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Effect of pressure on the isoconversional in situ combustion kinetic analysis of Bati Raman crude oil

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ABSTRACT

Knowledge of the chemical kinetics of an oil is critical for the success of an in situ combustion (ISC) project. Chemical kinetics studies help to formulate reaction schemes which help to understand the various reactions and conditions that favor the propagation and sustainability of combustion front in crude oil oxidation. The objective of this study is to investigate the effect of pressure on the kinetic analysis of in situ combustion and to understand the kinetics of Bati Raman crude oil, a 12° API crude from the Southeastern part of Turkey. In this study, ramped temperature oxidation (RTO) experiments with effluent gas analysis (EGA) are conducted at various pressures of 690, 1034, 1380, and 1724 kPag on Bati Raman crude oil. The experiments are conducted with clean non-reactive sandstone; crushed and sieved at a certain size. The isoconversional method generates an isoconversional fingerprint which shows changing reaction mechanisms on a plot of activation energy versus conversion or average temperature. Activation energies are evaluated from the fingerprints generated at the various pressures. In addition, reaction schemes are formulated for each operating pressure with associated stoichiometric coefficients and activation energy values. The results indicate that estimated activation energy values in the HTO region are increasing with increasing pressure. On the other hand, there is not a clear trend in low temperature oxidation (LTO) region. LTO activation energy values stay fairly constant with increasing pressure. Reaction schemes were proposed for Bati Raman crude oil at different operating pressures using the various regions of reaction mechanisms deconvolved on the generated isoconversional fingerprints. There is a close proximity of the stoichiometry of the reactions at different pressures which may be indicative of a good trend of consistency in the reaction schemes. Importantly, this work illustrates the effect of pressure on the isoconversional kinetic analysis of Bati Raman crude oil as well as kinetic schemes, generated based on the experiments, to be used in simulation studies.

1. Introduction

In situ combustion (ISC) is defined as the injection of air (or oxygen enriched air) into a reservoir to oxidize a small portion of the hydrocarbon in place to generate heat to reduce the oil viscosity and thus to increase the mobility of oil to improve recovery. ISC, though not limited to heavy oils, has been applied mostly to heavy oils, however, has never been as popular as steam injection. Operational problems, past failures, and lack of predictive tools such as reliable combustion simulators could be listed as the limiting factors.

ISC is a complex process involving mass and energy transport, phase behavior and chemical kinetic. The characteristic of ISC is the formation of different zones within the reservoir due to variations in temperature that is a direct result of exothermic chemical reactions between oil and oxygen. Therefore, it is important to understand the reaction kinetics of a given oil for ISC to be able to control/optimize the conditions and reactions to keep the combustion front sustained throughout the process.

Kinetics reactions during ISC involve a set of complex parallel and series reactions. These reactions are usually grouped into three: low temperature oxidation reactions (LTO), middle temperature reactions (MTR), and high temperature oxidation (HTO) (Fassihi, 1981). LTO reactions occurs below 600 K. Moore et al. (1997) explains that the temperature for LTO reactions is oil specific and the LTO is characterized by a negative temperature region (NTGR) where oxygen consumption declines even though temperature increases. Coke – a carbonaceous substance to be burnt as fuel to sustain the combustion front within the reservoir is laid on the rock matrix during middle temperature reactions (MTR). Above 673 K, high temperature reactions (HTO) takes place. HTO reactions are heterogeneous reactions of coke with oxygen. These reactions are exothermic and provides the energy to sustain combustion. A detailed review of combustion kinetics is given

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Nomenclature

A	Arrhenius constant in the Arrhenius reaction rate equation
C	Concentration, mol/m^3
CO_T	Total CO_2 production, moles
CO_{2T}	Total CO_2 production, moles
E	Activation energy, J/mol
***f*(*C*)**	Reaction model
K(T)	Rate constant
O_{2T}	Total O_2 consumption, moles
R	Universal gas constant, J mol^{-1} K^{-1}
R_c	Reaction rate,mol/ m^3 s
$s_{i,j}$	Stoichiometric coefficients
T	Temperature, K
t	Time, s
X	Conversion

elsewhere (Cinar, 2011).

The oil sample used in this study is from the Bati Raman field located in the southeastern part of Turkey. It is the largest known oil field in the country with an estimated original oil in place (OOIP) of 1.85 billion barrels (Kantar et al., 1985). The primary production of this naturally fractured carbonate reservoir was quite low (around %2 of initial oil in place) due to unfavorable oil properties; high viscosity (450–1000 cp), low API gravity (12), and low solution gas oil ratio (18 scf/bbl) (Kantar et al., 1985). The field has been flooded with carbon dioxide in an immiscible manner since 1986 and the total recovery to date is marginally over 6% OOIP (Sahin et al., 2012).

