

KINETICS OF ISOTHERMAL AND NON-ISOTHERMAL PYROLYSIS OF OIL SHALE

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The kinetics of decomposition of Huadian oil shale was studied by non-isothermal and isothermal methods. The non-isothermal weight loss was recorded at different heating rates (2, 5, 10, 15 and 20 K/min) up to 873 K. Two non-isothermal methods were applied for determination of kinetic parameters: the direct Arrhenius plot method and integral method. The isothermal weight loss studies were carried out for one hour at different temperatures 623, 648, 673, 698 and 723 K. Activation energy and frequency factor were calculated.

The kinetic parameters evaluated from isothermal and non-isothermal kinetic data were compared with each other. As for the two non-isothermal analysis models, the integral method shows lower deviation and hence provides a better fit of the data. The average results of non-isothermal experiments were similar to kinetic parameters determined by isothermal analysis.

Introduction

In China, oil shale deposits are widespread in many regions, the proved reserves amount to about 32 billion tonnes presenting a potential energy source [1]. The exploitation of oil shale in China represents a valuable potential of liquid hydrocarbons and energy, which can alleviate the pressure on energy shortage.

Kerogen in oil shale is such a complicated heterogeneous mixture of organic compounds that the pyrolysis kinetics studied is undoubtedly a sum of many different reactions that give the oil product. For the energy potential of oil shale to be maximized, the conversion processes of oil shale to oil should be studied varying process conditions such as heating rate, final temperature, and particle size [2–4] for obtaining the optimal ones. It is necessary to study the mechanism of pyrolysis and to determine the rate of decomposition.

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In order to predict the course of thermal degradation of oil shale, accurate values of the kinetic parameters of decomposition are required. Several investigations have been carried out on kinetics of kerogen decomposition in oil shales [5–9]. Working under isothermal conditions, Hubbard and Robinson [5] used the mechanism of two-step first-order reactions to describe the decomposition of kerogen to bitumen and subsequently bitumen to oil:



where $k > k'$ at $T < 300$ °C.

Braun and Rothman [9] have analysed more completely the Hubbard and Robinson data. They showed that the oil production kinetics could be explained more accurately by taking into account, in the data analysis, an initial thermal induction period. The activation energies and frequency factors for each step of the proposed two-step mechanism were obtained. Later, Khraisha [10] studied the isothermal decomposition of Jordanian oil shales. They described the reaction as two consecutive first-order reactions, and the activation energies were determined for each stage. However, the most difficult thing in the isothermal kinetic experiments is temperature control of the reactor and its content. This difficulty arises due to a long, initial heat-up period or a large temperature gradient inside the particle and across the reactor diameter. The non-isothermal pyrolysis offers certain advantages over the classic isothermal method [11, 12]. First, this analysis eliminates the errors caused by the thermal induction period; second, it permits a rapid scan of the whole temperature range of interest. Therefore, many researchers have employed the non-isothermal technique to study oil shale pyrolysis [8, 12, 13]. For the purpose of data comparison both isothermal and non-isothermal experiments were made [8]. The results of non-isothermal experiments showed that oil formation process can be quite accurately represented as a first-order reaction. Torrente and Galán [12] also studied thermal decomposition of oil shales using isothermal and non-isothermal thermogravimetric analyses. Among the three methods, the direct Arrhenius plot method, the integral method and the differential method, used in non-isothermal conditions, the integral method yields lower deviation and hence provides a better fit of the data.

Here we studied the isothermal and non-isothermal decomposition of Huadian oil shale. The data were analysed to determine the kinetic parameters under isothermal conditions using and comparing two non-isothermal kinetic models: the direct Arrhenius plot method and the integral method.

Experimental

Sample

The oil shale samples used in this work were obtained from the Huadian Basin in northeast of China. The Fischer assay results and other properties of

the sample are given in Table 1. Before the experiments the sample was ground and sieved to the size of less than 200 meshes to eliminate the effects of heat transfer and mass transfer in oil shale particles on the kinetic parameters. The crushed shale sample was put into an oven and kept there at a constant temperature of 378 K for about two hours to eliminate moisture.

