STUDY ON PYROLYSIS OF PARTICULATE OIL SHALE WITH AN IMPROVED THERMOGRAVIMETRIC APPARATUS*

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ABSTRACT

In the usual study on the pyrolysis of particulate oil shale weight loss and temperature measurements are made separately. In the present work a China-made LCT-1 thermogravimetric apparatus was modified to measure the center temperature and surface temperature of sample particle simultaneously with weight loss measurement. Cylindrical particles of Fushun and Maoming oil shales of 2-10 mm equal height diameter were used. Weight loss measurements and temperature histories enabled the investigation of the influence of particle size and heating temperature on pyrolysis time in an accurate and convenient way. At a constant heat-up rate of 5°C/min, for a shale cylinder of 10 mm diameter, the center temperature was slightly lower than the surface temperature, and the difference in temperature for Fushun oil shale was only 2°C, while for Maoming oil shale it was 4°C. An overall first order reaction model was used to describe the pyrolysis process of particulate oil shale. For Fushun oil shale the retorting time required was proportional to the diameter squared, while for Maoming oil shale it was proportional to the particle diameter. This difference could be accounted for by more developed lamination of the latter. The results obtained could be used for reference for design and production of particulate oil shale retorting.

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* Study supported by National Science Foundation.

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INTRODUCTION

In recent years extensive investigations have been made on the pyrolysis and oxidation of pulverized oil shale with differential thermal analysis (DTA) and thermogravimetry (TG) both in China and in other countries[1-5]. However, shale particles or lumps rather than fines are used in retorting. Granoff and Nuttall reported study on the pyrolysis of particulate oil shale[6], with separate determination of weight loss and temperature difference. In the present study, a China-made DTA-TG combined apparatus was modified to determine weight loss and center-surface temperature difference simultaneously. Shale samples of dozens to hundreds mg in weight and of diameter up to 10 mm could be used.

DESCRIPTION OF APPARATUS

Flow diagram of LCT-1 DTA-TG apparatus

The apparatus is a combination of DTA and TG, the ordinary flow diagram is shown as in Fig. 1. Reference and sample are put separately into two crucibles(1) in the electric furnace (2). Thermocouples are connected to the base of crucible pans (3). These two thermocouples are connected and welded in series with opposite ends. The thermal response of decomposition of sample is fed into differential heat magnifier, and then to the recorder (11). The off balance due to weight change in decomposition is transmitted through sample support rod(8), photoelectric displacement sensor and thermogravimetric detector to the recorder (11) which generates weight change curve continuously.

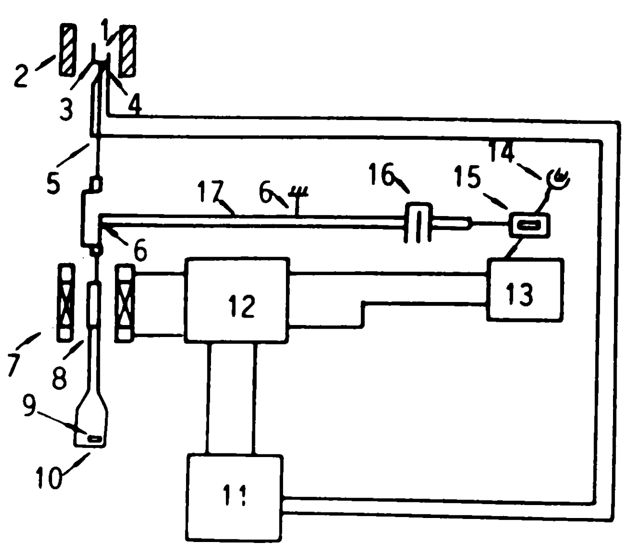

Fig. 1. Schematic drawing of apparatus

1. crucible, 2. electric furnace, 3. pan, 4. thermocouple, 5. sample rod, 6. metallic band, 7. coil, 8. permanent magnet, 9.weight in balance, 10. weight pan, 11. recorder, 12. servomagnifier, 13. photoelectric cell, 14. lamp, 15. shield, 16. regulating cock, 17. balance beam

