

Reaction mechanism and kinetics of pressurized pyrolysis of Chinese oil shale in the presence of water

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Abstract: A study of reaction mechanisms and chemical kinetics of pressurized pyrolysis of Chinese Liushuhe oil shale in the presence of water were conducted using an autoclave for simulating and modeling in-situ underground thermal degradation. It was found that the oil shale was first pyrolyzed to form pyrobitumen, shale oil, shale gas and residue, then the pyrobitumen was further pyrolyzed to form more shale oil, shale gas, and residue. It means that there are two consecutive and parallel reactions. With increasing temperature, the pyrobitumen yield, as intermediate, first reached a maximum, then decreased to approximately zero. The kinetics results show that both these reactions are first order. The activation energy of pyrobitumen formation from oil shale is lower than that of shale oil formation from pyrobitumen.

Key words: Oil shale, pyrobitumen, pressurized pyrolysis, in-situ underground retorting, reaction mechanism, chemical kinetics

1 Introduction

Shale oil from oil shale retorting is an important petroleum alternative. In recent years, due to high crude oil prices, much more attention has been paid to oil shale utilization. Oil shale can be retorted after it is mined from underground deposits. Oil shale can also be retorted in-situ underground by introducing hot gas and/or hot air to heat and pyrolyze it to produce shale oil. The in-situ retorting process is suitable for treating deeply buried deposits. Many large oil companies are conducting in-situ retorting tests in the United States and other countries. This process is conducted underground at high pressure and usually in the presence of water. So, the theoretical study is important for development of oil shale through the in-situ oil shale retorting process.

Many studies of the reaction mechanism and chemical kinetics of oil shale pyrolysis at normal pressure have been undertaken in the past several decades, providing a theoretical basis for the above-ground retorting of oil shale (Allred, 1966; Bruan and Rothman, 1975; Li et al, 1987; Li et al, 1995; Johannes and Zaidenstal, 2008; Al-Ayed, 2011). A total of eight models of pyrolysis kinetics have been developed. These are: a first-order pyrolysis model for the overall process, a first order model for different stages, an nth order pyrolysis model for the overall process, a maximum pyrolysis reaction rate model, a parallel first order pyrolysis model, a parallel and consecutive pyrolysis model (pyrobitumen as

pyrolysis intermediate model), an infinite parallel pyrolysis model, and a consecutive first order pyrolysis model (Qian et al, 2010).

However, only a few papers aimed at the pressurized pyrolysis of oil shale for modeling in-situ underground retorting, have been reported recently (Hoda et al, 2010; Arbabi et al, 2010).

In this paper, the reaction mechanism and kinetics for pressurized pyrolysis of Chinese Liushuhe oil shale were studied in the presence of water using an autoclave to simulate and model in-situ underground thermal degradation. The results could provide a theoretical basis for in-situ retorting of oil shale.

2 Experimental

2.1 Samples

Liushuhe oil shale, from Linkou County, Heilongjiang Province, China, was used. The oil shale was crushed, sieved and dried to 3.2-6 mm. The Liushuhe oil shale deposit is buried underground at a depth of 500 m, suitable for in-situ pyrolysis.

2.2 Apparatus

Fisher Assay was conducted according to Sinopec standard (SH/T 0508-92), using an aluminum apparatus made by Beijing Purenergy Company. Total organic carbon (TOC) was determined according to China's National Standard (GB/T 476-2001: Ultimate analysis of coal), with the apparatus

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Received November 30, 2011

(Type TOC-01) made by Jiangsu Skyray Instrument Company.

A laboratory autoclave (Type WYF-1), made by Nantong Huaxing Oil Equipment Co. Ltd, with a volume of 0.2 L and maximum working pressure of 50 MPa, was used for pressurized pyrolysis of oil shale.

2.3 Fischer assay and TOC determination

The oil shale Fischer assay and total organic carbon (TOC) determination were carried out according to the standards mentioned above, and the results are shown in Table 1.

Table 1 Fischer assay and TOC data of Liushuhe oil shale, dry basis

Oil yield wt%	Char yield wt%	Water yield wt%	Gas yield wt%	TOC wt%
11.6	64.9	8.75	14.7	49.5

Table 1 shows that the Liushuhe oil shale has a high shale oil yield and high TOC.