Table 1. Fischer assay data and properties of Huadian oil shale (% , dry basis)

Kerogen type	Fischer assay				Proximate analysis			Elemental analysis			
	oil	coke	water	gas	Volatiles	Ash	CO ₂	C	H	N	S
I	17.88	69.85	6.21	6.06	29.48	64.17	5.01	23.69	3.93	0.66	0.83

Apparatus and procedures

Thermogravimetric analysis (TGA) of the shale samples was undertaken using a NETZSCH simultaneous thermal analysis apparatus STA 449 /F/3. The specifications of the equipment are: measurement range from 5 g to 10 g, sensitivity 0.1 µg, maximum temperature (P = 1 bar) 1600 °C, maximum heating rate 50 K/min. The 4-mg samples were put into an alumina holder and pyrolysed in the argon atmosphere with flow rate of 50 ml/min. *Prior to* heating, the system was vacuumized three times to eliminate oxygen.

Weight loss data *versus* time or temperature were taken under two sets of operating conditions, non-isothermal and isothermal. For non-isothermal test, the sample was heated from room temperature to 873 K at heating rates 2, 5, 10, 15 and 20 K/min. For isothermal test, the furnace temperature was brought to the final temperature at rate 5 K/min and hold at designated temperatures 648, 673, 698, 723 and 748 K, for up to one hour. The temperature recorded was that of the sample which will eliminate the temperature error between the furnace and the sample.

Mathematic models

Analysis of weight loss data

The extent of conversion, or fraction of the material pyrolysed, α , was defined by the expression:

$$\alpha = \frac{W_t}{W_0}, \quad (1)$$

where W_t is weight loss quantity after time “ t ”, minutes, W_0 is total weight loss quantity after complete pyrolysis of oil shale kerogen.

According to the reaction theory, kinetic equation for decomposition of solid matter is usually written as:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n, \quad (2)$$

where $k=A \cdot e^{-E/RT}$ is reaction rate constant, A is frequency factor, E is activation energy, R is gas constant, and T is temperature. When assuming that oil shale pyrolysis is the first-order reaction, the rate of kerogen decomposition is given by:

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} (1-\alpha). \quad (3)$$

Non-isothermal analysis

Considering constant heating rate $\beta = dT/dt$, we will obtain the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1-\alpha). \quad (4)$$

In the present study, two models were used to evaluate the kinetic parameters: (1) direct Arrhenius plot method; and (2) integral method.

Direct Arrhenius plot method. At using this method, taking the logarithm of both sides of Eq. (4) yields the following equation:

$$\ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{dT}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}. \quad (5)$$

The values of E and A for individual runs were calculated basing on Eq. (5) by plotting the experimental value of $\ln(1/(1-\alpha) \cdot d\alpha/dT)$ against $1/T$.

Integral method. At using this method, the approximate integration of Eq. (4) results in Eq. (6):

$$\ln\left[\frac{-\ln(1-\alpha)(E+2RT)}{T^2}\right] = \ln\frac{AR}{\beta} - \frac{E}{RT}. \quad (6)$$

By using linear regression of $\ln[-\ln(1-\alpha)(E+2RT)/T^2]$ vs. $1/T$ in Eq. (6), the activation energy and frequency factor can be obtained by the slope and intercept from regression line. During the regression, the initial value of activation energy has to be given in advance. When the calculated activation energy equals the given activation energy, the regression will be stopped.

Isothermal analysis

For the isothermal decomposition of kerogen Eq. (2) was integrated to give:

$$\ln(1-\alpha) = kt. \quad (7)$$

Thus, from Eq. (7), for the first-order kinetics a plot of $\ln(1-\alpha)$ against t will yield a straight line, with a slope equal to $-k$. Thereafter, the Arrhenius plot was used to determine the values of activation energies and frequency factors.