Modification

Two pairs of thermocouples were passed through a four-holed porcelain tube, which served as sample support rod. The hot end of one pair of thermocouple was inserted into the center hole of shale sample botton, its cold end was connected to the junction on thermogravimeter recorder; a temperature recorder was connected in parallel to determine shale center temperature and thermogravimetric curve. The hot end of the other thermocouple was made into spiral shape in close contact with the external surface of shale sample, its cold end was connected to the DTA junction and input to the recorder. Surface temperature instead of differential heat was shown. In this way, thermogravimetric curve, shale center temperature and surface temperature could be determined simultaneously.

SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS

Oil shale from Fushun and Maoming was cut and made into cylinders of equal diameter height, 3, 4, 7, 9, 10 mm in size. From the principles of heat transfer and experimental verification, the heat transfer behavior of an equal diameter height cylinder was approximately the same as that of a spherical particle in retorting. A hole of 1.5 mm diameter was drilled in the center of cylinder bottom, where a thermocouple was embedded to determine the center temperature.

Shale sample was placed directly on the support rod. Heating of the sample was program-controlled at a heat-up rate of 5°C/min, with high purity nitrogen of 110 cc/min as carrier gas. Decomposition of sample began at about 330°C, and came to completion at 520°C.

EXPERIMENTAL RESULTS

1. For sample size less than 10 mm the center-surface temperature

difference was insignificant. Only negligible temperature difference was found at lower temperatures, at a temperature as high as 500°C, the temperature difference for Fushun oil shale was only 2°C, and for Maoming oil shale 4°C. This could be possibly ascribed to smaller porosity and in turn greater heat conductivity of the more compact Fushun oil shale.

2. The weight loss curve from experiment could be transformed into conversion versus retorting temperature, as shown in Fig. 2.

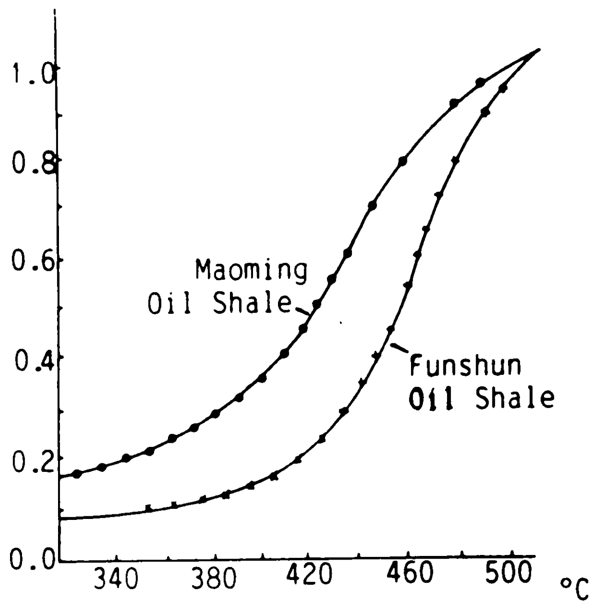

Fig. 2. Conversion versus Retorting Temperature
for Maoming and Fushun Oil Shales (10 mm)

From Fig. 2, at the same temperature the pyrolysis conversion was higher for Maoming oil shale than for Fushun oil shale.

3. From the experimental results, the relationship of conversion and retorting temperature for different particle sizes and different oil shales were obtained. Under the present experimental conditions there was little difference in the center and surface temperatures. The average temperature of center and surface temperatures was used as the retorting temperature. An overall first-order reaction model was used for data treatment. Apparent activation energy and apparent frequency factor A were obtained with differential method, as shown in Table 1 and 2. The reaction equation was as follows:

$$\frac{dx}{dt} = k(1-x) = A\, e^{-E/RT}(1-x) \qquad (1)$$

where x--conversion of pyrolyzable matter in oil shale

k--reaction rate constant min-1

t--reaction time min

A--apparent frequency min^{-1}

E--apparent activation energy KJ/mol

R--gas constant (8.3 KJ/K.mol)

From Tables 1 and 2, the correlation coefficients of experimental data with least mean square fitting were all greater than 0.99, which proves it reasonable to treat pyrolysis data of shale particles smaller than 10 mm with the overall first order reaction model. The time required for retorting at constant temperature could be calculated from E, A, k:

$$t = \frac{1}{k} \ln(1-x) \qquad (2)$$

The retorting time for a conversion x of 0.9 was shown in Tables 1 and 2.

