Low-temperature oxidation of Lloydminster heavy oil: Kinetic study and product sequence estimation

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HIGHLIGHTS

- Low temperature oxidation (LTO) region was divided into four different subzones.
- Kinetic parameters have been calculated for each subzone of LTO.
- Activation energy was positive for two subzones and negative for the other two.
- Elemental ratios of LTO residues provide insights for product sequence estimation.
- Product sequence and kinetic parameters are instrumental for numerical modeling.

ARTICLE INFO

ABSTRACT

Low-temperature oxidation (LTO) of Lloydminster heavy oil samples was investigated for a basic understanding of the reaction kinetics and an estimation of the product sequence. Ramped temperature oxidation experiments and isothermal experiments at seven different temperatures from 50 to 350 °C were performed to observe the thermal oxidation behavior of this heavy oil and to find kinetic parameters of the oxidation during LTO. The results reveal that there were four different subzones within the LTO zone. This is similar to previous findings for an Alaska heavy oil. The first and third subzones had positive activation energies, whereas the second and fourth subzones had negative activation energies. Compared to the sample from Alaska, the Lloydminster heavy oil exhibited higher derivative weight loss values, a higher order of reaction and lower activation energy. From each isothermal experiment, an elemental analysis conducted on the residue suggested that aldehyde is a major LTO product in the first subzone; alcohols and ketones are the major products in the second subzone; hydroperoxide and carboxylic acids dominate the third subzone; and, ketones and hydroperoxide are the major products of the fourth subzone.

1. Introduction

Khansari et al. determined four temperature subzones during the low-temperature oxidation (LTO) process for an Alaskan heavy oil using thermogravimetric analysis. The first and third temperature subzones, ranging from 50 to 150 °C and 200 to 250 °C, respectively, both had overall reactions with positive activation energies. Both the second and fourth subzones, from 150 to 200 °C and from 250 to 350 °C, respectively, had reactions with negative activation energies [1]. The authors then proposed that each of the four subzones may be connected to the LTO products, but did not report data to establish which products were dominantly produced within each temperature subzone.

If the products from the reactions within each temperature subzone can be controlled, this would have large implications for upgrading within heavy oil reservoirs during in situ combustion (ISC) processes. In ISC, there are three zones: (1) LTO, (2) thermal cracking (TC), and (3) high-temperature oxidation (HTO). LTO provides fuel that is combusted under HTO conditions, on the condition that there is sufficient oxygen supplied to the system. If the temperature is maintained within a specific temperature range, there is the potential to control the types of products generated during LTO within a reservoir, thereby providing the capability to yield value-added products from the reservoir during the recovery process. For instance, if the heating value of the LTO products is not high enough to keep the fire front sustainable, the operating temperature can be altered to generate LTO products with higher heating values.

Tadema used thermogravimetry analysis to investigate the combustion of a crude oil sample in the presence of sand and dis-

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covered that two oxidation regions exist: LTO and HTO. Tadema did not break down the two oxidation regions further [2]. Moore found that there was a temperature interval between LTO and HTO, where an increase in temperature led to a decrease of the oxygen uptake rate. This interval is often referred to as the negative temperature gradient interval. As with Tadema, Moore did not break down the LTO and HTO regions into subintervals [3].

Yannimaras and Fassihi et al. investigated the effect of LTO on the composition and viscosity of different crude oils. According to their results, LTO had no significant effect on light oil samples, but led to dramatic changes in heavy oil properties. For example, they showed that the viscosity of a heavy oil sample from Monterey that had undergone LTO was raised from 54,300 cP at 85 °F to 791,151 cP at 350 °F [4,5]. Freitag and Verkoczy investigated LTO of the SARA (saturate, aromatic, resin and ashphaltene) fractions of two different oil samples mixed with reservoir sand and found that the order of reaction with respect to the oxygen concentration varied from half to one, as the temperature was raised. The result implied that the rate of reaction strongly depended on the oxygen purity [6].

