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The oxidation of heavy oil: Thermogravimetric analysis and non-isothermal kinetics using the distributed activation energy model

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ABSTRACT

The oxidation behavior and kinetics parameters of heavy oil oxidation are highly required to understand the reactivity of crude oil and gain novel recovery routes. In this contribution, thermogravimetric analysis was employed to investigate the oxidation behaviors of one typical kind of Chinese heavy oil, and the distributed activation energy model (DAEM) was applied to obtain accurate kinetic parameters of oxidation reactions from 30 to 550 °C and to bring new insights on the complex reactions and mechanistic understanding. The three stage oxidation – low-temperature oxidation (200 to 320 °C), plateau section (320 to 350 °C), and high-temperature oxidation (above 350 °C) – was observed in the non-isothermal oxidation experiments. E vs. V/V^* curve of whole oil oxidation follows similar pattern to the thermogravimetric profile. Thus, low-temperature oxidation and high-temperature oxidation are regarded as two character zones of heavy oil oxidation. The apparent activation energies at low temperatures are around 100 kJ/mol, and at high temperatures are about 190–230 kJ/mol. The curves predicted from kinetic parameters afford a good approach with the experimental data demonstrating the reliability of the available kinetic parameters.

1. Introduction

Petroleum is the most important energy source for our world. Among the oil resource, heavy crude oils serve as major feedstock for the economics of petroleum development for the reason that the resources of heavy oil in the world are more than twice those of conventional light crude oil [1]. The heavy oil (<20° API) exploitation can be compatible to conventional oil if new approaches are applied to facilitate its recovery and moderate its quality detractors and environmental impact [2]. Among a variety of enhanced oil recovery technologies, in situ combustion (ISC) has been regarded as one of the most promising strategies, which is achieved by burning a small fraction of oil though injecting air into the reservoir in order to reduce the viscosity, enable flow of the unburned fraction and improve oil recovery [1]. However, the process control is a great challenge. To guarantee a successful implement, developing an accurate reaction kinetics model is highly required for numerical simulation to forecast and improve the design and field performance.

With the advantage of fast and accurate characterization, thermal analysis technique has been widely employed in investigations of thermal properties of various systems. The first attempt to use thermogravimetric (TG) data to understand the kinetics of oil combustion was performed by Tameda [3] in 1959. After that, more and more efforts have been made to apply thermal analysis methods to oil oxidation [4,5]. Both the first-order Arrhenius method and Coats–Redfern (C–R) approximation [6] have been applied to evaluate kinetic parameters such as activation energy and frequency factor. Mahinpey's group [7,8] investigated the pyrolysis and combustion kinetics of Neilburg oil, its asphaltenes and Fosterton oil using Arrhenius model. They found that the observed activation energies of whole oil were about 130 kJ/mol and the apparent order of oxidation reactions varied at different temperatures for isothermal combustion of coke. In their another work [5], low-temperature oxidation of an Alaska heavy oil was investigated using isothermal and ramped temperature thermogravimetry and the kinetic parameters of isothermal and non-isothermal reactions were calculated based on the differential method and Segal–Fatu approach, respectively. Kök [9] reported non-isothermal kinetics and feasibility study of medium grade crude oil. Three different kinetic methods, Arrhenius, C–R, and Ingraham–Marrier, were applied to determine the kinetic parameters. Hu [10] used C–R model to estimate kinetic parameters of KekeYa light oil oxidation in low temperature oxidation (LTO) and high temperature oxidation (HTO) regions. The average activation energies in LTO and HTO were 26.68 and 153.05 kJ/mol, respectively. Since a first-order reaction with respect to oil concentration over the oxidation process is assumed in these two methods, the real situations, especially of these complex materials, is not fully described yet. The kinetic equations proposed by Zsako and Vyazovkin, which has been utilized in the kinetic study of oil generation [5,11] and degradation [12], are considered as excellent model-free kinetics methods. However,

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the components in the heavy oil is extremely complex, the oxidation process of complex systems with various reactions are not well described by a simple combination of small number of reactions. An accurate kinetic model to describe the oxidation behavior of heavy oil and elucidate their reaction mechanism is highly required.

Among various kinetic models to describe the complex reaction systems, the distributed activation energy model (DAEM) provides a very effective route for the kinetic analysis of complicated reaction systems. It assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously, which is considered most suitable for the systems with complex reactions and has been widely used in the study of pyrolysis of biomass [13], coal [14], oil shale [15], and asphaltenes [16,17]. Li's group have carried out pioneering works on the applications of DAEM to the kinetic analysis of pyrolysis [18,19], hydropyrolysis [20], gasification [21], combustion [22], and even simulated distillation [23]. Herein, we apply the DAEM in the analysis of heavy crude oil oxidation to obtain accurate kinetic parameters and bring new insights on the complex reactions and mechanistic understanding.

