

THERMOGRAVIMETRIC KINETICS STUDY ON SOME CHINESE OIL SHALES

LI SHUYUAN, YOU ZHE
QIAN JIALIN*, GUO SHAOHUI

School of Chemical Engineering, University of Petroleum
Changping 102200, Beijing, China

In this work the pyrolysis of oil shale kerogen was investigated by using TGA apparatus. The overall first-order reaction model has been successfully used (correlation coefficient exceeds 0.99) to simulate weight loss data (T-x curve) for type I kerogen. For kerogens of types I, II and III, Friedman method can be reasonably used. Much work has been done on reaction kinetics of Fushun and Maoming oil shales. The results showed that the apparent activation energies of Fushun and Maoming shales are about 160 KJ/mol. This paper presents reaction kinetics of some Chinese oil shales compared with Fushun and Maoming oil shales. It was found that the activation energies of most oil shales studied range from 160 KJ/mol to 170 KJ/mol. These results provide important information for shale oil industry in China.

Introduction

Oil shale is an important source of energy. It can be used as a substitute for petroleum. The development of oil shale in the world mainly depends on the price of natural petroleum. It has been said that when the price of petroleum reaches to \$35/barrel, the cost of shale oil can compete with it. Oil shale resources in China are the fourth in the world [1]. It is estimated that there are 400 billion tons of oil shale, equivalent to 16 billion tons of shale oil. At present, the price of petroleum is rising impelling various countries to develop oil shale industry. This paper presents the pyrolysis kinetics of oil shales from Chinese several different areas in comparison with oil shales from Fushun and Maoming deposits.

* Corresponding author.

Experimental

Eight oil shale samples were taken from Jilin Huadian Gonglangton fourth (HD-1) and eleventh (HD-2) seams, Heilongjiang Yilan coal mine (YL-3, YL-4), Gansu Tianzhu Tianmalong oil shale mine (QZ-5, QZ-6), Fushun (FS-7) and Maoming (MM-8). Rock-Eval analysis data of oil shales are given in Table 1.

Table 1. Rock-Eval Analysis Data of Several Chinese Oil Shales (Air-Dried)

| Sample | TOC, % | S ₁ | S ₂ | S ₃ | S ₁ + S ₂ | PI | S ₂ /S ₃ | HI | OI | PC, % |
|--------|--------|----------------|----------------|----------------|---------------------------------|------|--------------------------------|----------|----|--------|
| | | mg/g | | | | | | mg/g TOC | | |
| HD-1 | 30.65 | 2.50 | 262.18 | 5.59 | 264.48 | 0.01 | 46.90 | 855 | 18 | 21.97 |
| HD-2 | 36.81 | 1.42 | 108.19 | 8.52 | 109.61 | 0.01 | 12.70 | 294 | 23 | 9.10 |
| YL-3 | 34.84 | 2.69 | 123.03 | 1.01 | 125.72 | 0.02 | 121.81 | 353 | 3 | 10.43 |
| YL-4 | 34.34 | 2.48 | 105.21 | 7.27 | 107.69 | 0.02 | 14.47 | 306 | 21 | 8.94 |
| QZ-5 | 14.44 | 1.76 | 115.19 | 2.05 | 116.95 | 0.02 | 56.19 | 798 | 14 | 9.71 |
| QZ-6 | 47.85 | 4.31 | 295.15 | 4.52 | 299.46 | 0.01 | 65.30 | 617 | 9 | 24.86 |
| FS-7 | 16.51 | 3.76 | 112.92 | 2.96 | 116.68 | 0.03 | 38.15 | 684 | 18 | 9.68 |
| MM-8 | 13.40 | 1.62 | 91.62 | 0.47 | 93.24 | 0.02 | 194.94 | 684 | 4 | 7.74 |
| CFG-9 | 6.28 | 1.61 | 29.32 | 1.25 | 30.93 | 0.05 | 23.46 | 467 | 20 | 2.567 |
| CFG-10 | 12.18 | 1.57 | 71.76 | 1.12 | 73.33 | 0.02 | 46.07 | 589 | 9 | 6.086 |
| CFG-11 | 17.85 | 2.49 | 122.88 | 1.50 | 125.37 | 0.02 | 81.92 | 688 | 8 | 10.406 |

Notes: S_1 – content of free hydrocarbon; S_2 – content of pyrolysis hydrocarbon; S_3 – content of carbon dioxide; PI – condensate index; HI – hydrogen index; OI – oxygen index; PC – potential carbon. The value of S_2/S_3 , called type index, can be used to determine the types of oil shale kerogen: for type I, $S_2/S_3 > 20$; for type II, $S_2/S_3 = 2.5\text{--}20$; for type III, $S_2/S_3 = < 2.5$.

