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INVESTIGATION ON THE PYROLYSIS OF FUSHUN OIL SHALE AND ESTONIAN KUKERSITE LUMPS

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ИССЛЕДОВАНИЕ ПИРОЛИЗА КРУПНОКУСКОВОГО ФУШУНЬСКОГО ГОРЮЧЕГО СЛАНЦА И ЭСТОНСКОГО СЛАНЦА-КУКЕРСИТА

Abstract

In the present work, oil shale lump pyrolysis apparatus was used to measure weight loss and intraparticle temperature profile for the lumps (20—50 mm in diameter) of Fushun oil shale and Estonian oil shale which is called kukersite. A pyrolysis model was uniquely developed which took into account both the pyrolysis reaction and intraparticle heat transfer. On the basis of experimental data, oil shale pyrolysis kinetic parameters were then determined by using the developed model. Furthermore, the effects of various variables (temperature, lump size and heating rate) on oil shale pyrolysis were investigated during experimentation. It was found that model predictions agree reasonably well with experimental data.
(Keywords: oli shale lump; model; temperature gradient)

Introduction

Up to now, only two countries in the world, China and (former) USSR (in particular Estonia), have oil shale industry in operation since decades ago. In the recent years, cooperation between two countries on the research and development of oil shale has been enhanced. Therefore, it is very necessary to carry out some research work on the comparison of the pyrolysis of oil shale from China and Estonia.

In the oil shale retorting processes, oil shale lumps rather than fines have been usually used as feedstock. From previous studies [1—3], it is found that the pyrolysis of oil shale lumps is much more complicated than pyrolysis of oil shale fines. The former involves not only chemical reactions, but also heat transfer, mass transfer, sample disintegration, etc. Because of poor thermoconductivity of oil shale, intraparticle heat transfer becomes the controlling step during the pyrolysis of oil shale lumps. Evidently, the investigation on intraparticle heat conduction will be the key to the overall pyrolysis of oil shale lumps.

In spite of the rather extensive research in this field, no one has developed a comprehensive model which takes into account both the pyrolysis reaction and heat transfer within the lump. Although a lot of work on the pyrolysis of oil shale fines has been performed at home and abroad, oil shale fines are not representative of the lumps that are used in the present retorting processes. Consequently, research work for developing a model to describe the retorting of oil shale lumps is of significance for the design and operation of oil shale retorts.

Experimental

1. Apparatus

In this study, the experimental apparatus was specially designed and constructed to obtain weight loss and intraparticle temperature profile. The schematic diagram of the apparatus is shown in Fig. 1.

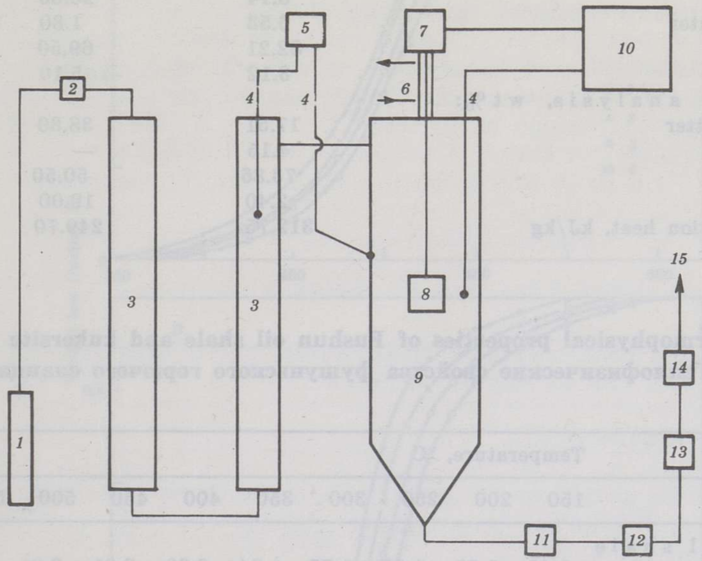

Fig. 1. Schematic diagram of experimental apparatus: *1* — gas carrier; *2* — flowmeter; *3* — gas preheater; *4* — thermocouple; *5* — temperature controller; *6* — cooling water; *7* — load cell; *8* — sample; *9* — reactor; *10* — recorder; *11* — electrostatic precipitator; *12* — ice bath; *13* — mass flowmeter; *14* — G. C.; *15* — vent