In this contribution, the oxidation performances of one typical kind of Chinese heavy crude oil, Xinjiang oil, were investigated by thermogravimetric analysis (TGA). The proper kinetics parameters, which are expected to predict the TG behavior of heavy oil oxidation, were obtained in particular reference to the DAEM method developed by Miura and Maki [24]. The main objective of this contribution is not only to explore the oxidation behavior and estimate kinetics parameters of heavy oil oxidation in the whole temperature range, but also to provide new insight into the oxidation reaction mechanism.

2. Experimental

The heavy oil used in this study was from Xinjiang Oil Field. The crude oil was separated from the sand to eliminate any catalytic effects arising from metals and subsequently devolatilized under inert atmosphere at 300 °C for 3 h to eliminate the influence of light component volatilization on TG profiles prior to the TG experiments. The elemental analysis was performed by an elementary analyzer (Elementar, Vario EL III). The non-isothermal oxidation experiments were conducted in a sensitive thermo-balance (Mettler Toledo, TGA/DSC-1) at a heating rate of 1, 3, 5, 10, and 20 °C/min from 30 to 550 °C in Al crucibles. The sample was weighted about 5 mg and was flatly spread on the bottom of the crucible to avoid the slow mass transfer of oxygen. In order to ensure adequate oxygen content for oxidation, we chose a mixed gas flow of oxygen and nitrogen in a ratio of 90/10 with a constant flow rate of 100 mL/min. The same experiment was repeated at least twice to ensure the repeatability and the accuracy of the experimental data.

3. Kinetics model

The DAEM, originally proposed by Vand [25] in 1942, has been widely used in systems with complex reactions. The DAEM model assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously. The change in the total weight is given by

$$1-V/V^{*}=\int_{0}^{\infty}\exp\left(-k_0\int_{0}^{t}\mathrm{e}^{-E/(\mathrm{R}T)}\mathrm{d}t\right)f(E)\mathrm{d}E \tag{1}$$

where V is the total volatiles evolved by time t, V^{*} is total volatiles of the sample, $f(E)$ is a distribution curve of the activation energies representing the differences in the activation energies of many first-order irreversible reactions, and k_0 is the frequency factor corresponding to the E value.

The distribution curve $f(E)$ is defined to satisfy

$$\int_{0}^{\infty}f(E)\mathrm{d}E=1. \tag{2}$$

For the process with a constant heating rate, β, temperature, T, against time, t, follows

$$T=T_0+\beta t. \tag{3}$$

Substituting Eq. (3) into Eq. (1), the following equation can be available:

$$1-V/V^{*}=\int_{0}^{\infty}\exp\left[-(k_0/\beta)\int_{0}^{T}\mathrm{e}^{-E/(\mathrm{R}T)}\mathrm{d}T\right]f(E)\mathrm{d}E. \tag{4}$$

The focus of the DAEM method is the estimation of $f(E)$ and k_0, with which the weight change of any heating profile can be predicted.

The conventional method is to assume the distribution curve $f(E)$ to be a Gaussian distribution with mean activation energy E_0 and standard deviation σ, and k_0 to be a constant dependent on reaction system to avoid the complexity of the analysis. However, the two assignments do not always reflect real situations.

Miura and Maki [24,26] develop a simple method to determine $f(E)$ and $k_0(E)$ from three sets of experimental data without assuming any functional forms for $f(E)$ and $k_0(E)$. According to their theory, it is approximated that only one reaction occurs at the specified T and β, which is given mathematically by

$$\mathrm{d}V/\mathrm{d}t\cong\mathrm{d}(\Delta V)/\mathrm{d}t=k_0e^{-E/(RT)}(\Delta V^{*}-\Delta V). \tag{5}$$

This indicates that the overall rate $\mathrm{d}V/\mathrm{d}t$ is approximated by the rate of the j-th reaction at the temperature at which only the j-th reaction is occurring. Thus, in Eq. (5), ΔV, ΔV^{*}, E, and k_0, respectively, are the amount of evolved, the total volatile content, the activation energy, and frequency factor for the j-th reaction.

