kJ mol^{-1}; n—reaction order; R—universal gas constant, kJ mol^{-1} K^{-1}; t—time of combustion process, min; T—particle temperature at time t, K; α—the ratio of actual mass loss to total mass loss at a given stage of the reaction:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}$$

where m_0, m_t, and m_∞ are the initial, the actual, and the final mass of the sample, respectively.

Coats–Redfern method was used to solve the kinetic Eq. 1. Table 3 gives the calculation results, showing that retorting temperature has a little effect on the combustion kinetic parameters of shale chars in the low-temperature stage. With increasing the retorting temperature, the activation energy of shale char gradually ascend. In addition, the activation energy value of all shale chars is somewhat higher than that of oil shale, resulting from that most of organic matters with lower pyrolysis temperature have released from solid particles during retorting oil shale.

Residence time

Curves in Fig. 3 illustrates the effect of residence time on the combustion process of shale chars 1#–4# obtained in different residence time at a constant retort temperature of 430 °C; indicating that mass loss in the low-temperature stage of combustion process decreases evidently with increasing retorting residence time to 40 min. However, further increasing residence time from 40 to 60 min has little effect on the mass loss of shale char in the low-temperature stage. In addition, the combustion TG and DTG curves of all shale chars in the high-temperature stage are very similar. Figure 4 presents the ignition phenomena of these shale chars, showing that the ignition temperature of shale char ascends and its ignition mechanism shifts from homogeneous to heterogeneous as the residence time increases.

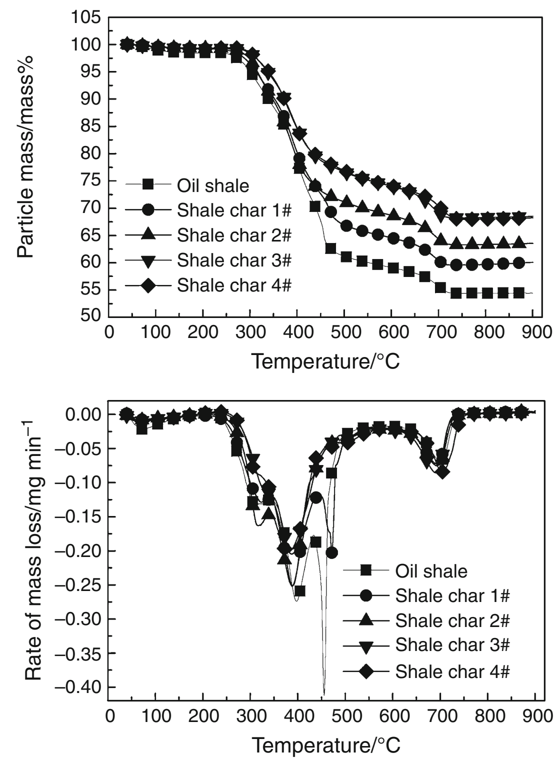

Fig. 3 Effects of residence time on the combustion of shale chars

According to the general decomposition mechanism of kerogen within oil shale [25–27], upon heating, the kerogen within oil shale is initially converted to bitumen at retorting temperatures ranging from 300 to 425 °C, and then to shale oil, non-condensable gas and coke. As a result, kerogen within shale chars 1#–4# obtained at the retorting temperature of 430 °C should have partly decomposed to bitumen. During retorting oil shale to prepare shale chars 1#–4#,

Table 3 Effects of retorting temperature on combustion kinetic parameters of shale chars

	Temperature range/°C	E/kJ mol^{-1}	A/min^{-1}	n	Correlation coefficient
Oil shale (<0.60 mm)	250–550	90.04	5.388×10^{6}	1.6	0.976
	550–735	172.27	1.377×10^{9}	1.0	0.954
Shale char 3#	250–550	119.76	1.583×10^{9}	2.0	0.975
	550–735	182.72	6.378×10^{9}	1.0	0.968
Shale char 5#	250–550	130.49	7.519×10^{9}	2.0	0.974
	550–735	170.99	1.071×10^{9}	1.0	0.956
Shale char 6#	250–550	136.11	1.759×10^{10}	2.0	0.979
	550–735	175.19	1.923×10^{9}	1.0	0.958
Shale char 7#	250–550	134.62	1.145×10^{10}	2.0	0.981
	550–735	178.42	3.146×10^{9}	0.9	0.964

