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COMBUSTION OF OIL SHALE PARTICLES UNDER ELEVATED PRESSURES

CHANGTAO YUE, SHUYUAN LI*
State Key Lab of Heavy Oil Processing,
University of Petroleum
Changping, Beijing 102200, China

Experiments on rapid combustion of Fushun and Maoming oil shale particles (3–11 mm) were carried out in a pressurized thermogravimetric analyzer. The effects of particle diameter, temperature and pressure on combustion process were investigated. Oil shale conversion values versus time at different temperatures and pressures were obtained. Kinetic parameters of the process were determined. The overall first-order reaction model was found to fit experimental data.

Introduction

Boilers can be used to burn poor solid fuels with low content of organic matter, such as lignite, oil shale, etc. Oil shale power stations have been built in Germany, Israel, Estonia and Brazil. In Huadian, China, a power equipment burning oil shale has been operating for many years. At present, some oil shale power stations are planned to be constructed in Jilin province. A lot of work on coal combustion has been published at home and abroad [1–5].

In this work, rapid combustion experiments on oil shale particles in a pressurized thermogravimetric analyzer were carried out to simulate their combustion behavior in fluidized-bed boiler. The effects temperature, pressure, and particle size were investigated.

Experimental

Samples used in this work were taken from Fushun and Maoming deposits, China. The data on their elemental and proximate analysis as well as on composition of oil shale ashes are given in Tables 1–3 [6].

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[*] Corresponding author: e-mail: syli@www.bjpeu.edu.cn

Table 1. **Analysis of Fushun and Maoming Oil Shales (dry basis)**

No.	Samples	Fischer Assay, wt%				Proximate analysis, wt%			Calorific value, kJ/kg
		Oil	Coke	Water	Gas	Volatiles	Ash	CO_2	
F832	Fushun	6.8	88.0	2.7	2.5	17.10	77.36	2.91	5701
M811	Maoming	8.8	84.1	3.7	3.4	22.80	71.94	1.40	7294

Table 2. **Elemental Analysis of Fushun and Maoming Oil Shales, wt% (dry, ash free)**

Samples	C	H	O	N	S	H/C
Fushun	79.07	9.93	7.02	2.12	1.68	1.51
Maoming	79.41	9.64	8.23	1.63	1.09	1.46

Table 3. **Composition of Fushun and Maoming Oil Shale Ashes, wt%**

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$
Fushun	61.93	25.82	8.61	1.26	1.69	0.69
Maoming	62.85	21.78	8.98	0.95	1.51	3.93

Combustion experiments were carried out in a pressurized thermogravimetric analyzer. The main element of the analyzer is a vertical reactor made of a stainless-steel tube (l = 200 mm, ∅ = 40 mm). The sample basket – a stainless-steel cylinder with equal height and diameter of 15 mm – is hung at the top of the reactor. Combustion temperature was measured by a thermocouple positioned just below the sample basket. The reactor was first charged with air to a given pressure and then heated to a given temperature. After some time needed for regulation, the basket with oil shale particle was put into the reactor, and the sample was burnt rapidly. The signal of oil shale weight loss during burning was directed into a computer system by a weight sensor. In the experiments, spherical samples of different diameters were tested and the effects of experimental conditions – temperature and pressure – investigated.

The diameters of the samples used in experiments were 3, 5, 7, and 11 mm (the weights 0.0325, 0.151, 0.413 and 1.602 g, respectively) to simulate combustion of oil shale fines (less than 10 mm) in industrial boiler burning oil shale. Operating pressures used were 0.1, 0.5 and 0.9 MPa and combustion temperatures 700, 800 and 900 °C, while operating temperature in an industrial boiler is about 850 °C.

Results and Discussion

Kinetic Parameters of Combustion

During the experiments, heating rate of samples was very high, up to 500–1000 °C /s. So, the effects of the heating-up period can be ignored and oil shale can be considered to be burnt at constant temperature. In addition, for oil shale particle small size (less then 10 mm), intra-particle temperature gradient may be considered negligible. Based on two reasons above, a simple overall first-order reaction model at constant temperature was used to describe rapid combustion of oil shale particles. Kinetic equations can be written as follows:

$$-\ln(1-x) = kf(p)t \qquad (1)$$

$$k = A\exp(-E/RT) \qquad .(2)$$

where *A* refers to frequency factor,

E is activation energy;

k is rate constant;

R is general gas constant;

t is reaction time;

T is reaction temperature;

x is combustion conversion;

f(*p*) is pressure factor.

