

STUDY OF THE COMBUSTION MECHANISM OF OIL SHALE SEMICOKE IN A THERMOGRAVIMETRIC ANALYZER

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Oil shale semicoke, formed in retort furnaces, is a source of severe environmental pollution and is classified as a dangerous solid waste. For the industrial application of oil shale semicoke in combustion, this present work focused on the thermal analysis of its combustion characteristics. The pyrolysis and combustion experiments of semicoke were conducted in a Pyris thermogravimetric analyzer. From the comparison of pyrolysis curves with combustion curves, the ignition mechanism of semicoke samples prepared at different carbonization temperatures was deduced, and was found to be homogeneous for semicoke samples obtained at lower carbonization temperature, shifting to heterogeneous with an increase in the carbonization temperature. The effect of carbonization temperatures and heating rates on the combustion process was studied as well. At last, combustion kinetic parameters of semicoke were calculated with the binary linear regression method, showing that activation energy will increase with increasing the heating rate.

Keywords: combustion mechanism, oil shale semicoke, thermal analysis

Introduction

Oil shale, a fine-grained sedimentary material with organic matter called kerogen, is rich and widespread in the world. Provided that oil shale is retorted to produce shale oil, the reserves of shale oil are about 475Gt [1]. The current decrease in the reserves of conventional energy resources has motivated many countries, including China – rich in oil shale – to investigate efficient means to use oil shale as an alternative energy as soon as possible.

In China, there are two conventional technologies available for utilizing oil shale resources: one is retorting oil shale to produce shale oil and fuel gas, and the other is burning oil shale to generate electricity. For the conventional oil shale retorting industry, there are three vital problems to solve: (1) fine oil shale particles (<10 mm) will be abandoned, leaving only 80% of oil shale to be utilized; (2) semicoke, formed in retort furnaces, is a source of severe environmental pollution and is classified as a dangerous waste, containing several toxic compounds, such as water-soluble phenols, sulphide sulphur, polynuclear aromatic hydrocarbon (PAH) [2]; (3) compared with petroleum industries, it has higher costs and processing complexities. There are also problems to deal with in the conventional oil shale-fired technology: (1) oil shale-fired pulverized furnaces and grate-fired furnaces have high-temperature corrosion, environmental pollution and slag-bonding problems [3]; (2) oil shale-fired bubbling fluidized bed furnaces have scale-up problems in boiler capacity,

as well as a high carbon content of fly ash. To improve the availability of oil shale, many specialists recommend burning oil shale in a circulating fluidized bed (CFB) with satisfactory combustion efficiency, low SO₂ and NO_x emission, adaptability to low-grade fuel, etc. Long operation experiences with many oil shale-fired CFB boilers have shown that burning oil shale in CFB furnaces is the cleanest and most economic of all the oil shale-fired utilization modes [3, 4]. The growth of petroleum price, and the development of heavy industries, however, make burning oil shale in CFB furnaces face new challenges: (1) the uncertainty of petroleum prices, its growing worldwide consumption and limited availability have motivated many countries rich in oil shale resources to investigate more efficient means to produce and use shale oil as an alternative; (2) the oil shale utilization in combustion will not soon become competitive without a significant governmental kick-start; (3) the comprehensive utilization of primary energy sources has an appreciable economic efficiency, and burning oil shale in CFB furnaces is not the optimal utilization of oil shale with higher shale oil content.

Recently, many researchers put forward a comprehensive utilization mode for oil shale [5, 6]: firstly, oil shale is retorted to produce shale oil and fuel gas in a retort furnace; secondly, the semicoke formed in the retort furnace is fed to a CFB furnace to burn, in order to generate high-pressure steam and electricity via a traditional steam-electric power mode; lastly, oil shale ash discharged from the CFB furnace

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Table 1 Analytical data for Huadian oil shale

Proximate analysis ^a		Ultimate analysis ^a /mass%	
Moisture/mass%	2.90	C	31.63
Volatile matter/mass%	41.89	H	4.370
Ash/mass%	51.61	O	7.764
Fixed carbon/mass%	3.60	N	0.726
Net calorific value/kJ kg ⁻¹	8374	S	1.000