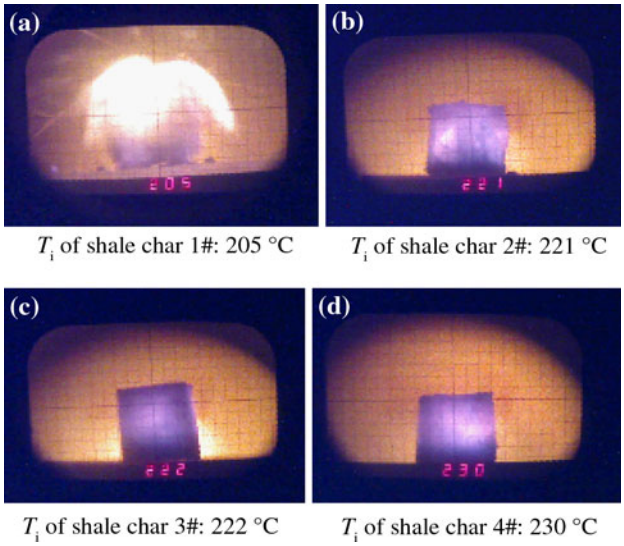

Fig. 4 Effects of residence time on ignition temperature and mechanism of shale chars

with increasing residence time at a constant retorting temperature, bitumen gradually converts to shale oil and non-condensable gases leaving from solid particles, and correspondingly residual organic matters within shale chars decrease gradually. Shale char 1# was obtained by retorting oil shale at 430 °C only for 6 min, lower retorting temperature and shorter residence time make more organic matters remain in solid particles. From Table 2, its volatile content is 33.48%, far more than other shale chars, resulting in lower ignition temperature and larger mass loss in the low-temperature stage. The longer retorting residence time, the less residual organic matters within shale char. As a result, in the low-temperature stage, the mass loss of shale char decreases and ignition temperature increases with increasing residence time. With combustion of shale char progressing to the high-temperature stage, most organic matters have burnt out in the low-temperature stage and residual organic matters within oil shale and four shale char samples are similar. The combustion of these organic matters resulted in a similar combustion process of high-temperature stage together with the decomposition of inorganic matters within particles.

Table 4 gives the kinetic parameters of shale chars 1#–4#, calculated from TG and DTG curves by the Coats–Redfern method. It was found that the activation energy increases slightly with increasing the residence time, attributed to that organic matters with low boiling point and pyrolysis temperature gradually decrease with increasing residence time.

Other retorting factors

Figure 5 gives the combustion TG and DTG curves of shale chars 7#–9# obtained from oil shale with different

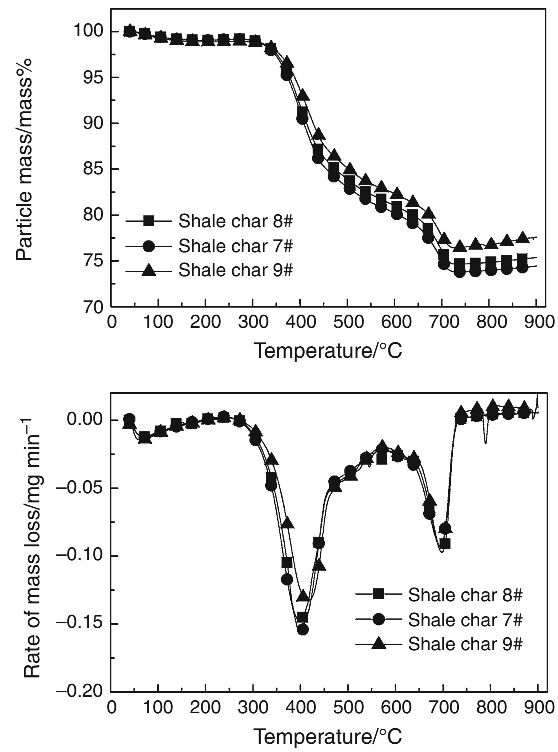

Fig. 5 Effects of particle size on the combustion of shale chars

Table 4 Effects of residence time on combustion kinetic parameters of shale chars

