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MECHANISM AND MATHEMATICAL MODEL OF HUADIAN OIL SHALE PYROLYSIS

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In this paper, pyrolysis characteristics of oil shale obtained from Huadian, China, are investigated by thermogravimetry method. The effect of operating conditions, such as particle size, heating rate on the pyrolysis process is analyzed, and kinetic parameters of pyrolysis at different heating rates are calculated using a two-stage Arrhenius model that is solved by the Freeman-Carroll method.

On the basis of these experimental results and theoretical analysis, a mathematical model, fully suitable for the pyrolysis characteristics of oil shale, is developed: mass loss rate is described by a two-stage intrinsic kinetics equation for reducing the calculation error; pyrolytic heat value of volatile is contained in energy equation, and density equation is considered as well, due to the release of a large amount of volatiles in pyrolysis process. Thermogravimetric experimental data are used to validate the described models.

Keywords: *mathematical model, oil shale, pyrolysis, thermogravimetry*

Introduction

Operation experiences with many oil shale-fired circulating fluidized bed (CFB) boilers have proven that burning oil shale in circulating fluidized beds is the cleanest and most economic of all the oil shale-fired utilization modes [1, 2]. Further studies on fundamental performance, for example combustion, pyrolysis, pore structure, are very important for improving the operation of CFB boilers and designing large-scale CFB boilers.

Han *et al*. have studied the combustion mechanism of Huadian oil shale by using thermal analysis techniques [3], and developed the mathematical model of combustion of oil shale [4]. Pyrolysis, a reaction by which the solid organic matter within fuel is converted to oil, gas and char, has an important effect on combustion performance of fuel. For example, if volatile of fuel releases before ignition, its ignition behaviour is usually homogeneous. Many experiments on pyrolysis of oil shale have been carried out at the final experiment temperatures lower than 550°C [5–8], and these studies mainly aim at oil shale retorting. In addition, it is well known that oil shale from different deposits may have quite different and complicated structure and chemical-mineralogical composition that will affect chemical performance.

For providing important pyrolysis information for studying combustion characteristics of Huadian oil shale, this paper studied its pyrolysis characteristics by thermogravimetric analysis in more detail and modeled the pyrolysis process.

Experimental

Oil shale

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

Temperature-programmed pyrolysis tests of oil shale particles were performed in a STA 409 thermogravimetric analyzer with the mass accuracy of 2 μg. Thermocouples measuring the ambient temperature were close to oil shale samples. In every experiment, approximately 4.9 mg of samples were heated from room temperature to 900°C at heating rates of 10, 20, 30 and 40°C min^{-1}. A gas flow rate of 100 mL min^{-1} N_2 was used as ambient gas. It is reasonable to consider that the temperature value measured by the thermocouples is approximate to the surface tempera-

Table 1 Proximate and ultimate analysis of Huadian oil shale (on an air-dry base)

Proximate analysis/	mass/%	Ultimate analysis/mass%	
Moisture	2.90	C	31.63
Volatilbe matter	41.89	H	4.370
Ash	51.61	O	7.764
Fixed carbon	3.60	N	0.726
Low heating/kJ kg^{-1}	8374	S	1.000

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Table 2 Ash component analysis of Huadian oil shale, (mass%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O
52.9	17.74	6.56	14.78	2.99	0.55	0.89	1.27

ture of oil shale particle because of low heating rate and small sample mass.

The thermogravimetric experiments are representative, due to the high precision thermogravimetric analyzer and standard sampling method.

Results and discussion

Effect of particle size on pyrolysis

Figures 1 and 2 present pyrolysis TG and DTG curves of oil shale with different particle diameters at a heating rate of 20°C min^{-1}, respectively.

From Fig.1, there are two obvious mass losses for every pyrolysis TG curve, which has also been presented by other oil shales, for example Pakistani [9], and Thailand [10] oil shale. In this present work, mass loss in the low-temperature stage (300–500°C) is about 25% of the initial mass, and only 10% in the high-temperature stage (600–730°C). The mass loss in the low-temperature stage should be attributed to volatile decomposition, due to lower pyrolysis temperature. Similar to the pyrolysis mechanism of coal [11], a portion of the low-temperature pyrolyzed substance of oil shale would crack, agglomerate or combine metallic elements to form an intermediate product that can sedimentate inside solid particles, and which will decompose in high-temperature conditions. Thus, the authors inferred that the pyrolysed substances during the high-temperature stage involve the intermediate product and carbonate minerals [10]. Comparison of the four curves in Fig. 1 shows that particle diameter in the studied range of particle size has a very slight effect on the pyrolytic process and final pyrolysis degree of oil shale.