^aair dry base**Table 2** Proximate analysis for semicoke samples prepared under different carbonization temperatures

Sample	SC ₄₀₀	SC ₅₀₀	SC ₆₀₀	SC ₇₀₀
Carbonization temperature/°C	400	500	600	700
Moisture/mass%, ad	0.16	0.07	0.03	0.02
Volatile matter/mass%, ad	26.44	20.13	9.07	7.28
Ash/mass%, ad	66.1	71.4	81.4	84.1
Fixed carbon/mass%, ad	7.3	8.4	9.5	8.6
Net calorific value/kJ kg ⁻¹ , ad	7420.6	5738.5	2250.5	1456.0

ad: air dry base

will be used as a raw building material. In the whole utilization system, the retort technology and the ash processing technology are relatively mature; however, the CFB combustion technology using oil shale semicoke as fuel is a new technology including combustion characteristics of semicoke, CFB design, etc. Thermogravimetric analysis has been extensively used as a means of studying combustion and pyrolysis characteristics of oil shale [7–9]. The objective of this work is to study the combustion mechanism of oil shale semicoke by using a Pyris thermogravimetric analyzer.

Experimental

Semicoke sample

In this work, oil shale was obtained from Huadian, China. The analytical data are given in Table 1. According to the National Standards of China, oil shale was sampled, ground and sieved to the experimental samples ($d < 0.2$ mm). The semicoke samples for this work were prepared by retorting oil shale samples at carbonization temperatures of 400, 500, 600 and 700°C in a high-temperature electric resistance furnace at atmospheric pressure and heating rates of 1.5–3.5°C min⁻¹. The proximate analysis for them is shown in Table 2.

Method

Programmed combustion and pyrolysis tests of oil shale semicokes were performed in a Pyris thermogravimetric analyzer with a mass accuracy of 0.1 µg and a temperature precision of ±2°C. Approximately 10.34 mg of samples were heated from 50 to 950°C at heating rates of 20, 40, 60 and 80°C min⁻¹. A gas flow rate of 80 mL min⁻¹ was used; ambient gas was N₂ for pyrolysis experiments, and pure oxygen was used as the reactive gas for combustion tests. The experimental results were representative due to the high-precision thermogravimetric analyzer and standard sampling method.

Results and discussion

Ignition mechanism of semicoke

Ignition, considered as the process initiating combustion phenomenon, is very important due to its influence on flame stability, pollutant formation and emission, and flame extinction. In practice, the ignition behaviour of fossil fuels can be decisive to identify the optimal location for their injection into industrial combustors [10]. After heated up to a certain temperature, fossil fuels will separate into two major product components, i.e. gaseous volatiles and solid char particles, due to the pyrolysis of carbonaceous constituents. Since both components are combustible, either the homogeneous ignition of volatile or heterogeneous ignition of the char follows the pyrolysis in the course of further heating to higher temperatures. In the homogeneous mechanism, the

initial step is pyrolysis and subsequent ignition of volatiles, followed by ignition of the char. The heterogeneous reaction involves the direct attack of oxygen on the solid particles. There are generally several criteria to indicate ignition. For example, a sudden increase in particle temperature [11], the inflection of a temperature-time profile [12], or visual

