Fuel 234 (2018) 604–608

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Reaction schemes and characteristics in crude oil oxidation process using a TGA testing method

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ARTICLE INFO

Keywords:
Crude oil
Oxidation
Thermogravimetric experiment
Reaction stage
Kinetic parameters

ABSTRACT

Stage characteristics of heavy oil oxidation is important for ignition and production control of fire flooding. A thermogravimetric (TG) experiment is carried out to study the oxidation process on a certain heavy oil sample mixing with quartz sand. Firstly, based on multicomponent theory of heavy oil, four stages corresponding to earlier low temperature oxidation (LTO), later LTO, fuel deposition and high temperature oxidation (HTO) are identified. The kinetic parameters of each oil oxidation stage are calculated by the Coats-Redfern integral method. It demonstrates that the orders of reaction have a great influence on the results of calculation. Then logical and reasonable reaction equations are derived out based on the mechanism of staged crude oil oxidation. The result shows that phase boundary reaction (also known as interfacial reaction, which is defined as a chemical reaction that occurs on a two phase contact interface.) is the main reaction at the stage of low temperature oxidation. And three dimensional diffusion reactions are primary at the stage of high temperature oxidation reaction. Finally thermogravimetric analysis of different viscosity crude oil verifies that the kinetic process of oxidation is determined by reaction mechanisms. And different mechanisms appears at different reaction stages.

1. Introduction

In recent years, scholars and experts at home and abroad show greatly interest in air injection technology [1,2]. This technology can be applicable to both in-situ combustion on heavy oil reservoir and air or air foam drive on light oil reservoirs. In a large number of indoor experiments and pilot tests for air flooding, many valuable experiences have been summarized, and at the same time, a certain understanding of the reaction mechanism of air flooding has been obtained [3–7].

The oxidation of crude oil is a complex and mixture system with very complicated reactions of oxidation-combustion process. The oxidation process of crude oil was divided into four stages (Vossoughi, 1983): Crude oil distillation, Low temperature oxidation (LTO), First combustion and Second combustion [8]. Belgrave (1993) and Alipour (2014) improved the division method of Vossoughi when establishing the in-situ combustion model. The oxidation process of crude oil was divided into three stages: LTO, Thermal cracking and High temperature oxidation (HTO) [9,10]. Before combustion or HTO, low temperature oxidation reactions can occur with the heavy oil components that can produce acid, aldehyde, ketone, alcohol and ester like compounds [9]. Ren [11] realized that the thermal cracking of crude oil can be divided into two stages: Splitting decomposition and Coking. Not only the reaction stages can be detailed separated, but also the mechanism of reaction at each stage. Deeply understanding of the oxidation characteristics at each stage can provide parameters for the numerical simulation and a theoretical basis for the follow-up field design of ignition power. It is greatly necessary to explore systematic division method of the oxidation process on the basis of the limitation of the existed division methods.

Most researchers always concentrate on the activation energy of the reaction when using the thermogravimetric to analyze crude oil oxidation kinetics. And they simply take oxidation reaction order n as 0 or 1 [12–14], which will affect the determination of kinetic parameters, and further affect the calculation of the reaction rate and the understanding of the intrinsic mechanism [15]. Based on a series of TGA experiment on heavy oil, the crude oil oxidation process is subdivided by the joint reaction mechanism and thermogravimetric curve. According to the physicochemical process of each oxidation reaction stage, the reaction mechanism function is determined and the kinetic parameters are calculated. Furthermore, the problems that should be paid attention to in the calculation of the intrinsic mechanism and the kinetic parameters of each reaction stage are analyzed in depth.

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https://doi.org/10.1016/j.fuel.2018.06.076
Received 6 February 2018; Received in revised form 29 May 2018; Accepted 19 June 2018
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2. Thermogravimetric experiment of heavy oil

2.1. Experimental design

When using pure oil samples for the thermogravimetric test, the oil samples begin coking which results in blockage of gas passages. The bottom sample can participate in the reaction only after the surface layer coke is consumed. Therefore, pure oil samples are difficult to be in a homogeneous reaction state.

In the thermogravimetric experiment, compared with pure oil samples, the oil sand samples heated by oil sands are uniformly heated and closer to the actual reservoir conditions. Tang Junshi et al. has verified this point in the thermogravimetric experiment [16].

In order to let the oil sample participate in the reaction uniformly, pure quartz sand of particle size for 80–120 mesh is added and then mix them according to the proportion of 1:9, quality of crude oil is 24 mg, quality of quartz sand is 216 mg. It makes samples sufficient adsorption on the surface of the quartz sand. The quartz sand particles can not only provide effective channels for the circulation of oxygen, but also closer to the actual conditions of the reservoirs. Therefore, a specified additional proportion of quartz sand is required.

Oil sample is from Liaohe oilfield. The viscosity of degassed oil on the ground is 1362.5 mPa·s. The density of oil is 0.9464 g/cm^3 (20 °C) and the asphaltene content precipitated by n-pentane is 30%–40% (quality percentage), which belong to a normal heavy oil.

The experiment was carried out under atmospheric pressure. The initial temperature was set at 20 °C and the reaction termination temperature was 650 °C. Three heating rates were set 3 °C/min, 5 °C/min and 7 °C/min respectively.