High viscosity of Bati Raman oil makes it attractive for thermal methods. The kinetics of Bati Raman crude oil has been studied for the last 30 years. Kok and Okandan (1994) estimated the kinetics parameters for Bati Raman oil (with crushed limestone) by using the reaction tube, thermogravimetric analysis (TGA), and differential thermogravimetric analysis (DTGA). Later, Kok and Karacan (1997), by separating the oil into their saturate, aromatic, resin, and asphaltene (SARA) fractions using the column chromatographic techniques, applied kinetic analysis on whole crude oil and their fractions by thermogravimetric analysis (TD/DTG). RTO kinetic experiments were also conducted with crushed limestone samples mixed with Bati Raman crude oil (Kok and Bagci, 2004). Also the effects of clay content and pressure on combustion reaction parameters were investigated by Bagci (2005a, 2005b) as well as the reaction kinetics of wet combustion (Bagci, 2006). Recently, Kok and Gul (2013) performed a differential scanning calorimetry (DSC) analysis on both the oil and its SARA fractions.

Literature have shown that all these kinetic studies were performed with limestone-Bati Raman oil mixtures as the reservoir is composed of carbonates. Naturally, in all the studies above, kinetic experiments were conducted with limestone because the authors did not want to ignore any effects due to carbonates. Generally, ISC kinetic studies are performed with crushed – matrix samples to eliminate any effects of permeability, however, the particle size is chosen according to the surface area of the matrix for any design purposes. In some cases oxygen diffusion into the matrix could be so limited that the reactions are controlled with oxygen diffusion not with kinetics. In this approach the idea is to eliminate any physical conditions that would mask chemical kinetic effects. Similarly, in our study effluent gas analysis is preferred over any method that is based on the weight of sample as weight also changes due to phase behavior and it is difficult to differentiate between thermodynamic and kinetic effects.

In situ combustion is not only a chemical reaction of oil with oxygen but also an interaction between rock and oil. Not only physical properties of rock (e.g. surface area), but also rock mineralogy has an important impact on reaction kinetics. It is observed that carbonates favor combustion (Cinar, 2011). Abundance of metallic sites such as calcium and magnesium could catalyze the reactions. Without any rock interaction, ISC kinetics is still a complex process as it involves a heterogeneous reactant composed of hydrocarbons with various chemical structures. Our approach here is to target this very complex phenomenon by eliminating one factor at a time. In that sense, the experiments were conducted with clean non-reactive sandstone; crushed and sieved at a certain size. In this study we focus on the effect of kinetic experiments' operating pressure on the activation energy values obtained from isoconversional analysis.

Formulation of reaction models from kinetic experimental studies help to understand reaction mechanisms for successful field scale applications. Parameters such as activation energy derived from kinetic cell experiments are used to formulate reaction models which are used in a simulator at least at laboratory scale to investigate the performance before expensive field pilots are conducted. In this study, ramped temperature oxidation (RTO) with effluent gas analysis (EGA) is employed to probe the reaction kinetics of Bati Raman crude oil. Using the differential isoconversional method by Friedman (1964), isoconversional fingerprints are generated using consumed oxygen and produced carbon oxides.

Since its first introduction to the petroleum engineering literature by Cinar et al. (2009), many researchers employed the technique (Glatz et al., 2011; Bazargan et al., 2013; Chen et al., 2014; Gundogar and Kok, 2014; Zhao et al., 2015). The isoconversional methods provide estimates of activation energy at the extent of conversion without any prior knowledge of the reaction model. They are very useful for the cases where the reaction model is not known or hard to form. The main difference over the conventional methods is the requirement of various experiments at different heating rates. The resulting graphs of activation energy versus conversion (or average temperature) is called the isoconversional fingerprint which indicates changes in the activation energy over the conversion or average temperature (Cinar et al., 2009).

In this study, activation energy values are evaluated from stabilized parts of the fingerprints and the effect of pressure on the activation energy is studied. Various reaction models are proposed for Bati Raman oil based on the regions of reaction mechanisms deconvolved on the fingerprints at the various operating pressures of 690, 1034, 1380 and 1724 kPag used in this study.

Effect of partial pressure of oxygen on the kinetics of in situ combustion is well known (Wilson et al., 1963; Bousaid and Ramey, 1968). Changing the operating pressure of the experiments, changes the partial pressure of oxygen. For instance, increasing the pressure also increases the partial pressure of oxygen which in turn increases the rate of oxidation reactions. Several researchers investigated the effect of operating pressure on the combustion tube tests (Wilson et al., 1963; Moore et al., 1990; Greaves et al., 1990, Cazarez-candia and Cruz-Hernandez, 2012). Wilson et. al. (1963) observed that increasing the operating pressure of combustion tube tests increases the peak temperature and combustion front velocity at low air flux. Greaves et al. (1990) concluded that the stoichiometry of the reactions are independent of operating pressure. Similar to Wilson et al. (1963), Cazarez-candia and Cruz-