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A method based on the Harcourt and Esson equation to estimate the catalytic effect of metallic additives on light crude oil

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ABSTRACT

This paper provides the research on four different metallic additives during the combustion process and kinetic behavior of crude oil based on the Harcourt and Esson equation. The oil-only sample and oil-metal additive mixtures were studied by TG/DTG and DSC. The results indicate that Dagang crude oil exhibites three regions low temperature oxidation (LTO), fuel deposition and high temperature oxidation (HTO) during the heating process. The metal additives show obvious catalytic effects on the oil and $ZnSO_4$. The exotherm increment benefits the high pressure air injection (HPAI) process. Based on the Harcourt and Esson equation, the activity energy requirement presents different values and trends in the LTO and HTO processes. Compared with the TG/DSC profile and activity energy, $ZnSO_4$ shows a positive effect on Dagang light crude oil during the HPAI process.

1. Introduction

High pressure air injection (HPAI) is generally considered an efficient method to heat and drive the oil in the reservoir. For the HPAI process, first, the process must reduce the viscosity of the oil. Second, the drive mechanism must be used to move the mobilized oil to a production well. In-situ combustion (ISC) was once believed to be concomitant in the whole process in heavy oil only because of the ignition requirement [1]. However, the ability of spontaneous ignition of the oil makes the application of the HPAI technique in light oil reservoir quite real [2,3]. Between the injection and production periods, three reactions are known which include low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO) being identified [4]. For the light crude oil, distillation and pyrolysis causes a huge mass drop in the LTO process. Thus, the lack of fuel deposition causes insufficient fuel supply for the HTO process [5,6]. It is therefore crucial to accelerate and strengthen the process of fuel deposition. Metallic additives have been proven to possess the ability to catalyze both hydrocarbon oxidation and cracking reactions for most crude oils [7–9]. Thus, most of the research has been focused on the sample mixed with both rock and metal additives or clay. It is also important and necessary to explore the effect of the metallic additives acting on the crude oil separately during the in situ combustion process.

TG/DTG (thermogravimetry/derivative thermogravimetry) and DSC (differential scanning calorimetry) are the effective methods to study the ISC process. In 1959, Tadema used thermal analysis to investigate in situ combustion and he found the LTO and HTO regions from the DTA curves [10]. Vossoughi and Drici [11] applied the DSC and DTA methods to analyze the combustion process in the presence and absence of metal oxides. He observed that in the presence of a large surface area such as with silica, surface reactions are predominant and are unaffected by small amounts of metal oxide present. Mustafa Versan Kök has also used DSC–TG curves to determine the heat value and reaction parameters for crude oils. He also used TG/DSC curves to evaluate the effect of clay and clay-metallic additive mixtures on the combustion process [4,12–17]. In the meantime, different kinetic methods were developed to analyze the kinetic parameters (the activation energy, pre-exponential factor and reaction model) from the data obtained by means of thermal analysis methods such as TG (thermogravimetry), DSC (differential scanning calorimetry) and DTA (differential thermal analysis) [18,19]. Coats and Redfern developed an integral method which can be applied to TG/DTG data, assuming the order of the reaction [13]. Ingraham and Marrier developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics [20]. Kök developed a classic model for the in situ combustion process. This model assumes that the oxidation rate of the total sample is dependent only on the rate constant [4,13]. In all of these models, the temperature dependence of the process rate is typically parameterized through the Arrhenius equation. Based on the TG/DSC data, the mass and heat

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flow changes occur not only as the variation of time but also with the variation in temperature. In 1996, David Dollimore developed a method based on the Harcourt–Esson equation to calculate the reaction rate (k). This method is also based on TG data, however it directly established the relationship between the mass variation and temperature and it also added the rate of heat (β) [21–27]. We used this method to investigate and analyze the catalysis effects of different metallic additives on the light crude oil during the ISC process and calculated the activation energy and pre-exponential factor.

2. Experimental procedure

In this study, the crude oil sample used in the experiment was obtained from the Gangdong zone in the Dagang oilfield (Tian Jin, China). The formation temperature is 67.5 °C and the oil viscosity and density at surface conditions (25 °C, 1 atm) are respectively 14.5 mPa s and 0.85 g/cm^3. The properties of the crude oil are given in Table 1, and the hydrocarbon distribution of the oil sample is given in Fig. 1. At surface conditions, most of the light components (C1–C5) were separated from the samples. From the figure, it can be observed that more than 68% of the oil compounds centralized in the group C5–C15, almost 8% of the group, containing a high hydrogen content. At reservoir condition (67.5 °C, 16.5 MPa), it is believed that the heavier fractions are transformed into a carbonaceous deposit with a low hydrogen content which is able to benefit the fuel deposition process.