The oil shales used in this work were ground and sieved < 0.075 mm to ignore the intraparticle temperature gradient of oil shale. Kinetic data were obtained by using a WCT-A thermogravimetric analyzer (TGA). Samples of about 20 mg were placed on the sample holder and pyrolyzed in the nitrogen atmosphere. The flow rate of nitrogen was kept constant at 40 mL/min. Pyrolysis was carried out at a constant heating rate of 5 °C/min. Samples HD-2 and YL-4 have been pyrolyzed at different heating rates of 2.5, 5, 10 and 15 °C/min. The final temperature of pyrolysis was 600 °C, and it was maintained until no more mass loss was observed.

Kinetic Model

The mathematical model used to analyze TGA data for determination of pyrolysis kinetics has been used by many researchers [2–10]. Assuming that oil shale pyrolysis occurs according to the overall first-order reaction, the corresponding equation can be written as follows:

$$\frac{dx}{dt} = k(1-x)^n = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x)^n \quad (1)$$

where x – fraction of kerogen undergoing conversion

t – time, s

k – reaction rate constant, s^{-1}

n – reaction order

A – apparent frequency, s^{-1}

E – apparent activation energy, J/mol

R – gas constant, 8.314 J/mol · K

T – absolute temperature, K

If the first-order reaction model is used to describe oil shale pyrolysis, Equation (1) can be written as

$$\frac{dx}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x) \quad (2)$$

At a constant rate of heating, $m = dT/dt$, we can obtain

$$\frac{dx}{dt} = \frac{A}{m} \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x) \quad (3)$$

Using the integration method, Equation (3) becomes

$$\int_0^x \frac{dx}{1-x} = \int_{T_0}^T \frac{A}{m} \cdot \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

Equation (4) is approximately integrated to get the following equation:

$$\ln\left[\left(-\frac{\ln(1-x)}{T^2}\right) / \left(1 - \frac{2RT}{E}\right)\right] = \ln \frac{AR}{mE} - \frac{E}{R} \cdot \frac{1}{T} \quad (5)$$

The data of fractional conversion x versus temperature T can be used in Equation (5). For a series of experimental data of x - T , Equation (5) may be solved by using the least square method to obtain kinetic parameters E and A .

