A new reaction model for low temperature oxidation of heavy oil: Experiments and numerical modeling

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ABSTRACT

ISC (in situ combustion) based enhanced heavy oil recovery is complex because there are numerous chemical reactions taking place simultaneously. The complexity arises due to the immense number of components reacting through many different reaction paths where the geology and oil saturation vary spatially within the reservoir. It is known that there are four major classes of reactions taking place within ISC: LTO (low temperature oxidation), HTO (high temperature oxidation), TC (thermal cracking), and aquathermolysis. Within the reservoir, during ISC, LTO and TC reactions play a major role by providing fuel for HTO. In many reaction schemes in the literature, the LTO interval is considered as a single reactive zone spanning a single temperature range. In this work, a new reaction scheme is proposed based on analysis of previously published thermogravimetric data where the LTO reaction temperature range is separated into four temperature subranges each with its own dominant reaction products. The new reaction model was implemented in a numerical model that revealed that it was able to represent the four LTO temperature subranges. In comparison, a numerical model using a previously published LTO reaction model with a single temperature range was not able to represent the behavior of LTO.

1. Introduction

Heavy and extra heavy (bitumen) oil reservoirs, given their relatively high oil viscosity at original reservoir conditions, with the exception of cold production of lower viscosity heavy oils, are typically recovered by using EOR (Enhanced Oil Recovery) methods. In common practice, for oils with viscosity greater than about 50,000–100,000 cP, these methods are generally thermal-based EOR processes such as cyclic steam stimulation or steam-assisted gravity drainage [13]. Another thermal EOR process, ISC (in situ combustion), has shown promise but has not yet been demonstrated as a commercial recovery process.

In ISC, a portion of the oil within the reservoir is combusted to generate heat and combustion gas. The net heat generated by multiple reactions leads to a reduction of the viscosity of the oil and the combustion gas generated provides a drive mechanism to move mobilized oil to the production well. If steam is generated during the reactions, this also helps to distribute heat within the reservoir which raises the oil mobility. Steam, after condensation, produces hot water which can also displace the mobilized oil to the production well. During ISC inside the reservoir, there are at

least three major temperature ranges where different classes of reactions are occurring. The first is LTO (low temperature oxidation), which generally operates in the temperature ranging from the reservoir temperature to about 350 °C, called the LTO temperature window. LTO produces oxygenated hydrocarbons with negligible amounts of carbon oxides. The second range is HTO (high temperature oxidation), which operates in the temperature interval between about 400 and 800 °C, where the fuel within the reservoir is converted to carbon oxides and water. The third is TC (thermal cracking, also known as pyrolysis) which breaks down the original oil as well as LTO products to coke and gases. In the presence of water, aquathermolysis (hydrous pyrolysis) also occurs which produces additional carbon dioxide and hydrogen sulfide. TC operates throughout the entire range of temperature but is mostly found in the temperature range from about 350 to 450 °C. Since the temperature within the reservoir depends directly on heat transfer, the TC, LTO, and HTO temperature ranges also correspond to physical zones at the reaction front within the reservoir. Physically, TC and LTO occur where the temperature and oxygen concentration are lower than that in the HTO zone. TC may occur ahead of the LTO zone where temperatures are elevated but all of the oxygen has been consumed. HTO occurs on the zone where oxygen content is rich and TC and LTO have previously deposited coke and oxygenated oil.

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Understanding the LTO zone is of a great importance since its products play a significant role with respect to the sustainability of the combustion process. Although LTO products are essential for a technically successful ISC recovery process, producing too much LTO products (especially for heavy oil containing large amounts of asphaltene) can potentially harm oil recovery since the liquid product of LTO reactions can have viscosities greater than that of the original oil and other products, associated also with TC, and can block pores leading to reduced production rate [3,17].

Ref. [9] investigated LTO of hydrocarbons and showed that in addition to CO and CO_2, alcohol, aldehyde, ketone, carboxylic acid, and hydroperoxide were also reaction products. Ref. [9] also proposed two governing mechanisms for the LTO region. In the first mechanism, LTO generates mostly hydroperoxide as an initial product whereas in the second mechanism, LTO generates mainly aldehydes at the early steps of the reactions. The first mechanism is predominant when the hydrocarbon concentration is much higher than the oxygen concentration. The second mechanism occurs when the concentration of oxygen is significant compared to that of hydrocarbon. In later research [10], showed that for hydrocarbons with high carbon number, the second mechanism prevails. They did not present any information about the kinetics of the LTO reactions. Ref. [6] showed that the major products of LTO include oxygenated hydrocarbons such as alcohols, aldehydes, hydroperoxides, ketones, carboxylic acids and water. Although Burger and Sahuquet provided a data set for calculation of heats of reaction for the oxidation of these LTO products, they did not consider any product sequences, including oxidation of products, during the LTO region.

