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An experimental investigation of the in-situ combustion behavior of Karamay crude oil

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ABSTRACT

The Karamay Field (Xinjiang, China) has crude oil that is 11.8° API and is a potential candidate for in-situ combustion (ISC). During ISC, air is injected into a reservoir to oxidize a small portion of the hydrocarbons present thereby generating heat and pressure that enhance recovery. We have conducted a screening study to evaluate the likelihood of the success of ISC in Karamay. Questions of interest for Karamay include the fraction of the crude oil that is converted to fuel, the quantity of particular crude-oil components that become fuel for ISC, and the ability to propagate a combustion front through porous media. To investigate ISC properties of the oil, true boiling point fractions were collected from Karamay crude oil and the kinetics of oxidation of each fraction in porous media were measured using ramped temperature oxidation (RTO) and compared to the whole crude oil. The isoconversional approach is used to interpret the RTO results of each boiling point fraction to obtain the activation energy characteristics of each boiling point fraction.

With increasing boiling point and, consequently, molecular weight, the ignition temperature as well as the temperature for the onset of oxidation increases. Fuel availability increased with pseudocomponent density. The 500+°C boiling point fraction presents reaction kinetics most similar to the whole crude oil indicating that the crude-oil components in this fraction contribute the most to fuel production. Reaction kinetics of the whole oil appeared to be favorable for successful propagation of a combustion front. Importantly, this prediction was validated using displacement tests in a 1 m long combustion tube filled with reservoir sands. The Karamay crude oil demonstrated significant in-situ upgrading as a result of ISC. The gravity of the produced oil was 19.3° API. Our results add to the knowledge base of conditions for successful ISC as well as significant upgrading.

1. Introduction

Heavy oil is found within the shallow formations of the Karamay oil field (Xinjiang Province, China). There are 5 heavy oil deposits and the oil grades from heavy to extra heavy to super heavy. Initial oil saturations are in excess of 70% in some zones. The various reservoirs are described as cemented, permeable sands (300–5000 mD) with significant heterogeneities including frequent mud stringers. Despite the sands being designated as cemented, sand production is noted in many wells during thermal recovery (Wang et al., 2010). Reservoirs are generally delineated by various faults. The lithology is typically medium fine-grained sandstone with good sorting, and consolidated with cement-based materials that provide a medium strength formation. Cementation types are mainly controlled by contact manner, and occur with intergranular pores. Reservoir porosity varies from 28.5% to 30.7% with an average of 29.3%. The range of permeability is from 599 mD to 1584 mD with an average of 900 mD. Oil saturation ranges from 59.8% to 68.6% with the average of 64.0%.

No clear development scenario has emerged at Karamay. Thermal recovery techniques used within Karamay include cyclic steam stimulation, steam-assisted gravity drainage (SAGD), steamflood, and in-situ combustion (ISC). Hybrid techniques are under consideration such as SAGD followed by ISC. Hence, ISC potential needs to be evaluated.

ISC is accepted as an enhanced oil recovery (EOR) method applicable to a wide range of reservoir and crude-oil types and, importantly, ISC is thermally efficient. Although the effectiveness of ISC has been proven by lab experiments, pilots, and field tests, challenges remain regarding field application. To evaluate field applicability, an evaluation incorporating a series of lab experiments and numerical

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Nomenclature

α	conversion
T	temperature
C	oxygen consumption
$C^0_{O_2}$	initial concentration of oxygen
C_{O_2}	oxygen concentration at time t
A	pre-exponential or frequency factor
E	activation energy
n	hydrogen/carbon atomic ratio of fuel
m	CO_2/CO concentration ratio produced
t	time
FA	fuel availability

simulation is typically completed as described, for example, by Cinar et al. (2009), Hasçakır et al., 2011, Lapene et al. (2011), Gutierrez et al. (2012), Kovscek et al. (2013). During the evaluation process, the measurement of parameters such as effective activation energy, reaction frequency factor, fuel availability, and the ability to propagate a combustion front in the laboratory are believed to be crucial steps. The burning quality of the crude oil is determined through such experiments.

In this study, experiments were conducted to investigate the fuel availability of various pseudocomponents and whole crude oil. Pseudocomponents were obtained by true boiling point distillation (TBP). Activation energy of TBP pseudocomponents and whole crude oil were interpreted using RTO experiments with the isoconversional method. Combustion tube experiments were integral to this study to establish (i) predictability of the kinetic cell result and (ii) that a fire front should propagate in this system. Upgrading affects calculated by oil gravity and viscosity variation of produced oil from combustion tube experiments were also measured. The remainder of this introduction discusses methods to measure and interpret the kinetics of crude-oil oxidation as well as a selection of results from the literature.