Results and discussions

Non-isothermal analysis

Figure 1 shows the weight loss data of oil shale as a function of temperature at different heating rates. This figure has certain important features: total weight loss of oil shale is about 17.5% and no decomposition of carbonates is observed when the temperature increases to 873 K. The weight loss mostly occurred between 603 K and 873 K, which is attributed to the release of hydrocarbons.

The data on the relationship between conversion and temperature can be obtained by using Eq. (1) (Fig. 2). As the temperature increases, the conversion of oil shale also increases, because the processes of oil shale pyrolysis are continuous and irreversible.

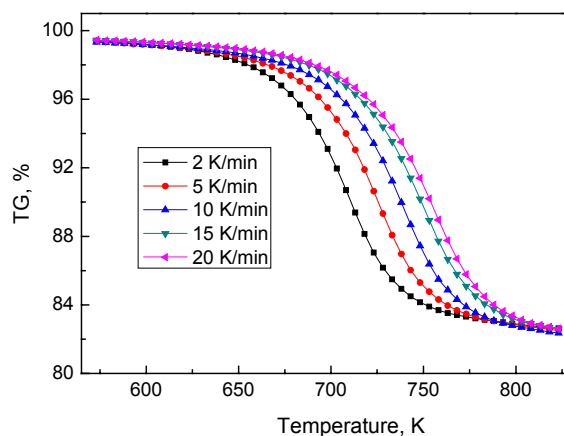


Fig. 1. The weight loss of oil shale at different heating rates.

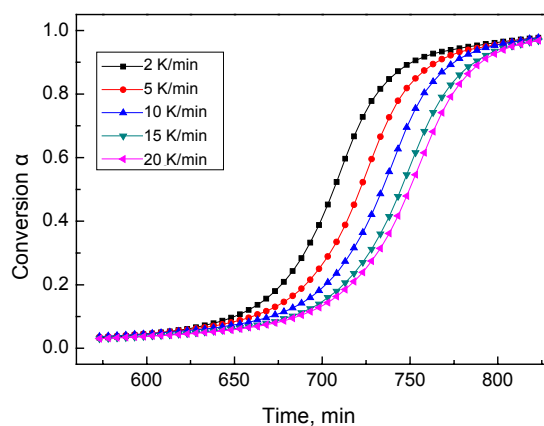


Fig. 2. The conversion vs. time at different heating rates.

Furthermore, there is a shift in the weight loss data to higher temperatures as the heating rate increases, because the rate of heat transfer at various heating rates is different, and the exposure time to a particular temperature at the higher heating rate is shorter, as well as the effect of the kinetics of decomposition [14–16].

In the present study, two methods were applied for determination of the kinetic parameters: the direct Arrhenius plot method and the integral method. Figures 3 and 4 show the plots for the direct Arrhenius plot method and the integral method at different heating rates. The almost full fit indicates the validity of assuming the first-order decomposition mechanism for conversion between 6 and 90% of oil shale kerogen.

The kinetic parameters obtained using the direct Arrhenius plot method and the integral method are given in Table 2. From Table 2 we can found that different heating rates give different activation energies and frequency

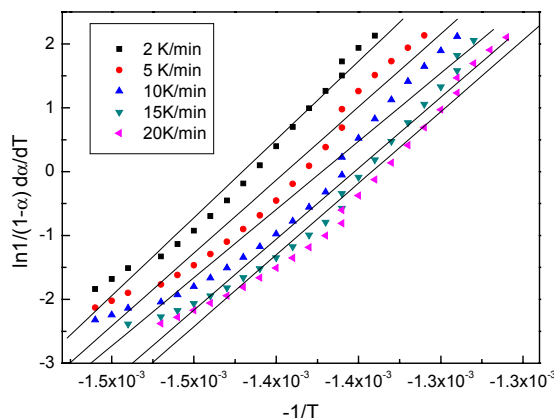


Fig. 3. Direct Arrhenius plot method for different heating rates.

