DRYING MECHANISM AND KINETICS MODEL OF LUMP-SIZE MAOMING OIL SHALE WITH HIGH MOISTURE CONTENT

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ABSTRACT

The drying process of Maoming oil shale (moisture content 19%, lump size 30-60 mm) has been studied with weight loss and temperature distribution observations of a single lump shale. Three stages of drying process can be shown as: (1) uniform diffusion and surface evaporation of free moisture below 105-110°C, (2) shrinking core evaporation of free moisture at constant temperature of 105-110°C, (3) evaporation of adsorbed water (capillary water) at 110-250°C. Different models for each stage fit well laboratory measurements.

INTRODUCTION

Maoming oil shale is characterized by high porosity and developed capillarity. Its moisture content can be as high as 13-22%, which causes reduced retort throughput. Thermal disintegration of lump shale in retort results in uneven gas flow and higher resistance. The drying of particulate Maoming oil shale has been reported[1]. The present work is concerned with lump shale used in commercial retorts.

EXPERIMENTAL

Description of apparatus

A set of thermogravimetric drying apparatus was designed for studying lump shale, as shown in Fig. 1.

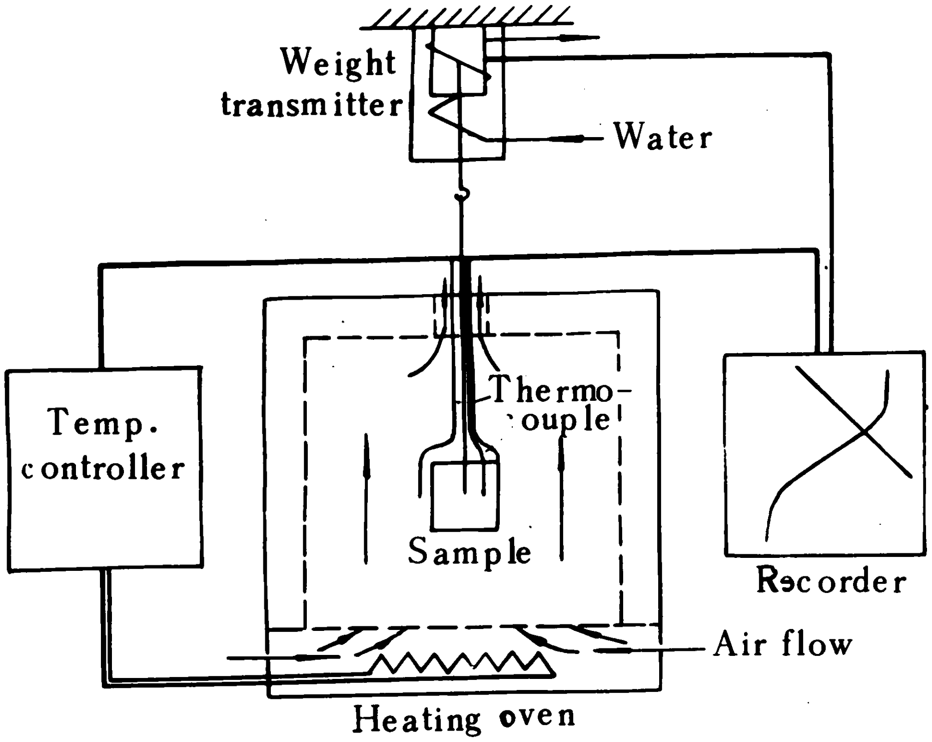


Fig. 1. Schematic drawing of apparatus

The sample was suspended under a transducer by a chromel wire in the center of a drying oven with direct contact of hot air. The transducer was surrounded by a water jacket to maintain constant temperature. Several thermocouples were inserted to different radial positions of the sample. The temperatures at center, surface and other positions could be measured and recorded.

Sample preparation

Samples were cut and ground to cylinders of equal-length-diameter, 30, 40, 50, 60mm in size. Different ways of attaining high moisture content, such as soaking or spraying with water were tried but failed to simulate the real situation in Maoming. Finally the sample was buried in damp soil for 4-5 days, and the capillary diffusion helped to reach a high moisture content of 19% without disintegration.