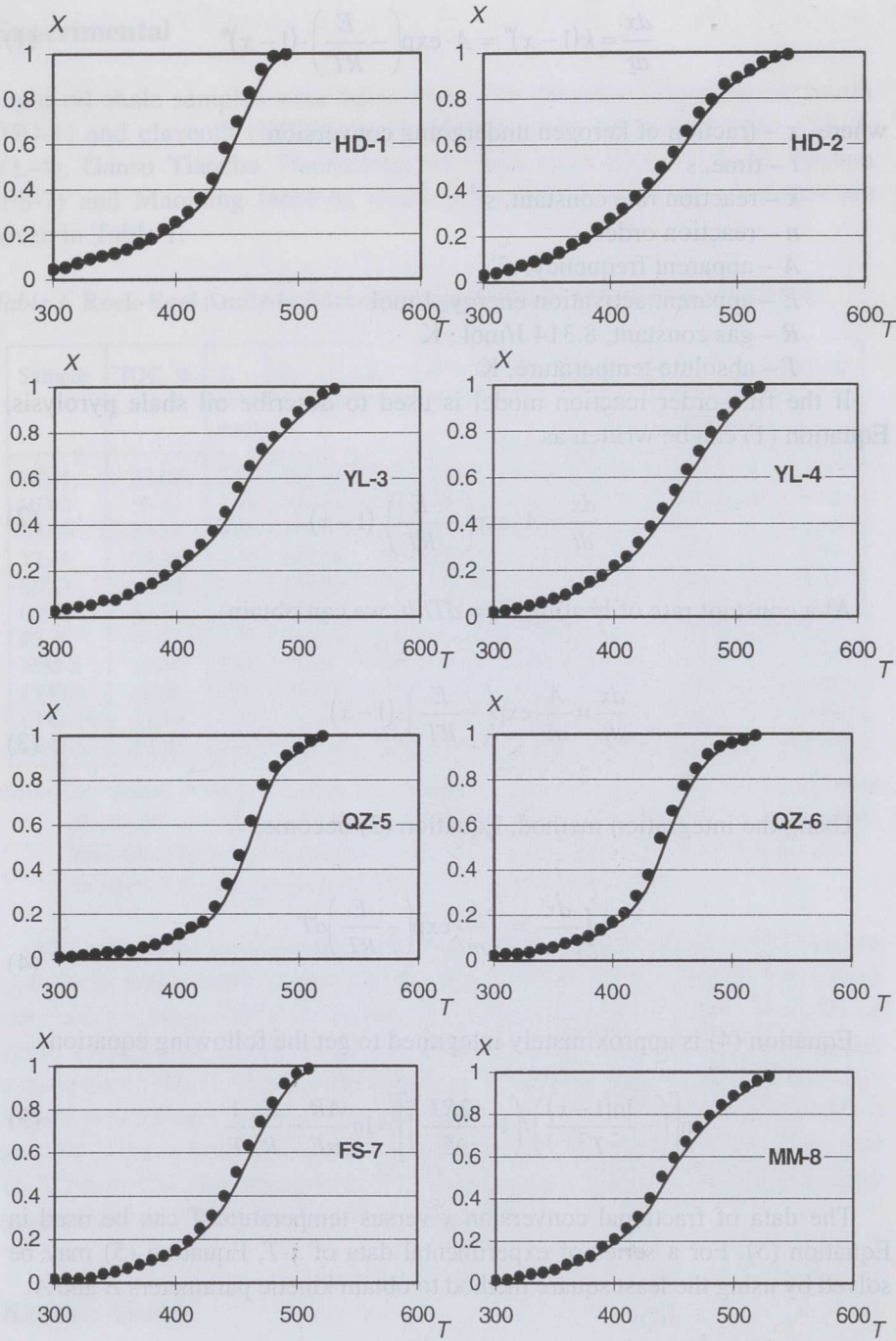


Fig. 1. Fractional conversion vs temperature for different oil shales

Results and Discussion

Oil shale kerogen type indices S_2/S_3 are given in Table 1. When this index exceeds 20, it indicates type I. Type index of II1 oil shale kerogen is between 5 and 20. Type index of II2 – between 2.5 and 5. Type index of III oil shale kerogen is less than 2.5. According to Table 1, type indices of the samples HD-2 and YL-4 are between 5 and 20. They belong to type III1. Type indices of other samples exceed 20. They all belong to type I oil shale kerogen. The experimental data of all samples were treated with overall first-order reaction model, and the samples HD-2 and YL-4 also with Friedman method to obtain their kinetic parameters at different temperatures.

Figure 1 shows T - x curves of all oil shales obtained from experimental data measured at heating rate of $5^\circ\text{C}/\text{min}$.

Figure 2 gives T - x curves of HD-2 and YL-4 obtained from experimental data at different heating rates (2.5, 5, 10 and $15^\circ\text{C}/\text{min}$). According to Fig. 1, pyrolysis of oil shale begins at about 300°C , ends at about 550°C . According to Figures 1 and 2, oil shale pyrolysis occurs mainly between 400 – 500°C . The values of kinetic parameters E and A are given in Table 2.