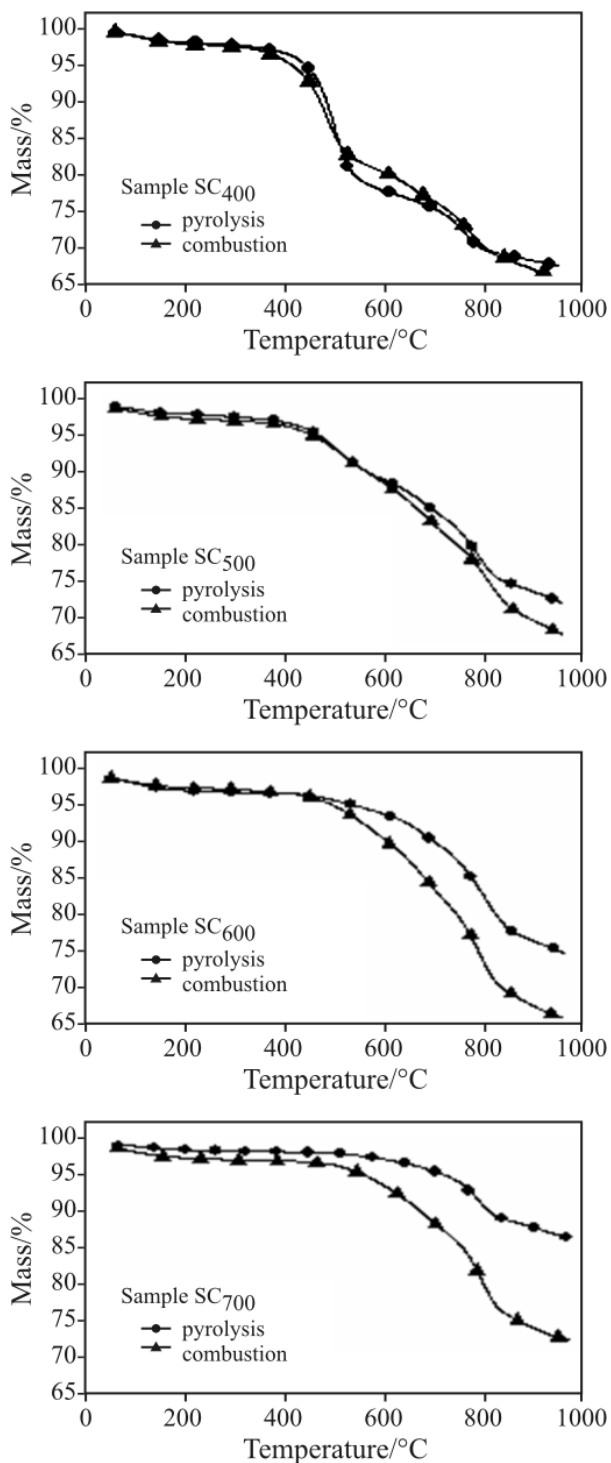


Fig. 1 Comparison of pyrolysis and combustion TG curves of four samples at the heating rate of 60°C min⁻¹

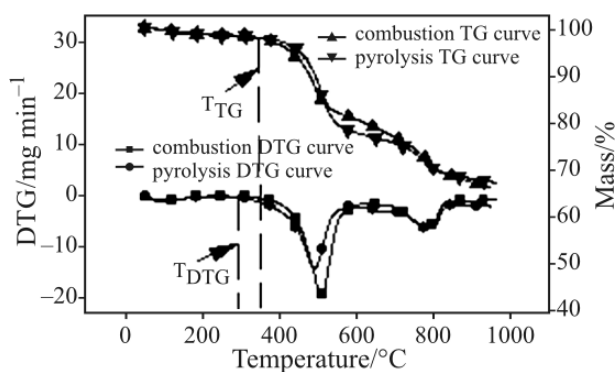


Fig. 2 Calculation of the ignition temperature of sample SC₄₀₀

observations on the emission of light of flashing and the changes of gas composition [13]. In addition, Arenillas *et al.* [10] deduced the ignition mechanism of coal from the comparison of pyrolysis curves with combustion curves. In this paper, the authors adopted Arenillas *et al.*'s method. Figure 1 compares pyrolysis curve of each semicoke sample with its combustion curve at the heating rate of 60°C min⁻¹. For samples SC₄₀₀ and SC₅₀₀, a noticeable initial mass loss under pyrolysis conditions takes place as the same way as that under combustion conditions, which means that the volatiles are released due to the increase in the temperature, and are independent of ambient gas species. In the presence of oxygen the volatiles can ignite because of low ignition temperature. Thus, the ignition behaviour of samples SC₄₀₀ and SC₅₀₀ is homogeneous. However, for samples SC₆₀₀ and SC₇₀₀, the mass loss during pyrolysis is different from that during combustion and occurs later, indicating that both volatiles and char burn, and the ignition mechanism is thus heterogeneous. Combined with the conclusion that the ignition behaviour of oil shale is homogeneous [14], the ignition mechanism of oil shale semicoke will shift from homogeneous to heterogeneous with an increase in the carbonization temperature.

