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Using DSC/TG/DTA techniques to re-evaluate the effect of clays on crude oil oxidation kinetics

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ABSTRACT

This study was performed to re-evaluate the exothermic behavior of crude oil+clay minerals by differential scanning calorimetry (DSC) technique from the view of thermal analysis. It is observed that KekeYa crude oil shows much greater amount of heat generation at low temperature oxidation (LTO) stage than high temperature oxidation (HTO) stage, which may be due to the high content light components of crude oil. Besides, all clay minerals exhibited a good catalytic effect on oil oxidation, especially in HTO stage. In this paper, it revealed that illite shows the highest catalytic ability for crude oil oxidation which is slightly different from the conclusion of smectite as the best catalyzer in our previous study performed by thermogravimetry/derivative thermogravimetry (TG/DTG) techniques. However, kaolinite was not the best catalytic agent for crude oil oxidation concluded in the two studies. Some new recognition was achieved by comparing the results with previous study. The kinetic computations based on a single heating rate may be not accurate and reliable, which should be responsible for the difference of clay catalytic ability. The calculated kinetics parameters of different models do not show significant variation which can provide important guidance for better understanding the catalytic effect of different clays on crude oil oxidation as well as reservoir simulation studies. Hence, we can unitize this difference for reasonably adjusting oxidation kinetics parameters obtained by different kinetic models to match experimental results.

1. Introduction

Among various enhanced oil recovery technologies, air-injection process characterized by abundant gas source, low cost and wide application range, has been regarded as one of the most promising strategies, which has received considerable attention recently. There are two main forms of air injection: one is high pressure air injection (HPAI) for light oil reservoirs, the other is in-situ combustion (ISC) for heavy oil reservoir. Both two methods involved oxidation behavior of crude oil, which played an important role in improving oil recovery process. Many different thermal analysis (TA) techniques such as thermogravimetry/derivative thermogravimetry (TG/DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), had been widely applied to study the oxidation behavior of crude oil. In order to get a better understanding of oxidation mechanism, much works had been conducted using TA techniques in recent decades.

Vossoughi et al. (1983) applied TG and DSC techniques to study the effect of sand, silica and kaolinite on crude oil combustion. It was observed that addition of kaolinite to the crude oil could reduce the activation energy significantly, which indicated that kaolinite had a catalytic and surface area effect on oil oxidation. Kök et al. (1997a, 2004) used high pressure thermogravimetric analysis (HPTG) to estimate the oxidation behavior of oil – limestone mixtures. The experimental result showed that compared to oil – sand mixture, the oil – limestone mixture had a lower temperature region for LTO reaction but a little higher temperature region for HTO reaction. They explained that it maybe the different porosities of the matrices lead to the difference, which did not take the effect of matrix composition into consideration. Besides, Kök (2011) investigated the Thermal-oxidation behavior of three different oils in limestone matrix using TG/DTA technique. The results indicated that two distinct reaction regions were identified known as LTO and HTO, respectively. In Kök's (2006) another work, the influence of clay on crude oil combustion behavior was investigated through TG/DTA at three different heating rates (10, 15, 20 °C/min). The result revealed that it was the catalytic properties of clay that reduced the activation energies

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of all the reactions. This observation is similar to the results concluded by Ranjbar (1993), indicating that clay minerals enhanced fuel deposition (FD) during the pyrolysis process as well as catalyzed fuel oxidation. Moreover, with the increasing of clay content in the matrix, the amount of fuel increased while the activation energy decreased. Furthermore, Kök and Gundogar (2009) gave more details about the effect of clay concentrations on the thermal behavior and kinetics of heavy crude oil by TG/DTG. It was observed that as the clay content in the porous matrix increased from 5 to 20 wt%, activation energy values were decreased from 12.1 to 8.1 kJ/mol for LTO and 118.2 to 96.2 kJ/mol for HTO respectively. But the clay type was not given. Ni et al. (2014) also pointed that the addition of cutting with clay and metal salts resulted in a shortened FD stage and higher peak temperature in LTO region.

Most study focus on studying the influence of cutting and rock composition on oil oxidation behavior, little attention was paid to quantify the contribution of clay minerals type on crude oil oxidation. In our previous study, the influence of the four kinds of clay minerals including kaolinite, smectite, illite, and chlorite on oil oxidation behavior was respectively investigated by TG/DTG techniques. We found that smectite had the best catalytic ability, then illite was ranked second followed by chlorite and kaolinite (Jia et al., 2012a). However, the kinetics analyses were based on a single heating-rate which may be lack of reliability and should be avoided (Tanaka, 2005; Vyazovkin et al., 2011). Whilst this method was still accepted for many engineering application field due to its simple and convenient to obtain plausible kinetics parameters before conducing expensive experimental and simulation work. Kök (2012) observed that activation energies of heavy crude oil combustion exhibiting the same trend but different value as the clay content increased at different heating rate. Gundogar and Kök (2014) used TG/DTG/DSC to investigate the combustion behavior of Kastel oil at different heating rates. They observed that activation energy was insensitive to the heating rate. So the reliability of the results based on a single heating-rate has always been a controversial issue.

