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Water and aromatics fraction interaction at elevated temperature and their impact on reaction kinetics of in-situ combustion

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ABSTRACT

Performance predictions of the In-Situ Combustion (ISC) process is a challenge as it involves complicated chemical reactions, fluids movement, phase changes, and heat and mass transfer. This study investigates how oil type and water presence can affect the ISC performance, based on using a combination of combustion tube and Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) experiments.

Combustion tube experiments were conducted with two different crude oil without water ($S_{wi} = 0\%$) and with the presence of water ($S_{wi} = 34\%$). Experimental conditions were kept constant (3 L/min air injection rate and 100 psig pack pressure) for all four experiments conducted with two different oil samples.

To determine the chemical reactions that occurred during combustion tube experiments, the initial crude oil samples and their Saturates, Aromatics, Resins, and Asphaltenes (SARA) fractions were subjected to TGA/DSC experiments under air injection at two constant heating rates with and without water addition. Because two heating rates were observed during combustion tube experiments, 5 °C/min was used to represent the slow heating region (Steam Plateau, Evaporation and Visbreaking) and 20 °C/min was used to mimic the rapid heating region (Cracking Region and Combustion Zone).

To better understand the complicated mutual interactions of functional groups in crude oil, TGA/DSC experiments were repeated on normal-decane (an alkane), decanal (an aldehyde), decanone (a ketone), and decanol (an alcohol) which represent the low temperature oxidation (LTO) products. Note that these chemicals have a constant carbon number (C10).

The combustion tube experiments showed that Oil 1 was able to burn for both conditions (with and without water), while Oil 2 could only sustain combustion with water. To determine the reason for this difference, the burning behavior of the crude oils and their individual SARA fractions with and without water additions was studied through TGA/DSC experiments. At the high heating rate (20 °C/min), heat generation does not vary for both crude oil samples. However, at the low heating rate (5 °C/min), Oil 1 generates a higher amount of energy at high temperature oxidation (HTO) zone. We observed similarities between the decanone (a ketone) burning behaviors with aromatics fractions for Oil 1 which indicates that the aromatics fraction may contain ketone functional groups as LTO products. Upon burning, ketones generate higher energy than any LTO products. Therefore, Oil 1 may have functional groups in its structure more like ketones which promotes its combustion more than Oil 2. While presence of water does not change the burning behavior of Oil 1, we observed that the aromatics fraction of Oil 2 in the presence of water generates components similar to decanol (an alcohol) burning behavior. Note that alcohols generate more heat than aldehydes upon burning which explains the enhancement of Oil 2 burning behavior in the presence of water. However, aldehydes produced less energy than ketones. As a result, the combustion performance of Oil 2 was poorer than Oil 1. These results suggest that the chemical structure of the aromatics fraction is critical for the success of ISC. Water and aromatics fraction interaction at elevated temperature favors ISC reactions.

1. Introduction

In-situ combustion (ISC) is a thermal enhanced oil recovery (EOR) method in which air is injected into an oil reservoir and a combustion front sweeps the reservoir in the direction of the gas flow toward the production well (Ramey, 1971). ISC is promising not only because it

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Table 1
Characterization of Crude Oil Samples with density, viscosity, and the weight percent of SARA fractions (Prakoso et al., 2015).

Sample	Gravity, °API	Viscosity, cP	SARA fractions, wt%			
			Saturates	Aromatics	Resins	Asphaltenes
Oil 1	7.97	251,000	12.70	42.11	22.93	22.26
Oil 2	8.19	53,200	23.60	20.00	21.90	34.30

results in a greater oil displacement efficiency, but also it increases the produced oil quality by significantly lowering its viscosity (Martin et al., 1958; Sarathi, 1998). However, besides the main concerns on technical, environmental, and economic feasibility, the complex chemical reactions make ISC performance prediction difficult, resulting in limited field application (Yang and Pope, 1998; Abuhesa and Hughes, 2008) which is the focus of our paper. The heterogeneous nature of the reservoirs makes the chemical reactions more complicated to estimate (Hascakir and Kovscek, 2014; Aleksandrov and Hascakir, 2015; Ismail et al., 2016). For performance prediction of ISC, some simplified reaction models are implemented which use several different crude oil fractionations (Moore et al., 1992; Kok, 1993; Bagci, 1998; Ambalae et al., 2006; Murugan et al., 2009; Klock and Hascakir, 2015; Ismail et al., 2016; Ismail and Hascakir, 2017). Saturates, Aromatic, Resins, and Asphaltenes (SARA) fractionation is one of the most widely used methods to determine the reaction kinetics (Kok, 1993; Bagci, 1998; Speight, 1999; Klock and Hascakir, 2015). Accordingly, while in in-situ combustion, the role of aromatics and resins fractions is still not very clear; saturates are well-known as the "ignitor" for combustion (Verkoczy and Freitag, 1997; Sarathi, 1998) and asphaltenes are the fuel source (coke) of combustion (McCain, 1990; Mullins et al., 2012). The coke formation and burning reactions are the key reactions determining the success of ISC (Coats and Redfern, 1964; Hascakir and Kovscek, 2014).

