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Oxidation Kinetics Analysis of Crude Oils with Different Viscosities

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Abstract: In order to compare the oxidation kinetics parameters of crude oils with different properties in the process of crude oil oxidation, six different crude oil samples were selected to analyze the oxidation characteristics of crude oils with different properties. In order to study the oxidation of crude oil, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) synchronous analyzer were used for crude oil in the oxygen environment between 25 °C and 900 °C at a heating rate of 20 °C/min. The experimental results were based on crude oil oxidation using TGA and DTG experimental data to evaluate the oxidation mechanism of different crude oils, so as to better understand the situation in the oxidation reaction process. At the same time, the oxidation stage of crude oil was divided according to DSC data. Arrhenius method was used to analyze the oxidation kinetic parameters of crude oils with different properties, and the activation energies and pre-exponential factors of different crude oils were calculated. The experimental results show that the oxidation stage of crude oil can be divided into three stages: low-temperature oxidation, fuel deposition, and high-temperature oxidation. The low-temperature oxidation reaction begins at 280 °C, and the high-temperature oxidation reaction occurs at 400 °C. The low-temperature oxidation activation energy of an oil sample is 39.73–77.74 kJ/mol. The activation energy of the high-temperature oxidation is in the range of 106.27–264.47 kJ/mol. The activation energy of crude oil in the low-temperature oxidation stage increases with the increase of crude oil viscosity and decreases with the increase of crude oil viscosity in the high-temperature oxidation stage. Therefore, during the high-temperature oxidation stage, high-viscosity crude oil is more prone to reactions.

Keywords: crude oil; oxidation reaction; reaction kinetics; viscosity; heavy oil; kinetic parameters

1. Introduction

Laboratory experiments and field tests confirmed that, compared with water injection, air injection can increase oil recovery by 14–23% [1–3]. One of the keys of this technology is whether the injected O_2 can oxidize well with the reservoir crude oil [4]. Therefore, oxidation kinetics of crude oil became the basic theory of air injection to enhance oil recovery [5]. In addition, it is of great significance to understand the propagation of combustion front in porous media [6,7]; furthermore, the combination of oxidation reaction kinetic parameters and numerical simulation can provide a basic research method for air injection projects [8].

Crude oil oxidation kinetic parameters include activation energy, pre-exponential factor, and reaction mechanism function. At present, the experimental methods for calculating the kinetic parameters of crude oil oxidation include thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), differential scanning calorimeter (DSC), accelerated rate calorimetry (ARC), etc. [9,10] Scholars usually use the TGA method to study the oxidation process of heavy oil under atmospheric pressure because of the low content of

dissolved gas in heavy oil and the small difference in oil composition between surface condition and formation condition. The TGA method can measure the conversion rate of crude oil in each oxidation stage at different heating rates. Based on the conversion rate of crude oil combined with the Arrhenius equation, the oxidation kinetic parameters of crude oil in different oxidation stages can be obtained by differential method or integral method [11,12].

Kok et al. [13,14] used thermal analysis techniques (TGA-DTG, and DSC) to study the oxidation behavior of heavy- and medium-grade crude oils. Higher activation energy values were obtained in heavy and medium crude oils. They discussed that the higher the asphaltene content in crude oil, the higher the activation energy and heat release (the asphalt has a high content of bitumen, high activation energy, and releases a large amount of heat). Other parameters such as heating rate, clay minerals, and metal additives also have an important influence on the oxidation behavior of crude oil. Gundogar et al. [15] reported the oxidation behavior of light and medium crude oil under atmospheric air and calculated the activation energy using different kinetic models. Results showed that activation energy at the high-temperature oxidation (HTO) stage is significantly higher than that at the low-temperature oxidation (LTO) stage. The studies indicate that heavier oils with greater asphaltene content had a greater influence on the oxidation heat release and activation energy [16]. Liu et al. [17] used thermogravimetric analysis to explore the influence of chemical composition of crude oil on oxidation kinetics; the higher the content of colloid and asphaltene in crude oil, the greater its reaction rate and energy demand in the low-temperature oxidation (LTO) stage. As well, more coke deposits were generated in the fuel deposition (FD) stage, which was positive for high-temperature combustion. The LTO stage generally presents an endothermic trend; energy accumulation is essential to the subsequent reaction. In recent years, more attention has been paid to the effects of aromatics, resins, and asphaltenes on the oxidation behavior of heavy crude oil, and catalysts have been considered to reduce the reaction temperature and improve the reaction speed [18,19].

The high content of colloid and asphaltene is one of the important reasons for the high viscosity of crude oil. Previous studies have confirmed that colloid and asphaltene are important factors affecting the activation energy of the reaction. Although the oxidation behavior of crude oil has been studied extensively for many years, scholars pay more attention to the kinetic parameters of the three stages (LTO, FD, and HTO), but the relationship between the oxidation kinetic parameters and the properties of crude oil (e.g., viscosity) is less discussed or only heavy and light oil's oxidation kinetic parameters are compared: no one has systematically studied the effect of crude oil weight at different oxidation stages on the activation energy. In this article, six kinds of crude oil with different viscosities were conducted by synchronous thermal analysis technology [20] of TGA, DTG, and DSC, in order to analyze the heat release in different oxidation stages of different samples, and the kinetic parameters were calculated for each stage. Finally, based on the published references data as supplementary [21], the relationship between activation energies and oil viscosities of different samples at different oxidation stages was given.

