

THERMAL ANALYSIS STUDIES ON COMBUSTION MECHANISM OF OIL SHALE

X. X. Han*, X. M. Jiang and Z. G. Cui

Institute of Thermal Energy Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Combustion and pyrolysis experiments of Huadian oil shale have been conducted using a STA409 thermogravimetric analyzer. The effect of various factors on combustion of oil shale is studied. Particle size has little effect on combustion process of oil shale; starting temperature of combustion mass loss and ignition temperature of oil shale decrease with increasing O₂ concentration of ambient gas; increase of heating rate can result in ignition temperature, burn-out temperature and maximum rate of combustion mass loss increasing. Homogeneous ignition mechanism of oil shale is ascertained using a hot state microscope.

Activation energy was determined using Arrhenius model that is solved by Freeman–Carroll method. Calculation results show activation energy will increase with heating rate.

Keywords: combustion, ignition, oil shale, thermal analysis

Introduction

Oil shale, a sapropelic deposited rock containing organic combustible materials, is greatly different from coal in formation and structure. Especially, oil shale has higher volatile and ash content than coal, which makes large difference in physical and chemical performance between oil shale and coal. So, combustion performances of coal are incompletely fit to oil shale. Furthermore, combustion mechanism research on oil shale is very important for design of oil shale combustion devices.

The use of small-scale tests for an initial evaluation of the reactivity of fuel is a far more rapid and cheaper method than pilot-scale testing. Thermogravimetric analysis has been extensively used for the combustion and reactivity characterization of different materials and blends. 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 [1–3]. 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.

Operation experience of many oil shale-fired circulating fluidized bed boilers has proven that burning oil shale in circulating fluidized bed is economic and

clean [4, 5]. The objective of this work is to provide fundamental information for the industrial combustion application of Huadian oil shale by studying combustion mechanism through thermal analysis.

Experimental

The oil shale samples used in this work were from Huadian, China. According to the national standards of China, the oil shale samples were sampled, ground and sieved to the four experimental samples that were 75.66, 110.05, 200.21 and 290.40 μm in average particle diameter measured using the MAM5004 particle size analyzer. The analytical data and ash mass content are shown in Tables 1 and 2.

Ignition phenomenon is observed and photographed using a Leitz II-A heatable stage microscope with high definition video camera. And the experimental conditions are: (1) sample size of $3\times 3\times 3\text{ mm}^3$; (2) 100% O₂ concentration with flow rate of 500 mL min^{-1} ; (3) heating rate of $10^\circ\text{C min}^{-1}$.

Programmed pyrolysis and combustion tests of oil shale particles were performed in a STA409 thermogravimetric analyzer with the mass accuracy of 2 μg . Thermocouple measuring the ambient temperature was close to oil shale sample. Approximately 4.6 mg of samples were heated from room temperature to 900°C at the heating rate of 10, 20, 30 and $40^\circ\text{C min}^{-1}$. A gas flow rate of 100 mL min^{-1} was used; ambient gas was N₂ for pyrolysis experiment and mixture gas with 20% O₂ and 80% N₂ was used as

* Author for correspondence: hanxiangxin@sjtu.edu.cn

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** Ash analysis of Huadian oil shale (mass%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O
52.9	17.74	6.56	14.78	2.99	0.55	0.89	1.27

the reactive gas for the combustion test. It is assumed that temperature value measured by the thermocouple is approximate to that of oil shale samples because of low heating rate and small sample mass.

The thermogravimetric experiments are representative because of the high precision thermogravimetric analyzer and standard sampling method.