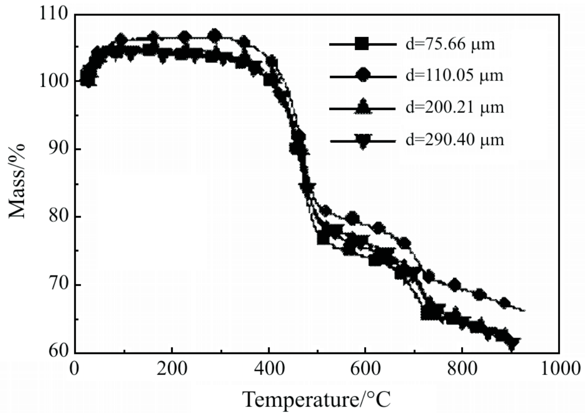

Fig. 1 Pyrolysis TG curves of oil shale with different particle diameters

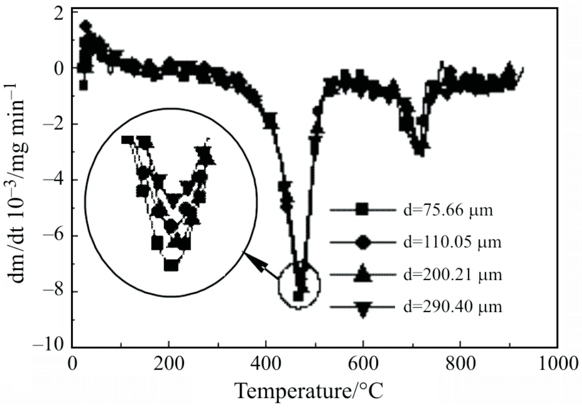

Fig. 2 Pyrolysis DTG curves of oil shale with different particle diameters

From Fig. 2, there are two evident peaks for every pyrolysis DTG curve. The maximum peak value in the low-temperature stage is evidently more than that in the high-temperature stage, showing that the mass loss rate in the low-temperature stage is faster. Partial enlarged drawing in Fig. 2 can present that mass loss rate will somewhat increase with particle diameter decreasing.

Based on Figs 1 and 2, the higher mass loss and pyrolysis rate in the low-temperature stage means that a large amount of volatile matter will sharply erupt, so that it is possible that solid particles may be enwrapped by volatile, making it difficult for ambient gas to contact the surface of solid particles, and providing an ideal condition for homogeneous ignition. And although particle diameter has an effect on pyrolysis degree and mass loss rate in the studied range of particle diameter, the effect is slight enough to be omitted. When particle diameter is enough large, it will possibly affect pyrolysis process because of the mass transfer resistance of ash layer and the complexity of pore structure.

Effect of heating rate on pyrolysis

Figures 3 and 4 present pyrolysis TG and DTG curves of oil shale particle (*d*≈110.05 μm) at different heating rates, respectively.

In this work, increasing the heating rate from 10 to 40°C min^{-1}, causes an increase in pyrolysis degree at the final temperature. Weitkamp and Gutberlet [12], and Williams and Ahmad [9] suggest that the pyrolysis processes of heating rate higher than 10°C min^{-1} may be a diffusion-limited process controlled by heat and product diffusion. They suggested

