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Low-temperature oxidation of light and heavy oils via thermal analysis: Kinetic analysis and temperature zone division

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ABSTRACT

This research is intended to investigate low-temperature oxidation (LTO) behavior and kinetics of light and heavy oils and to divide their LTO intervals. Ramped thermogravimetry/derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) experiments and isothermal TG experiments with different temperature intervals were used to characterize LTO behavior and to obtain kinetic parameters determined by Ozawa–Flynn–Wall (OFW) and general reaction rate models. The results indicated that there were three (two) distinct variation trends about the conversion rate versus temperature for light (heavy) oil in the LTO region, manifesting the LTO interval of light (heavy) oil should be controlled by multiple-step mechanisms and divided into at least three (two) reaction subintervals. The LTO interval of both light and heavy oils used could be subdivided into three temperature intervals inferred from the variation trend of activation energy over temperature for ramped experiments. Additionally, the LTO region of both light and heavy oils held three subzones in the aspect of isothermal tests. For light oil, the reaction rate augmented from 50 to 250 °C where the activation energy was positive, while it reduced from 250 to 350 °C coupled with negative activation energy. As for heavy oil, the reaction rate presented an increasing trend in the first and third subintervals (50–150 °C and 250–350 °C) with positive activation energy and a declining trend in the second subinterval (150–250 °C) with negative activation energy. It is believed that this research can add new insights to the LTO interval division of crude oil regarding to the isothermal and non-isothermal conditions, which are of significance for understanding LTO reaction pathways and mechanisms.

1. Introduction

A descending oil production from conventional and mature reservoirs is a dominating concern for oil companied and thus, numerous researchers have put appreciable emphasis on how to enhance oil recovery effectively and economically to meet accelerating demand for petroleum (Jia et al., 2012). Up to the date, the high pressure air injection (HPAI) technique has been regarded as a valid EOR method with a series of advantages such as, heat release, low cost and widespread availability, compared to conventional gas injection (nitrogen, carbon dioxide etc.) (Yuan et al., 2015). It has been successfully carried out in the Buffalo Field with substantial incremental oil outputs and satisfactory economic benefits (Kumar et al., 2010).

Currently, quite a few literature covered that the oxidation reaction mode of the crude oils mainly involved the following three regions: LTO, fuel deposition (FD) or middle-temperature oxidation (MTO), and high-temperature oxidation (HTO). Of these reactions, LTO has been demonstrated to be principal and complex (Mahinpey et al., 2010; Murugan et al., 2009, 2010). For light oil reservoirs, oxygen contained in air injected can be consumed through spontaneous LTO at the reservoir temperature to generate flue gas (mainly includes nitrogen, carbon dioxide and light hydrocarbons) to displace oil, coupled with a possible thermal release which produces a significant impact on the oil recovery mechanisms. Especially, whether the oxygen concentration can be reduced to the safe level of 3–5% in practical application largely depends on a sequence of reactions between oil and oxygen during LTO region (Chen et al., 2013; Ren et al., 2002). As for heavy oil reservoirs, the LTO zones are very crucial owing to its products play a vital role with respect to the sustainability of the HTO or in-situ combustion (ISC) process. But if too much LTO products with viscosities greater than that

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of the crude oil are generated, they also potentially worsen the following oxidation reactions and crude oil recovery (Khansari et al., 2014b; Li et al., 2017a,b). Therefore, a comprehensive understanding of LTO reactions of both light and heavy oils is needed urgently to ascertain whether these rections can bring about more beneficial effects on improving oil recovery.