2. Experimental Section

2.1. Materials

There are 6 kinds of crude oil used in this experiment. Before the experiment, the samples were dehydrated and impurities were removed; the water content of the dehydrated oil sample after treatment is less than 0.5%. According to Table 1, sample 1 is light with a viscosity of 9.6 mPa·s and a API gravity of 31.2. Samples 2–3 are ordinary heavy oil, with viscosities between 66–574 mPa·s and API gravities between 22.9–20.4. The viscosity of samples 5 and 6 is much higher than that of the other ones, the API gravities are less than 20. (API gravity = 141.5/SG − 131.5, SG is the ratio of crude oil density to pure water density at 4 °C under standard atmospheric pressure).

Table 1. Samples viscosities and API gravities (50 °C).

Sample No.	Viscosity/(mPa·s)	API Gravity
1#	9.6	31.2
2#	66	22.9
3#	105	22.1
4#	574	21.4
5#	2053	19.6
6#	2927	18.3

2.2. Experimental Apparatus and Procedure

The crude oil oxidation process was implemented by TGA/DSC synchronous thermal analyzer (Mettler Toledo TGA/DSC3$^+$, Figure 1). TGA/DSC synchronous thermal analyzer can simultaneously measure mass signal and heat release signal, and it has TGA and DSC analysis function. The experimental temperature is 25–900 °C, and the protective gas is nitrogen with a flow rate of 50 mL/min. The reaction gas is air, and the flow rate is 20 mL/min. The reaction gas passes over the surface of the crucible and causes the sample to undergo an oxidation reaction, then the surplus reaction gas is eliminated together with the protective gas.

Figure 1. Mettler Toledo TGA/DSC3$^+$ synchronous thermal analyzer.

The procedures are as follows: (1) Switched on the software system and set the temperature range as 25–900 °C and the heating rate as 20 °C/min; (2) Empty ceramic crucible was placed in the furnace body, the gases tubes were connected, the reaction gas was air, the protective gas was 99.99% high purity nitrogen; (3) The baseline calibration was first executed to improve the TG/DSC thermal analysis accuracy, and repeated three times for stability; (4) Blank curves were recorded as correlation data; (5) Oil sample was placed in the ceramic crucible with the mass around 10–20 mg; (6) TG/DSC synchronous tests were carried out on 6 oil samples under the same experimental conditions; (7) TG-DTG and TG-DSC curves were drawn and analyzed, respectively, using the testing data of different oil samples; (8) Kinetic parameters were calculated according to Arrhenius kinetic theory [22].

3. Results and Discussion

3.1. TG-DTG Analysis

TG-DTG curve can dynamically reflect the weight loss rate of oil samples during oxidation. The horizontal coordinate is temperature, the vertical coordinate of TG curve is the residue mass fraction of the sample at a certain temperature, and the vertical coordinate of DTG curve is the derivative of conversion rate to reaction time. The larger the absolute value is, the faster the oxidation reaction rate is.

As shown in Figure 2, when the temperature is below 140 °C, the TG curve is flat, and the weight loss rate basically remains unchanged. The main reason for weight loss

is volatile light hydrocarbon components. When the temperature is higher than 140 °C, the weight loss rate increases rapidly, among which, the weight loss rate of oil sample 6 is the lowest at low-temperature, because oil sample 6 is ordinary heavy oil class ii with high content of colloid and asphaltene and heavy components, and it does not undergo oxidation easily at low temperature. Oil sample 1 has the highest weight loss rate at the low-temperature oxidation stage, mainly because of the high content of light components in oil sample 1, which is conducive to the occurrence of spontaneous combustion of crude oil in the oxidation process. The weight loss rate of oil samples 3 and 4 in the low-temperature oxidation stage is between that of oil sample 1 and oil sample 6, because the light component content of oil samples 3 and 4 is smaller than that of oil sample 1, while the gelatinous asphaltene content is larger than that of oil sample 1. The thermogravimetric curve shifts to the right as the viscosity of crude oil increases.
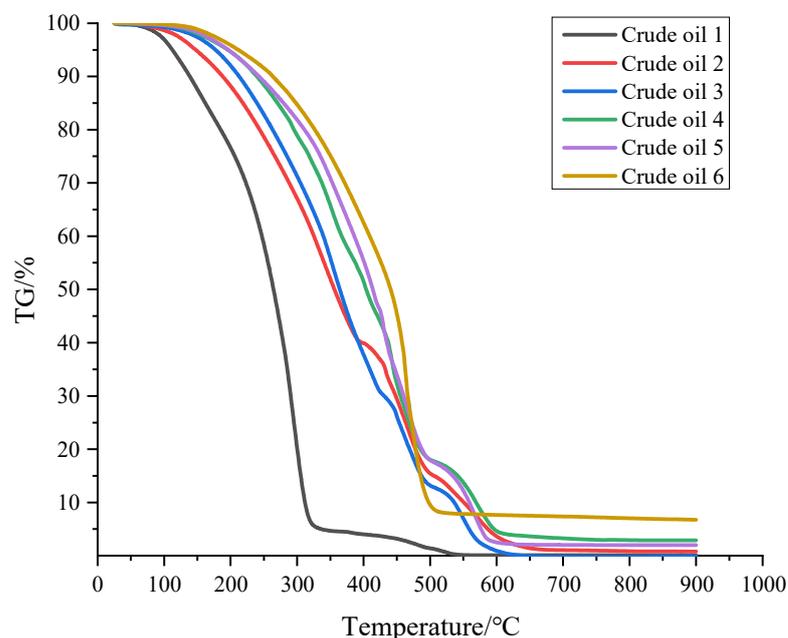
Figure 2. TG curves of crude oil samples.