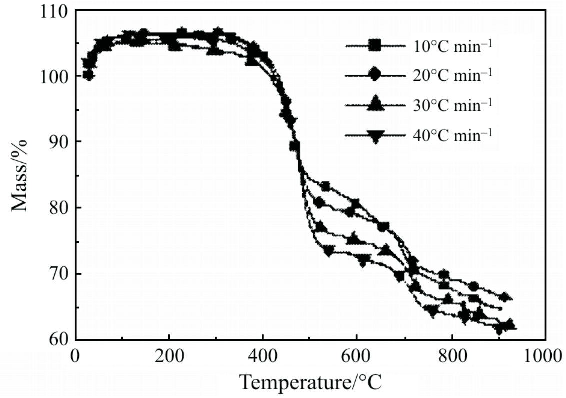

Fig. 3 Pyrolysis TG curves at different heating rates

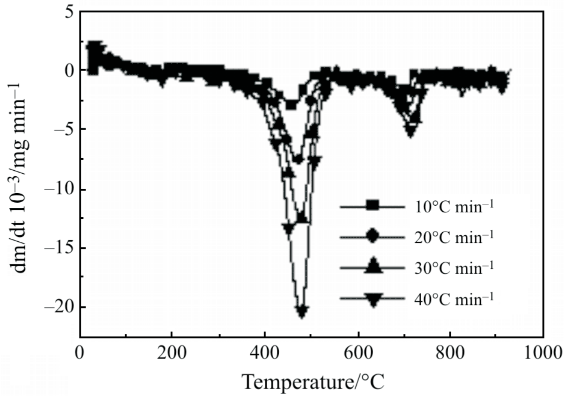

Fig. 4 Pyrolysis DTG curves at different heating rates

that the extent of diffusion control increases at high heating rates because products are generated faster than they can diffuse out of the pores, consequently secondary coking reactions will occur. However, according to DTG curves of Figs 3 and 4, the pyrolysis degree and mass loss rate increases with heating rates, showing diffusion control is not a major factor in pyrolysis process for Huadian oil shale.

Kinetic parameter of pyrolysis

According to reaction rate theory, whether for the low-temperature or high-temperature stage, kinetic equation of oil shale pyrolysis may be written as follows:

$$\frac{dm}{dt}=-A_i\exp\left(-\frac{E}{RT}\right)f(m)$$

where $f(m)=m^n$.

Freeman-Carroll method is used to solve the kinetic equation. Table 3 gives calculation results, showing that the activation energy in the low-temperature stage will decrease with an increase in the heating rate, however, in the high-temperature stage the value will increase with increased heating rate. In fact, the relationship between activation energy and heating rate is very complex. Williams and Ahmad [13] studied the effect of heating rate on the pyrolysis process of Pakistan oil shale using the thermogravimetric analysis. In their studies, the thermogravimetric data were analyzed to determine the kinetic parameters of activation energy and pre-exponential factor using two methods, the Arrhenius and Coats-Redfern analyses, showing that there was no clear relationship between activation energy and heating rate: in some cases, for example the Salt Range oil shale, the activation energies were very similar irrespective of heating rate; however, in other cases, there were significant differences in the calculated activation energies, in relation to heating rate, for example, the Kark oil shale. Consequently, it is concluded that the discrepancies in the activation energy for oil shale decomposition is not perhaps surprising, in that variations will occur depending on the type of oil shale and type of pyrolysis.

Pyrolysis model

A variety of approaches have been used to model the complex pyrolysis and combustion process of fuel. The simplest attempts are empirical and employ global kinetics, in which Arrhenius expressions are used to correlate mass loss rate with temperature [14, 15]. In addition, some characteristics of oil shale must be considered in the pyrolysis model:

- Two evident mass losses in the pyrolysis process of oil shale mean that a two-stage kinetic equation should be adopted for reducing the calculation error.
- A large amount of released volatiles will greatly decrease particle density.

Table 3 Kinetic parameters of Huadian oil shale at different heating rates

ϕ/°C min^{-1}	Low-temperature stage			High-temperature stage		
	A_1/min^{-1}	E_1/kJ mol^{-1}	n_1	A_2/min^{-1}	E_2/kJ mol^{-1}	n_2
10	0.75	226.87	3.70	1.54	20.87	0.68
20	3.31	153.77	2.73	3.81	30.14	0.83
30	4.51	83.05	1.85	21.86	113.2	2.02
40	7.66	52.21	1.66	667.20	189.70	3.62

- Because of the high content of volatile, the pyrolytic heat value of volatile matter should be included in any energy equation.
- Oil shale has high ash content, causing the particle diameter of oil shale to become nearly unidiameter during the pyrolysis process.

Mathematical model of pyrolysis

Intrinsic kinetics equation

According to the Arrhenius equation, the reaction rate equation of oil shale pyrolysis may be written:

$$\frac{\mathrm{d}m}{\mathrm{d}t}=-A_\mathrm{i}\exp\left(-\frac{E_\mathrm{i}}{RT}\right)m^\mathrm{n} \qquad (1)$$

Energy equation

According to differential equation of heat conduction: $\rho c_\mathrm{p}\frac{\partial T}{\partial t}=div(k\cdot gradT)+q_\mathrm{v}$, the pyrolysis energy equation is described as follows:

$$\rho_\mathrm{p}c_\mathrm{p}\frac{\partial T}{\partial t}=\lambda\left(\frac{\partial^2 T}{\partial r^2}+\frac{2}{r}\frac{\partial T}{\partial r}\right)+\Delta H\frac{\mathrm{d}\rho_\mathrm{p}}{\mathrm{d}t} \qquad (2)$$

Particle density equation

Since particle diameter maintains nearly constant in the pyrolysis process, a large amount of volatiles released will make particle density decrease. Particle density equation at time t may be thus described as follows:

$$\frac{\mathrm{d}\rho_\mathrm{p}}{\mathrm{d}t}=\frac{6(\mathrm{d}m)}{\pi d_p^3\mathrm{d}t} \qquad (3)$$