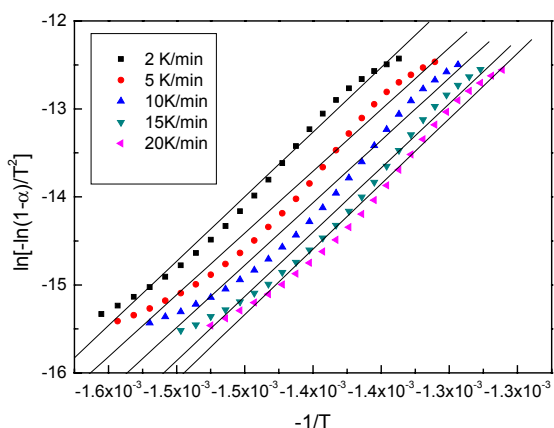


Fig. 4. Integral method for different heating rates.

Table 2. Kinetic parameters calculated for different heating rates

Heating rates, K/min	Arrhenius plot method			Integral method		
	E , kJ/mol	A , s ⁻¹	R	E , kJ/mol	A , s ⁻¹	R
2	129.61	2.46×10^6	0.9879	127.56	6.41×10^7	0.9910
5	133.41	8.62×10^6	0.9828	123.58	4.49×10^7	0.9831
10	137.14	3.71×10^7	0.9888	123.83	7.73×10^7	0.9895
15	137.36	4.09×10^7	0.9914	130.80	2.40×10^8	0.9865
20	135.86	4.33×10^7	0.9914	131.44	3.27×10^8	0.9866

factors. The values of activation energies and frequency factors increase a little with increasing rate in the case of both methods. The kinetic parameters are in good correlation with heating rates due to the compensation effect, which has also been studied by other researchers [17, 18]. Variations in values of both activation energies and frequency factors and the related compensation effect are attributed to variations in thermal lag at different heating rates [19].

The error in direct Arrhenius plot method is induced by the derivative da/dT value. The error in the integral method results from the approximate integration. In terms of conversion, calculated data are more reliable than the instantaneous rates measured in our experiments. Although small-time increments were used, the rates measured are based on the average of true instantaneous rate over the interval, as has shown by other researchers [15, 16, 20, 21]. Therefore, the kinetic parameters obtained using the integral method are recommended, since the errors are smaller. However, in respect of the computational process, the direct Arrhenius plot method is simpler than the integral method.

Isothermal analysis

Isothermal thermogravimetric analysis was performed at temperatures 648, 673, 698, 723 and 748 K (Fig. 5). Under isothermal conditions, increasing temperature decreases pyrolysis time to reach the same extent of conversion. In addition, the conversion of oil shale kerogen depends on the final pyrolysis temperature. As shown in literature [14, 22–24], higher pyrolysis temperature results in higher conversion of kerogen, the duration of pyrolysis remaining similar.

For the evaluation of rate constants, the experimental data of isothermal pyrolysis were regressed linearly by Eq. (7). The results are shown in Fig. 6. The linear correlation coefficients of each curve exceed 0.99. The linear regression of $\ln k$ vs. $1/t$ was used to determine activation energy and frequency factor by slope and intercept. The activation energy in the case of isothermal analysis is 141.52 kJ/mol, and the linear correlation coefficient close to one (results are shown in Table 3).

The kinetic parameters of isothermal experiments are compared with the averaged non-isothermal kinetic data obtained, the corresponding values of activation energies are given in Table 2. The results are shown in Table 4. Both isothermal and non-isothermal analysis give similar values of activation energy and frequency factor.

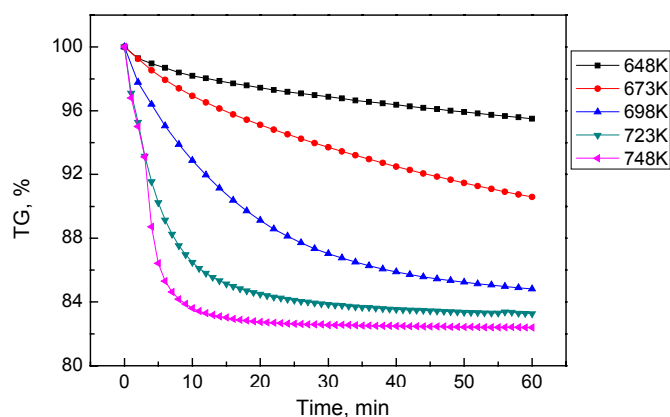


Fig. 5. The weight loss data at different isothermal conditions.