Kok and Gul (2013) studied the thermal characterization and kinetics of six Turkish crude oils (light and medium type) with TG/DTG and DSC methods under atmospheric air. The results revealed that light crude oils were more susceptible to LTO reactions and apparent activation energies determined by the model free and model fitting kinetic approaches in LTO zone were much lower than those in HTO. After the above work, Kok et al. (2017) further investigated the crude oil characterization using TG coupled with Fourier transform infrared (FTIR) and TG coupled with mass spectrophotometry (MS) techniques. In their research, CO, CO_2 and ethane was found in low temperature intervals and light-weight and condensable gases such as toluene (C_7H_8) was also observed with the temperature. After analyzing the experimental results of TG and pressurized differential scanning calorimetry (PDSC) comprehensively, Li et al. (2009) reported the oxidation behavior for light and medium crude oils was significantly different from those of bitumen considering the temperature intervals where oxidation reactions were imperative. Additionally, they also proved that distillation was a key factor for light oil in terms of influencing heat flow and mass loss from liquid phase characteristics. Zhao et al. (2016) investigated the LTO behavior of light crude oil using ramped temperature oxidation (RTO) experiments with varying temperature intervals. The results indicated that oxygen addition reaction of the light oil occurred over the temperature range of 120–200 °C. Besides, the kinetic parameter, apparent activation energy, of the light oil determined by the model-free method (Friedman method) varied from 160 to 350 kJ/mol in the temperature region of 205–230 °C. Khansari et al. (2012) studied the LTO of an Alaska heavy oil through one ramped and six isothermal TG experiments between 100 and 350 °C. In their study, four temperature intervals, ranging from 100 to 150 °C, 150 to 200 °C, 200 to 250 °C and 250 to 350 °C, were divided during the LTO process according to the variation trend of kinetic parameters (reaction order, rate constant, and activation energy) from a first-order, general reaction rate model. More recently, Khansari et al. (2014a) further researched the LTO of Lloydminster heavy oil using TG analysis. The results revealed that there were four subzones in the LTO stage, which was similar to previous findings for an Alaska heavy oil. Besides, they also evaluated the main products within each temperature subzone via elemental analysis method. Murugan et al. (2010) examined the effect of LTO on the pyrolysis and combustion of heavy oil. The results testified that the residue formed during LTO process was more coke-like in nature, and frequency factor and activation energy was augmented for coke combustion with LTO. Li et al. (2017a, 2017b) investigated the LTO characteristic and kinetics of the ordinary heavy and ultra-heavy oils based on the TG/DSC tests, scanning electron microscope (SEM) observations and isothermal oxidation experiments coupled with effluent gas analyses. They pointed out that oxygen addition reaction upgraded the nature of heavy oil and sequent condensation reactions and inter-reactions accelerated the coke deposition with CO_2 generation. After the oxidation, a declining trend was found in the HTO activation energies of both ordinary heavy and ultra-heavy oils, whereas the LTO activation energy of ordinary heavy and ultra-heavy oils were improved by 43.5% and reduced by 28.4%, respectively. Meyers et al. (1990) studied the effect of LTO on viscosity and fractions of different crude oils and reported that the viscosity of a heavy oil sample after LTO increased to 791151 mPa s at 350 °F from 54300 mPa s at 85 °F, while there was no obvious augment in light oil samples. Niu et al. (2011) implemented sets of small-batch reactor (SBR) experiments using pure oil components, such as wax, anthracene, n-hexadecane and typical light and heavy oil samples for studying the LTO reaction process. The measured values of reaction rates of typical light and heavy oil samples evidenced that heavy oils could be more readily oxidized than light oils at low temperatures. Also, they proposed the LTO reaction mechanisms and paths of the hydrocarbon oxidation process. Liu et al. (2017) studied the interaction between saturates, aromatics and resins during pyrolysis and oxidation of heavy oil. It was claimed that as saturates co-oxidized with aromatics or resins, both the onset temperatures of LTO were augmented. Wang et al. (2018) suggested that the LTO mechanisms can be applied for heavy oils to utilize the thermal effect.

The LTO of light and heavy oils has obtained widespread attention as evidenced by above literature review. Although some meaningful information, such as, reaction intervals and mass loss and peak temperatures, kinetic triplets and heat enthalpy have been already used to elucidate the LTO behavior of crude oils, but it is still not fully understood. Also, the temperature interval division within the LTO region for light and heavy oils regarding to ramped and isothermal process has been rarely performed. Hence, in this paper, the LTO behavior of light and heavy oils was further studied through a series of non-isothermal TG/DSC and isothermal TG tests. Moreover, the LTO temperature interval of light and heavy oils were divided according to the variation trend of kinetic parameters obtained from ramped tests with OFW method and isothermal ones with general reaction rate model.

2. Experimental section

2.1. Materials

The light and heavy oils used were respectively taken from Mahu and Fengcheng blocks in Xinjiang oilfiled (Junggar Basin, China). The physical properties and SARA fractions of the crude oils are listed in Table 1. The oil SARA fraction tests were performed according to ASTM D2549.

2.2. Ramped temperature oxidation experiments

The experiments were conducted using NETZSCH STA 449F3 PC/PG (NETZSCH, Ltd., German) with DSC and TG-DTG modules over the temperature range of roughly 25 to 700 °C. Prior to the tests, thermal analysis systems were calibrated as the methods described by Kok (2011). The procedures involved placing oil samples (~20 mg), setting constant heating rates (5, 10 and 15 °C/min) and air flow rate (50 ml/min), then commencing the experiment. All the runs were performed twice to guarantee the accuracy of experimental data and the experiments showed good consistency with standard errors of ± 1 °C.

Table 1
Properties and SARA fractions of crude oils.

Oil type	API (°, 20 °C)	Density (g/cm^3, 20 °C)	Viscosity (mPa·s, 100 °C)	SARA fractions (wt%)				Element analysis (wt%)			
				S	A_1	R	A_2	C	H	O	N
Light oil	42.03	0.8154	1.6	70.96	19.14	8.52	1.27	**79.07**	**16.34**	**2.28**	**0.86**
Heavy oil	17.18	0.9517	412	35.64	20.78	28.30	15.28	**82.3**	**11.9**	**3.47**	**0.41**

Notes: S-saturates, A_1-aromatics, R-resins, A_2-asphaltenes.