Because E and k_0 are constants, Eq. (5) can be integrated for a constant heating rate β as

$$1-\Delta V/\Delta V^{*}=\exp\left(-k_0\int_{0}^{t}\mathrm{e}^{-E(\mathrm{R}T)}\mathrm{d}t\right)\cong\exp\left(-\frac{k_0\mathrm{R}T^2}{\beta E}\mathrm{e}^{-E/(\mathrm{R}T)}\right). \tag{6}$$

The differential expression (Eq. (5)) and the integral expression (Eq. (6)) can be rewritten as

$$\ln\left[d(V/V^{*})/dt\right]=\ln\left[k_0(\Delta V^{*}/V^{*})(1-\Delta V/\Delta V^{*})\right]-E/(\mathrm{R}T) \tag{7}$$

and

$$\ln\left(\beta/T^2\right)=\ln(k_0R/E)-\ln\left[-\ln(1-\Delta V/\Delta V^{*})\right]-E/(\mathrm{R}T). \tag{8}$$

The V/V^{*} values should be equal for different β values when only the j-th reaction is occurring. The Arrhenius plot of $\ln(\beta/T^2)$ vs. $1/T$ at the same V/V^{*} value determines the E and k_0 value corresponding to the V/V^{*} value. Since the DAEM model requires no assumptions and the procedure is simple, the Miura and Maki method has achieved wide acceptance since proposed.

4. Results and discussion

4.1. TG analysis

Fig. 1 shows the TG and the derivative thermogravimetric (DTG) curves for oil oxidation. The oxidation weight loss of the oil sample starts at about 180 °C and completes at about 470 °C. The oxidation process involves three main stages: LTO, plateau section, and HTO. The first

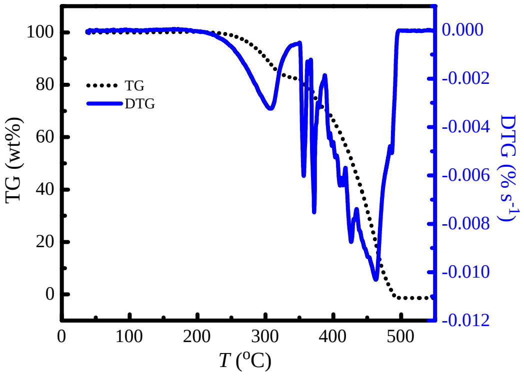

Fig. 1. TG and DTG curves of whole oil oxidation (O_2 90 mL/min, N_2 10 mL/min, 5 °C/min).

stage of LTO is ranging from 200 to 320 °C, during which the DTG profile exhibits a small broad peak, indicating a gentle weight loss rate. The second stage, plateau section, has a narrow temperature range of about 320 to 350 °C with little weight loss. This is attributed from the fact that the reaction rate is very low in this temperature range and/or the induction period for oxidation reactions with high activation energy. In the third stage above 350 °C, known as HTO, the weight sharply decreases to zero with a total weight loss of about 80 wt.%, while the DTG curve presents several overlapping peaks. The observations coincide with those reported in the previous publications [5,8,27].

The TG and DTG results suggest two character zones of oxidation weight loss rate. It is indicated that different kinds of reactions occur in the two zones. However, the direct evidence at molecular scale is still unavailable yet to well identify the two reaction zones. It is anticipated that the main reactions in the LTO region are probably partial oxidation of carbon atoms at the ends of carbon chains or on branch chains [5][28], while in the HTO region oxidation reactions of carbon atoms on the main chains are more common. To obtain more detail information from the TG results, the kinetic analysis is carried out as follows.

4.2. Effects of heating rate on TG

Fig. 2 shows TG curves for oil oxidation at a heating rate of 1, 3, 5, 10, and 20 °C/min. The profile is shifted to higher temperature and the temperature limits of LTO and HTO zones become less outstanding with the increase of the heating rates. Because of huge thermal hysteresis at high heating rate, there is not enough time for oil samples to reach thermal equilibrium state with a rapid increase of the furnace temperature. Consequently, the measured mass loss curve shifts with temperature ramp rate. If the time is too limited, the LTO reactions are expected to be incomplete before the HTO reactions become dominating, and as a result, the platform on TG profiles even disappears (as observed in the curve at 20 °C/min). Heat accumulation from oxidation also occurs at high heating rates, which results in fierce combustion when a critical point is reached. When the heating rate is 20 °C/min, a convex-shaped curve at 450 °C is detected.