Рис. 1. Принципиальная схема аппаратуры для эксперимента: *1* — носитель газа; *2* — расходомер; *3* — подогреватель газа; *4* — термопара; *5* — регулятор температуры; *6* — охлаждающая вода; *7* — секция загрузки; *8* — образец; *9* — реактор; *10* — регистрирующий прибор; *11* — электростатический осадитель; *12* — ледяная ванна; *13* — расходомер для определения потери массы; *15* — вентиляционное отверстие

Experimentation was divided into two parts: determination of weight loss and measurement of temperature gradients within the lump. In the first part, a single oil shale sample was supported in a stainless steel mesh basket which was suspended by a stainless steel rod from a load cell mounted at the top of the reactor. The load cell which measured sample weight loss was interfaced with a recorder which converted the signal into weight readings. In the second part, under the same experimental conditions, three microthermocouples were inserted into the center, half radius and at the surface of sample, respectively, to obtain the local temperature profile.

2. Main experimental conditions

Sample: Fushun oil shale (China) and kukersite (Estonia)

Sample shape: regular cylinder

Sample size: 20 mm, 30 mm, 40 mm, 50 mm, in diameter and in height.

Heating rate: 2 °C/min and 5 °C/min

Final temperature: 550 °C—600 °C

Gas carrier: nitrogen with high purity

Table 1. **Analysis data of Fushun oil shale and kukersite**
Таблица 1. **Основные характеристики фушуньского горючего сланца и кукерсита**

	Fushun oil shale	Kukersite
Fischer assay, wt%:		
Oil	8.14	23.60
Pyrolysis water	6.53	1.80
Char	82.21	69.50
Gas	3.12	5.10
Proximate analysis, wt%:		
Wolatile matter	17.51	38.80
Moisture	4.15	—
Ash	73.86	50.50
CO_2	2.40	19.00
Pyrolysis reaction heat, kJ/kg	312.75	249.70

Table 2. **Thermophysical properties of Fushun oil shale and kukersite**
Таблица 2. **Теплофизические свойства фушуньского горючего сланца и кукерсита**

Indices	Temperature, °C									
	150	200	250	300	350	400	450	500	550	600
Fushun, oil shale										
C_{ps}, kJ/(kg·K)	1.40	1.55	1.66	1.77	1.94	2.20	2.61	3.21	4.07	5.21
$a \times 10^8$, m^2/s	35.86	34.66	33.46	32.27	31.07	29.87	28.67	27.47	26.27	25.08
Kukersite										
C_{ps}, kJ/(kg·K)	1.06	1.13	1.21	1.32	1.52	1.85	2.43	1.64	1.35	1.29
$a \times 10^8$, m^2/s	—	19.0	—	17.8	—	15.1	—	14.6	—	25.6

3. Sample properties
The properties of oil shale samples are summarized in Tables 1 and 2 [4—6].

4. Experimental data
The typical weight loss data are shown in Fig. 2.

Model and theory

1. Kinetic equations
According to the mass action law, the overall first order reaction equation for solid fuel pyrolysis can be written as follows:

$$dX/dt = Ae^{-E/RT}(1 - X) \qquad (1)$$

In the consideration of constant heating condition, $dT/dt = \beta$, the integration of eq. (1) gives eq. (2):

$$1 - X = \exp[-1/\beta \cdot ART^2/(E + 2RT) \cdot \exp(-E/RT)] \qquad (2)$$

Substition of eq. (2) into eq. (1) yields the pyrolysis rate:

$$dX/dt = A \cdot \exp[-E/RT - ART^2/(E + 2RT) \cdot 1/\beta \times \times \exp(-E/RT)] \qquad (3)$$