TG and DTG curves of different oil samples at the same heating rate are shown in Figure 3. The oxidation characteristics of crude oil can be divided according to the temperature range and reaction rate of exothermic reaction. TG-DTG curve shows that the reaction rate peak of each crude oil sample is different. The first peak occurs at 300–400 °C, and the main reaction type is a low-temperature oxidation reaction between crude oil and oxygen [23]. The second peak occurs at 500–600 °C, and the reaction type is a high-temperature oxidation reaction between oil coke and oxygen. The weight loss rate of each oil sample showed a characteristic of multi-peak fluctuation, which was mainly caused by the fact that the oil sample used in the experiment was pure oil, and the air swept over the sample surface. After the crude oil on the surface became coking, the internal oil sample could not fully contact with oxygen and the oxidation was incomplete. The peak reaction rate of oil samples 1–2 is around 300 °C, and that of oil samples 3–6 is around 350 °C to 450 °C. The peak area of oil samples 5–6 is larger than that of others, which further indicates that the thicker crude oil is, the lower the content of light hydrocarbon components is, and the weight loss is slower in the low-temperature oxidation reaction stage. On the whole, the peak reaction rate shifted to the right with the increase in crude oil viscosity.
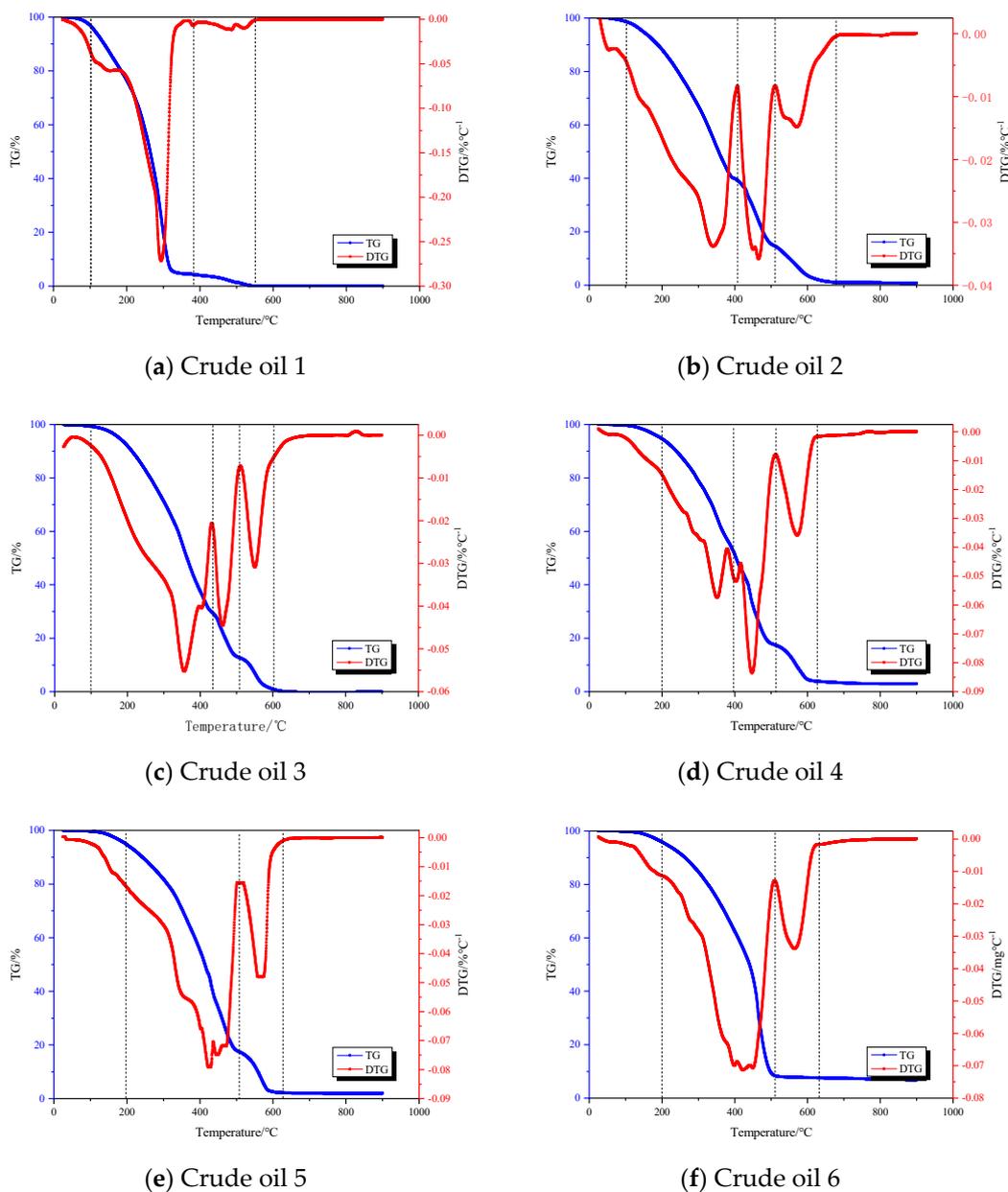
(**a**) Crude oil 1