2.2. Experimental method

A German Netish thermogravimetric analyzer is used in this experiment. First, open the furnace and put the experimental matching sample on the tray and then turn on the gas (reactive gas flow is 120 ml/min). The experimental conditions parameters are set by control software.

Thermogravimetric analysis is carried out at different heating rates of 3 °C/min, 5 °C/min and 7 °C/min. Then the original data is equidistantly thinned. The obtained TGA curve is shown as Fig. 1.

Based on the previous study, the oxidation reaction of the crude oil system can be divided into four successive stages [17]. The four stages mainly include earlier LTO (< 180 °C), later LTO (180 °C–350 °C), fuel deposition (350 °C–440 °C) and HTO (> 440 °C) . The fuel deposition stage is neither dominated by high temperature oxidation reactions nor by low temperature oxidation reactions, so it should be defined as an independent section.

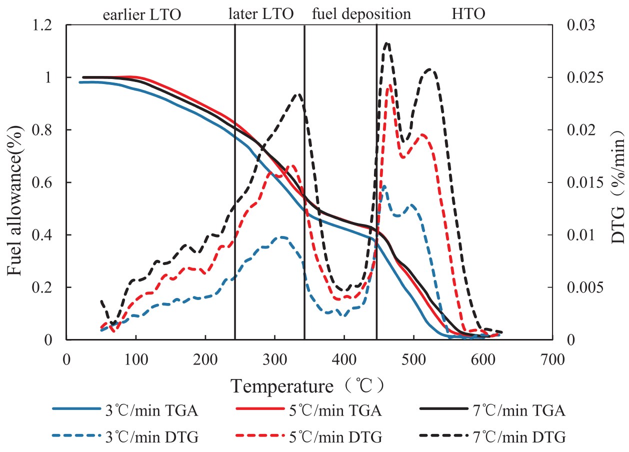

Fig. 1. TGA curve and mass loss rate curve at different heating rate.

70 °C–241 °C, earlier low temperature oxidation (LTO): at this stage, the weight loss is caused by volatilization of water and light hydrocarbon components below the temperature of 100 °C [18–22]. The LTO reaction is dominant above 100 °C.

241 °C–351 °C, the later LTO stage: the weight loss rate increased obviously. There is a severe low-temperature oxidation reaction at this stage. The oil sand weight loss rate is significantly increased and the reaction generated heat increased rapidly.

351 °C–455 °C, the fuel deposition stage: the weight loss rate decent and the reaction is continued. The reaction is analyzed and supposed to be the fuel deposition stage.

455 °C–549 °C, high temperature oxidation stage: the heavy oil starts to burn and the oxidation reaction is intense with large amount of heat, in which heavy oil fully oxidized in oxygen, and the product is CO_2, water and a small amount of nitrogen oxides, so weight loss is rapid at this stage.

From Fig. 1, crude oil oxidation rate presents obvious characteristics of stages, which is basically consistent with the divided stage described before. The curve of the LTO stage presents two-peak shape when the heating rate is 5 °C/min and the second peak is notably higher than the first one when the rate is 7 °C/min, which becomes a strong low temperature oxidation stage. At the thermal cracking stage, due to the production which is oil and solid coke, the weight loss rate is very low. When it comes to high temperature oxidation stage, the weight loss rate once again reaches the peak and the curve even has the same threshold temperature of HTO reaction though the heating rates are variable. As is shown in the dotted line (455 °C), maybe it is caused by that both the coke and insufficient cracked oil conducted HTO reaction [4].

With the increase of heating rate, the oxidation rate of oil sand increases as a whole, and there are two peaks in the weight loss curve of the low temperature oxidation stage and the high temperature oxidation stage. It is well known that the ignition points of different hydrocarbon components are different. The reason for the two peaks is both the coke and insufficient cracked oil conducted HTO reaction. Generally speaking, coke can burn at about 455 °C. So the first peak of the two-peak curve of HTO stage should be caused by the weight loss of the coke and the second peak is caused by the combustion of uncracked crude oil [23].

3. Selection of oxidation kinetics calculation method

At present, the calculation of oxidation kinetic parameters based on TG experiment is mainly composed of an integral method or a differential method. Due to the uncertainty of the experiment itself, the experimental data will fluctuate and the error of the differential method is large. In this paper, Coats-Redfern integral method is used to calculate the oxidation kinetic parameters, and is convenient to smooth out the volatility of the experimental data and improve the reliability of the curve fitting. The main formulas of the Costs-Redfern integral method are shown as Eqs. (1) and (3) [24].

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{1}$$

$$G(\alpha) = \int_0^a \frac{d\alpha}{f(a)} \tag{2}$$

The mechanism function is set to $f(\alpha) = (1-\alpha)^n$, so the commonly used Coats-Redferm functions [24] are can be written as below:

$$\begin{cases} \ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT},\ n \neq 1 \\ \ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}(1-\frac{2RT}{E})\right] - \frac{E}{RT},\ n = 1 \end{cases} \tag{3}$$

In Eq. (3), $\alpha = (w_0 - w_t)/(w_0 - w_f)$,α—The remaining amount of raw materials,%; w_0—initial fuel weight, mg; w_t—The weight of Raw material at a certain moment, mg; w_f—The weight of the remaining solids

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