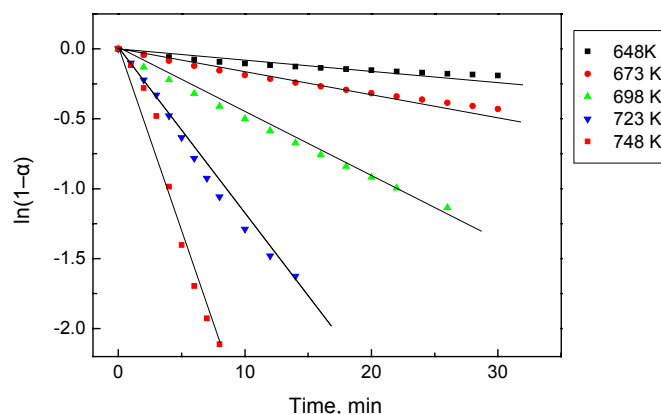


Fig. 6. The curve of $\ln(1-\alpha)$ vs. t at different isothermal conditions.

Table 3. The results of isothermal analysis

Temperature, K	k	Correlation coefficient
648	0.0074	0.9198
673	0.0155	0.9971
698	0.0472	0.9940
723	0.1237	0.9916
748	0.2101	0.9865
Relationship $\ln k - 1/T$	$\ln k = 21.294 - 17022/T$ ($R^2 = 0.9911$)	
Activation energy, kJ/mol	141.52	
Frequency factor, s^{-1}	1.77×10^9	

Table 4. Comparison of isothermal and non-isothermal-derived kinetic parameters

Method	E , kJ/mol	A , s ⁻¹
Isothermal experiments	141.52	1.77×10^9
Direct Arrhenius plot method (averaged data)	134.68	2.64×10^7
Integral method (averaged data)	127.44	4.86×10^7
Non-isothermal experiments (averaged data)	131.06	3.75×10^7

Conclusions

The isothermal and non-isothermal pyrolysis of oil shale from the Huadian Basin showed distinctly different decomposition curves depending on pyrolysis temperature and heating rate, but the thermal decomposition routes are not fundamentally different, both being continuous and irreversible.

Basing on isothermal experiment data, it was concluded that the conversion of oil shale depends on the final pyrolysis temperature, and higher temperature of pyrolysis contributes to higher conversion extent. During non-isothermal pyrolysis, with increase in heating rate a shift in conversion curves to higher temperatures was observed. The values of activation energy E and frequency factor A and the related compensation effect result from variations in thermal lag at different heating rates.

The data were examined to determine kinetic parameters using isothermal and non-isothermal analysis. Among the two non-isothermal analysis models, the integral method yields lower deviation and hence provides a better fit of the data. The isothermal analysis gave results similar to those of the non-isothermal analysis (averaged data) for determination of kinetic parameters.

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REFERENCES

1. Qian, J., Wang, J., Li, S. Oil shale development in China // Oil Shale. 2003. Vol. 20, No. 3S. P. 356–359.
2. Nazzari, J. M. The influence of grain size on the products yield and shale oil composition from the pyrolysis of Sultani oil shale // Energ. Convers. Manage. 2008. Vol. 49, No. 11. P. 3278–3286.
3. Ahmad, N., Williams, P. T. Influence of particle grain size on the yield and composition of products from the pyrolysis of oil shales // J. Anal. Appl. Pyrol. 1998. Vol. 46, No. 1. P. 31–49.