(**b**) Crude oil 2

(**c**) Crude oil 3

(**d**) Crude oil 4

(**e**) Crude oil 5

(**f**) Crude oil 6

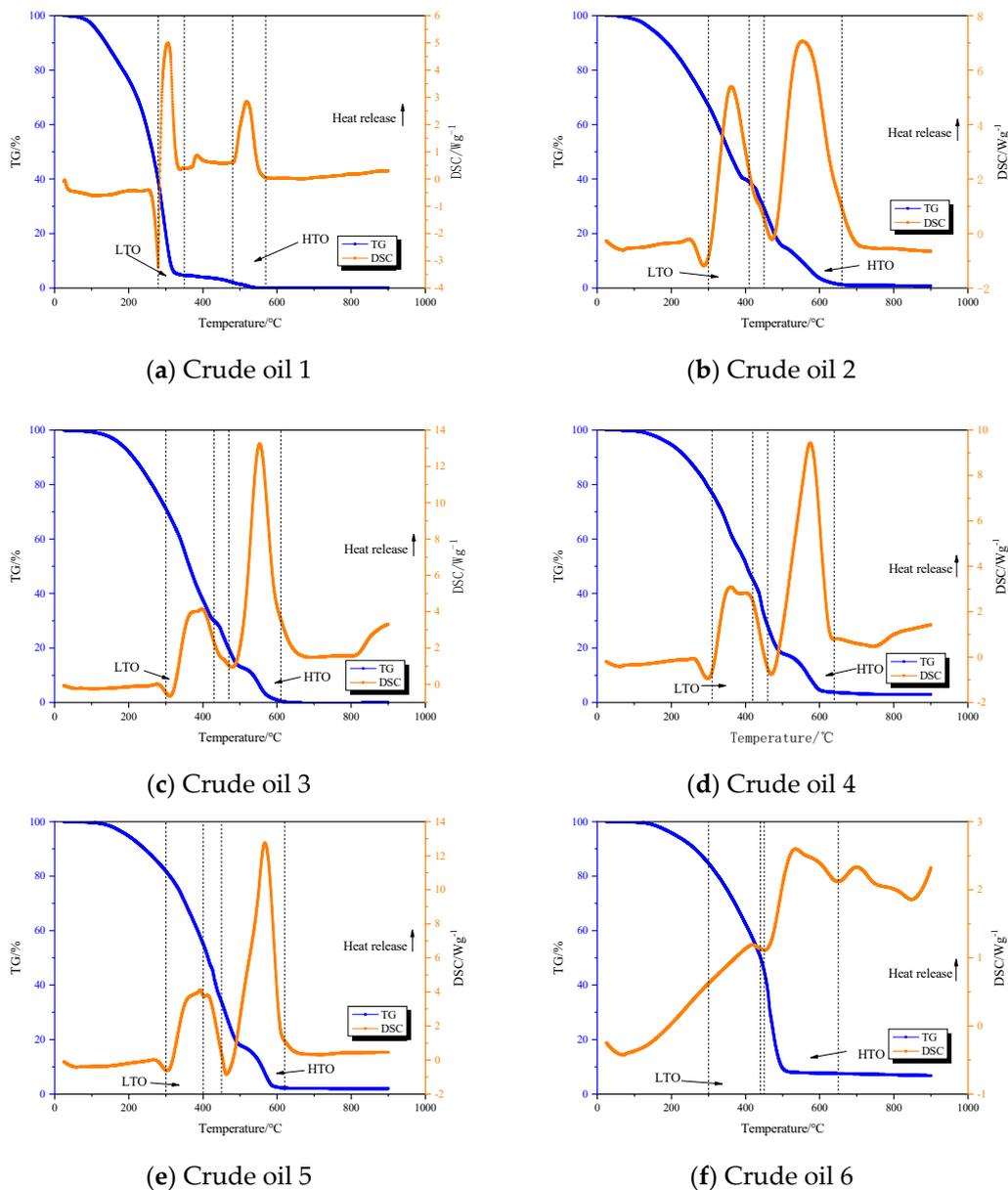**Figure 3.** TG/DTG curves of crude oil samples.

According to the TG experimental results of crude oils with different properties, the mass changes before and after the reaction were analyzed to obtain the mass loss rate. The results are shown in Table 2. The average mass loss rate of oil samples 1–2 was 98.765%, that of oil samples 3–4 was 97.49%, that of oil samples 5–6 was 97.68%. In general, the mass loss rate of ordinary heavy oil was less than that of light oil samples.

Table 2. Changes in the quality of crude oil samples.