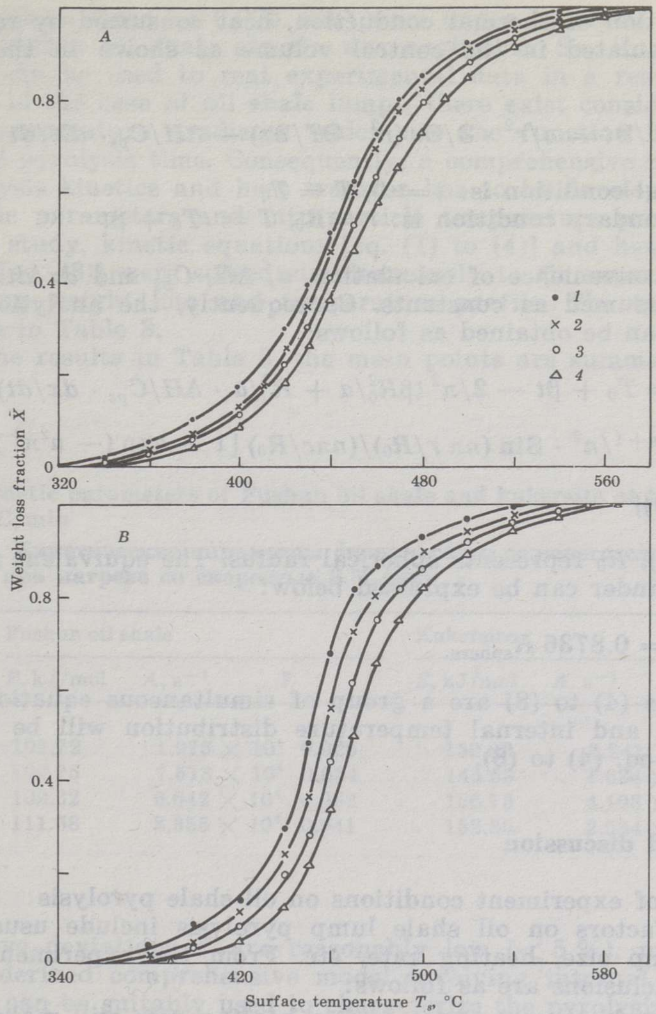

Fig. 2. Weight loss fraction vs. sample surface temperature for Fushun oil shale lump (*A*) and for kukersite lump (*B*) with different diameters: *1* — 20 mm; *2* — 30 mm; *3* — 40 mm; *4* — 50 mm (heating rate 2 °C/min)

Рис. 2. Зависимость потери массы от температуры поверхности куска для фушуньского горючего сланца (*A*) и кукерсита (*B*) при различных диаметрах кусков: *1* — 20 мм; *2* — 30 мм; *3* — 40 мм; *4* — 50 мм (скорость нагрева 2 °С/мин)

During the pyrolysis of lumped oil shale, internal tempratures at different locations are not uniform. As a result, pyrolysis conversion X is a function of radius r. Volume average $\bar{X}$ of local conversion X can be expressed by eq. (4):

$$1 - \bar{X} = 3/R_0^3 \int_0^{R_0} (1 - X) r^2 \, dr \qquad (4)$$

$\bar{X}$ can be experimentally obtained as a function of the temperature of oil shale lump surface.

2. Heat transfer equation

The heat balance of the internal control volume can be expressed by the summation of thermal conduction, heat consumed by reaction and heat accumulated in the control volume as shown in the following equation:

$$\partial T/\partial t = a/r^2 \cdot \partial/\partial r\,(r^2 \cdot \partial T/\partial r) - \Delta H/C_{ps} \cdot dX/dt \qquad (5)$$

The initial condition is: $t = 0$, $T = T_0$ (6)
and the boundary condition is: $r = R_0$, $T = T_0 + \beta t$ (7)

For the convenience of calculation, a, ΔH, C_{ps} and dx/dt are approximately assumed as constants. Consequently, the analytical solution of eq. (5) can be obtained as follows:

$$T = T_0 + \beta t - 2/\pi^2\,(\beta R_0^2/a + R_0^2/a \cdot \Delta H/C_{ps} \cdot dx/dt) \times$$
$$\times \sum_{n=1}^{\infty} \{(-1)^{n+1}/n^2 \cdot \mathrm{Sin}\,(n\pi\, r/R_0)/(n\pi r/R_0)\,[1 - \exp\,(- n^2\pi^2 \times$$
$$\times\, a/R_0^2 \cdot t)]\} \qquad (8)$$