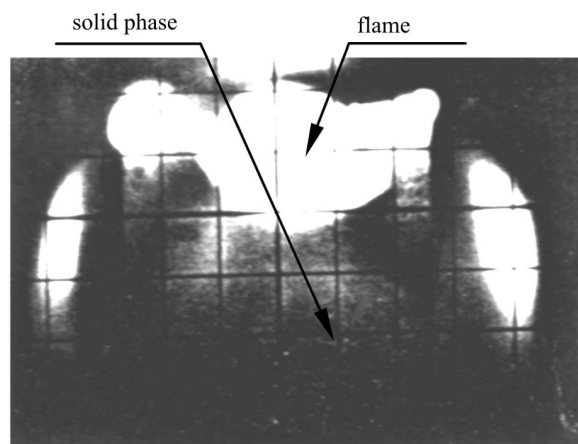
Results and discussion

Ignition mechanism

Ignition is considered as the process initiating the combustion phenomenon and it is a relevant step due to its influence on flame stability, pollutant formation and emission, and flame extinction. In practice, the ignition behaviour of coal can be decisive to identify the optimal location for their injection into industrial combustors [1]. After heated up to a certain temperature, fossil fuel 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 whole sample particle. Understanding the ignition behaviour of fuel is of utmost importance for the design of boilers and control of the combustion process.

Usually, there are several criteria to indicate ignition. For example, jump of particle temperature [6], inflection of temperature–time profile [7] or visual observation with measured gas composition [8]. In this work, ignition mechanism is judged using the Leitz II-A heatable stage microscope. In ignition experiment under the heatable stage microscope, oil shale

particle began to ignite at 208°C in ambient gas of 100% O₂. The ignition phenomenon observed at ignition moment through the heatable stage microscope is presented in Fig. 1. Clear flame appears outside oil shale particle and solid phase is dark, which means it is pyrolyzed volatile that is burning. The authors judged by the appearance that ignition behaviour of oil shale is homogeneous under such an operating condition.

**Fig. 1** Ignition experiment phenomenon under heatable stage microscope

It is well known that both ignition temperature and ignition mechanism depend on the type and operating conditions of the test apparatus besides inherent properties of fuel. Is ignition behaviour of oil shale still homogeneous with changing operating conditions of the test apparatus?

From the above ignition experiment, volatile is a very important factor for the ignition of oil shale. Pyrolysis experiment can directly reflect pyrolysis property of fuel volatile. So the authors adopted pyrolysis experiment to study volatile release property of oil shale. Figure 2 presents pyrolysis TG curves of oil shale with different particle diameters at heating rate of 20°C min⁻¹. Figure 3 presents pyrolysis TG curves

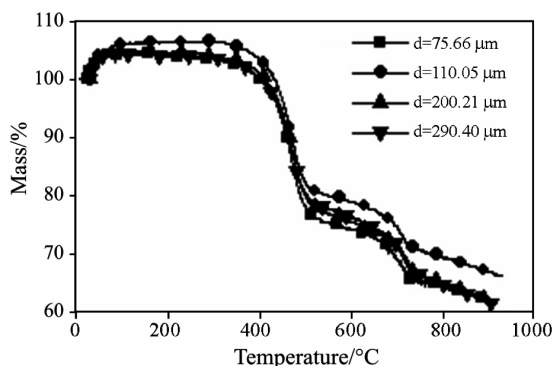


Fig. 2 Pyrolysis TG curves of oil shale with different particle diameters

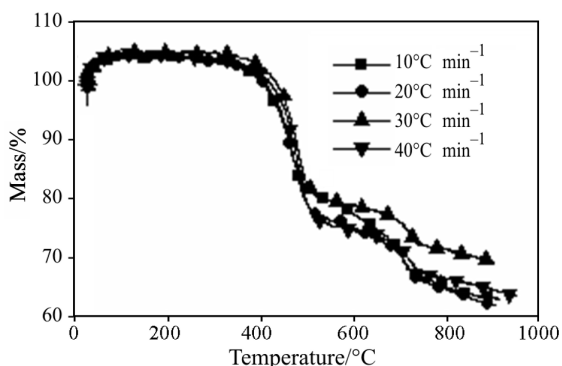


Fig. 3 Pyrolysis TG curves of oil shale at different heating rates

of oil shale of 200.21 μm in average diameter at different heating rates.

From Figs 2 and 3, there are two evident mass losses for every pyrolysis curve: about 25% of the initial mass for low-temperature stage (350–500°C); only 10% of the initial mass for high-temperature stage (650–730°C). And it seems that heating rate and particle diameter have little effect on pyrolytic temperature and pyrolyzed volatile amount of low-temperature stage. Pyrolytic temperature of about 350°C is lower than that of coal. 25% mass loss in low-temperature stage means that a large amount of volatile will sharply erupt so that it is possible that solid particle will be wrapped by volatile and O_2 molecules of ambient gas are very difficult in contacting the surface of solid particle. Thus, fast release of abundant volatile can provide a good condition for homogeneous ignition of oil shale.

