Journal of Petroleum Science and Engineering 169 (2018) 673–682

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

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

EPR as a complementary tool for the analysis of low-temperature oxidation reactions of crude oils

Seyed Saeed Mehrabi-Kalajahi[a,b], Mikhail A. Varfolomeev[a,*], Chengdong Yuan[a], Dmitrii A. Emelianov[a], Khasan R. Khayarov[a], Alexander I. Klimovitskii[a], Alexander A. Rodionov[c], Sergei B. Orlinskii[c], Marat R. Gafurov[c], Igor S. Afanasiev[d], Gennadii D. Fedorchenko[d], Elena V. Lubnina[d]

[a] *Butlerov Institute of Chemistry, Kazan Federal University Russia, Kremlevskaya str. 18, 420008, Kazan, Russia*
[b] *Research Center for Oil and Gas Exploration, Shahid Beheshti University, Tehran, Iran*
[c] *Institute of Physics, Kazan Federal University, Kremlevskaya str. 18, 420008, Kazan, Russia*
[d] *JSC Zarubezhneft, Moscow, 101990, Russia*

ARTICLE INFO

Keywords:
Crude oil
In-situ combustion
Air injection
Oxidation
EPR
Free radical concentration

ABSTRACT

Air injection is a promising method for enhanced oil recovery (EOR) in both conventional and unconventional oil sources. It is widely accepted that oxidation reactions between oil and injected air determine the success of an air injection process. In this study, electron paramagnetic resonance (EPR) was introduced as a new route to investigate the occurrence of low-temperature oxidation (LTO) and its behavior by monitoring the signals of free radicals. The EPR experiments were conducted for the different crude oil samples (light, medium and heavy) heated in both static air and flow air (air-bubbling) conditions under different temperatures from 25 °C to 180 °C. The results showed that the free-radical concentrations exhibited a good correspondence on the heating temperature. Furthermore, nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) experiments were carried out to help to analyze the oxidation process and verify the EPR results. It turned out that the EPR results can be well supported by NMR, FTIR and DSC data, which indicates that proposed EPR monitoring method can be applied as a fast and low-cost technique to investigate LTO under mild reaction conditions. Simultaneously, the combination of EPR, NMR, FTIR and DSC can help to better understand the LTO mechanism and to monitor the application of in-situ combustion technique in the field.

1. Introduction

In recent decades, air injection techniques (including high-pressure air injection and in-situ combustion) have attracted great attention for enhanced oil recovery (EOR) in both the conventional and unconventional oil resources (heavy oil, bitumen, and shale oil, etc.) (Yuan et al., 2018a,b; Hascakir et al., 2013). In an air injection process, when air is injected into reservoirs, it will lead to a series of oxidation reactions (Zhao et al., 2016) which are the decisive factor that determines if the air injection process is successful or not (Sakthikumar et al., 1995; Chen et al., 2012; Gargar et al., 2015; Deniz-Paker and Cinar, 2017).

A lot of studies have been focused on investigating the oxidation process. The dominant view indicates that the entire oxidation process of crude oils can be divided into three distinct reaction stages (Tadema, 1959; Kok and Gul, 2013; Gargar et al., 2014) that are known as low-temperature oxidation (LTO), fuel deposition (FD) and high-temperature oxidation (HTO) (Dong et al., 2013; Pu et al., 2015; Yuan et al., 2015). The LTO, which usually occurs below 350 °C (Tadema and Wiejdema, 1970; Moore, 1993; Li et al., 2009), is the earliest but considered as the most complicated stage of oxidation process. The extent of the LTO directly reflects whether the air injection process will be in an expected mode in reservoir (Varfolomeev et al., 2016; Kok et al., 2017). LTO process is still less well-understood due to the complex reaction mechanism (Freitag and Verkoczy, 2005; Burger and Sahuquet, 1972). In a real air injection process, when the air is injected into the reservoir, LTO reaction occurs at the reservoir temperature in a slow manner, and free-radicals chain branching reaction where free radicals are produced through C-C, C-H and C-heteroatom bond breakings (Al-Marshed et al., 2015; Freitag, 2016) is believed to be the main reaction route (Wilk et al., 1986; Fofana et al., 2015).

* Corresponding author.
E-mail addresses: vma.ksu@gmail.com, mikhail.varfolomeev@kpfu.ru (M.A. Varfolomeev).

https://doi.org/10.1016/j.petrol.2018.05.049
Received 22 January 2018; Received in revised form 5 May 2018; Accepted 17 May 2018
Available online 19 May 2018