	Temperature range/°C	E/kJ mol^{-1}	A/min^{-1}	n	Correlation coefficient
Shale char 1#	250–550	93.07	9.784×10^6	1.7	0.976
	550–735	179.13	3.713×10^9	0.9	0.962
Shale char 2#	250–550	109.93	3.897×10^8	2.0	0.978
	550–735	180.82	4.781×10^9	1.0	0.961
Shale char 3#	250–550	119.76	1.583×10^9	2.0	0.975
	550–735	182.72	6.378×10^9	1.0	0.968
Shale char 4#	250–550	125.44	4.070×10^9	2.0	0.961
	550–735	163.73	3.813×10^8	1.1	0.948

Table 5 Effects of particle size on combustion kinetic parameters of shale chars

	Temperature range/°C	E/kJ mol^{-1}	A/min^{-1}	n	Correlation coefficient
Shale char 8#	250–550	137.52	1.806×10^{10}	2.0	0.978
	550–735	175.45	2.059×10^{9}	0.9	0.957
Shale char 7#	250–550	134.62	1.145×10^{10}	2.0	0.981
	550–735	178.42	3.146×10^{9}	0.9	0.964
Shale char 9#	250–550	137.85	1.538×10^{10}	2.0	0.982
	550–735	176.40	2.310×10^{9}	0.9	0.961

particle sizes, and Table 5 gives the combustion kinetic parameters. Since these shale chars were obtained from oil shale with different particle sizes at the retort temperature of 520 °C in the residence time of 20 min, most of organic matters within oil shale have been removed and the content of residual organic matter within shale chars is almost equal [10], resulting in a similar combustion history. Similarly, changing heating rate during retorting oil shale has little on the combustion characteristics of shale char, just as shown in Fig. 6 and Table 6. Therefore, it was concluded that particle size and heating rate in the studied limit have far smaller effect on the combustion characteristics of shale char than retorting temperature and residence time, which has further proven the conclusions obtained in the previous related works [9].