Sample Name	Initial Mass/mg	Final Mass/mg	Mass Loss Rate/%
Crude oil 1	26.595	0.378	98.58
Crude oil 2	10.3	0.1085	98.95
Crude oil 3	13.295	0.1604	98.79
Crude oil 4	16.7	0.6361	96.19
Crude oil 5	18.5	0.382	97.94
Crude oil 6	16.1	0.415	97.42

3.2. TG-DSC Analysis

In order to more accurately differentiate each sample of oxidation reaction stage, the quality of crude oil samples was drawn according to the results of the measurement unit of heat release rate curve (DSC curve). As shown in Figure 4, DSC curve trends upward as the exothermic peak and downward for absorption of heat. According to the curve change rule, these regions can be precisely divided into the low-temperature oxidation, fuel deposition, and high-temperature oxidation stages of each crude oil. Each stage has different characteristics of crude oil oxidation reaction.

(**a**) Crude oil 1

(**b**) Crude oil 2

(**c**) Crude oil 3

(**d**) Crude oil 4

(**e**) Crude oil 5

(**f**) Crude oil 6

Figure 4. TG/DSC curves of crude oil samples.

As shown in Figure 4, the low-temperature oxidation reaction began to occur at 280 °C and the high-temperature oxidation reaction occurred at 450 °C.

The lower limit of temperature in the low-temperature oxidation stage is about 280 °C, and the upper limit is about 400 °C. In this stage, oxygenation reaction and further polycondensation reaction of oxidized derivatives form heavy components with large molecular weight. At this stage, oxidative and exothermic phenomena were observed on the DSC

curve, but the thermal effect was weak, and the mass loss rate of crude oil samples was still caused by the volatilization of light hydrocarbon components.

　　　The fuel deposition stage is the excessive stage of low-temperature oxidation reaction to high-temperature oxidation reaction, and the lower limit of temperature is about 400 °C while the upper limit is about 450 °C. The DTG curve shows that the conversion rate of crude oil sample has obvious change, and the DSC curve shows that the heat release rate of crude oil sample per unit mass has obvious change. The reason for weight loss is mainly caused by volatilization of short-chain hydrocarbons produced by alkyl side chains and weak chemical bond fractures of some oxygen-containing derivatives.

　　　The lower limit of temperature at the high-temperature oxidation stage is 450 °C, above which the second conversion rate peak and heat release rate peak of unit mass crude oil sample appear on DTG and DSC curves, and the corresponding reaction is the combustion reaction of solid coke. When the reaction temperature is higher than 450 °C, pyrolytic coke and light hydrocarbon are generated by the pyrolysis reaction of crude oil. Pyrolytic coke mainly comes from colloidal and asphaltene components with large relative molecular weight, high viscosity, and complex aromatic ring structure, and the formation process does not need oxygen action. The non-hydrocarbon gases produced by the reaction are mainly CO_2, CO, and H_2O.

　　　By analyzing different crude oil TG-DSC curves, the sample crude oil oxidation reaction stage was divided according to the DSC peak, as shown in Table 3. With the increase of crude oil viscosity, the crude oil oxidation temperature interval gradually increases; with the increase of crude oil viscosity, the heat release in the high-temperature oxidation stage increases significantly. This is mainly because the combination of low-viscosity crude oil and light hydrocarbon content is high; the low-temperature oxidation stage is accompanied by a large number of light hydrocarbons that undergo volatilization and have heat absorption characteristics, at the same time, the oxygenation and bond break in the low-temperature oxidation stage are also endothermic reactions, so they offset part of the heat released by oxidation, resulting in a low comprehensive heat release of low-viscosity crude oil at this stage.
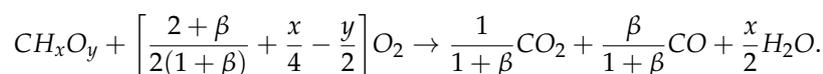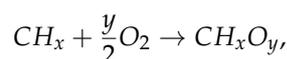
Table 3. Classification of crude oil samples oxidation stages.

Sample Name	LTO/°C	Fuel Deposition Stage/°C	HTO/°C
Crude oil 1	280–350	350–480	480–570
Crude oil 2	300–410	410–450	450–660
Crude oil 3	300–360	360–450	450–610
Crude oil 4	310–420	420–450	450–640
Crude oil 5	300–400	400–450	450–620
Crude oil 6	300–410	410–420	420–650

3.3. Oxidation Reaction Models at Each Stage

3.3.1. Reaction Model for Low-Temperature Oxidation Stage

　　　Crude oil oxidation is a complex series of reactions. In the low-temperature oxidation stage, the two-step reaction scheme proposed by Clara et al. [24] can be utilized:

$$CH_x + \frac{y}{2}O_2 \rightarrow CH_xO_y,$$

$$CH_xO_y + \left[\frac{2+\beta}{2(1+\beta)} + \frac{x}{4} - \frac{y}{2}\right]O_2 \rightarrow \frac{1}{1+\beta}CO_2 + \frac{\beta}{1+\beta}CO + \frac{x}{2}H_2O.$$

CH_x and CH_xO_y are the fuel and polar compounds for the reaction, respectively. Polar compounds include aldehydes, ketones, alcohols, and carboxylic acids. Fuel is the oxidized part of crude oil. In the first oxidation reaction, CH_x is consumed to form polar compounds, but no combustion occurs. The second step is a combustion reaction, where oxygen reacts with polar compounds to generate CO, CO_2, and water.