The present study was carried out to re-evaluate the effect of clays on crude oil oxidation kinetics using DSC techniques based on a single heating-rate. In this paper, the influence of individual clay mineral on light crude oil thermal behavior was investigated by DSC technique while the thermal behavior of crude oil in air and nitrogen environment was also respectively analyzed by TG/DTA experiments. Three kinetics models were used to analyze DSC curves to gain kinetic data, which was different from the previous study. In addition, the obtained results were compared to previous kinetic parameters achieved by TG/DTG techniques. The main objective of this study is not only to broaden the recognition of the effect of clays on oil oxidation behavior, but also to provide some suggestions on how to select kinetic analyses method for thermal recovery in petroleum engineering field.

2. Experimental

The crude oil used in this study was light crude oil from KekeYa oilfield of Tarim basin of China. The properties of the oil were shown in Table 1. The clays used were from Zhibo Zhisheng Chemical, Shandong province, China, with an effective content of more than 96.0%. The main minerals contained by each clay and their relative percentage content were summarized in Table 2. All clay samples were crushed into the same size (50–60 mesh), avoiding the influence of surface effect.

The thermal analysis of crude oil was performed by TG/DTG/DTA. Air and nitrogen were injected to flow through the oil sample to obtain the experiment data respectively. The details of the experimental equipment and design were given elsewhere (Jia et al., 2012a). The tests of oil+clay mixtures were conducted using NETZSCH STA 409 PC/PG system with DSC module. Experiments were conducted at a heating rate of 10 °C/min over the temperature range of 30–600 °C at atmospheric pressure with a constant air mass flow rate of 10 ml/min. Sample weight for each test was around 33 mg and the oil saturation in the oil+clay mixture was 50%. The DSC system was calibrated to ensure accuracy of temperature readings before the experiments. Besides, all experiments were performed twice for repeatability.

Table 1
The properties of sample oil (Jia et al., 2012a).

Properties	Oil
API gravity/°	44.3
Viscosity (at 25 °C, 0.1 Mpa)/mPa s	3.7
Density (at 25 °C, 0.1 Mpa)/g cm^{-3}	0.805
Light component (C_{5-16})/%	70.55
Medium component (C_{17-26})/%	29.10
Heavy component (C_{27+})/%	0.35

Table 2
Chemical analysis of clay samples (Jia et al., 2012a).

Clay	Mineral/wt%				
	SiO_2	Al_2O_3	Fe_2O_3	MgO/CaO	Na_2O/K_2O
Kaolinite	45.67	37.20	0.29	0/0.72	0
Smectite	64.32	20.74	3.03	2.30/0	2.61/0
Illite	34.90	35.60	1.00	0	0/9.91
Chlorite	46.80	9.02	1.49	31.60/0	0

3. Kinetic theory

Since crude oil is a complex mixture of hydrocarbons with widely varying chemical and physical properties, the oxidation of crude oil is a complicated phenomenon characterized by numerous reactions proceeding simultaneously. In this research, three methods were used to obtain the kinetic data of oil+clays mixtures oxidation reaction through DSC curves. Because the experiment sample size is very small and the sample is surrounded by excess air flow, the oxidation progress may not be dependent on the oxygen concentration, so it is reasonable to assume that the reaction can be described by first-order kinetics.

3.1. Method 1

It is supposed that non-isothermal reaction can be approximately equal to isothermal reaction in infinitesimal time interval, so the reaction rate can be described by the following form:

$$\frac{d\alpha}{dt}=kf(\alpha),$$

where t is the reaction time, min, α is the fraction of sample reacted already at a certain time t,%, k is the reaction rate constant, min^{-1}, $f(\alpha)$ is the conversion function. The relationship between temperature and the reaction rate constant can be described by Arrhenius equation

$$k=A\exp(-E/RT),$$

where A is the Arrhenius constant, min^{-1},T is the temperature, K, and E is the activation energies, kJ mol^{-1}, R is the gas constant, kJ mol^{-1} K^{-1}. This model assumes that the reaction is first-order kinetics ($n=1$), and the conversion function was of the form