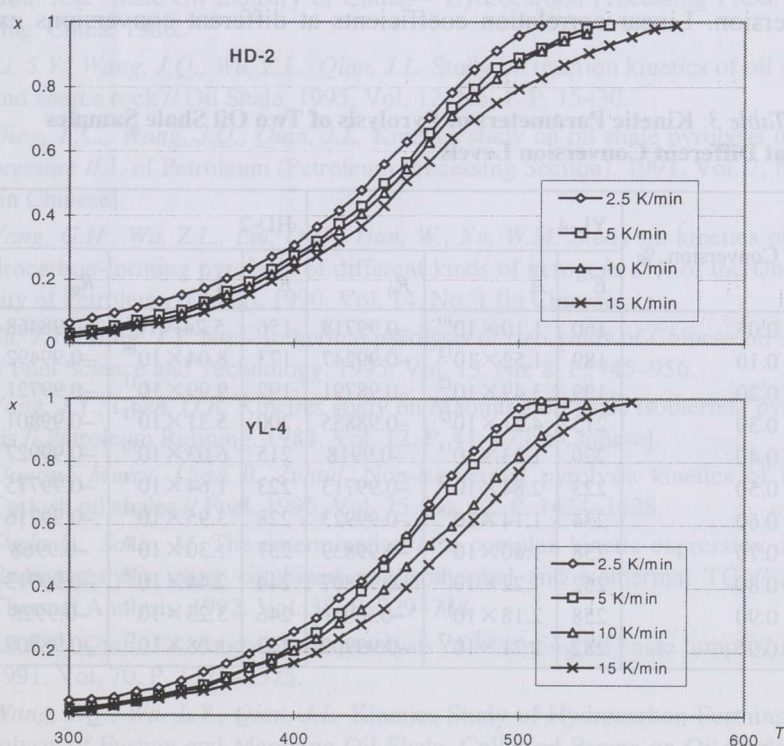


Fig. 2. Fractional conversion vs temperature at different heating rates

Table 2. Kinetic Parameters of Pyrolysis of Eight Oil Shale Samples

| Sample | A, KJ/mol | E, min ⁻¹ | R |
|--------|-----------|-------------------------|----------|
| HD-1 | 158 | 1.22 × 10 ¹¹ | -0.99219 |
| HD-2 | 151 | 3.96 × 10 ⁹ | -0.99409 |
| YL-3 | 161 | 7.09 × 10 ¹⁰ | -0.9975 |
| YL-4 | 163 | 5.35 × 10 ¹⁰ | -0.9925 |
| QZ-5 | 186 | 6.94 × 10 ¹² | -0.99669 |
| QZ-6 | 170 | 9.04 × 10 ¹¹ | -0.99693 |
| FS-7 | 169 | 2.05 × 10 ¹¹ | -0.99491 |
| MM-8 | 168 | 5.69 × 10 ¹¹ | -0.99709 |

Compared with FS-7 and MM-8, other oil shales lie in same range with Fu-shun and Maoming ones. Correlation coefficients of all oil shales exceed 0.99. This shows that the overall first-order reaction model is feasible for treating the pyrolysis data of all Chinese oil shales. Kinetic parameters *E* and *A*, and coefficient *R*₀ of HD-2 and YL-4 at different conversions are presented in Table 3. Activation energies increase with increasing fractional conversion. Linear correlation coefficients at different conversions exceed 0.98.

In Tables 2 and 3, *R*₀ represents linear correlation coefficient, which is used to measure the feasibility of the kinetic model. If the absolute value of *R*₀ is more close to unity, the first-order kinetic model will be more accurate to describe oil shale pyrolysis.

Activation energies for most oil shales range from 160 to 170 KJ/mol. HD-2 has the lowest activation energy (151 KJ/mol), and QZ-5 has the highest one (186 KJ/mol).

Table 3. Kinetic Parameters of Pyrolysis of Two Oil Shale Samples at Different Conversion Levels

| Conversion, % | YL-4 | | | HD-2 | | |
|---------------|----------|-------------------------|-----------------------|----------|-------------------------|-----------------------|
| | <i>E</i> | <i>A</i> | <i>R</i> ₀ | <i>E</i> | <i>A</i> | <i>R</i> ₀ |
| 0.05 | 160 | 1.10 × 10 ¹⁰ | -0.99718 | 156 | 5.24 × 10 ⁹ | -0.98468 |
| 0.10 | 189 | 1.52 × 10 ¹² | -0.99247 | 173 | 8.04 × 10 ¹⁰ | -0.99492 |
| 0.20 | 199 | 3.49 × 10 ¹² | -0.98791 | 192 | 9.99 × 10 ¹¹ | -0.99721 |
| 0.30 | 213 | 4.21 × 10 ¹³ | -0.98835 | 200 | 5.31 × 10 ¹² | -0.99801 |
| 0.40 | 220 | 1.13 × 10 ¹⁴ | -0.9918 | 215 | 6.03 × 10 ¹³ | -0.99927 |
| 0.50 | 223 | 2.84 × 10 ¹⁴ | -0.99713 | 223 | 1.64 × 10 ¹⁴ | -0.99775 |
| 0.60 | 234 | 1.14 × 10 ¹⁵ | -0.99923 | 228 | 3.95 × 10 ¹⁴ | -0.99716 |
| 0.70 | 238 | 1.60 × 10 ¹⁵ | -0.99839 | 237 | 1.30 × 10 ¹⁵ | -0.9968 |
| 0.80 | 252 | 1.22 × 10 ¹⁶ | -0.99807 | 244 | 2.44 × 10 ¹⁵ | -0.99913 |
| 0.90 | 258 | 2.18 × 10 ¹⁶ | -0.9986 | 246 | 3.23 × 10 ¹⁵ | -0.9928 |
| 0.95 | 282 | 2.71 × 10 ¹⁷ | -0.99902 | 273 | 1.08 × 10 ¹⁷ | -0.98909 |

Conclusions

- Overall first-order reaction model is feasible for treating the pyrolysis data of type I oil shales.

- Activation energy of the most oil shales ranges from 160 KJ/mol to 170 KJ/mol. HD-2 has the lowest (151 KJ/mol), and QZ-5 the highest (186 KJ/mol) activation energy.
- Linear correlation coefficient for type I kerogen exceeds 0.99, and 0.98 for type III.
- Oil shale pyrolysis occurs with the highest rate between 400 and 500 °C. The process begins at about 300 °C and ends at about 600 °C.
- According to the Friedman method, the activation energy increases with the increasing of fractional conversion.

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