So, the authors thought that ignition behaviour of oil shale is homogeneous whether operating conditions change or not because oil shale has high volatile content and low pyrolysis temperature that can offset the effect of changing operating conditions of the test apparatus on ignition behaviour. However, although operating conditions has little effect on ignition behaviour of oil shale, they will greatly influence combustion process, which will be introduced in the following thermogravimetric analysis.

Thermogravimetric analysis

Effect of particle size on combustion

Figure 4 shows combustion TG curves of Huadian oil shale with different average diameters at the heating rate of $10^\circ\text{C min}^{-1}$. Similar to combustion TG curve of Ulukisla oil shale [9], combustion TG curves of Huadian oil shale also have two evident mass losses: about 28% of the initial mass for low-temperature stage (280–500°C); less than 10% of the initial mass for high-temperature stage (620–730°C). After ambient temperature exceeds 730°C , mass loss become more and more small and combustion is close to terminal. Based on Fig. 4 and the analysis of ignition mechanism, combustion behaviour is homogeneous and burning matter is volatile in the low-temperature stage; but in the high temperature stage, matter involving in combustion includes fixed carbon and residual volatile, and combustion behaviour is heterogeneous. Although many literatures [10, 11] have proved ignition behaviour and combustion process of coal are greatly influenced by particle diameter, four TG curves in Fig. 4 are very similar, which shows particle diameter has little effect on combustion process of oil shale. The same result can be obtained at another three heating rates.

Although particle size has little effect on combustion process of oil shale, it has an important effect on porosity structure and burn-out degree of oil shale particle. Because oil shale has high ash content, mass transfer resistance of ash layer will gradually increase and become major controlling factor in burning rate of fixed carbon in the high temperature stage. Burn-out degree of coke will decrease with increasing particle size.

There exists a slight mass gain of 3–5% for combustion TG curves in the temperature range of 25–60°C in Fig. 4. The authors speculated that the cause was that oil shale would adsorb a certain ambient gas in the initial stage of the thermogravimetric experiments. But compared with total mass loss of oil shale, the mass gain is so slight that the effect of it on combustion process of oil shale is negligible.

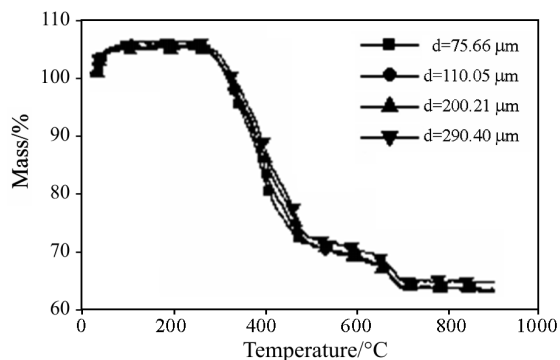


Fig. 4 Combustion TG curves of oil shale with different particle diameters

Effect of O₂ concentration on combustion

Figure 5 presents combustion and pyrolysis TG curves of oil shale of 110.05 μm in average particle diameter at the heating rate of 10, 30 and 40°C min⁻¹. How O₂ concentration affects combustion of oil shale can be obtained by comparing combustion curve at any heating rate with pyrolysis curve because all the conditions of combustion experiment, such as experimental installation, are identical to those of pyrolysis experiment except ambient gas (ambient gas of pyrolysis experiment is 100% N₂, but a mixture gas of 80% N₂ and 20% O₂ for combustion experiment).