Ref. [4] proposed a reaction scheme for LTO, HTO, and TC of bitumen and determined its associated stoichiometry and kinetic parameters. In their reaction scheme, asphaltenes, gas and coke are products of TC reactions; asphaltenes and coke are products of LTO reaction; and carbon oxides and water are products of HTO reactions. Their TC model was not able to predict early generation of maltenes from asphaltenes.

Ref. [22] presented a reaction scheme for LTO of bitumen based on both batch reactor and combustion tube experiments. Their LTO products were basically the same as the major LTO products described by Burger [6]. Based on their experimental results, Ren et al. found that alcohols and aldehydes were produced during the earlier stages of LTO and hydroperoxides were formed later on. The hydroperoxides participated in further reactions producing other major LTO products. They also revealed that carbon monoxide and carbon dioxide were gaseous products of LTO. They did not provide estimates for kinetic parameters associated with their LTO reaction scheme to fit their experimental observations.

Ref. [12] in a series of experiments on heavy oil, showed that the LTO reactions up to 250 °C for a mixture of saturates with one or more of the SARA (Saturates, Aromatics, Resins and Asphaltene) fractions replicated the LTO behavior of the saturates alone. From their experimental results, they concluded that the aromatic, resin and asphaltene fractions had a minor effect on the overall LTO reaction rate of the whole oil. Thus, they divided the LTO reactions into two groups: first, the kinetics of the saturate fraction, and second, the kinetics of non-saturates (aromatics, resins, and asphaltenes). However, they did not propose a reaction scheme for the two groups.

Ref. [20] studied the LTO reactions of SARA pseudocomponents for both light and heavy oil samples. Based on their proposed reaction mechanism, the initial products of LTO included aldehyde and alcohol groups. In their reaction model they selected n-hexadecane, wax (basically n-octadecane and n-dodecane), antheracene, and asphaltene to represent each one of the SARA pseudocomponents. They concluded that n-hexadecane and antheracene are not very reactive and need to reach a certain temperature to participate in oxidation reactions.

Ref. [16] examined the kinetics of oxidation of tar sands by using differential scanning calorimetry and TGA (thermogravimetric analysis). He concluded that there exist three dominant reaction stages consisting of volatilization/desorption stages and a high temperature cracking/combustion stage. Ref. [14] investigated LTO reaction kinetics using TGA. Based on TGA results and elemental studies of the products over temperature subintervals within the LTO temperature window, they found that the LTO temperature window could be separated into four distinct temperature subranges with different behaviors and different dominant products. These LTO products were basically the same that were discovered by Burger [6].

In the literature, there are many experimental and simulation investigations on the LTO zone for heavy oil and bitumen. In nearly all of the models generated within these studies, the LTO zone is considered as a single reactive zone [2,3,5,8,11,17,19]. Furthermore, in most of these studies, the heavy oil is characterized by its Saturates, Aromatics, Resins and Asphaltene (SARA) fractions. Ref. [1] established two models for LTO reactions for bitumen based on sand-free and water-free oxidation experimental data. Their model included SARA fractions but they lumped saturates and aromatics together as a single pseudo component and assumed that asphaltene and coke are produced together. Although their reaction models are based on SARA pseudocomponents, it cannot represent the individual behaviors of saturates or aromatics during LTO.

The results from the literature reveal that a comprehensive reaction model (with stoichiometry and kinetic parameters) for LTO of heavy oil and bitumen that deals with the families of products generated within the LTO temperature window is not yet available. Here, a new reaction scheme for each subrange within the LTO temperature window has been developed based on published TGA experimental data. Since the LTO zone provides fuel for burning front, the quality and quantity of LTO residues significantly affect the sustainability of ISC recovery processes.

2. Methods and materials

Table 1 lists the key characteristics of the heavy oil (from the Lloydminster area of Western Canada) used in the experiments described here. Prior to the oxidation experiments, the oil was separated from its host sand and brine water to eliminate any catalytic effects arising from metals and salt on oxidation reactions that might exist. Then industrial quartz sand (Sil Industrial Mineral Inc.) was mixed with clean oil to prepare an oil sand sample with mass ratio of about one part oil to about four parts sand (the sample consists of about 82% sand by mass). Air was utilized as an oxidation agent for the LTO reactions.

Details of the experimental methods and materials used to obtain the data used here are described in Ref. [15]. To be complete, a brief description is provided here. Thermogravimetric analysis (TGA) is an analytical technique where, during the course of

Table 1
The physical properties of heavy oil sample from Lloydminster [15].

Density (g/ml)	
15 °C	0.9728
25 °C	0.9661
API (15 °C)	13.95
Viscosity (mPa s)	
25 °C	3026
40 °C	808
SARA analysis (wt.%)	
Saturate	22.41
Aromatic	50.65
Resin	26.95
Asphaltene	7.67