EFFECT OF INDUCTION ON THE KINETICS OF OIL SHALE PYROLYSIS

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Introduction

Exploitation of the energy potential of oil shale deposits has been a continuing interest in energy research for many decades. The importance of oil shale reserves has been increasing because of the dwindling energy supply. Extraction of oil and gas from oil shale is based on the principle of retorting the oil shale. Retorting may be performed above the ground (*ex situ* retorting). It may also be done in place, where the oil shale formation occurs (*in situ* retorting). Common to all retorting processes is oil shale pyrolysis. To predict the decomposition behavior of oil shale during retorting, knowledge of the pyrolysis kinetics is necessary.

1. Kinetics of Oil Shale Pyrolysis

Studies of the kinetics of oil shale pyrolysis can be

dated back to the early nineteenth century, when Engler⁶⁾ first examined the pyrolytic mechanism of oil shale. Since then a number of investigations have been made by different researchers.^{2,3,5,8-10)} Among these investigations, that by Hubbard and Robinson⁹⁾ was regarded as the most extensive. Their experimental data on Colorado oil shale pyrolysis have been widely used for verifying various kinetic models.

Colorado oil shale contains approximately 13% organic matter, the rest being ash and carbonaceous residue. The organic matter appears in soluble and insoluble forms. The soluble component, known as natural bitumen, accounts for less than 8% of the organic content in this oil shale. The insoluble organic matter, known as kerogen, is the most important of the organics present. Upon heating, kerogen decomposes to bitumen, which in turn decomposes further to oil, gas and carbon residue. Although the various products of kerogen decomposition had been identified and reported by many investigators,

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relatively little was known about the decomposition mechanism.

Based on the previous experimental evidence, Allred¹⁾ proposed the following reaction sequence

where k_1 and k_2 are the rate coefficients. The reaction sequence explains the consecutive nature of the decomposition reaction, but it does not yield good predictions of the various products as compared to the observations of Hubbard and Robinson.⁹⁾ Recognizing the inadequacy of his model, Allred¹⁾ suspected that the bitumen produced in the first step of the decomposition reaction may have a catalytic role in further accelerating the pyrolytic reaction.

The suggestion of Allred prompted Fausett *et al.*⁷⁾ to propose a more sophisticated model. Their model can be represented by

where A_1 is the kerogen, A_2 the bitumen, A_3 the oil and gas and A_4 the carbon residue. The rate equations for the above reaction sequence are given by

$$\frac{dX_1}{dt} = -k_1X_1 - (k_3 + k_4 + k_5)X_1X_2 \quad (1)$$

$$\frac{dX_2}{dt} = -k_1X_1 - k_2X_2 + k_3X_1X_2 \quad (2)$$

$$\frac{dX_3}{dt} = k_2X_2 + k_4X_1X_2 \quad (3)$$

$$\frac{dX_4}{dt} = k_5X_1X_2 \quad (4)$$

with the initial condition

$$t=0; \quad X_1=1, \quad X_2=X_3=X_4=0 \quad (5)$$

The predicted maximum concentrations of bitumen, oil and gas based on this second-order kinetics are about the right order of magnitude when compared with the experimental data of Hubbard and Robinson.⁹⁾ However, Eqs. (1) and (4) predict much earlier occurrences of the maximum conversions for bitumen and oil and gas than the observed data. In

other words, the predicted conversion profiles of bitumen, oil and gas shift to the left when compared to the experimental ones, suggesting that there is a delay in kerogen decomposition.

Braun and Rothman³⁾ proposed the following reaction scheme:

where K represents the kerogen, B the bitumen, G_1 and G_2 the gas produced in the first and second reactions, A the oil and C_1 and C_2 the carbon residues produced in the first and second reactions. These authors also considered a constant induction (delay) for kerogen decomposition and bitumen, oil and gas productions. Based on the above reaction scheme, the bitumen and oil productions are given by

$$\frac{B}{K_0} = \frac{k_1f_1}{k_2-k_1} \{ \exp[-k_1(t-t_0)] - \exp[-k_2(t-t_0)] \} \quad (6)$$

$$\frac{A}{K_0} = \frac{f_1f_2}{k_2-k_1} \{ k_2[1 - \exp(-k_1(t-t_0))] - k_1[1 - \exp(-k_2(t-t_0))] \} \quad (7)$$

in which f_1 and f_2 are the fractional conversions to bitumen and oil, t_0 the induction and K_0 the initial kerogen concentration. The new model retains the simplicity of Allred's.¹⁾ Eq. (7) well predicts the oil production, but Eq. (6) fails to do so for the bitumen, revealing the deficiency of the kinetic model. Hence, without further refinement, the simple model of Braun and Rothman³⁾ seems to be inadequate also. Since then, no further progress has been made in improving the decomposition kinetic model of oil shale pyrolysis.