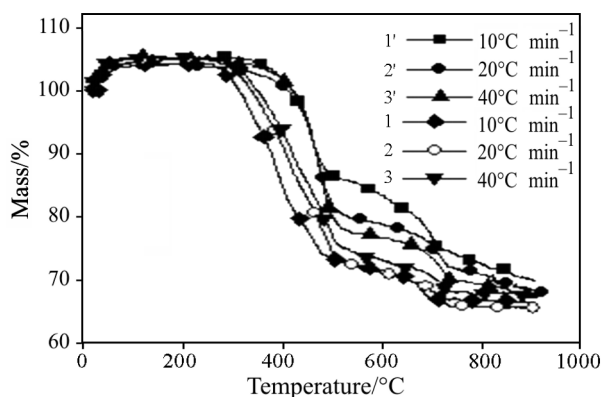


Fig. 5 TG curve comparison between combustion and pyrolysis at different heating rates

In Fig. 5, lines 1, 2 and 3 describe combustion TG curve at the heating rates of 10, 30 and 40°C min⁻¹ respectively; lines 1', 2' and 3' describe pyrolysis TG curve at the heating rates of 10, 30 and 40°C min⁻¹ respectively. Starting temperature of pyrolysis mass loss is represented as T_p ; starting temperature of combustion mass loss is expressed as T_c . Values of the two characteristic temperatures at the three heating rates above are shown in Table 3. Based on Table 3, T_p decreases and T_c increases with increasing heating rate. Moreover, T_p is always greater than T_c at the same heating rate and the difference between T_p and T_c becomes small with increasing heating rate.

According to Fig. 5 and Table 3, there has been a certain mass loss (8–12% of the initial mass) for combustion TG curves before ambient temperature reaches the starting temperature of pyrolysis mass loss. The authors think there are two possible reasons: one reason is that fixed carbon of oil shale has been burning, which results in mass loss advance of combustion; the other reason is ascribed to volatile release advance. On basis of analysis of homogeneous ignition mechanism of oil shale, the first possible reason is rejected and it should be volatile release advance that result in earlier mass loss of combustion than that of pyrolysis. By comparing experimental conditions of pyrolysis with that of combustion, the unique difference is ambient

Table 3 Characteristic temperature of oil shale at different heating rates

Heating rate/°C min ⁻¹	Starting temperature/°C	
	pyrolysis	combustion
10	393	270
30	373	292
40	361	300

gas: O₂ concentration of pyrolysis experiment is 0%, but O₂ concentration of combustion experiment is 20%. O₂ molecules of ambient gas increase and are physicochemically adsorbed on the surface of oil shale particle when particles of oil shale are heated in the combustion experiment; adsorbed O₂ molecule may react with oil shale functional group of unsaturated bond to form a new chemical bond called as intermediate compound, C_xO_yH_z [12]. Moreover, Krishnaswamy's [13] cited active sites to explain the low-temperature oxidation mechanism: active sites of coal will physico-chemically absorb O₂ of ambient gas to form complex, which will possibly release a certain heat energy that will be accumulated within oil shale particles. When total heat value of ambient heat and heat released by physical and chemical adsorption reaction of O₂ exceeds pyrolytic heat value of oil shale volatile, a great deal of volatile will sharply release although ambient temperature don't reach pyrolysis temperature of oil shale. Volatile begins to ignite because of low ignition temperature of it subsequently. Based on the above analysis, the authors refer that starting temperature of combustion mass loss will further decrease with increasing O₂ concentration of ambient gas because more and more O₂ molecules are adsorbed on the inner and outer surface of oil shale particles and react with active sites to release heat. The conjecture is in agreement with conclusion of many literatures [14–16]. But, when O₂ molecules absorbed by oil shale reach saturation degree, further increase of O₂ concentration will have little influence on the starting temperature of combustion mass loss.

In addition, volatile of Huadian oil shale has low ignition temperature and can instantly burn after released. Accordingly decrease of starting temperature of combustion mass loss with whether decreasing heating rate or increasing O₂ concentration will result in ignition temperature of oil shale decreasing subsequently.

