Fuel 225 (2018) 336–342

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Low temperature oxidation of crude oil: Reaction progress and catalytic mechanism of metallic salts

Tengfei Wang*, Weipeng Yang, Jiexiang Wang, Shem Kalitaani, Zhiyu Deng

Institute of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, People's Republic of China

ARTICLE INFO

Keywords:
Light oil
Low temperature oxidation (LTO)
Reaction progress
Metallic salts
Catalytic mechanism

ABSTRACT

Low Temperature Oxidation (LTO) reaction between crude oil and oxygen is a main reaction during the air flooding progress. The oxygen consumption rate and the reaction progress are both major factors affecting the air flooding result. Static oxidation experiments and Thermogravimetric-Fourier Transform infrared (TG-FTIR) tests have been conducted to research the LTO reaction progress, the catalytic universality of metallic salts on the oxygen consumption capacity of crude oil, and the catalytic reaction mechanism. The results show that in the progress of the low temperature oxidation of crude oil, oxygen reacts with crude oil to produce H_2O, CO_2 and oxygenated hydrocarbons such as carboxylic acid, alcohol, and phenol. In the early stages, the reaction products were mainly oxygenated hydrocarbons, while CO_2 was a main product in the latter stages of the reaction. In the LTO reaction, the oxygen addition and the bond scission reactions existed simultaneously, but the oxygen addition reaction was dominant at the beginning of the reaction. As the reaction progresses, the bond scission reaction is gradually enhanced. From this research, it has been noted that the metallic catalyst precursor can effectively promote the LTO reaction through both the oxygen addition and bond scission reactions. The chain initiation reaction and chain propagation reaction are the main factors limiting the oxidation of crude oil. The metallic catalyst precursor can increase the formation rate of organic peroxides and promote the oxidation reaction of crude oil. The injection of the metallic catalyst precursor during air flooding can improve the safety and widen the application of air flooding technology. The catalytic effect on the oxidation of crude oils has good universality.

1. Introduction

Air injection Enhanced Oil Recovery (EOR) technology is popular both in heavy and light oil reservoirs for its various advantages, such as low cost and unlimited gas supply. The major application of air injection in heavy oil reservoirs is In-situ Combustion (ISC). During ISC, the injected air can reduce the oil viscosity and drive it to the production wells due to the heat and flue gas generated during the exothermic combustion reactions between the oxygen in air and coke generated by heavy components in the oil [1–3]. Differing from ISC, air flooding in light oil reservoirs can be viewed as an indirect flue gas flooding. The reason for this is that the oxygen in injected air can be consumed gently during the spontaneous LTO with light oil, and plenty of flue gas will be generated at the same time; thus, the gas actually performing the flooding is the generated flue gas [4–6]. For some deep light oil reservoirs with low permeability, the reservoir temperatures and pressures are high enough to sustain a fast LTO reaction rate. In some cases, even a spontaneous ISC can occur when the heat generation rate of LTO is higher than the heat loss rate of the reservoir caprocks; this is the so-called High Pressure Air Injection (HPAI) process [7,8]. However, the coke generated as fuel of combustion reaction is limited, and the combustion front is unstable in the HPAI process due to the lack of heavy components in the light oils. LTO is still the major mechanism of oxygen consumption in the HPAI process. In this study, the main concern is air flooding applied in light oil reservoirs.

Air flooding technology has been applied successfully in several light oil reservoirs such as the MPHU, West Hackberry, Coral Creek, Ekofisk, Buffalo and Horse Creek oilfield in recent years [9–19]. However, the safety issue is still an obstacle for its wide application. The challenge during the air injection process is how to prevent the oxygen in the injected air from reaching the production wells and hence avoid the explosion risk in the wellbore. In addition to increasing the well space between the injection and production wells, accelerating the consumption rate of the oxygen injected using a catalyst is an effective and easily implementable method to improve the air flooding safety. The catalyst injected into the reservoir will have full contact with the oil

---

* Corresponding author.
E-mail address: wangtengfeiforever@126.com (T. Wang).

https://doi.org/10.1016/j.fuel.2018.03.131
Received 30 August 2017; Received in revised form 19 March 2018; Accepted 20 March 2018

and air during the flow process in the reservoirs; thus, it is practical and feasible to use catalysts to enhance the oxygen consumption.

Currently, studies on accelerating the oxidation rate of crude oil are mainly based on metal salts or metal oxides and are mainly aimed at the high temperature oxidation catalysis applied in the ISC process. Bagci [19], Ramirez [20,21], Fassihi [22,23], Drici [24], Shallcross [25], and Castanier [26] investigated the effects of metal elements (such as iron, copper, magnesium, molybdenum, cobalt, nickel, titanium, vanadium, cadmium and tin) on the oxidation of crude oil by combustion tube experiments and Thermogravimetric- Differential Scanning Calorimetry (TG-DSC) experiments. The results show that the metal elements can effectively promote the high temperature oxidation of crude oil, improve the combustion efficiency, increase the propagation speed of the combustion front and increase the crude oil yield.

In our previous research [27], the effect of organometallic salts on the LTO reaction was studied. The results showed that the transition metal complexes had a catalytic effect on the LTO reaction of crude oil: which can significantly improve the LTO reaction rate. The LTO reaction rate when cobalt naphthenate is added was increased 5.09 times compared to that of the pure oil (crude oil without an additive) at 70 °C and 16 MPa. Saturates and aromatics are converted to resins and asphaltenes during LTO, and the addition of metallic salts can enhance the conversion. Organometallic salts can significantly reduce the activation energy of the LTO reaction, and ease the reaction. The reaction progress and catalytic mechanism were not investigated in the previous work [27], and this is the focus of this paper.