Zhu *et al.* [15] compared several thermogravimetric analysis methods used to determine the ignition temperature, and finally recommended the following equation to calculate the ignition temperature:

$$T_i = \frac{T_{TG} + T_{DTG}}{2} \quad (1)$$

where T_{TG} is the temperature corresponding to the demarcation point between combustion TG curve and pyrolysis TG curve of sample; T_{DTG} describes the temperature corresponding to the demarcation point between combustion DTG curve and pyrolysis DTG curve of sample; T_i is the ignition temperature.

Figure 2 illustrates the T_{TG} and T_{DTG} of sample SC₄₀₀ at the heating rate of 80°C min⁻¹, from which the ignition temperature T_i of sample SC₄₀₀ can be obtained. In the same way, the ignition temperatures

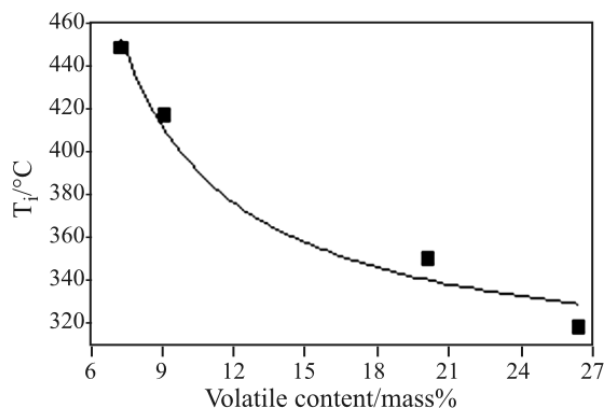


Fig. 3 Curve of ignition temperature vs. volatile content

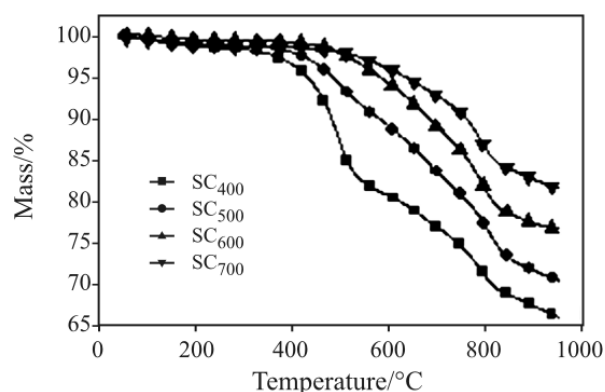


Fig. 4 Combustion TG curves of semicokes at the heating rate of $80^{\circ}\text{C min}^{-1}$

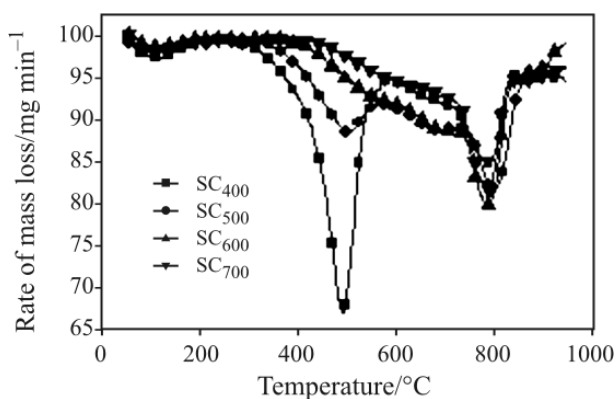


Fig. 5 Combustion DTG curves of semicokes at the heating rate of $80^{\circ}\text{C min}^{-1}$

of the other semicoke samples were also worked out. Figure 3 shows the relation of ignition temperature vs. volatile content (i.e. the carbonization degree of semicoke). According to Fig. 3, the ignition temperature of semicoke evidently increases with a decrease in the volatile content.