β is molar CO/CO_2 ratio, and the values of x, y, and β are influenced by oil and temperature.

3.3.2. Reaction Model for Fuel Deposition Stage

There are two simultaneous reactions at this stage:

$$R - CH_xO_y \rightarrow R' - CH_xO_y + H_2 + C_nH_{2n+2},$$

$$R' - CH_xO_y + \cdots R' - CH_xO_y \rightarrow Coke.$$
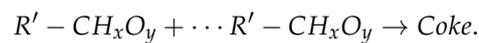
On the one hand, the macromolecular chain and the ring chain break to form small molecule hydrocarbons, and the crude oil is modified; on the other hand, small molecule hydrocarbons are repolymerized to form coke, which is used as fuel for the next stage [25].

3.3.3. Reaction Model for High-Temperature Oxidation Stage

This stage is a combustion reaction, in which the coke formed in the previous stage reacts with oxygen, and the products are carbon oxides and water. Murugan et al. [26] describe coke combustion using the following equation:

$$Coke + O_2 \rightarrow CO_x + H_2O.$$
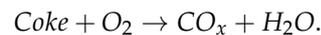
3.4. Kinetics of Oxidation of Crude Oil

3.4.1. Kinetic Mechanism of Oxidation Reaction

Crude oil oxidation, pyrolysis, and combustion reactions are complex and continuous reaction processes, because the crude oil contains a large number of hydrocarbons, there are multiple complex intermediate reactions in oxidation; in order to understand this complex process, it is necessary to study the dynamics of the process.

In the TG experimental reactor, oxygen was in excess and the crude oil content was small. Kok et al. [22] proposed a simple model to calculate kinetic parameters by using Arrhenius kinetic theory. It is assumed that the oxidation rate of the crude oil sample depends only on the reaction rate, the reaction order, and the remaining mass of the sample. Oxidative combustion of crude oil can be approximated as a first-order reaction, expressed by the chemical reaction rate equation:

$$\frac{d\omega}{dt} = k\omega \tag{1}$$

$$\omega = \frac{m_0 - m_2}{m_0 - m_1} \tag{2}$$

$$k = A exp\left(-\frac{E}{RT}\right) \tag{3}$$

Assuming first-order kinetics,

$$\frac{d\omega}{dt} = \omega A exp\left(-\frac{E}{RT}\right) \tag{4}$$

Taking the logarithm of both sides,

$$log\left(\frac{\frac{d\omega}{dt}}{\omega}\right) = log A - \frac{E}{2.303RT} \tag{5}$$

$\frac{d\omega}{dt}$—the rate of mass change, mg/°C

m_0—sample initial mass, mg

m_1—sample finial mass, mg

m_2—sample middle mass, mg
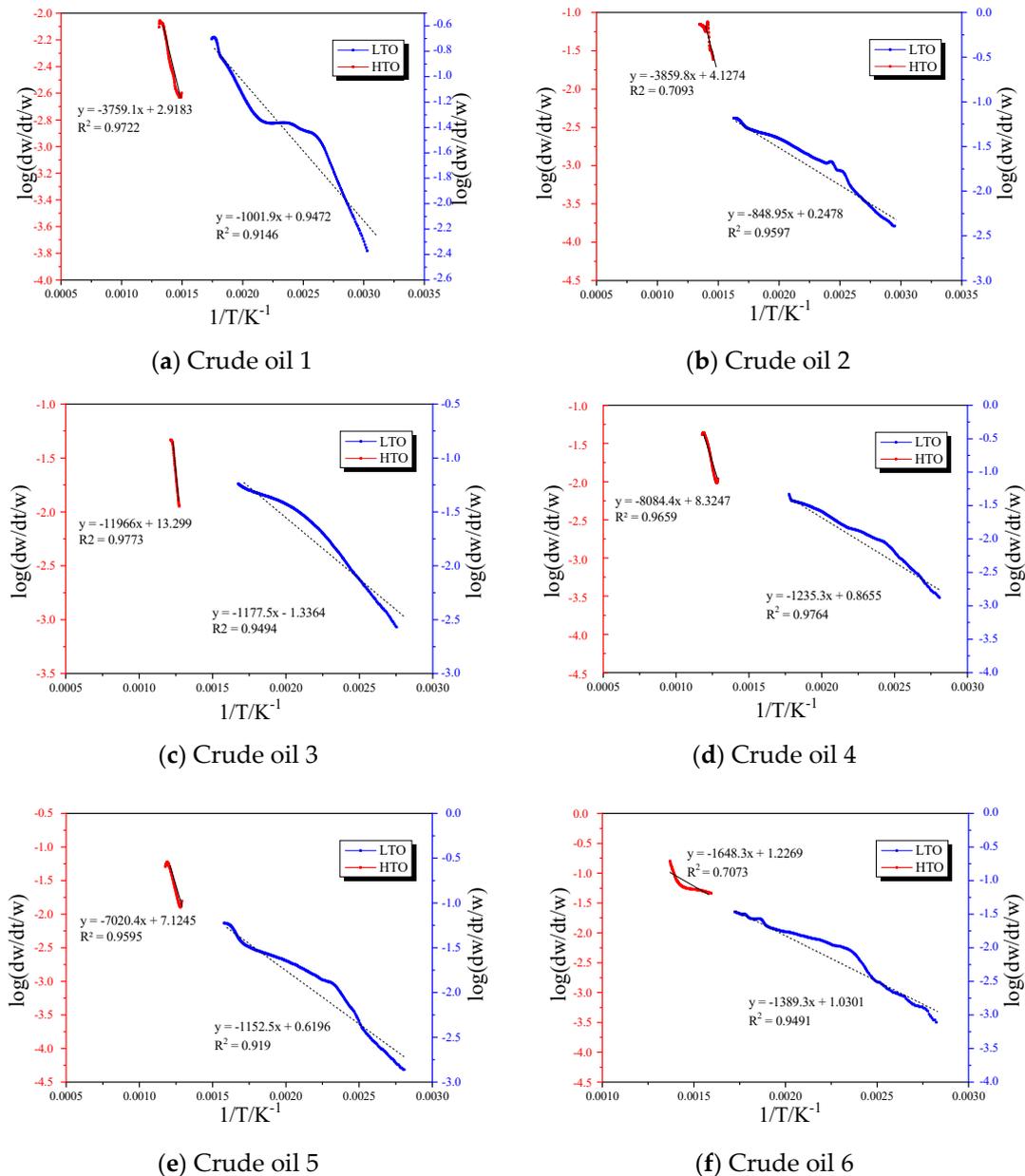
T—temperature, K