The *x-t* data obtained at the same temperature can be regressed linearly using Equation (1). The value of *kf*(*p*) can be obtained from regression slope. For other temperatures, *E* and *A* can be determined using Equation (2). Pressure factor *f*(*p*) can be calculated using the data of experiments carried out at different pressures. Combustion kinetics of oil-shale 5-mm particles can be described as follows:

Maoming oil shale

$$k = 19.23\exp(-44900/RT) \qquad (3)$$

$$f(p) = 0.0881 + 0.122p - 0.0282p^2 \qquad (4)$$

Fushun oil shale

$$k = 63.54\exp(-50600/RT) \qquad (5)$$

$$f(p) = 0.0865 + 0.132p + 0.0276p^2 \qquad (6)$$

where *p* is absolute pressure, MPa.

All correlation coefficients exceeded 0.99 when linear regression was used. The overall first-order reaction model was found to be feasible to describe oil shale combustion behavior. According to the regression results, activation energy needed for Fushun oil shale combustion was higher than that for Maoming oil shale. However, both values are low. The results coincide with literature data [7].

Equation (1) includes pressure factor *f*(*p*), a parameter which considers the effects of pressure on combustion process. This factor is greater for Fushun oil shale. Both pressure and temperature exhibit important effects on Fushun oil shale. The reaction rate constant *k* of this shale combustion is also high. So, Fushun oil shale is easier to burn than Maoming one. As for selecting operating conditions for commercial boiler burning Fushun oil shale, shorter residence time can be used to increase boiler capacity.

Combustion Conditions

Temperature

The *x-t* curves of Maoming oil shale combustion at different temperatures are shown in Fig. 1. Fushun oil shale has similar trends in the same operating conditions. At higher temperature *x-t* curves become sharper, and combustion time is shorter. According to the Arrhenius equation, the relationship between reaction rate constant and temperature obeys exponential function. Therefore, temperature has greater effect on oil shale combustion than pressure and particle size. To increase boiler capacity higher temperatures are to be used.