In eq. (8), R_0 represents spherical radius. The equivalent radius of a regular cylinder can be expressed below:

$$R_{\mathrm{cylinder}} = 0.8736\, R_{\mathrm{sphere}} \qquad (9)$$

Equations (4) to (8) are a group of simultaneous equations. Kinetic parameters and internal temperature distribution will be determined by solving eq. (4) to (8).

Results and discussion

1. Effects of experiment conditions on oil shale pyrolysis
Effective factors on oil shale lump pyrolysis include usually temperature, lump size, heating rate, etc. From the experimental results, several conclusions are as follows:
(1) A larger lump size and a higher heating rate will make the intrapartical temperature gradient bigger and thus result in a higher initial and final pyrolysis temperature, due to the poor thermal conductivity of oil shale lump. Therefore, in oil shale lump retorting processes, if heating rate will be increased to raise unit's capability, a higher temperature has to be chosen as the final retorting temperature and the oil shale must be heated at that temperature for a sufficient time. Otherwise, the retorting process will be incomplete, which may result in lower shale oil yield.
(2) With a rise in surface temperature of oil shale lump, intraparticle temperature gradient will increase gradually. The temperature gradient reaches maximum near the highest pyrolysis rate, which may be attributed to the considerable pyrolysis reaction heat. From this phenomenon, it is clear that internal thermal conduction is a controlling step in overall pyrolysis of oil shale lump.
(3) Internal temperature gradient depends on the thermal conductivity of oil shale lump. For Fushun oil shale with the lump size of 50 mm, maximum temperature difference between surface and center is about 31 °C at the heating rate of 2 °C/min, while for kukersite, it is about 74 °C.
2. Kinetic parameters of oil shale pyrolysis

When oil shale fines (< 0.075 mm) were under pyrolysis, temperature gradient within oil shale sample was negligible. So, intrinsic kinetic equation can be used to reat experimental data in a reasonable way. However, in the case of oil shale lumps, there exist considerable intraparticle temperature gradients which are the function of lump diameter and pyrolysis time. Consequently, a comprehensive model involving pyrolysis kinetics and heat transfer has to be developed to obtain the kinetic parameters and intraparticle temperature profile.

In this study, kinetic equations [eq. (1) to (4)] and heat conduction equation [eq. (8)] were solved simultaneously to fit experimental data concenrning weight loss and temperature profile. The typical results are shown in Table 3.

From the results in Table 3, the main points are summarized as follows.

Table 3. **Kinetic parameters of Fushun oil shale and kukersite at heating rate of 2 °C/min**

Таблица 3. **Кинетические параметры фушуньского горючего сланца и кукерсита при нагреве со скоростью 2 °C/мин**

Lump size, mm	Fushun oil shale			Kukersite		
	E, kJ/mol	A, s^{-1}	F	E, kJ/mol	A, s^{-1}	F
20	101.72	1.975×10^4	0.026	150.00	3.241×10^7	0.031
30	109.75	7.518×10^4	0.034	145.58	1.634×10^7	0.038
40	109.32	6.642×10^4	0.032	156.73	4.193×10^7	0.042
50	111.58	8.355×10^4	0.041	152.35	2.534×10^7	0.029

(1) Relative deviations F are reasonably low (< 5 %), which implies that the derived comprehensive model involving internal temperature gradients can be suitably used to characterize the pyrolysis of oil shale lumps.

(2) Heating rate and lump size have little effect on kinetic parameters of oil shale lumps. For that reason, the kinetic results from this study can be taken as intrinsic kinetic parameters which is independent of temperature gradient.

(3) During the pyrolysis of oil shale lumps, apparent activation energy for kukersite proved to be higher than that for Fushun oil shale.

3. Intraparticle temperature profile

As mentioned above, the kinetic parameters were obtained by using the solutions of simultaneous equations. In the meantime, intraparticle temperature profile was determined as well. The typical results from experiment and calculation are summarized in Tables 4 and 5.