4.3. Kinetic analysis using DAEM method

DAEM method was applied to describe the kinetic of heavy oil oxidation. As shown in Fig. 3, the Arrhenius plot of $\ln(\beta/T^2)$ vs. $1/T$ was performed to obtain the activation energy E and the frequency factor k_0 at each selected level of conversion for $\beta = 1, 3, 5$ °C/min. TG profiles with low heating rates are selected to reduce the impact of thermal hysteresis and heat accumulation and obtain kinetic parameters for more reliable analysis. Since the slope and intercept are sensitive to the linearity of the $\ln(\beta/T^2)$ vs. $1/T$ relationship, the linear regression was held with linearity (R^2) to be above 0.9 in this contribution.

Both the Arrhenius and C–R models [7,8,10] have the assumption that the oil oxidation rate is only related to oil concentration. In contrast, the DAEM method provides accurate apparent activation energies without any assumptions of overall reaction order. Fig. 4 illustrates activation energy vs. conversion relationship of whole oil oxidation. Corresponding to the TG curve, E vs. V/V^* curve can be divided into three stages: In the first stage (LTO), the conversion is less than 20%, and the apparent activation energies are around 100 kJ/mol. The activation energy jumps rapidly from 100 kJ/mol to about 250 kJ/mol in the second stage (plateau section) with no obvious weight loss. The average apparent activation energies of the third stage are about 190–230 kJ/mol. The difference of activation energies between LTO and HTO indicates two groups of characteristic reactions in the whole temperature range, while the similarity of activation energies indicates the same or similar kind of reactions in each stage.

The activation energy E and frequency factor k_0 have a positive correlation. They nearly meet the exponential relationship (Fig. 5), which is in accordance with those reported in the literatures [25,29]. The exponential relationship is described as:

$$k_0 = ae^{bE} \tag{9}$$

where a and b are positive constants that are depended on reaction systems. The relation of k_0 vs. E given by Eq. (9) is known as “compensation effect”. The compensation effect remains the same in different regions since a and b are nearly constants (Fig. 5).

Using the E and k_0 obtained by DAEM, the TG profiles were predicted by Eq. (6) without any mathematical fitting techniques (Fig. 6). The TG curves for $\beta = 1, 3, 5$ °C/min were employed to estimate E and k_0. The model fits well with experiment results, which indicates that $R^2 > 0.9$ is enough to calculate E and k_0 with high accuracy. Fig. 6(b) shows that the V/V^* vs. T relationships for $\beta = 10$ and 20 °C/min are well predicted except in the ranges with extremely high reaction rate

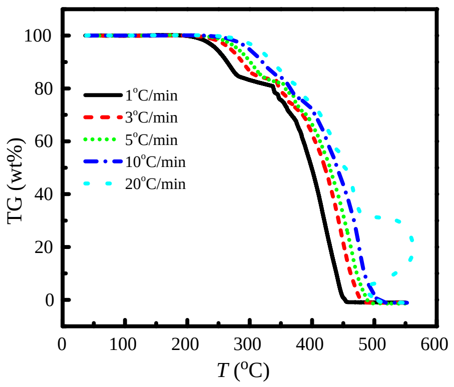

Fig. 2. TG profiles of oil oxidation at different heating rates.

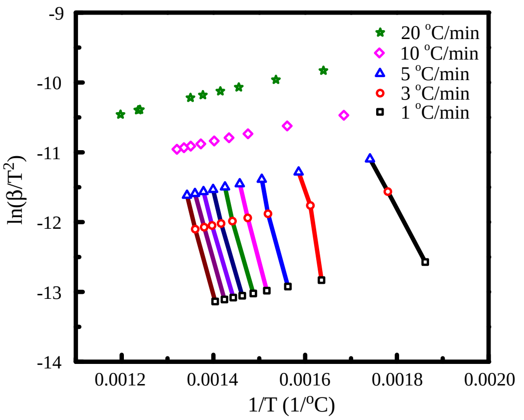

Fig. 3. The Arrhenius plot of $\ln(\beta/T^2)$ vs. $1/T$ at selected conversion values.

