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Comprehensive investigations into low temperature oxidation of heavy crude oil

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ABSTRACT

Due to the significance of low temperature oxidation (LTO) process on the subsequent oxidation reactions and oil recovery for in situ combustion (ISC), this work aimed at conducting a series of comprehensive investigations into LTO of heavy crude oil. The LTO behavior of heavy oil was analyzed by static oxidation experiments. Then the alterations in oil characteristics due to LTO were investigated through coke content measurements, flammability tests and scanning electron microscopic (SEM) observations. Additionally, the effect of LTO on thermal behavior and kinetics of heavy oil was researched using thermogravimetry (TG)/differential scanning calorimetry (DSC) technique. The results showed that the temperature played a crucial role in LTO of heavy oil. Almost no coke was deposited at 80 °C. The amount of coke deposition at 160 °C averaged 0.346 g coke/g oil, which was roughly 4.2 times higher than that at 120 °C. The oxidized oil at 160 °C possessed the most superior flammability at ambient temperature and atmospheric pressure in comparison to that at 80 and 120 °C. The surface morphologies of oxidized oil at 160 °C and its formed coke were quite rough, which boosted the subsequent combustion reactions. The results of TG/DSC unravelled that the oxidized oils were subjected to higher mass loss and exothermic effect at the fuel deposition (FD) and high temperature oxidation (HTO) stages as compared to crude oil. After the static LTO, the activation energy in the LTO and FD stages for heavy oil was increased, while that in the HTO stage was reduced. Compared with crude oil and oxidized oils, the coke deposited during the static LTO presented the highest thermal release and reaction activity in the HTO interval. This paper can provide some new insights regarding LTO mechanisms of heavy oil to rich the ISC technology.

1. Introduction

With the sustainable energy demand growth coupled with the depletion of conventional light and medium oilfields, the increasing attention has been put on the heavy oil reservoirs with a huge amount of reserves (Larter et al., 2008). However, it is still a challenge for heavy oil being produced economically and efficiently due to its high viscosity and poor flow property in porous media. Various thermal recovery technologies, including ISC, steam-assisted gravity drainage (SAGD), steam flooding, in situ electrical heaters etc., have been proven to be promising strategies regarding the exploitation of heavy oil reservoirs (Pu et al., 2015a). For ISC, oxygen-enriched gas or air is firstly injected to the target zone with the aim of producing a variety of oxidation reactions between crude oil and air in place, followed by the generation of some oxygenated compounds and coke. A combustion front induced by self-ignition or an external burner will propagate downstream slowly by the sequent air flow. Distinctive thermal effects along with miscible and/or immiscible flue gas flooding boost the production of heavy oils (Kovscek et al., 2013; Zhao et al., 2016).

As reported by most researchers, the ISC process can generally be categorized into three main stages, that is, LTO, FD and HTO (Huang and Sheng, 2017; Kok and Gundogar, 2013; Li et al., 2017b). With regard to heavy oil reservoirs, the LTO reactions are notably vital since the LTO products have significant influences on the sustainability of combustion front. Nevertheless, if an excess of LTO products with viscosities much greater than that of the crude oil are formed, they will

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Table 1
SARA fractions and basic properties of heavy crude oil.

Viscosity at 40 °C (mPa·s)	Density at 40 °C (g/cm^3)	SARA composition (wt%)				Element analysis (wt%)					HHV (J/gr)
		saturates	aromatics	resins	asphaltenes	C	H	O	N	S	
17418	0.9435	28.09	31.45	32.86	7.60	84.75	12.13	1.51	1.15	0.46	−43286.3 ± 37.6

HHV: Higher heating value.

generate an adverse effect on the subsequent oxidation reactions and oil recovery (Khansari et al., 2014b; Li et al., 2017a). Therefore, detailed investigations into LTO behavior and mechanisms of heavy oil are needed urgently with the intent of ensuring the superior performance of ISC method.