The metallic additives chosen to perform this experiment were $ZnSO_4$, $AlCl_3{\cdot}6H_2O$, $CuSO_4$ and $SnCl_4$. Considering the influence of clay and rock, this research chooses to test the mixtures of the oil and metallic salts separately. A NETZSCH STA 409 PC/PG (NETZSCH, Ltd. German) with a TG/DSC model was used for the thermal analysis. In the thermal study, a constant mass flow of air at the rate of 50 (mL min^{-1}) at atmospheric pressure and a temperature range from 25 to 600 °C with a heating rate of 10 °C min^{-1}. Prior to the experiments, the DSC system was calibrated for temperature readings using indium as the reference standard. The TG/DTG system was calibrated with calcium oxalate monohydrate for the temperature readings and silver was used in order to correct for buoyancy effects. All of the samples were prepared according to ASTM standards (D2013-72) and the weights of the oil-only and oil-metallic salt mixtures were around 25 mg. The mass ratio of oil and metallic salts is 9:1. All experiments were performed three times to demonstrate the reproducibility.

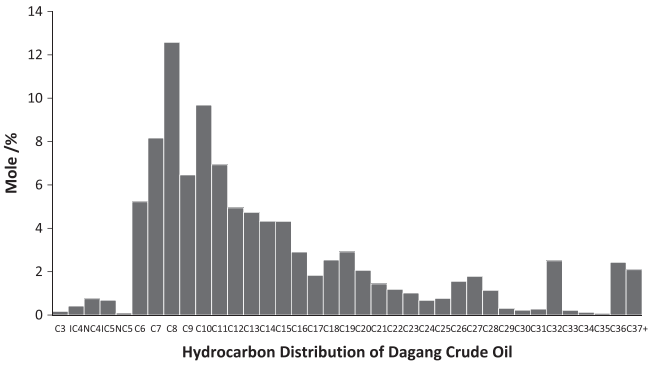

Fig. 1. Hydrocarbon distribution of oil sample.

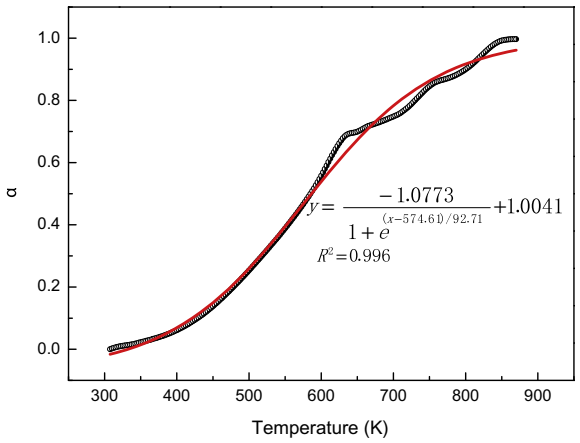

Fig. 2. Characteristic α vs. temperature in kelvin of Dagang crude oil.

3. Kinetic theory

Kinetics deals with the measurement and parameterization of process rates [19]. The rate can be parameterized in terms of three major variables: temperature (T), extent of conversion (α), and pressure (P) as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \tag{3.1}$$

In this equation, k is the reaction rate, $h(P)$ is the pressure function and $f(\alpha)$ is a function of the component fraction α. In most conditions, $h(P)$ is ignored in kinetic computational methods used in the area of the thermal analysis.

Based on the kinetic curve characteristic fitted by the Boltzmann function as given in Fig. 2, the reduced type of Dagang crude oil is sigmoidal (sometimes also called autocatalytic) [19]. This model represents those processes whose initial and final stages demonstrate, respectively, the accelerating and decelerating behavior so that the process rate reaches its maximum at some intermediate values of the extent of conversion. The Avrami–Erofeev models provide a typical example of the sigmoidal kinetic as follows:

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{3.2}$$

In this equation, n is the reaction order. The combustion reactions were assumed to be fist-order. So the function of $f(\alpha)$ is:

$$f(\alpha) = 1 - \alpha \tag{3.3}$$

Instead of the Arrhenius expression, an alternative equation was put forward by Harcourt and Esson, namely:

$$k = CT^m \tag{3.4}$$

where C is constant and m is also a positive constant.

So for the reaction of oil, the specific reaction rate is then defined as:

$$\frac{d\alpha}{dt} = CT^m(1-\alpha) \tag{3.5}$$

In non-isothermal kinetic studies, the usual method of analysis is simply to utilize three relationships. The first is to relate the temperature (T) with the rate of heating (b) as follows:

$$T = T_0 + bt \tag{3.6}$$

where T_0 is the starting temperature. Combining this with the kinetic expression will lead to the following:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \times \frac{dt}{dT} = \frac{kf(\alpha)}{b} \tag{3.7}$$

Table 1
The properties of the Dagang crude oil.

Physical properties			SARA analysis (wt%)			Elemental analysis (wt%)			
Density (g/cm^3)	Viscosity (mPa s)	API	Saturates	Aromatics	Resins + Asphaltenes	C	H	N	S
0.851	14.5	34.8	83.72	14.37	1.12	84.71	14.33	0.02	0.21