4. Shen, M. S., Lui, A. P., Shadle, L. J., Zhang, G. Q., Morris, G. J. Kinetic studies of rapid oil shale pyrolysis: 2. Rapid pyrolysis of oil shales in a laminar-flow entrained reactor // *Fuel*. 1991. Vol. 70, No. 11. P. 1277–1284.
5. Hubbard, A. B., Robinson, W. E. US Bureau of Mines Report of Investigation, No. 4744, 1950.
6. Allred, V. D. Kinetics of oil shale pyrolysis // *Chem. Eng. Progr.* 1966. Vol. 62, No. 8. P. 55–60.
7. Coats, A. W., Redfern, J. P. Kinetic parameters from thermogravimetric data // *Nature*. 1964. Vol. 201, No. 4914. P. 68–69.
8. Campbell, J. H., Koskinas, G. H., Stout, N. D. Kinetics of oil generation from Colorado oil shale // *Fuel*. 1978. Vol. 57, No. 6. P. 372–376.
9. Braun, R. L., Rothman, A. J. Oil-shale pyrolysis: Kinetics and mechanism of oil production // *Fuel*. 1975. Vol. 54, No. 2. P. 129–131.
10. Khraisha, Y. H. Kinetics of isothermal pyrolysis of Jordan oil shales // *Energ. Convers. Manage.* 1998, Vol. 39, No. 3-4. P. 157–165.
11. Lee, S. *Oil Shale Technology*. – USA: Florida, Boca Raton, CRC Press Inc., 1991. P. 52.
12. Torrente, M. C., Galán, M. A. Kinetics of the thermal decomposition of oil shale from Puertollano (Spain) // *Fuel*. 2001. Vol. 80, No. 3. P. 327–334.
13. Li, S., Qian, J. Study of the pyrolysis of Maoming oil shale lumps // *Fuel*. 1991. Vol. 70, No. 12. P. 1371–1375.
14. Thakur, D. S., Nuttall Jr., H. E. Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry // *Ind. Eng. Chem. Res.* 1987. Vol. 26, No. 7. P. 1351–1356.
15. Rajeshwar, K. Thermal analysis of coals, oil shales and oil sands // *Thermochim. Acta*. 1983. Vol. 63, No. 1. P. 97–112.
16. Xue, H., Li, S., Wang, H., Zheng, D., Fang, C. Pyrolysis kinetics of oil shale from Northern Songliao basin in China // *Oil Shale*. 2010. Vol. 27, No. 1. P. 5–16.
17. Olivella, M. A., de las Heras, F. X. C. Nonisothermal thermogravimetry of Spanish fossil fuels // *Oil Shale*. 2006. Vol. 23, No. 4. P. 340–355.
18. Olivella, M. A. Study of sulfur in fossil fuels. PhD. Thesis. – Universitat Politècnica de Catalunya (ed), Manresa, 2000. 325 pp.
19. Grønli, M., Antal, M. J., Várhegyi, G. A round-robin study of cellulose pyrolysis kinetics by thermogravimetry // *Ind. Eng. Chem. Res.* 1999. Vol. 38, No. 6. P. 2238–2244.
20. Williams, P. T., Ahmad, N. Influence of process conditions on the pyrolysis of Pakistan oil shales // *Fuel*. 1999. Vol. 78, No. 6. P. 653–662.
21. Li, S., Yue, C. Study of different kinetic models for oil shale pyrolysis // *Fuel Process. Technol.* 2004. Vol. 85, No. 1. P. 51–61.
22. Williams, P. T., Ahmad, N. Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis // *Appl. Energ.* 2000. Vol. 66, No. 2. P. 113–133.
23. Skala, D., Sokic, M., Kopsch, H. Oil shale pyrolysis – a new approach to the kinetic investigation of different kerogen type samples // *Thermochim. Acta*. 1988. Vol. 134. P. 353–358.
24. Dogan, O. M., Uysal, B. Z. Non-isothermal pyrolysis kinetics of three Turkish oil shales // *Fuel*. 1996. Vol. 75, No. 12. P. 1424–1428.

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