Table 1. Pyrolysis of Fushun Oil Shale of Different Particle Sizes

Particle size mm		11.1	9.2	4.3	2.6
Apparent activation energy KJ/mol		144.63	170.96	162.60	165.11
Apparent frequency factor min^{-1}		1.1×10^{9}	9.3×10^{10}	4.5×10^{10}	6.9×10^{10}
Correlation coefficient		0.992	0.994	0.990	0.993
Reaction rate constant k min^{-1}	520°C	0.3218	0.5117	0.8153	0.8948
	500°C	0.1825	0.2616	0.4301	0.4678
	480°C	0.1004	0.1291	0.2193	0.2363
	460°C	0.0535	0.0613	0.1078	0.1150
Retorting time at constant temp. min (conversion 90%)	520°C	7.16	4.53	2.83	2.57
	500°C	12.6	8.80	5.35	4.92
	480°C	22.9	17.8	10.5	9.74
	460°C	43.1	37.6	21.4	20.0

Table 2. Pyrolysis of Maoming Oil Shale of Different Particle Sizes

Particle size mm		10.7	9.3	4.5	3.2
Apparent activation energy KJ/mol		90.71	98.65	114.53	125.82
Apparent frequency factor min^{-1}		$5.3x10^5$	$1.9x10^6$	$3.1x10^7$	$1.8x10^8$
Correlation coefficient		0.987	0.992	0.994	0.990
Reaction rate constant	520°C	0.5683	0.6159	0.8548	0.9832
k min^{-1}	500°C	0.3930	0.4181	0.5449	0.6002
	480°C	0.2701	0.2781	0.3391	0.3570
	460°C	0.1819	0.1809	0.2045	0.2064
Retorting time at	520°C	4.65	3.74	2.69	2.34
constant temp. min	500°C	5.86	5.51	4.23	3.83
(conversion 90%)	480°C	8.53	8.28	6.79	6.45
	460°C	12.66	12.73	11.30	11.10

4. The apparent activation energy and apparent frequency factor decreased with increasing particle size, which signified inclusion of heat transfer and diffusion in apparent activation energy. The decrease of reaction rate constant with increasing particle size seemed reasonable from the corresponding decrease of E and A. The reaction rate constant of Maoming oil shale decreased from 0.983 min^{-1} to 0.568 min^{-1}, when the particle size increased from 3.2 mm to 10.7 mm (at 520°C). The reaction rate constant of Fushun oil shale decreased from 0.898 min^{-1} to 0.320 min^{-1}, when the particle size increased from 2.6 mm to 11.1 mm (at 520°C).

5. The time required for retorting increased with increasing particle size. From least mean square regression, the retorting time at constant temperature for Maoming oil shale was proportional to particle size, while that for Fushun oil shale was proportional to particle size squared, as shown in Figs. 3 and 4 respectively.

These two relationships were reasonable with correlation coefficients greater than 0.98. Fushun oil shale was affected by particle size to a larger extent than Maoming oil shale. This was probably due to significant lamination of Maoming oil shale. The fissured shale facilitated diffusion of decmposition products. On the other hand, less apparent fissure eould be found in compact Fushun oil shale.