Effect of carbonization degree on combustion characteristics

Figures 4 and 5 show combustion TG and DTG curves of semicoke samples at the heating rate of $80^{\circ}\text{C min}^{-1}$, respectively. According to the change tendency of TG curves, the whole combustion history may be divided into three stages: low-temperature stage (the initial temperature of mass loss to 530°C), transition stage ($530\sim 730^{\circ}\text{C}$), and high-temperature stage ($730\sim 850^{\circ}\text{C}$). According to Fig. 4, the following points of similarities and differences can be obtained:

- The initial temperature of mass loss increases with increasing carbonization temperature.
- In the low-temperature stage, the mass loss of sample SC₄₀₀ is evidently greater than that of samples SC₅₀₀, SC₆₀₀ and SC₇₀₀. And the demarcation point of sample SC₄₀₀ between the low-temperature stage and the transition stage is obvious, however, the demarcation point of samples SC₅₀₀, SC₆₀₀ and SC₇₀₀ is so indistinct that the two stages may merge into a stage.
- In the high-temperature stage, the combustion process of all the samples is similar.

In Fig. 5, there exist two peak temperatures in the DTG curve of sample SC₄₀₀, showing that evident mass loss happens twice. As used herein, the ‘peak temperature’, is the temperature at which the mass loss rate is at its maximum. The peak temperature in the low-temperature stage evidently decreases with increasing carbonization temperature, and samples SC₆₀₀ and SC₇₀₀ have no peak temperature in the low-temperature stage. However, in the high-temperature stage, the peak value and shape of four DTG curves are very similar. Furthermore, it can also be found from the DTG curves that the initial temperature of mass loss increases with increasing carbonization temperature.

The authors ascribed these mentioned differences above to the carbonization degree. Usually, it is very easy for volatiles of oil shale to release and ignite under the low-temperature condition. As a result of lower carbonization temperature, sample SC₄₀₀ has higher volatile content than the other samples. So, the initial temperature of its mass loss is lower and mass loss is faster. With increasing carbonization temperature, the residual volatiles within semicoke samples decrease and become difficult to be pyrolyzed as well, resulting in that the initial temperature of mass loss increases and mass loss becomes slow. In the high-temperature stage, almost all the volatiles within semicoke samples have been pyrolyzed, and the matter involving in combustion and decomposition reactions is similar for the four samples and mainly contains fixed carbon, mineral substance and organic substance difficult to

Table 3 Kinetic analysis of oil shale semicoke at different heating rates

Heating rate/ °C min ⁻¹	Low-temperature stage			High-temperature stage		
	<i>E</i> /kJ mol ⁻¹	<i>A</i> /s ⁻¹	<i>n</i>	<i>E</i> /kJ mol ⁻¹	<i>A</i> /s ⁻¹	<i>n</i>
20	59.91	709.87	1.14	108.69	1.1·10 ²⁸	1.50
40	67.98	9727.03	1.24	81.68	5.2·10 ³⁵	1.63
60	81.05	217850.69	1.63	80.45	2.0·10 ¹⁹	1.28