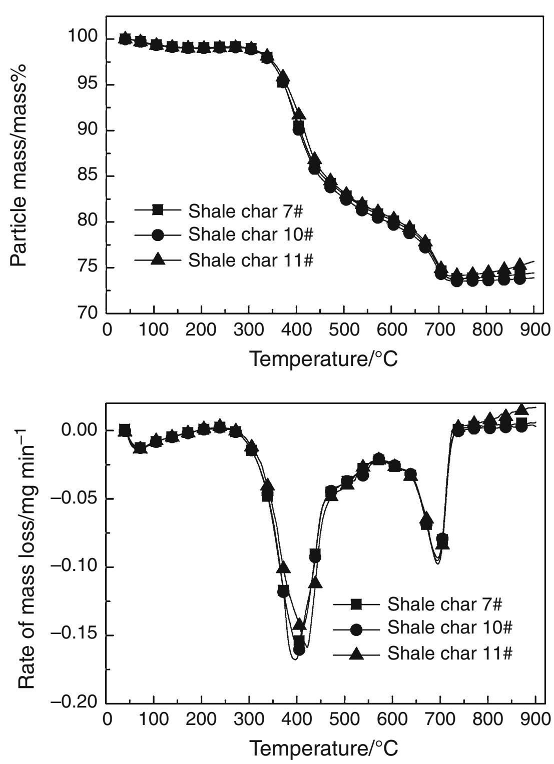

Fig. 6 Effects of heating rate on the combustion of shale chars

Comprehensive analysis of combustion of shale chars

According to the general decomposition mechanism of kerogen and the analysis of combustion characteristics of shale char, changing retorting factors can directly affect the content and components of organic matters within shale char, and then affect the ignition mechanism and the low-temperature stage of combustion process of shale char, in which retorting temperature and residence time play very important roles among four studied retorting parameters: with either elevating the retorting temperature or lengthening the residence time at a low retorting temperature, mass loss of the low-temperature stage of combustion decreases largely, ignition temperature ascends evidently and ignition mechanism shifts from homogeneous to heterogeneous. In addition, increasing retorting temperature from 490 to 520 °C or lengthening residence time from 40 to 60 min only has a slight effect on the combustion of shale char. However, elevating the retort temperature from 430 to 460 °C keeping the residence time of 40 min constant has more remarkable effect on the combustion process of shale char than increasing residence time from 40 to 60 min at a constant retorting temperature of 430 °C. Thus, the effect of only changing one retorting factor is limited on the combustion of shale char, and it is more important to simultaneously optimize retort temperature and residence time for high shale oil yield, good combustion characteristics of shale char and minimum retorting energy loss. For Dachengzi oil shale studied in this work, on the basis of both the combustion experiments of shale char and the analysis of the effect of retorting factors on shale oil yield [8], it was recommended that a set of retorting condition for the comprehensive utilization technology of oil shale is: retort temperature of 460–490 °C, residence time of 20–40 min, particle size of <3 mm, and low heating rate of <10 °C/min. For industrial retorting process of oil shale, the particle size of oil shale into the retorts is usually several decade millimeters, far larger than the particle size studied in this article. Accordingly, the residence time need to be properly lengthened for trying to retorting oil shale completely.

Table 6 Effects of heating rate on combustion kinetic parameters of shale chars

	Temperature range/ °C	E/kJ mol^{-1}	A/min^{-1}	n	Correlation coefficient
Shale char 11#	250–550	139.68	2.581×10^{10}	2.0	0.982
	550–735	181.39	4.786×10^{9}	0.9	0.963
Shale char 7#	250–550	134.62	1.145×10^{10}	2.0	0.981
	550–735	178.42	3.146×10^{9}	0.9	0.964
Shale char 10#	250–550	137.25	1.861×10^{10}	2.0	0.979
	550–735	180.32	4.036×10^{9}	0.9	0.965

Conclusions

For obtaining shale oil with a high yield and treating shale char efficiently, a series of fundamental experiments have been conducted for systemically studying the effects of retorting factors on shale oil yield and shale char characteristics, including retorting experiments of oil shale, pyrolysis experiments of shale char, and identification of organic matters within shale char, etc. On the basis of these previous studies, in this article, combustion experiments of shale chars obtained under different retorting conditions were performed with a Q5000IR thermogravimetric analyzer and a Leitz II-A heatable stage microscope, and the effects of retorting factors were discussed on the combustion characteristics of shale char. Combustion kinetic parameters of shale char were calculated by Coats–Redfern method. The main conclusions and recommendations are given below:

(1) Either increasing the retorting temperature from 430 to 520 °C or lengthening the residence time at a low retorting temperature will largely decrease residual organic matters within shale char, resulting in an ascent of ignition temperature of shale char, a decrease of mass loss in the low-temperature stage of combustion process and a shift of ignition mechanism from homogeneous to heterogeneous.

(2) Particle size and heating rate studied in this work have far smaller effect on the combustion characteristics of shale char than retorting temperature and residence time.

(3) On the basis of both the combustion experiments of shale char and the analysis of the effect of retorting factors on shale oil yield, it was recommended that an optimum retorting condition suitable for the comprehensive utilization technology of oil shale is: retort temperature of 460–490 °C, residence time of 20–40 min, particle size of <3 mm and low heating rate of <10 °C/min. For industrial retorting process of oil shale, some retorting parameters need to be adjusted properly for retorting oil shale completely.

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