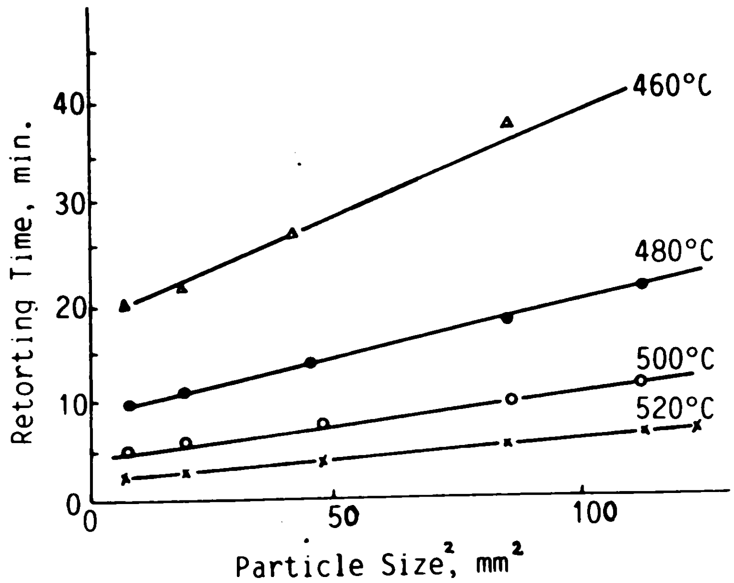

Fig. 3. Retorting Time versus Particle Size Squared for Fushun Oil Shale

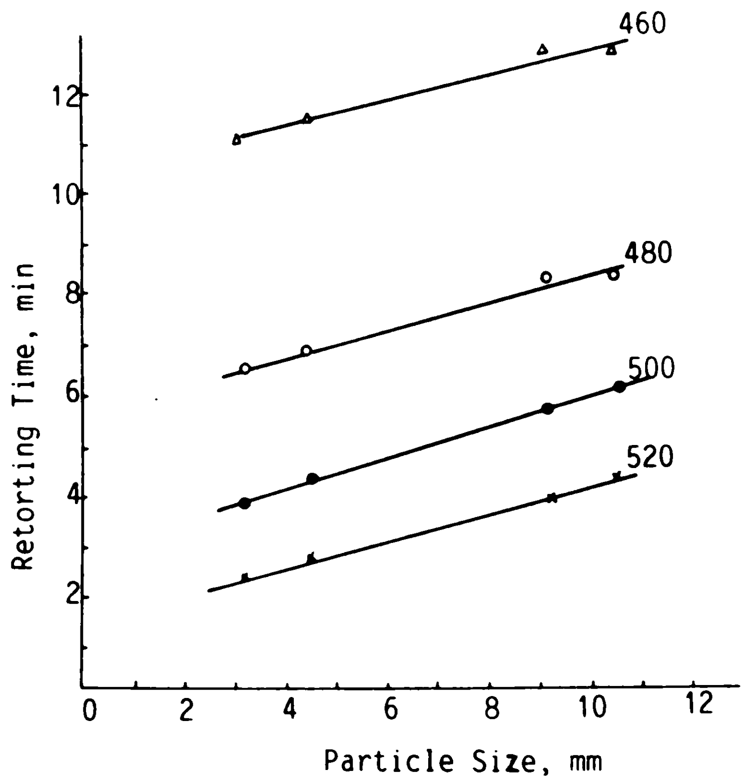

Fig. 4. Retorting Time versus Particle Size for Maoming Oil Shale

From Figs. 3 and 4, it was shown that in the interval of lower temperature of 460-480°C, the decrease in retorting time for a rise in temperature of 20°C was more than in the interval of higher temperature of

500-520°C, e.i., a rise in temperature would have a greater effect in reducing retorting time in the interval of lower temperature.

CONCLUSION

1. The modified LCT-1 DTA-TG apparatus is capable of handling samples from fines of dozens mg to particles of hundreds mg up to 10mm.It can be used for studying particulate materials.

2. Simultaneous determination of weight loss and center-surface temperature difference can be made with this modified apparatus.

3. For particle size less than 10 mm at a heat-up rate of 5°C/min little difference in center and surface temperatures is observed. An overall first-order reaction model can be used for data treatment.

4. In the size range of 2 to 10 mm, the retorting time of Maoming oil shale at constant temperature is proportional to particle size, while that of Fushun oil shale is proportional to particle size squared.

AKNOWLEDGEMENT

The authors are grateful to Prof. Zhu Yajie for his help.

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