Boundary conditions

$$r=d_\mathrm{p}/2,$$

$$-\lambda\frac{\partial T}{\partial r}=\alpha(T_\mathrm{B}-T_\mathrm{a})+\varepsilon\sigma F[(T_\mathrm{B}+273)^4-(T_\mathrm{a}+273)^4]$$

$$r=0, \qquad \frac{\partial T}{\partial r}=0$$

Initial conditions

$$t=0,\ T=T_0$$

where T_B is the ambient temperature around oil shale particle, K; $T_\mathrm{B}=T_\mathrm{s}=T_0+\Phi t$ for temperature-programmed ambient, however T_B=constant for constant temperature ambient, for example CFB furnaces.

Proving the mathematical model

For proving the pyrolysis model with the above thermogravimetric experimental data, the pyrolysis model can be simplified further, combined with the thermogravimetric experimental conditions.

Simplifying condition

The temperature distribution inside oil shale particles is uniform because of small particle diameter and low heating rate.

Simplifying model

On the basis of simplifying conditions, simplified mathematical model is described as follows:

$$-\frac{\mathrm{d}m}{m^\mathrm{n}}=\frac{A_\mathrm{i}}{\phi}\exp\left(-\frac{E_\mathrm{i}}{RT}\right)\mathrm{d}T \qquad (4)$$

Integrating (4), the final equation of pyrolysis model is expressed as follows:

$$\begin{cases}\ln\frac{m}{m_0}=\frac{A_\mathrm{i}}{\phi}\int_{T_\mathrm{Si}}^{T}\exp\left(-\frac{E_\mathrm{i}}{RT}\right)\mathrm{d}T & n=1\\ \frac{1}{1-n}(m_0^{1-\mathrm{n}}-m^{1-\mathrm{n}})=\frac{A_\mathrm{i}}{\phi}\int_{T_\mathrm{Si}}^{T}\exp\left(-\frac{E_\mathrm{i}}{RT}\right)\mathrm{d}T & n\neq1\end{cases} \qquad (5)$$

Initial conditions: $t=t_\mathrm{s}$, $T=T_\mathrm{s}$, $m=m_0$.

Activation energies E_i, pre-exponential factors A_i and reaction orders n of Eq. (5) have been given in Table 3. Figure 5 compares the model TG curve of oil shale particle ($d\approx110.05$ μm) with experimental TG curve under the heating rate of 20°C min^{-1}; Fig. 6 shows model TG curves of oil shale particle ($d\approx110.05$ μm) under different heating rates.

In Fig.5, the experimental TG curve has more mass gain (3–5%) in the temperature range of 25–60°C than shown by the model calculations. It is thought that the cause of this was that oil shale would

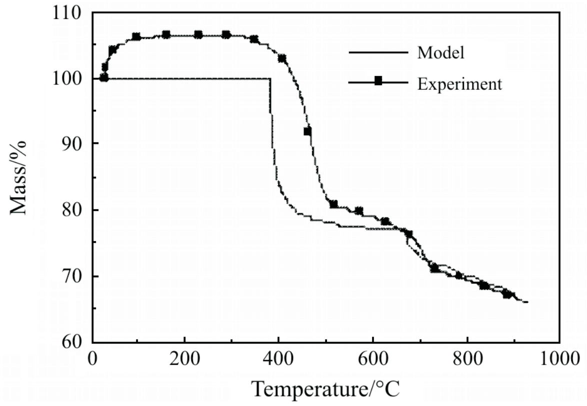

Fig. 5 TG curve comparison between experiment and model at ϕ=20°C min^{-1}

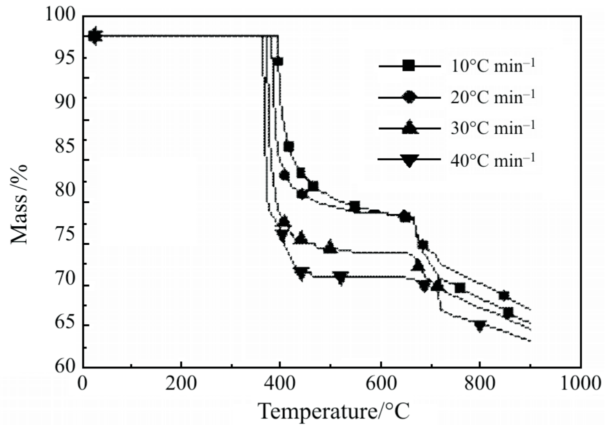

Fig. 6 Model TG curves at different heating rates

adsorb a certain ambient gas in the initial stage of the thermogravimetric experiments. Because mass of oil shale sample is only 4.9 mg, mass of N_2 absorbed can not be omitted, and will make measurement result increase, which makes the initial particle mass exceeds 100%. In the high-temperature stage, the experimental curve is close to the model curve.