It can be seen from the data listed in Tables 4 and 5 that the larger the lump the greater the temperature difference from surface to the center. Therefore, it is clear that the effect of lump size is very significant on the pyrolysis of oil shale lump.

Model predictions give a satisfactory fit to experimental data in constant heating stage. But, at isothermal stage above 550 °C, deviations between experimental and calculated data become high, which is possibly caused by the imperfectness of the model.

Table 4. **Temperature difference between surface and center of Fushun oil shale lumps (heating rate 2 °C/min)**
Таблица 4. **Разница между температурами поверхности и центра кусков кукерсита (скорость нагрева 2 °C/мин)**

Surface temperature, °C	φ, mm							
	20		30		40		50	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
150	3.0	1.9	4.0	4.4	8.0	7.8	11.0	13.0
200	3.0	2.1	5.0	4.6	8.0	8.3	12.0	13.2
250	3.0	2.1	5.0	4.8	8.0	8.7	12.0	13.5
300	3.0	2.2	6.0	5.0	9.0	9.2	13.0	14.6
350	3.0	2.9	6.0	6.2	10.0	11.5	15.0	15.9
400	4.0	4.5	7.0	9.0	12.0	14.7	20.0	21.2
450	4.0	5.4	9.0	12.0	18.0	20.0	31.0	33.0
500	4.0	3.2	12.0	8.0	20.0	17.7	31.0	34.2
550	3.0	2.7	10.0	8.0	20.0	15.0	26.0	24.0
Isothermal heating at 550 °C								
10 min	2.0	0	3.0	0	11.0	1.5	18.0	4.0
30 min	0	0	1.0	0	4.0	0.9	11.0	2.0
50 min	0	0	0	0	1.0	0	5.0	0

Table 5. **Temperature difference between surface and center of kukersite lumps (heating rate 2 °C/min)**
Таблица 5. **Разница между температурами поверхности и центра кусков кукерсита (скорость нагрева 2 °C/мин)**

Surface temperature, °C	φ, mm							
	20		30		40		50	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
150	5.0	3.8	9.0	8.2	12.0	16.3	26.0	25.5
200	5.0	3.5	9.0	8.0	14.0	15.4	26.0	24.1
250	6.0	3.9	10.0	8.9	16.0	15.6	26.0	24.3
300	6.0	4.2	10.0	9.0	17.0	16.5	28.0	28.8
350	7.0	4.8	12.0	11.0	19.0	18.5	32.0	35.0
400	8.0	6.9	15.0	13.2	22.0	26.5	38.9	42.0
450	14.0	12.5	29.0	26.5	35.0	33.5	54.0	58.6
500	15.0	10.6	30.0	26.0	42.0	39.2	74.0	70.0
550	8.0	4.5	19.0	11.5	32.0	25.7	50.0	39.1
Isothermal heating at 550 °C								
10 min	3.0	0	10.0	0	20.0	6.0	34.0	12.0
30 min	1.0	0	4.0	0	10.0	3.0	22.0	5.0
50 min	0	0	2.0	0	5.0	0	10.0	0

Under the condition that heating rate is 2 °C/min, and isothermal above 550 °C, the center temperature gets to 550 °C after more than one hour heating for a lump 50 mm in diameter, but the same center temperature will reach after 10 minutes heating for a lump 20 mm in diameter. This fact points out that this delay in retorting process can result in the burning of oil product to decrease oil yield. Also, oil released from the center of lump will be exposed to very high temperature as it escapes from the lump. As a result, further cracking of shale oil will be enhanced.

During the pyrolysis of oil shale lumps, kukersite has a larger temperature gradient than Fushun oil shale. For instance, at heating rate of 2 °C/min, maximum temperature difference of kukersite (50 mm in diameter) is up to 74 °C while for Fushun oil shale it is 31 °C. This is probably caused by poorer thermoconductivity of kukersite (see Table 2). As a result, retorting for kukersite will need high final temperature and longer retention.