There are two dominant reaction types observed during in-situ combustion which aid fuel (coke) formation: low temperature oxidation (LTO) and high temperature oxidation (HTO). LTO reactions take place below 300 °C. The products of these reactions are oxygenated hydrocarbons such as aldehydes, ketones, and alcohols (Burger and Sahuquet, 1972; Sarathi, 1998). These LTO products are further oxidized through HTO reactions which take place above 300 °C. The main product of HTO reaction is coke (carbon-rich residue) and combustion is primarily burning of coke (Sarathi, 1998). In combustion reaction, formed fuel (coke) is consumed with oxygen. Carbon dioxide, water, and carbon monoxide are produced with high amount of energy release. Combustion sustainability strongly depends on the energy generation through consumption of coke. The coke formation reactions are controlled by the LTO and HTO reactions.

Reservoir rock also contributes to the combustion reactions (Burger and Sahuquet, 1972; Burger et al., 1985; Cinar et al., 2011a,b; Kozlowski et al., 2015; Ismail et al., 2016; Aleksandrov et al., 2017; Ismail and Hascakir, 2017). The reservoir clays act as catalysts and reduce the activation energy barrier to initiate oxidation and combustion reactions (Kozlowski et al., 2015). Carbonates decompose more effectively when the reservoir pressure is low and the temperatures of in-situ combustion are high (Bogdanov et al., 1990) as carbonates start to decompose around 500 °C (Burger et al., 1985). The thermal energy ratio between the energy used to decompose carbonate (dolomites) and the energy used to burn crude oil is reported to be 0.20 (Ismail et al., 2016), indicating that endothermic energy from carbonate decomposition is relatively low compared to exothermic energy from crude oil burning. However, the thermal energy ratio between the crude oil burning in carbonates (dolomites) and crude oil burning alone is 1.75 (Ismail et al., 2016). Carbonates react with crude oil to produce higher exothermic energy and do not exhibit decomposition at combustion temperatures (Cinar et al., 2011a,b; Ismail et al., 2016) which appears to be promising for combustion.

Although previous studies investigate the combustion behavior of heavy oils (Verkoczy and Jha, 1986; Ambalae et al., 2006; Hascakir et al., 2013; Hascakir and Kovscek, 2014), the effect of water on in-situ combustion has not been well documented. However, the presence or the absence of formation water might significantly affect the in-situ combustion performance (Hascakir et al., 2011; Kudryavtsev and Hascakir, 2014). The interaction of bitumen with formation water during in-situ combustion is known as aquathermolysis or hydrous pyrolysis (Belgrave et al. 1994, 1997). Aquathermolysis results in the decomposition of asphaltic components, thus decreasing the concentration of the least-desired fractions and increasing oil mobility (Johnson and Romanowski, 1987; Brons and Siskin, 1994).

Hence, this paper discusses the ISC performance of two crude oil samples with two distinct properties. It investigates the impact of formation water on crude oil decomposition reactions through SARA (Saturates, Aromatics, Resins, and Asphaltenes) fractionation during in-situ combustion. Moreover, the reaction pathways were explained by interpreting the results of the control experiments on an alkane, an aldehyde, a ketone, and an alcohol.

2. Experimental procedure

The combustion behavior of two crude oils was examined in the scope of this study. The crude oils were characterized first with density at standard conditions and viscosity at 23 °C (Prakoso et al., 2015). Then, the crude oil samples were separated into their saturates, aromatics, resins, and asphaltenes (SARA) fractions by following the ASTM D2007-11 (ASTM, 2011). Characterization of the two crude oils is summarized in Table 1.

Note that the saturates fraction of crude oils are ignitors and asphaltenes are known as the source for fuel. Because Oil 2 has greater amount of saturates and asphaltenes than Oil 1, Oil 2 may be easier to ignite than Oil 1, and Oil 2 may form more fuel than Oil 1.

The crude oil samples and their n-pentane insoluble asphaltenes fractions were also analyzed for their elemental composition. Carbon and hydrogen weight percent was determined by using LECO Carlo Erba CHN analyzer and the metal content was determined by Thermo Intrepid Inductively Coupled Plasma (ICP) analyzer. Results in weight percent are given in Table 2. It should be noted that the other elements in Table 2 represent mainly oxygen. Thus, it can be concluded that the initial asphaltenes fraction of Oil 2 is highly oxidized already. However, it should also be noted that Oil 1 has more oxygen atoms (likely found in the form of oxygenated hydrocarbons) in its deasphalted oil than Oil 2.

After characterization studies were completed, four combustion tube experiments were conducted on these two different oil samples to observe the impact of crude oil composition on ISC behavior. In all four experiments, reservoir rock was simulated by using 20/40 mesh size Ottawa sand which has 32% porosity (Svrcek and Mehrotra, 1989; Hamm and Ong, 1995) and 34% of the pore space was filled with crude oil samples. In previous studies, the effect of initial oil and water saturations was studied on Oil1 (Kudryavtsev and Hascakir, 2014; Aleksandrov and Hascakir, 2015). Accordingly, at 34% initial oil saturation, below 34% initial water saturation values, it has been observed that combustion did not sustain. However, same oil saturation