Table 1. Moisture content after wetting

D mm	H mm	Weight after wetting (g)	Weight after drying (g)	Moisture %
30	30	43.6	36.7	18.5
40	40	103.6	87.0	19.0
50	50	195.3	163.4	19.5
60	60	338.0	283.5	19.2

Experimental conditions and data

All the drying experiments were carried out at a heat-up rate of 3°C/ min in the range of room temperature to 230-250°C. The weight loss was measured and recorded through the transducer. The shale moisture was reduced gradually, as shown in Fig. 2. It can be seen that the weight

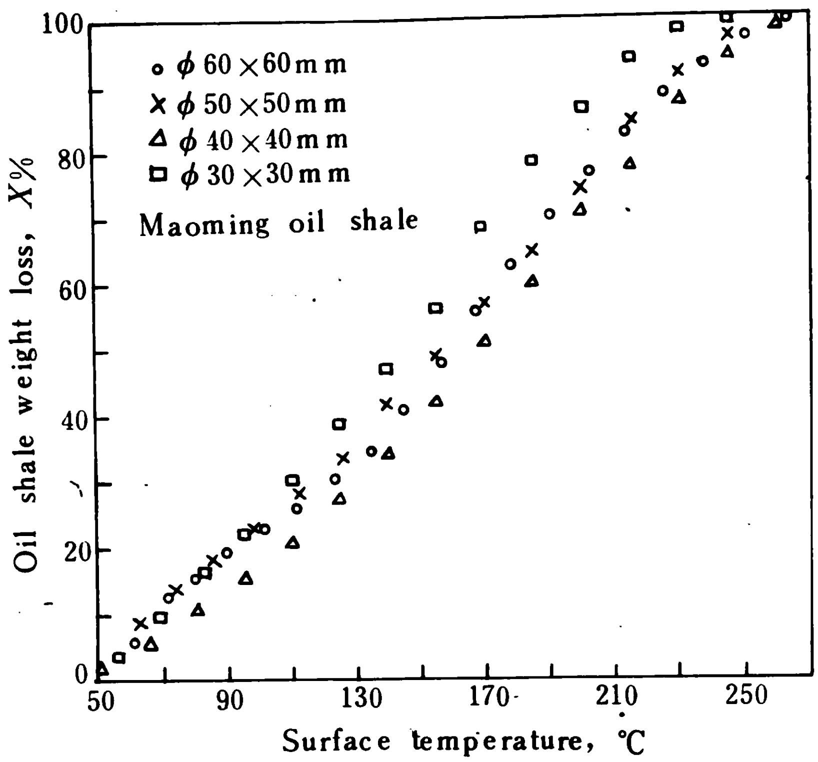


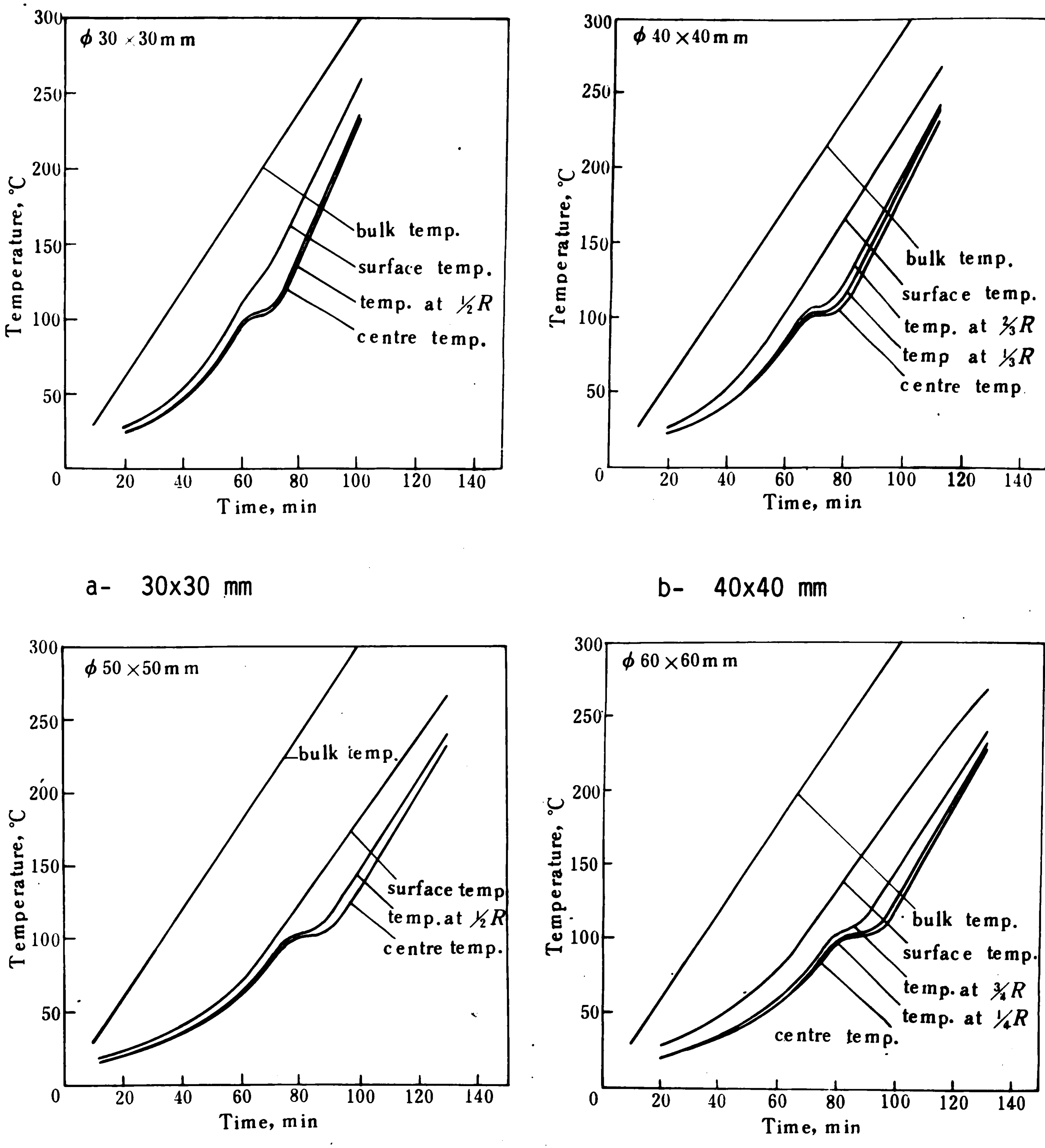
Fig. 2. Weight loss curve of oil shale samples with different diameters

loss curves behave similarly. Linear relationship can be observed until one fourth of the moisture is lost, after that the drying rate tends to decrease.

Several holes of 1.5 mm in diameter and one half cylinder height in depth were drilled at the center, 1/4 R, 1/2 R radial positions to hold 1.5 mm sheathed thermocouples. The surface temperature was measured by fastening securely the thermocouple on the sample surface. The temperature distribution is shown in Fig. 3a-d.

DRYING MECHANISM

Three distinct stages can be observed in the temperature profile shown in Fig. 3. The first stage: Oil shale is heated from room temperature to about 110°C. There exists a small radial temperature gradient.



a- 30x30 mm

b- 40x40 mm

c- 50x50 mm

d- 60x60 mm

Fig. 3. Temperature profile of a single lump shale

Free moisture held on the surface and in large capillaries diffuses uniformly towards the surface and evaporates. The surface temperature can be considered as the wet bulb temperature of the surrounding air flow. About 25% of the moisture is lost in 60-80 minutes. The second stage: The shale internal temperature is kept constant at about 110°C, while the surface temperature is increasing. The surface of evaporation of free moisture moves inward gradually in terms of shrinking core evaporation. In this stage, another 25% of the moisture is evaporated in 10-15 minutes, and the surface temperature reaches 160-170°C. The third stage: Both the internal temperature and the surface temperature increase linearly, and there exists an appreciable temperature gradient. The moisture adsorbed in small capillaries is evaporating. The smaller the pore diameter, the smaller the vapor pressure and the more diffulty will be in evaporation. The shale temperature is lower in the center and higher at the surface. The inner temperature gets higher until the moisture in internal small capillaries is lost.

At the end of the second stage and the beginning of the third stage, evaporation of moisture in small capillaries causes a pressure difference between large capillaries with no moisture and small capillaries. Disintegration takes place if the pressure difference is large enough to exceed the capillary strength.

DRYING MODELS

There are many drying models for the porousmedia[2,3,4]. In this study, three drying models were suggested to fit the three stages.