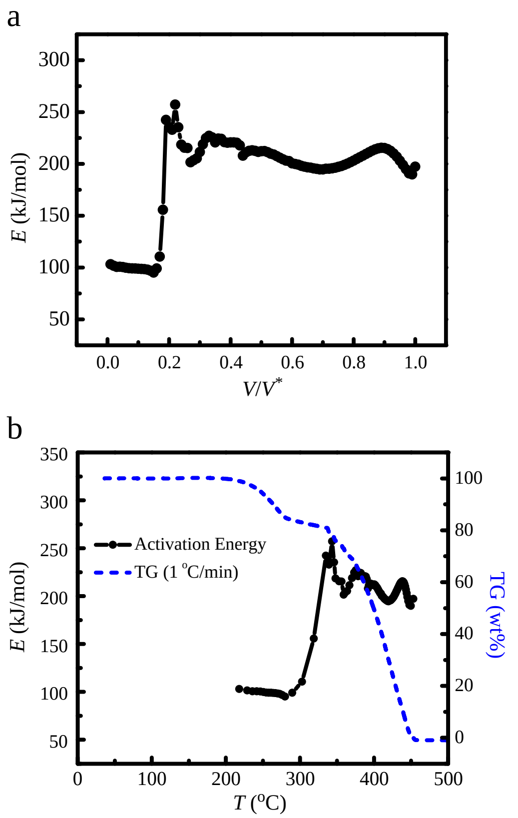

Fig. 4. Activation energy E vs. (a) conversion V/V^* and (b) temperature T relationship estimated for whole oil oxidation.

and heat-release rate when the system temperature is totally out of control. These findings indicate that the DAEM method is suitable to describe the heavy oil oxidation. The as-obtained E and k_0 are very useful to predict the kinetic behavior of heavy oil.

5. Conclusions

The oxidation of heavy oil can be divided into three main stages, that is, LTO (200–320 °C), plateau section (320–350 °C), and HTO (above 350 °C), observed from TG and activation energy profiles. Larger thermal hysteresis at higher heating rate induces the disappearance of platform and uncontrollability of sample temperature. LTO and HTO are regarded as two character zones of heavy oil oxidation. At low temperatures, the apparent activation energies of reactions are around 100 kJ/mol, while the apparent activation energies are about 190–230 kJ/mol at high temperatures. Two types of reactions in the LTO and HTO regions can be inferred. The oxidation behavior predicted from kinetic parameters offers a good approach with the experimental data. This work not only provides new insights on the type of reactions occurring, but also an accurate reaction kinetics model of heavy oil oxidation to understand the reactivity of crude oil and gain novel efficient recovery routes. It is also applicable to the underground heavy oxidation, which provides predictable results to understand the in situ oxidation behavior of heavy oil, facilitate its recovery, and moderate its quality detractors and environmental impact.

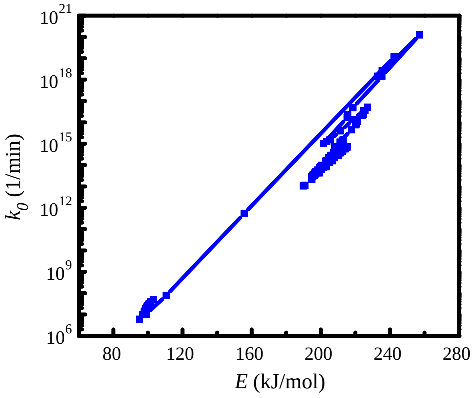

Fig. 5. k_0 vs. E relationship estimated for whole oil oxidation.

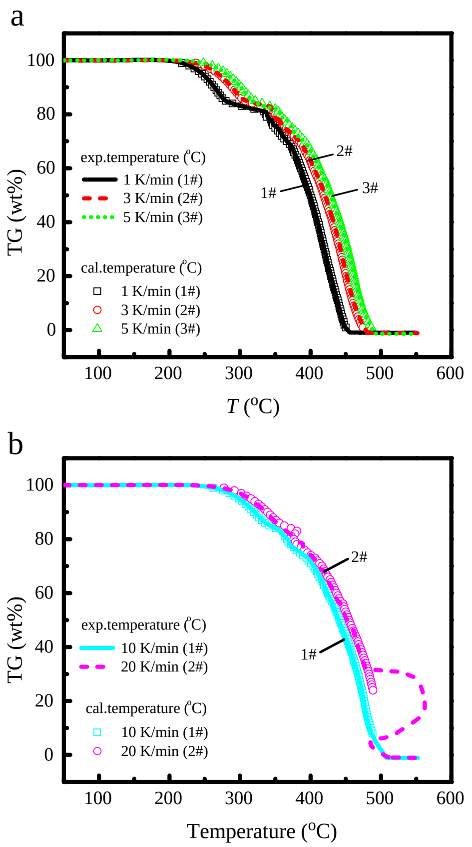

Fig. 6. Experimental and calculated TG curves at (a) $\beta = 1$, 3, and 5 °C/min, (b) $\beta = 10$ and 20 °C/min for whole oil oxidation.

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