Conclusion

1. The pyrolysis of Fushun oil shale and kukersite lumps was studied by using a single-lump reactor. A comprehensive model involving pyrolysis reaction and heat transfer was developed.
2. Kinetic parameters are the same for different lump sizes, which implies that it is a successful attempt to model lump-size oil shale pyrolysis by means of Arrhenius equation with the effects of intraparticle heat transfer taken into consideration.
3. Intraparticle heat transfer is a dominant factor in the pyrolysis of oil shale lumps. The results indicate that a higher heating rate and a larger lump size will make the intraparticle temperature gradient bigger.
4. The model predictions and experimental data basically agree with each other, which shows that the comprehensive model developed can be reasonably used to characterize the pyrolysis of oil shale lumps.
5. Kukersite has a larger temperature gradient than Fushun oil shale due to poorer thermoconductivity of kukersite.

Nomenclature

a — thermal diffusivity (m^2/s)
A — Arrhenius frequency factor (s^{-1})
C_{ps} — heat capacity of oil shale [kJ/(kg·K)]
E — apparent activation energy (kJ/mol)
F — relative deviation
r — radial distance (mm)
R_0 — radius of oil shale lump (mm)
R — gas constant [8.314 J/(mol·K)]
t — time (s)
T — temperature (K)
T_0 — room temperature (°C)
T_s — surface temperature of sample (°C)
X — conversion fraction of oil shale pyrolysis, as a function of temperature T and radius r
X — average conversion fraction for the whole oil shale lump
β — heating rate (°C/min)
ΔH — pyrolysis heat (kJ/kg)
ϱ_s — solid density of oil shale lump (kg/m^3)

ЛИ ШУЙ-ЯНЬ, ЦЯНЬ ЦЗЯ-ЛИНЬ

ИССЛЕДОВАНИЕ ПИРОЛИЗА КРУПНОКУСКОВОГО ФУШУНСКОГО ГОРЮЧЕГО СЛАНЦА И ЭСТОНСКОГО СЛАНЦА-КУКЕРСИТА

Резюме

Обычно для переработки горючих сланцев используется мелкокусковой сланец и сланцевая мелочь. Пиролиз крупнокускового горючего сланца пред-

ставляет собой более сложный процесс: наряду с химическими реакциями, его составляющими являются процессы тепло- и массопередачи, измельчение кусков и др.

Из-за низкой удельной теплопроводности горючего сланца решающим фактором при пиролизе крупнокускового сланца становится теплопередача внутри частицы. Однако, несмотря на интенсивные исследования, до сих пор не удалось разработать модель, в которой одновременно учитывались бы как реакция пиролиза, так и теплопередача в куске.

Для настоящего исследования была разработана аппаратура (рис. 1) для определения потери массы и изменения температуры внутри частицы.

Из образцов фушуньского сланца и эстонского кукерсита были изготовлены цилиндры с одинаковыми высотой и диаметром: 20, 30, 40 и 50 мм. Условия эксперимента были следующими: скорость нагрева 2 или 5 °С/мин, конечная температура нагрева 550—600 °С, газ-носитель — азот высокой чистоты.

Свойства образцов горючих сланцев охарактеризованы в таблицах 1 и 2; процесс потери массы иллюстрирует рис. 2.

В результате проведенного исследования была разработана модель, охватывающая как реакцию пиролиза, так и процесс теплопередачи.

Как оказалось, куски различных размеров имеют одинаковые кинетические параметры, и это указывает на то, что уравнение Аррениуса применимо и для моделирования процесса пиролиза крупнокускового сланца при условии, что при этом учитывается эффект внутрикусковой теплопередачи.

Внутрикусковая теплопроводность является доминирующим фактором при пиролизе кускового сланца. Чем выше скорость подъема температуры и больше размер куска, тем выше температурный градиент в нем.

Расчетные значения, полученные на основе разработанной модели, и экспериментальные данные в основном соответствуют друг другу, что подтверждает применимость общей модели для характеристики пиролиза крупнокускового горючего сланца.

По причине меньшей теплопроводности, кукерсит имеет более высокий температурный градиент, чем у фушуньского сланца.

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