(1) Uniform diffusion and surface evaporation of free moisture.For high moisture content, the diffusional effect is not controlling. The effect of low relative humidity in air flow can be neglected. The rate of moisture evaporation is affected by the moisture content and surface temperature.

$$\frac{dx}{dt} = K_1(1-X) = A_1 e^{-E/RT}(1-X) \qquad (1)$$

$$dT = \Phi\, dt \qquad (2)$$

$$\frac{dx}{dT} = \frac{A_1}{\Phi} e^{-E_1/RT}(1-X) \qquad (3)$$

where X--- weight loss, %
t--- time, min
T--- surface temperature, K
ϕ--- heat-up rate 3°C/min
A_1-- pre-exponential factor, min^{-1}
E--- apparent activation energy of evaporation, KJ/mol
k_1-- evaporation rate constant, related to the physical properties fo oil shale, evaporation surface area etc.

Integration of (3) gives

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right]=\ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \quad (4)$$

(2) Shrinking core model of free moisture evaporation

The evaporation surface of free moisture moves inward from shale surface to center. The drying rate is related to the area of evaporation surface.

$$\frac{dx}{dt}=k_2\frac{3/2\pi d^2}{3/2\pi D^2}=k_2\frac{d^2}{D^2}=A_2e^{-E_2/RT}\left(\frac{d}{D}\right)^2 \quad (5)$$

where d--- diameter of evaporation front surface
D--- diameter of shale cylinder

Assume the moisture is evenly distributed

then

$$1-X=\frac{d^3}{D^3} \quad (6)$$

$$\frac{dx}{dt}=A_2e^{-E_2/RT}(1-X)^{2/3} \quad (7)$$

Integrating (7)

$$\ln\left[\frac{1-(1-X)^{1/3}}{T^2}\right]=\ln\frac{A_2R}{3\phi E_2}\left(1-\frac{2RT}{E_2}\right)-\frac{E_2}{RT} \quad (8)$$

(3) Small-capillary adsorbed moisture evaporation model

Both the internal and surface temperatures increase linearly.

For a specific capillary diameter, the outer at the higher temperature side has its moisture evaporate first, while the inner at the lower temperature side has its moisture evaporate later. The surface of evaporation can be considered as moving inward and the shrinking core model, as equation (8), is also applicable. The temperature T is taken as the instantaneons temperature at the $\frac{1}{2}$R.

RESULTS AND DISCUSSION

The calculated results for each stage are listed in Tables 2-4.

Table 2. Evaporation model for the first stage

Lump size, mm	30x30	40x40	50x50	60x60
Temperature range, °C	room temp. ---110	room temp. ---120	room temp. ---120	room temp. ---135
E, KJ/mol	24.93	21.3	16.48	13.39
A, min^{-1}	72.23	13.57	3.70	1.25
Correlation coefficient	0.997	0.999	0.996	0.994

Table 3. Shrinking core model for the second stage

Lump size, mm	30x30	40x40	50x50	60x60
Temperature range,° C	116-145	125-155	112-140	130-156
E, KJ/mol	15.65	17.59	15.24	18.4
A, min^{-1}	3.18	3.50	2.39	4.45
Correlation coefficient	0.999	0.999	0.999	0.998

In this stage, E varies in the range of 15-18 KJ/mol and has nothing to do with lump size, the evaporation of free moisture at constant temperature can be considered independent of lump size.

Table 4. Shrinking core model for the third stage

Lump size, mm	30x30	40x40	50x50	60x60
Temperature range,° C	125-230	155-260	140-245	156-238
E, KJ/mol	18.05	18.88	16.25	16.15
A, min^{-1}	7.33	6.43	3.54	3.44
Correlation coefficient	0.999	0.999	0.994	0.999

CONCLUSIONS

1. Three stages exists in the drying process of Maoming oil shale. They are well represented by the surface evaporation model, shrinking core evaporation model and capillary adsorbed moisture evaporation model respectively. Good fit with laboratory data gives correlation cofficient

above 0.99.

2. The activation energy calculated are in the range of 16-26 KJ/mol, from which the evaporation can be taken as physical desorption.

3. When the free moisture in large pores no longer exists and the moisture adsorbed in small capillaries begin to evaporate, the pressure difference becomes large enough to exceed capillary strength, resulting in shale disintegration.

4. The study of drying of lump shale in the size range used in commercial retorts is helpful to production and design.

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