In Fig. 6, increasing the heating rate results in an increase in pyrolysis degree, which is coincident with experiment result shown by Fig. 3.

Conclusions

- In the pyrolysis process of Huadian oil shale, there are two obvious mass losses. Mass loss in the low-temperature stage is about 25% of the initial mass, and only 10% in the high-temperature stage. DTG curves shows that the mass loss rate in the low-temperature stage is evidently more than that in the high-temperature stage.
- High mass loss and pyrolysis rate of oil shale in the low-temperature stage means that large amounts of volatiles will sharply erupt to enwrap solid phase, which will provide an ideal condition for the homogeneous ignition of oil shale.
- Particle diameter has a very slight effect on the pyrolysis degree and mass loss rate of Huadian oil shale in the studied range of particle diameter, and mass loss rate and pyrolysis degree increases with heating rates increasing.
- On the basis of these above experimental results and theoretical analysis, a mathematical model of pyrolysis, fully suitable for the intrinsic property of oil shale, is developed: pyrolytic heat value of volatile is included in energy equation, and density equation is considered, due to the release of a large amount of volatiles in heating process; mass loss rate is described by a two-stage Arrhenius equation for reducing the calculation error. The thermogravimetric experimental data are used to validate the pyrolysis model.

Nomenclatures

A – pre-exponential factor, min^{-1}
c_p – specific heat at constant pressure, J kg^{-1} K^{-1}
d_p – particle diameter, m
E – activation energy, kJ mol^{-1}
F – radiation factor
ΔH – pyrolytic heat value, J kg^{-1}
m – remaining volatile mass, kg
n – reaction order
r – radial distance, m
R – universal gas constant, J mol^{-1} K^{-1}
t – time of pyrolysis process, min
t_s – time spent from room temperature to initial temperature of pyrolysis, min
T – pyrolysis temperature at time t, K
T_a – surface temperature of particle, K
T_B – ambient temperature, K
T_{max} – temperature corresponding the maximum rate of pyrolysis, K
T_s – initial temperature of pyrolysis process, K
α – convective coefficient of heat transfer, W m^{-2} K^{-1}
ε – emissivity of oil shale
λ – heat conduction coefficient, W m^{-1} K^{-1}
ρ_p – particle density, kg m^{-3}
σ – Boltzmann constant, W m^{-2} K^{-4}
ϕ – heating rate, °C min^{-1}

Subscripts

0 – initial moment of experiment
i – stage i of pyrolysis process

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References

1 A. Paist, Oil Shale, 21 (2004) 181.
2 X. M. Jiang, D. C. Liu, H. P. Chen, C. G. Zheng and Y. K. Qin, Oil Shale, 18 (2001) 73.
3 J. M. Nazzal, J. Anal. Appl. Pyrolysis, 62 (2002) 225.
4 S. Y. Li and C. T. Yue, Fuel Process. Technol., 85 (2004) 51.
5 N. Olukcu, J. Yanik, M. Saglam and M. Yuksel, J. Anal. Appl. Pyrolysis, 64 (2002) 29.
6 J. O. Jaber, S. D. Probert and P. T. Williams, Energy, 24 (1999) 761.
7 X.X. Han, X.M. Jiang and Z.G. Cui, J. Therm. Anal. Cal., 84 (2006) 631.

8 X.X. Han, X.M. Jiang and Z.G. Cui, Combust. Theory Model., 10 (2006) 145.
9 P. T. Williams and N. Ahmad, Fuel, 78 (1999) 653.
10 S. Sato and M. Enomoto, Fuel Process. Technol., 53 (1997) 41.
11 X. X. Sun and J. Y. Chen, Physicochemical Principle of Pulverized Coal Combustion, Wuhan, HUST Press, 1991, pp. 118–123.
12 A. W. Weitkamp and L. C. Gutberlet, Ind. Eng. Chem. Process. Des. Dev., 9 (1970) 386.
13 P. T. Williams and N. Ahmad, Applied Energy, 66 (2000) 113.
14 M. V. Kok, J. Therm. Anal. Cal., 79 (2005) 175.
15 M. V. Kok, G. Pokol, C. Keskin, J. Madarasz and S. Bagci, J. Therm. Anal. Cal., 76 (2004) 247.

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