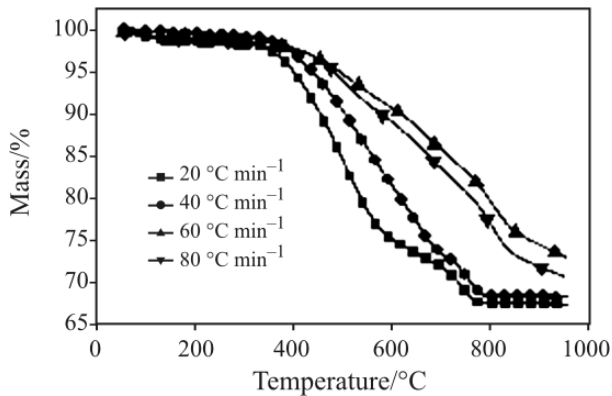


Fig. 6 Combustion TG curves of sample SC₅₀₀ at different heating rates

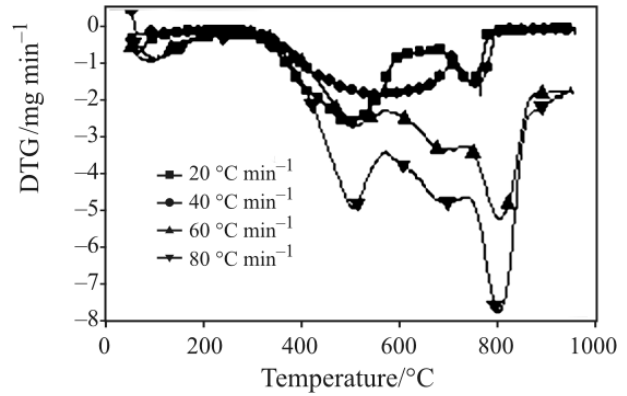


Fig. 7 Combustion DTG curves of sample SC₅₀₀ at different heating rates

decompose. So, the combustion history of the four samples is similar in the high-temperature stage.

Effect of heating rate on combustion characteristics

Figures 6 and 7 give combustion TG and DTG curves of sample SC₅₀₀ at different heating rates. According to Fig. 6, the burn-out degree of semicoke increases with a decrease in the heating rate, because low heating rate can lengthen the combustion time of semicoke particles and reduce the temperature gradient within the semicoke particle. However, the burn-out degree of sample SC₅₀₀ at the heating rate of 80°C min⁻¹ is a little higher than that at the heating rate of 60°C min⁻¹, which cannot show the above characteristic that the burn-out degree of semicoke increases with decreasing the heating rate. The authors ascribed a possible cause to the change in the porosity structure of particles in the combustion process. Figure 7 presents that the mass loss rate increases with increasing the heating rate. Both Figs 6 and 7 show that the heating rate has no evident effect on the initial temperature of mass loss.

Kinetic analysis of combustion

When the sample size is small, and with an excess air supply, the process of the reaction is independent of the concentration of oxygen [16]. It is therefore reasonable to assume that the oxidation can be described by the Arrhenius method [16, 17]. Based on

the Arrhenius equation, the combustion reaction rate equation of semicoke may be written as follows:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} (1-\alpha)^n \quad (2)$$

where *A* – pre-exponential factor, s⁻¹; *E* – activation energy, kJ mol⁻¹; *n* – reaction order; *R* – universal gas constant, J mol⁻¹ K⁻¹; *t* – time of combustion process, s; *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.

The binary linear regression method is used to solve the kinetic equation. Table 3 gives calculation results, showing that activation energy in the low-temperature stage will increase with increasing the heating rate.

Conclusions

As a result of current petroleum price growth and environmental pollution problem, the conventional technologies of oil shale become unavailable in the energy market. Accordingly, many researchers recommend a comprehensive utilization technology for oil shale. In the comprehensive utilization

technology, the circulating fluidized bed combustion technology using oil shale semicoke as fuel is regarded the most important. In this paper, the combustion mechanism of oil shale semicoke was studied by using a Pyris thermogravimetric analyzer, and the following conclusions can be drawn from the experimental results:

- From the comparison of pyrolysis curves with combustion curves, the ignition behaviour of oil shale semicoke will shift from homogeneous to heterogeneous with increasing the carbonization temperature, and accordingly the ignition temperature of semicoke will increase.
- The carbonization degree markedly influences the combustion history of the low-temperature stage of oil shale semicoke, and has little effect on the combustion of high-temperature stage.
- TG curves obtained at different heating rates show that lower heating rate can increase the burn-out of semicoke, and DTG curves show that mass loss rate will increase with increasing heating rate.
- Combustion kinetic parameters of semicokes were calculated with the binary linear regression method, showing that activation energy in the low-temperature stage will increase with increasing the heating rate.

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