Thermogravimetric (TG) analysis is a useful tool to study the oxidation reaction and was used to research the kinetics of the ISC process; for instance, the high temperature oxidation characteristics of crude oil [28,31,35] and the high temperature pyrolysis and combustion reaction of heavy oil [29,32,33]. The influence of metal additives and rock minerals on the ISC was also studied using TG analysis in combination with Differential Scanning Calorimetry (DSC) [24,30,36–38], Fourier Transform Infrared Spectroscopy (FTIR) [39] or pyrolysis/chromatography [34]. In this research, TG analysis combined with the FTIR test is used to investigate the LTO process.

In this study, the catalytic universality of metallic salts was studied based on the previous research [27], the LTO reaction progress and the influence of additives on the progress were also studied by applying TG-FTIR analysis. Then, the catalytic mechanism of the low temperature oxidation was analyzed.

2. Experimental section

2.1. Experimental devices and supplies

The catalytic universality of metallic salts was studied using the static oxidation experiment device (See Fig. 1), which is similar to the one used in the previous study [27]. The TG-FTIR test device consists of an STA6000 thermogravimetric analyzer and a PerkinElmer Fourier Infrared Spectrometer.

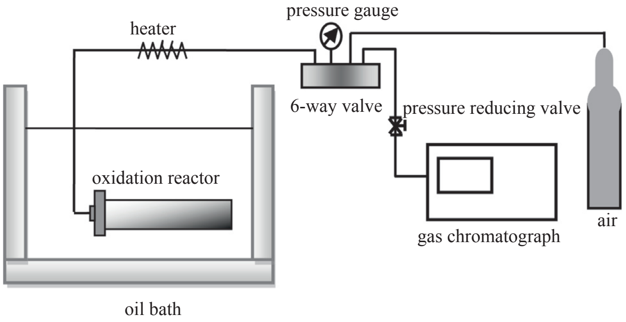

Fig. 1. Schematic of the static oxidation experiment device (oxidation reactor volume is 100 mL).

Table 1
The initial crude oil characterization.

Crude oil type	SARA composition/% (saturate/aromatics/resin/asphaltene)	Density/(g/cm^3)	Viscosity at 70 °C/(mPa·s)
Dong 69–57	70.91/16.07/9.78/3.24	0.850	2.14
An 234–47	66.50/18.16/10.78/4.55	0.876	4.62
SW 10–14	68.18/17.56/10.28/3.99	0.860	3.16

Three crude oils produced from different reservoirs in China are used to conduct the Catalyst-activated LTO (CLTO) experiments: Dong 69–57 and An 234–47 crude oil produced from the Dongzhi and An 83 reservoirs in the Changqing oilfield, and SW 10–14 crude oil produced from the Shiwu reservoir by the Northeast oil and gas company. The initial crude oil characterization is shown in Table 1. The organometallic salts used are copper naphthenate, manganese naphthenate, cobalt naphthenate and iron naphthenate. The composition of air used was 21% oxygen and 79% nitrogen.

2.2. Experimental procedure

2.2.1. Static oxidation experiment

After checking the integrity of the system, the oxidation reactor was filled with crude oil or the additive-added oil; then, the reactor was heated to 70 °C in an oil bath and retained for at least half an hour to reach thermal equilibrium in the reactor. After that, the reactor was filled with high pressure air until the experimental pressure was obtained. The pressure in the reactor was recorded during the experiments, and the changes in gas composition were analyzed at the end of the runs. The volume ratio of air to oil was 7:9 for blank runs and 8:7 for CLTO runs. The catalytic effect of the four additives on the LTO of the three oils was studied.

The additives dispersion procedure: The dehydrated crude oil was heated to 80 °C under a nitrogen atmosphere, and the catalyst precursor was dispersed in crude oil using an ultrasonic disperser, the concentration of metallic precursor in the oil sample used is 0.08 mol/L.

2.2.2. Thermogravimetrc – Fourier transform infrared (TG-FTIR) test

Two tests were conducted to study the oxidation behavior differences of pure crude oil and the oil containing a catalyst. 12 mg samples were used for both tests. The samples were placed in a ceramic crucible in a thermogravimetric analyzer (PerkinElmer, STA6000). Air at a flow rate of 30 mL/min was used to ensure an oxidation atmosphere. The sample was heated from 30 to 180 °C at 50 °C/min, and then kept at 180 °C for the test. Air was also used as a carrier gas during both tests. The evolved gas was carried by the carrier gas to the sample cell of the FTIR spectrometer. The FTIR sample cell temperature was kept at 180 °C, and the resolution was set at 1 cm^{-1}. The scanning range was 500–4000 cm^{-1}, the scanning wavenumber precision was better than 0.008 cm^{-1} and the absorbance precision was better than 0.05%. The spectrum based on the test time was recorded by software. The transfer line between the thermal analyzer and the infrared spectrometer was maintained at 180 °C to avoid condensation of the evolved gases with boiling temperatures less than 180 °C. The LTO reaction progress and the catalytic mechanism of the metallic salt were studied.

3. Results and discussion

3.1. Catalytic universality of the metallic salts

Catalytic universality in this paper refers to the wide range of crude oils in which a particular catalyst can be applied. A total of 15 static oxidation experiments were conducted at 70 °C and 16 MPa using different crude oils to research the catalytic universality of the metallic