E—activation energy, kJ/mol

R—gas constant, 8.314 J/(mol·K)

A—Arrhenius constant, 1/min

When $\lg[(d\omega/dt)1/W]$ is plotted vs. $1/T$, a straight line with a slope of $E/2.303\,R$ is obtained, and from the intercept, the Arrhenius constant can be estimated (Figure 5). The individual activation energies for each reaction region can be notionally attributed to different reaction mechanisms.

(**a**) Crude oil 1   (**b**) Crude oil 2

(**c**) Crude oil 3   (**d**) Crude oil 4

(**e**) Crude oil 5   (**f**) Crude oil 6

Figure 5. Arrhenius method to calculate the activation energy of different oxidation stages.

Due to the complexity of the oxidation and pyrolysis process of crude oil, the dominant reaction and process are different in different temperature ranges. Therefore, the activation

energy obtained by the above calculation method is apparent activation energy, rather than corresponding to a specific reaction.

3.4.2. Calculation of Oxidation Kinetic Parameters

The $\log((d\omega/dt)/\omega) - 1/T$ curve is plotted by Equation (5), as shown in Figure 5. The activation energy and pre-exponential factors of various oil samples were calculated by differential method through the slope and intercept of the fitted relationship curves of six kinds of crude oil, as shown in Table 4. The activation energy of oil samples 1–2 at the low-temperature oxidation stage is smaller, that of oil samples 3–5 at the low-temperature oxidation stage is larger, and that of oil sample 6 at the low-temperature oxidation stage is the largest. The activation energy of oil samples 1–2 at the high-temperature oxidation stage is larger than that of oil samples 3–6 at the high-temperature oxidation stage.

Table 4. Arrhenius Method to calculate the kinetic parameters of sample crude oil oxidation.

Sample Name	E/kJmol^{-1}		A/min^{-1}	
	LTO	HTO	LTO	HTO
Crude oil 1	50.49	264.47	2.5785	18.5098
Crude oil 2	39.73	249.04	1.2812	12.0165
Crude oil 3	62.84	230.05	0.2628	12.4100
Crude oil 4	66.91	185.02	2.3762	4.6598
Crude oil 5	61.08	106.27	1.8582	0.0876
Crude oil 6	77.74	115.97	2.8013	0.2923

The activation energy of the low-temperature oxidation stage is smaller than that of the high-temperature oxidation stage, while the frequency factor of the low-temperature oxidation stage is larger than that of the high-temperature oxidation stage. The activation energy of ordinary heavy oil is higher than that of light oil. With the increase of crude oil viscosity, the activation energy of the low-temperature oxidation phase gradually increases, and that of the high-temperature oxidation reaction phase gradually decreases.

3.5. Effect of Viscosity on Oxidation Kinetics of Crude Oil

With the increase of crude oil viscosity, crude oil of the low-temperature oxidation reaction temperature range is bigger and bigger, and the fuel deposition scope is smaller and smaller. This is mainly because the lower the viscosity, the more light components contained in crude oil, the less heavy components, the higher the reactivity; on the contrary, the higher the viscosity, the more heavy components contained in crude oil, the less light components, the lower the reactivity, so the greater the viscosity of crude oil, the longer the low-temperature oxidation stage.