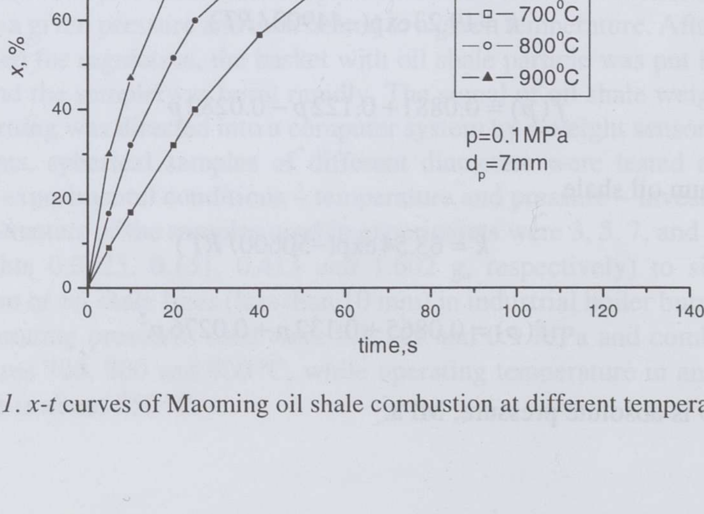

Fig. 1. x-t curves of Maoming oil shale combustion at different temperatures

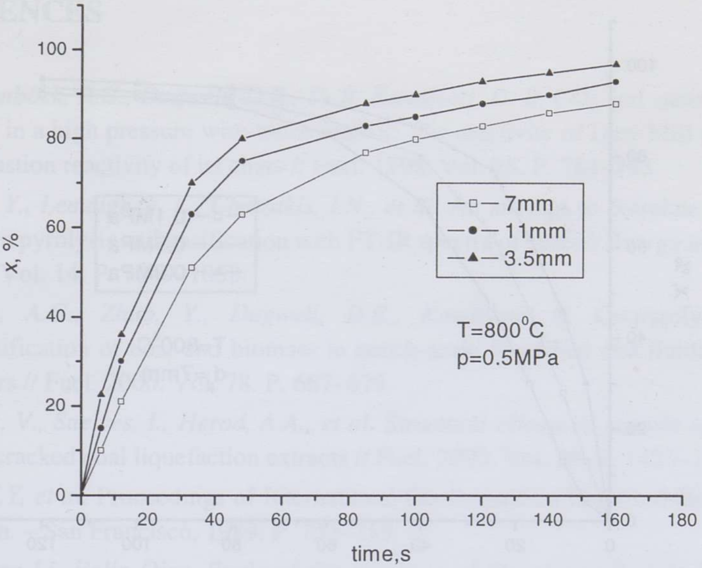

Fig. 2. x-t curves of combustion of different-size particles

Particle Size

Conversion curves of Maoming oil shale samples of different size are given in Fig. 2. Curves for 3- and 5-mm particles are overlapped showing that the effects of particle size can be ignored for diameters less than 5 mm. So, the kinetic parameters can be considered intrinsic, not affected by mass and heat transfer. The effect of size, however, becomes obvious for particles larger than 5 mm. In this case, mass and heat transfer strongly affect the process, and for complete combustion longer time is needed. Quantitative expression of particle size effects is difficult due to their very complicated nature. Oil shale particles may crack during combustion so changing the influence of mass and heat transfer.

Pressure

The *x-t* curves of the combustion process for Fushun oil shale obtained at different pressures are given in Fig. 3. One can see that with the increase in pressure and, thus, in the oxygen content of the gas phase, combustion rate increases and process time shortens. However, the effect of pressure decreases slowly with the elapsed time. The *x-t* curves for Maoming oil shale have similar trend. With the increase in the temperature and particle size, the effect of pressure becomes obvious. This can be explained by the fact that rapid combustion at higher temperatures needs more oxygen. Oxygen diffusion becomes a controlling step; so, the effect of pressure on combustion rate becomes more obvious. Large particles are more resistant to oxygen diffusion. Elevating the pressure favours oxygen diffusion and increases combustion rate.

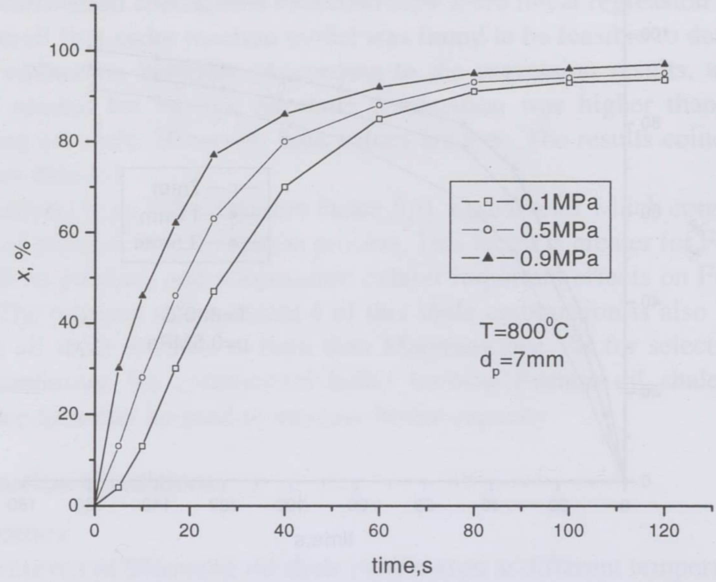

Fig. 3. *x-t* curves of Fushun oil shale combustion at different pressures

Time

The *x-t* curves obtained using different conditions show that the time needed for conversion of 90 % of the initial sample is shorter than the time needed for the residual 10 %. For example, 90 % conversion of 7-mm particles of Maoming shale at 900 ºC and 0.1 MPa was reached within less than 30 s (see Fig. 1), whereas burning of the residual 10 % needed about 100 s. So, combustion rate of volatile matter was high, while that of carbon residual slow. Selecting operating conditions for an industrial boiler when higher conversion degree is required, long residence time and high temperature are to be chosen.

Conclusions

1) Combustion of oil shale particles can be described by overall first-order reaction model. Activation energy of combustion for Fushun oil shale was estimated to be higher than that for Maoming one.
2) The temperature is the most important factor influencing the combustion process. With the increasing activation energy, the effect of temperature is enhanced.
3) Pressure and particle size also affect the process. High pressure and small size favor oil shale combustion.
4) Using of oil shales with better combustion characteristics enables to shorten residence time to increase boiler capacity.

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