2. Proposed Modification of the Kinetic Model

From the above discussion, it is apparent that none of the models currently available can well predict the observed data. The kinetic models of Fausett *et al.*⁷⁾ and Braun and Rothman³⁾ are definitely more refined than Allred's,¹⁾ but are still far from satisfactory. It appeared that modification of the model of Fausett *et al.*⁷⁾ by incorporating inductions for kerogen and bitumen decompositions and oil and gas production, respectively, would provide a better alternative. This turns out to be the case.

The model adopted here is based on that of Fausett *et al.*⁷⁾ but takes into account the inductions for various components. Braun and Rothman³⁾ considered a constant induction for kerogen and bitumen decompositions and oil and gas productions. An observation of the experimental data of Hubbard and

Robinson⁹⁾ reveals that the induction varies significantly from one species to another. Consideration of a constant induction for all components is inadequate. In the present study, Eqs. (1) to (4) of Fausett *et al.*⁷⁾ were adopted. These equations are subject to the following initial conditions:

$$t = < t_k; \quad X_1 = 1 \quad (8)$$

$$t = < t_b; \quad X_2 = 0 \quad (9)$$

$$t = < t_o; \quad X_3 = 0 \quad (10)$$

$$t = < t_c; \quad X_4 = 0 \quad (11)$$

in which t_k , t_b , t_o and t_c are the inductions for kerosen and bitumen decompositions and oil and gas productions, respectively. Because of the nonlinearity of the modified kinetic model, no analytic solutions were available and Eqs. (1) to (4) had to be integrated numerically⁴⁾ by the Runge-Kutta method. The inductions hence were determined empirically by best fit of the model predictions to the experimental data of Hubbard and Robinson⁹⁾ by Box's complex optimization scheme.¹¹⁾ The activation energies (E_i) and preexponential factors (k_{i0}) of the five kinetic parameters, k_1 to k_5 , can be represented by

Table 1. Activation energies and preexponential factors

i	k_{i0}	E_i , (kcal/g·mole)
1	7.04448e+03	20.3
2	3.40127e+10	37.4
3	1.90436e+10	33.8
4	1.39002e+08	28.2
5	9.77004e+08	31.0

Fig. 1. Comparison of model predictions and experimental data for bitumen, oil and gas, and carbon residue productions at 425°C

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right) \quad (12)$$

The values of k_{i0} and E_i are given in **Table 1**.

Figures 1 to 4 show comparisons of the model predictions (solid lines) with the experimental data for the productions of bitumen, oil, gas and carbon residue for temperatures ranging from 425 to 500°C. It is apparent that predictions and observations are in good agreement for all temperatures. If the induction times were excluded, as in the original model

Fig. 2. Comparison of model predictions and experimental data for bitumen, oil and gas, and carbon residue productions at 450°C

Fig. 3. Comparison of model predictions and experimental data for bitumen, oil and gas, and carbon residue productions at 475°C

Fig. 4. Comparison of model predictions and experimental data for bitumen, oil and gas, and carbon residue productions at 500°C

Fig. 5. Inductions of kerogen and bitumen decompositions, and oil and gas production vs pyrolytic temperature

of Fausett *et al.*,⁷⁾ the model predictions would shift toward the left in the figures.

The temperature-dependent inductions for various components are shown in Fig. 5. It is seen that the inductions for kerogen and bitumen decompositions are basically the same. The induction for oil and gas production is seen to be significantly larger than that of kerogen/bitumen decomposition. A common trend of the induction times is that they decrease with increase in pyrolytic temperature. According to this trend, the induction will disappear if the pyrolysis is conducted at a sufficiently high temperature.

Conclusion

It is shown in the present study that the kinetic

decomposition models of Allred¹⁾ and Braun and Rothman³⁾ are inadequate for representing the actual oil shale decomposition. Similarly, the model of Fausett *et al.*⁷⁾ without consideration of inductions is likewise deficient. However, modification of the Fausett *et al.*⁷⁾ to include induction and temperature dependence of induction allows close prediction when compared with the experimental data of Hubbard and Robinson.⁹⁾

Nomenclature

A	= oil concentration
A_1	= kerogen concentration
A_2	= bitumen concentration
A_3	= combined concentration of oil and gas
A_4	= concentration of carbon residue
B	= bitumen concentration
C_1, C_2	= carbon residue produced in the first and second reactions of the Braun and Rothman model ³⁾
E_i	= activation energy of the i -th reaction
f_1	= fractional conversion to bitumen from kerogen
f_2	= fractional conversion to oil from bitumen
G_1, G_2	= gas production in the first and second reactions of the Braun and Rothman model ³⁾
K_0	= initial kerogen concentration
k_1	= rate coefficient of kerogen decomposition
k_2	= rate coefficient of bitumen decomposition
k_3, k_4, k_5	= rate coefficient of kerogen and bitumen decomposition to other products
k_{i0}	= preexponential factor of the i -th reaction
R	= gas constant
t	= time
t_b	= induction for bitumen decomposition
t_c	= induction for carbon residue production
t_k	= induction for kerogen decomposition
t_o	= induction for oil and gas production
X_1	= mass fraction of kerogen
X_2	= mass fraction of bitumen
X_3	= mass fraction of oil and gas
X_4	= mass fraction of carbon residue

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