The Arrhenius method was used to obtain the oxidation kinetic parameters of crude oil with different viscosities, and the fitting comparison was made with the oxidation kinetic parameters of crude oil studied by predecessors. The relationship between viscosity and activation energy at the low-temperature oxidation stage is shown in Figure 6, and the relationship between viscosity and activation energy at the high-temperature oxidation stage is shown in Figure 7; the black dots represent the experimental data in this article, the red dots represent previous literature data, and the curves represent the fitting results of previous data. By comparing with previous literature, the oxidation kinetic parameters of dilute oil obtained in this work are all relatively high, which is because pure oil was selected for the experiment in this work, while oil sand was selected for the ratio experiment in the literature. Previous studies showed that the activation energy of pure oil was higher than that of oil sand [14,17,27–29]. At the same time, the heating rate in this paper is 20 °C/min, and the higher the heating rate, the higher the activation energy of crude oil. The results show that the activation energy of crude oil increases with the increase of crude oil viscosity in the low-temperature oxidation stage, decreases with the increase of crude oil viscosity in the high-temperature oxidation stage, and the range of activation energy reduction in

the high-temperature oxidation stage is larger. This is because the low-temperature stage mainly involves the volatilization of light components and the occurrence of oxidation reactions, forming aldehydes, ketones, carboxylic acids, and peroxides (peroxides further undergo bond cracking reaction). As the presence of oxygen promotes the reaction and the energy required for bond breaking of straight-chain alkanes is low, the activation energy is lower than the high-temperature oxidation stage. As the viscosity increases, the content of light components decreases, and the content of heavy components increases. Therefore, the activation energy of the reaction in the low-temperature oxidation stage increases with the increase of viscosity. In the high-temperature oxidation stage, the activation energy decreases with the increase of viscosity, which is also due to the generation of highly active substances such as hydroxyl radicals and highly active coke during the fuel deposition stage by the colloid. These substances have high activity and low activation energy. Therefore, the higher the colloid content, the higher the viscosity, and the lower the activation energy during the high-temperature oxidation stage [25].
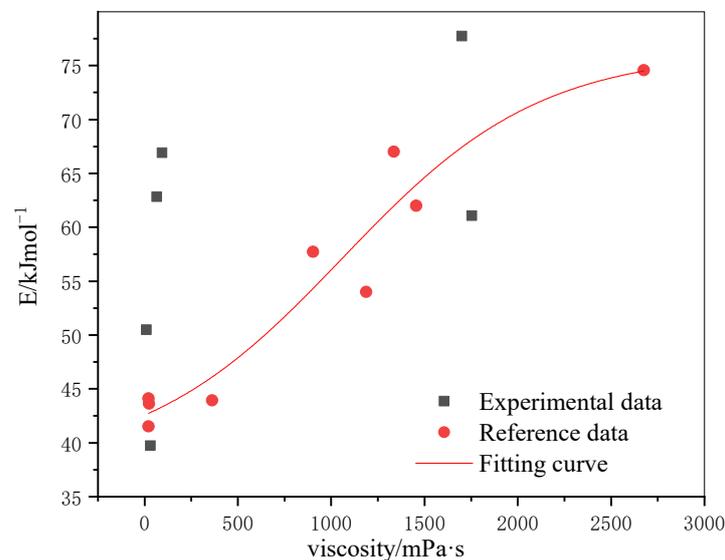

Figure 6. LTO stage viscosity–activation energy relationship diagram.
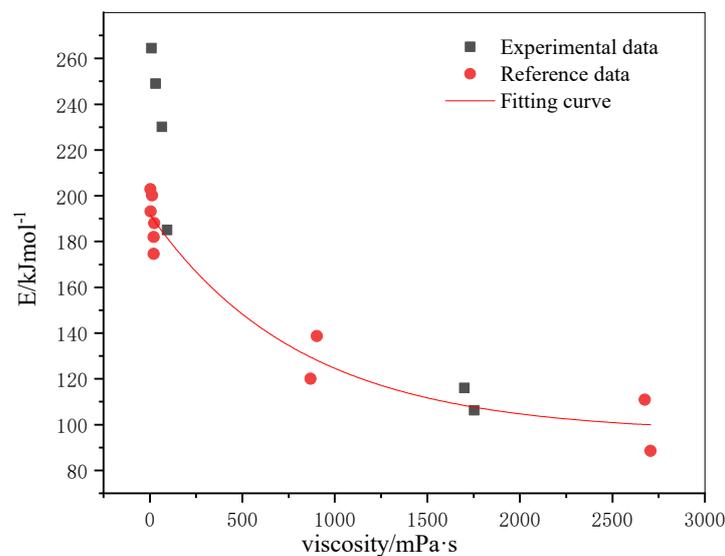

Figure 7. HTO stage viscosity–activation energy relationship diagram.

4. Conclusions

1. Light oil, ordinary heavy oil I, and ordinary heavy oil II can be divided into three reaction stages during the oxidation process: low-temperature oxidation stage, fuel deposition stage, and high-temperature oxidation stage.
2. After the analysis of the TG-DTG-DSC curve, different crude oils show obvious differences. The mass loss rate of light crude oil in the low-temperature oxidation stage is the largest, and the mass loss rate of ordinary heavy crude oil is smaller than that of light crude oil.
3. Arrhenius method calculated that the activation energy of oil samples with different properties was 39.73–77.74 kJ/mol in the low-temperature oxidation stage and 106.27–264.47 kJ/mol in the high-temperature oxidation stage.
4. The activation energy of crude oil increases with the increase of viscosity in the low-temperature oxidation stage and decreases with the increase of viscosity in the high-temperature oxidation stage.

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