In recent years, quite a few efforts have been reported on analyzing the LTO of heavy crude oil. Khansari et al. (2012) divided the LTO interval of an Alaska heavy oil into four subintervals on the basis of six isothermal TG tests. They proved that the first and third temperature intervals, ranging from 50 to 150 °C and from 200 to 250 °C, had overall endothermic reactions; the second and fourth temperature intervals, ranging from 150 to 200 °C and from 250 to 350 °C, had dominant exothermic reactions. After the above work, Khansari et al. (2014a) further investigated the LTO of Lloydminster heavy oil. In their study, in addition to the LTO interval division, the product sequence within each temperature subzone was also estimated. Pu et al. (2015b) characterized the LTO behavior of Tahe heavy oil via thermal analysis. The inflammable coke was formed after heavy crude oil being oxidized for 7 days at 120 °C and 40 MPa, implying that the heavy oil held a spontaneous combustion potential for high pressure air injection (HPAI) without ignition process. Murugan et al. (2010) investigated the effect of LTO on the combustion of heavy oil. It was claimed that the residue formed at the LTO stage was more coke-like in nature and kinetic parameters (activation energy, frequency factor and rate constant) were increased for coke combustion with LTO. Freitag (2010) evidenced that saturates contained a small amount of naturally occurring oxidation inhibitors that affected the LTO reaction rate and kinetics of heavy oil by quickly consuming an essential intermediate in the reaction chain. Cheng et al. (2015) studied the LTO of heavy oil using TG/DSC and pressure differential scanning calorimetry (PDSC) methods. It was found that the total amount of heat release in the LTO zone exhibited a linear relationship with oxygen partial pressure both in atmospheric and reservoir pressures. Kok (2011) analyzed the thermal behavior of medium and heavy crude oils in limestone matrix by TG/DSC technique. It was observed that heavy oil held higher activation energy in the LTO interval relative to medium oil. After that, Kok et al. (2017) characterized the oxidation behavior of crude oil using TG coupled with mass spectrophotometry (MS) technique. Some gases such as CO, CO_2 and C_2H_6 were observed in low temperature intervals. Li et al. (2017b) verified that compared to ordinary heavy oil, the ultra-heavy oil after LTO had more evident coke-like deposition with lower activation energy demand, which made it possible for ISC in the absence of chemical adjuvants. Very recently, Yuan et al. 2018a, 2018b utilized TG coupled with Fourier transform infrared spectroscopy (FTIR) technique to examine the oxidation behavior and kinetics of heavy crude oil. They indicated that the mass loss in the LTO interval was controlled by the evaporation of light components. For the heavy oil, the oxidized compounds formed after LTO were more temperature-stable and less volatile than in the medium and light oils.

Although the LTO of heavy oil has received extensive attention, corresponding investigations including the LTO behavior and precise role of LTO during the ISC process are still needed pressingly. In this paper, the LTO behavior of heavy oil was firstly evaluated. Then the alterations in oil characteristics due to LTO were studied in depth. Finally, the influence of LTO on thermal behavior and kinetics of heavy oil was further investigated. The primary objective of this study is not only to understand the LTO behavior of heavy oil, but also to explore the effect of LTO on the subsequent FD and HTO reactions. It is believed that this work can accelerate to have a deeper understanding regarding the LTO of heavy oil, which should be much significance for field applications of ISC.

2. Experimental section

2.1. Materials

The heavy crude oil was taken from Jiqi block in Xinjiang oil field (Junggar Basin, China). The basic properties and SARA fractions (saturates, aromatics, resins and asphaltenes) of this heavy oil are listed in Table 1. The SARA fractions were measured according to the standard method of NB/SH/T 0509–2010. All the chemicals used in the study, which contained heptane, ethanol, toluene, etc., were obtained by Chengdu Kelong Chemical Co., Ltd. and were used as received.

2.2. Isothermal oxidation experiments

The simplified diagram schematic is illustrated in Fig. 1 and corresponding apparatuses have been described in our previous research (Yuan et al., 2015). The experimental procedures were as follows. (1) The heavy oil sample was pumped into the oxidation reactor at an injection rate of 2 mL/min. The amount of oil sample taken up a quarter of the total volume of the oxidation reactor. (2) The compressed air was injected until the internal pressure of the reactor was increased up to 15 MPa at a constant temperature. (3) The static LTO experiment was terminated after 6 days. Actually, we did a sequence of isothermal oxidation experiments with different times of 2, 4, 6, 8 and 10 days. The results indicated that the oxygen consumption rate of heavy crude oil became very low after the oxidation time was increased up to 6 days. Therefore, we chose 6 days as a reference in this study. (4) The effluent gases compositions were measured using Agilent 7890B series gas chromatography (GC). Three experimental runs were performed under the temperatures of 80, 120 and 160 °C, respectively. The apparent hydrogen/carbon (H/C) ratio was defined as Eq. (1) (Mahinpey et al., 2007; Moore et al., 2002).

$$H/C = 4[\nu_o(\gamma_i/\nu_i) - CO_2 - 0.5CO - \gamma_o]/[CO + CO_2] \quad (1)$$

where y_i and y_o represent the concentration of injected and effluent O_2 (mol/%), respectively, and ν_i and ν_o are the concentration of injected and effluent N_2 (mol/%), respectively.

2.3. Characterizations of oxidized oils

The amount of SARA fractions contained in oxidized oils were measured as the method mentioned in section 2.1. Also, a portion of oxidized oils were washed with a certain amount of toluene to split the formed coke and residue, followed by drying in nitrogen environment at 100 °C. The flammability of oxidized oils at ambient temperature and atmospheric pressure was evaluated. FEI Quanta 450 scanning electron microscopy (SEM) was deployed for directly observing the microstructural characteristics of the oxidized oil at 160 °C, its formed coke and asphaltenes.