Effect of heating rate on combustion

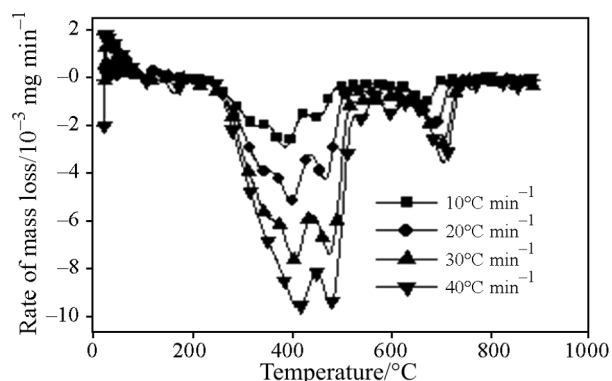
Combustion DTG curves of oil shale of 110.05 μm in average particle diameter at the heating rates of 10, 20, 30 and 40°C min⁻¹ are given in Fig. 6. There exist two peak temperatures in every DTG curve, which also shows evident mass loss happens twice. The peak

Table 4 Peak and burn-out temperature of oil shale at different heating rates

Heating rate/ $^{\circ}\text{C min}^{-1}$	Peak temperature/ $^{\circ}\text{C}$		Burn-out temperature/ $^{\circ}\text{C}$
	low-temperature stage	high-temperature stage	
10	393	680	724
20	411	700	746
30	415	710	760
40	422	719	760

Table 5 Kinetic analysis of oil shale at different heating rates

Heating rate/ $^{\circ}\text{C min}^{-1}$	Low-temperature stage			High-temperature stage		
	A/min^{-1}	$E/\text{kJ mol}^{-1}$	n	A/min^{-1}	$E/\text{kJ mol}^{-1}$	n
10	$1.04 \cdot 10^4$	27.26	1.51	$1.64 \cdot 10^{61}$	82.79	5.57
20	$1.06 \cdot 10^4$	78.18	-9.34	$1.92 \cdot 10^{60}$	99.83	5.38
30	$2.08 \cdot 10^4$	122.5	-9.56	$5.57 \cdot 10^{59}$	145.50	5.99
40	$2.47 \cdot 10^4$	152.2	-9.70	$2.58 \cdot 10^{57}$	195.56	5.14


Fig. 6 Combustion DTG curves at different heating rates

temperature is the temperature at which the rate of mass loss is at its maximum. For every DTG curve, the maximum rate of mass loss in the low-temperature stage is always greater than that in the high-temperature stage. And, either in the low-temperature stage or in the high-temperature stage, the maximum rate of mass loss will increase with heating rate. Burn-out temperature indicates a complete sample oxidation [17]. Table 4 gives the peak and burn-out temperature which will increase with heating rate.

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 oxygen concentration. It is therefore reasonable to assume that the oxidation can be described by the Arrhenius method [9]. According to the Arrhenius equation, the combustion reaction rate equation of oil shale may be written as follows:

$$\frac{dm}{dt} = -A \exp\left(-\frac{E}{RT}\right) m^n$$

where: A – pre-exponential factor, min^{-1} ; E – activation energy, kJ mol^{-1} ; m – residue combustible matter mass, kg; n – reaction order; R – universal gas constant, $\text{kJ mol}^{-1} \text{K}^{-1}$; t – time of combustion process, min; T – combustion temperature at time t , K.

Freeman–Carroll method is used to solve the kinetic equation. Table 5 gives calculation results and shows that activation energy increases with heating rate.

Conclusions

Preliminary experimental work on the combustion and pyrolysis of oil shale particles has been presented, using a thermogravimetric analyzer. Ignition mechanism of oil shale was ascertained using a heatable stage microscope. On this basis, the following conclusions are drawn from this study:

- Ignition mechanism of oil shale keeps homogeneous whether operating conditions change or not because oil shale has high volatile content and low pyrolysis temperature that can offset the effect of changing operating conditions of the test apparatus on ignition behaviour.
- There are two evident mass losses for oil shale in the combustion process: about 28% of the initial mass for low-temperature stage (280–500 $^{\circ}\text{C}$); less than 10% of the initial mass for high-temperature stage (620–730 $^{\circ}\text{C}$). Rate of mass loss in the low-temperature stage is greater than that in the high-temperature stage.

- Particle size has little effect on combustion of oil shale, but it has an important effect on burn-out degree of oil shale.
- Starting temperature of combustion mass loss and ignition temperature of oil shale decrease with increasing O₂ concentration of ambient gas because of physical and chemical adsorption reaction of O₂.
- Maximum rate of combustion mass loss, burn-out temperature, ignition temperature and activation energy will increase with increasing heating rate.

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