2.4 Pressurized pyrolysis experiments

Liushuhe oil shale particulates (30 g) and pure water (50 g) was put into the autoclave. In this case, water is oversaturated in autoclave at different temperatures and pressures. The autoclave was sealed, evacuated and heated according to the desired temperature increase from 15 °C to 200 °C for 5 hr, and from 200 °C to different final temperatures (275, 300, 320, 340, 360, 370 °C) with a heating rate of 2.5 °C/hr. After cooling, the exit valve was opened and the pyrolysis products were removed from the autoclave. The shale oil was condensed and separated from the pyrolysis water. The shale oil and pyrolysis gas were measured separately. The shale char residue was dried and weighed. Then it was extracted with dichloromethane in a Soxhlet extractor to get pyrobitumen as the pyrolysis intermediate.

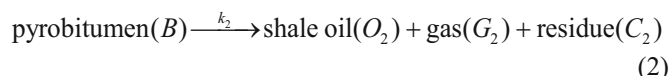
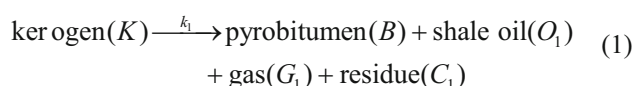
The product yields from Liushuhe oil shale at different final temperatures are shown in Table 2 (based on total organic carbon, TOC).

Table 2 Liushuhe oil shale pyrolysis yields at different final temperatures

Final temperature °C	Final pressure MPa	Shale oil g/gTOC	Shale gas g/gTOC	Pyrobitumen g/gTOC
275	4.5	0	0.168	0.0266
300	6.4	0.0002	0.183	0.0352
320	8.8	0.0165	0.220	0.0158
340	11.6	0.0701	0.249	0.0159
360	15.2	0.120	0.282	0.0062
370	17.8	0.159	0.297	0.0064

3 Reaction mechanism

We suppose that the oil shale pressurized pyrolysis proceeds as follows: at first the oil shale kerogen decomposes to form pyrobitumen and part of shale oil, gas and char residue, then the pyrobitumen decomposes to form another part of shale oil, shale gas and char residue. These are two consecutive and parallel reactions:



where k_1 and k_2 are the pyrolysis rate constants of kerogen and pyrobitumen, respectively.

4 Kinetic model

Based on the mass reaction law, the above two reactions may fit into the Arrhenius equation. Many researchers have found that oil shale kerogen is sapropelic and its pyrolysis reaction is first order (Li et al, 1987). So, the kinetic equations of kerogen pyrolysis, pyrobitumen pyrolysis and the shale oil formation may be written as follows:

$$\frac{dK}{dt} = -k_1 \times K = -A_1 \exp\left(\frac{-E_1}{RT}\right) K \quad (3)$$

$$\frac{dB}{dt} = f_1 \times k_1 \times K - k_2 B = f_1 A_1 \exp\left(\frac{-E_1}{RT}\right) K - A_2 \exp\left(\frac{-E_2}{RT}\right) B \quad (4)$$

$$\begin{aligned} \frac{dO}{dt} &= f_3 \times k_1 \times K + f_2 \times k_2 \times B \\ &= A_1 f_3 \exp\left(\frac{-E_1}{RT}\right) K + A_2 f_2 \exp\left(\frac{-E_2}{RT}\right) B \end{aligned} \quad (5)$$

where

- B : Weight fraction of pyrobitumen;
- O : Weight fraction of shale oil;
- K : Weight fraction of kerogen;
- k_1 : Rate constant of kerogen pyrolysis reaction (s^{-1});
- k_2 : Rate constant of pyrobitumen pyrolysis reaction (s^{-1});
- f_1 : Weight fraction of pyrobitumen formed from the kerogen pyrolysis;
- f_2 : Weight fraction of shale oil formed from the kerogen pyrolysis;
- f_3 : Weight fraction of shale oil formed from pyrobitumen pyrolysis;
- E_1 : Apparent activation energy of kerogen pyrolysis (kJ/mol);
- E_2 : Apparent activation energy of pyrobitumen pyrolysis (kJ/mol);
- T : Reaction temperature (K);
- R : Gas constant ($8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$);
- A_1 : Apparent frequency factor of kerogen pyrolysis (s^{-1});
- A_2 : Apparent frequency factor of pyrobitumen pyrolysis (s^{-1}).