For determination of activation energy, data processing using the isoconversional method is widely employed in the thermal kinetics area (e.g., Ozawa, 1965), but not necessarily ISC screening (Freitag and Exelby, 2006; McCall et al., 1984; McGhie, 1983; Vossoughi et al., 1982). Experimental methods for measuring crude-oil kinetic parameters fall into two categories: isothermal and non-isothermal methods. The isothermal method refers to experiments conducted at a series of constant temperatures, while non-isothermal methods are carried out with prescribed heating rates leading to a temperature history. Using the isothermal method, Bousaid and Ramey (1968) calculated the activation energy of reaction between the crude oil and oxygen at constant temperature. In later work examining multiple phase reactions of crude oil and air, Kök et al. (1997) found that kinetic parameters are varied and influenced by temperature, reaction procedure, pressure, and so on. Hence, when calculating the activation energy (E_a) and frequency factor (A) at different constant temperatures, many experiments are typically required. Ramped temperature oxidation (RTO) uses a linear increase of temperature and thereby provides an alternative to isothermal analysis. Results contain substantial information for each experiment conducted under a prescribed heating rate. The intermediate reaction process is detected by running the same experiments with different heating rates and analyzing results using the isoconversional principle. Cinar et al. (2009) provide, apparently, the first example of the isoconversional technique applied to crude-oil RTO experiments. Isoconversional analysis is more convenient than conventional methods of data interpretation (e.g., Li and Hwang, 1992; Farrauto et al., 1995).

For heavy oil that commonly has complex organic compounds with a wide carbon number distribution and variety of molecular structures as well as functional groups, chemical reactions between the heavy oil and O_2 are complicated and varied (e.g., Lapene et al., 2009). Series and parallel reactions occur via multiple steps. It is exceptionally difficult to determine exactly the elementary reactions and reaction intermediates even when using model oils in combination with the most advanced thermal kinetic apparatus and interpretation. For example, it is established that combusting diethyl ether with air produces twenty-seven intermediate and several final products (Agnew and Agnew, 1965).

Previous investigations of in situ combustion oxidation kinetics show the existence of at least two temperature regions over which oxygen consumption rates are significant (Burger and Sahuquet, 1972; Moore et al., 1999). Many researchers indicate that there are three different classes of chemical reactions occurring at different temperatures as combustion progresses. First, low temperature oxidation (LTO) happens in the “low” temperature regime ($T \leq 160$ °C) and mainly yields water and oxygen addition products including carboxylic acids, ketones, alcohols, and hydroperoxides (Burger and Sahuquet, 1972; Dabbous and Fulton, 1974; Moore et al., 1992). Second, the middle temperature reaction (MTR) region typically occurs from 250 to 400 °C. Fuel deposition or fuel formation reactions are completed as temperature increases (Benson, 1981). Finally, the high temperature oxidation (HTO) region appears above 450–500 °C. Bond scission reactions result mainly in production of carbon oxides. Even though these three temperature regimes are commonly quite distinct, it is difficult to establish sharp boundaries between them (Kök and Karacan, 1998).

A key factor in successful ISC is the formation of fuel from the crude oil. Various authors have considered the fuel-forming and oxidation properties of crude oils including, for example, Kök (1993), Cinar et al. (2011a), and Ambalae et al. (2006). They have differing interpretations. When considering the influence of components on combustion behavior, a general rule proposed is that the reaction rate constant for normal paraffins increases with increasing carbon number, while the activation energy decreases with increasing carbon number (Fabuss et al., 1964). Light volatile components are potentially combusted when temperature is elevated, concentration of fuel, and air flux are high enough (Barzin et al., 2010, 2013). Despite all of this prior research, no general correlation is established between viscosity, composition or density of the crude, and the thermo-oxidative characteristics of the oil (Kök et al., 2004).

2. Experimental

The apparatus are varied. True boiling point distillation (Petroleum Analytical Instrument Company, Dalian China) is used to prepare pseudocomponents (Fig. 1) following standard procedures (ASTM Standard D5236, 2013). Soxhlet Extraction Instrument (Petroleum Analytical Instrument Company, Dalian China) is used for water content measurement. Electric Dehydration Instrument (Petroleum Analytical Instrument Company, Dalian China) and electronic balances complete the apparatus for sample preparation. The kinetics cell is a plug flow type reactor whereas the combustion tube is 1.04 m in length and 0.075 m in diameter. Detailed information about the kinetic cell and combustion tube experimental apparatus and their operation are presented by Cinar