Substituting $\frac{dT}{dt} = \phi$ into Eqs. (3), (4), (5), and integrating Eq.(3), the result is put into Eqs. (4) and (5), thus the following equations can be obtained:

$$\begin{aligned} \frac{dy_1}{dT} &= \frac{f_1 A_1}{\phi} \exp\left[-\frac{E_1}{RT} - \frac{A_1 R T^2}{\phi(E_1 + 2RT)} \exp\left(-\frac{E_1}{RT}\right)\right] \\ &\quad - \frac{A_2}{\phi} y_1 \exp\left(-\frac{E_2}{RT}\right) \end{aligned} \quad (6)$$

$$\frac{dy_2}{dT} = \frac{f_3 A_1}{\varphi} \exp\left[-\frac{E_1}{RT} - \frac{A_1 R T^2}{\varphi(E_1 + 2RT)} \exp\left(-\frac{E_1}{RT}\right)\right] + \frac{A_2}{\varphi} f_2 y_1 \exp\left(-\frac{E_2}{RT}\right) \quad (7)$$

where y_1 is the weight fraction of pyrobitumen at temperature T . y_2 is the weight fraction of shale oil at temperature T . φ is the heating rate.

Based on the experimental data shown in Table 2, and using the Runge-Kutta and non linear least square regression methods, the kinetic parameters E_1 , E_2 , and A_1 , A_2 in Eqs. (6) and (7) can be calculated. The kinetic parameters for pressurized pyrolysis of Liushuhe oil shale are shown in Table 3.

Table 3 The kinetic parameters for pressurized pyrolysis of Liushuhe oil shale

f_1	f_2	f_3	A_1, s^{-1}	A_2, s^{-1}	$E_1, \text{kJ/mol}$	$E_2, \text{kJ/mol}$
0.600	0.842	0.060	9.30×10^5	8.75×10^{10}	112.3	188.0

5 Discussion

Based on the kinetic parameters, the shale oil yield and the pyrobitumen yield at a specific temperature in the range of 275-370 °C can be calculated by integration of Eqs. (6) and (7). The average deviations (F_1 and F_2) between the calculated and measured values for bitumen and shale oil yields at the final temperatures at high pressure can be obtained as follows: $F_1=0.015$, $F_2=0.073$. It means that the deviations are so small that the hypothesis of the pyrolysis reaction mechanism involving two consecutive and parallel pyrolysis reactions is sound under these conditions. It also indicates that the assumption that the pyrolysis reaction is first order is acceptable.

It is also shown that the apparent activation energy of oil shale kerogen pyrolysis forming pyrobitumen ($E_1=112.3$ kJ/mol) is smaller than that of the pyrobitumen pyrolysis ($E_2=188.0$ kJ/mol). Therefore, the reaction of kerogen pyrolysis forming pyrobitumen and shale gas and shale oil takes place first, and then the pyrobitumen pyrolysis reaction follows. These two reactions proceed in parallel. Therefore in the early period the net yield of the pyrobitumen increases, and reaches a maximum, then later, the pyrobitumen yield decreases while the shale oil and shale gas yields increase continually. This reaction mechanism is also proven by the experimental data shown in Table 2.

6 Conclusions

A reaction mechanism and kinetics study of pressurized pyrolysis of Chinese Liushuhe oil shale in the presence of water were conducted using an autoclave. Final temperatures of 275, 300, 320, 340, 360, 370 °C and corresponding final pressures of 4.5, 6.4, 8.8, 11.6, 15.2, 17.8 MPa were selected for simulating and modeling in-situ underground thermal degradation, and the following conclusions could be drawn:

1) From the experimental data, it is shown that the yield of pyrobitumen increases with increasing temperature

in the early period. After reaching a maximum, then it decreases gradually to approximately zero, indicating that the pyrobitumen is the intermediate product of oil shale pyrolysis. The yields of shale oil and shale gas always increase with the temperature ranging from 275 °C to 370 °C.

2) The reaction mechanism of pressurized pyrolysis can be described as two consecutive and parallel reactions. The oil shale kerogen at first pyrolyzes to form pyrobitumen and shale oil, shale gas and residue, then the pyrobitumen pyrolyzes to form moreshale oil, shale gas and residue.

3) The kinetic equations of two consecutive and parallel reactions can be formulated and derived for indicating the shale oil yield, and pyrobitumen yield. Based on the experimental data, the apparent activation energy and apparent frequency factor of these two equations can be obtained. The yield of shale oil and pyrobitumen can be calculated at any temperature in the range of 275-370 °C.

4) The calculated yield values of the shale oil and pyrobitumen agree well with the experimental data. The deviations are acceptable, indicating that the postulated reaction mechanism and the kinetic model provide a good model of the real conditions.

5) The results obtained could provide a theoretical basis for in-situ oil shale underground retorting.

Acknowledgements

Authors are grateful for financial support from the National Science and Technology Major Project of China (Grant No. 2008ZX05018) and from Taishan Scholar Constructive Engineering Foundation of Shandong province (No. ts20120518).

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