Phillips and Hsieh proposed two models for the kinetics of the oxidation reaction of a bitumen sample: the simple and complex models. They found that the complex model, which deals with bitumen as multiple reactants, explains the reaction complication more accurately [7]. Niu et al. investigated the LTO of SARA components for both light and heavy oil samples at different temperatures, pressures and water saturations. Their results showed different behaviors for each component. They also found that the heavier the oil, the greater the potential for oxidation [8].

Lerner et al. performed numerical simulations to study the displacement process and chemical reaction influence on reservoir recovery. They showed that the physical, chemical and fluid flow characteristics dramatically affected the ISC process [9]. Another numerical model was presented by Smith and Perkins [10], who had studied and simulated the heat transfer, vaporization, condensation and fluid flow pattern during wet ISC at reservoir conditions. They also obtained the kinetic data along with their simulation [10].

Bousaid and Ramey performed some isothermal oxidation experiments to study the burning rate of the ISC process. Carbon concentration, oxygen partial pressure and temperature were parameters that affected the rate of reaction at the combustion front. In addition, the porosity and presence of clay decreased the activation energy and, thus, increased the reactivity [11]. Freitag and Exelby carried out combustion tube tests for heavy oil and bitumen samples. Their results showed that the produced oil properties before steam breakthrough were drastically affected by steam distillation rather than thermal cracking [12].

Kok et al. used thermogravimetric analysis to investigate the kinetics of the oxidation reaction for whole oil and its SARA fractions. They calculated the kinetic parameters using the Coats and Redfern method for each experiment [13]. Alexander et al. performed the flood pot method to study the fuel availability for the ISC technique. Their results revealed that the fuel availability depended on the type of porous media, oil saturation and crude oil characteristics [14].

Walter described the pilot test and the techniques applied for oil recovery considering its economic aspects. He explained that, for the test site of a shallow oil sand reservoir, the applied pressure was low and the injection and production processes were more convenient and, thus, less expensive [15]. Benham and Poettmann studied the results reported from laboratory experiments and field tests using stoichiometric principals. They concluded that the fuel burned at the combustion front was partially coked residue and was affected by temperature rather than the crude oil [16].

Burger and Sahuquet showed that LTO products were oxygenated hydrocarbons, such as alcohols, aldehydes, ketones, hydroperoxides and carboxylic acids [17]. However, they failed to specify whether the products were specific to a particular temperature span within the LTO temperature range. Many researchers have conducted experiments on LTO reactions with construction of kinetic models [18–21].

Reaction schemes often rely on the use of pseudo-components, such as the SARA fractions or simply maltenes and asphaltenes, to represent the oil and products and although there are various investigations on different aspects of LTO from experimental to modeling to economic assessments, to date and to the best of the authors' knowledge, no reactions schemes have broken down the kinetics of LTO into temperature subzones with the associated distributions of products, which is the main achievement of the work documented here. The LTO temperature subzones and their reaction kinetics for a Lloydminster heavy oil have been investigated using both isothermal and ramped temperature oxidation reactions. The LTO product sequence has been estimated based on the elemental analysis. The results of the experiments have been compared to that of an Alaskan heavy oil.

2. Methods and materials

Table 1 lists the physical properties of the Lloydminster heavy oil sample. To eliminate catalytic effects that may arise from the presence of the minerals, metals and salts existing in reservoir sand, the oil was separated from the sand prior to the experimental analysis. The clean oil was then mixed with standard industrial quartz sand (Sil Industrial Mineral Inc.) with a mass ratio of one part oil to four parts sand. The compositional properties of the quartz sand is listed in Table 2.

The thermogravimetric analyzer (TGA, Perkin Elmer Model TGA 7 with TAC 7/DX controller) used in each experiment was purged initially with nitrogen (20 ml/min) for about 30 min to displace gaseous impurities within the system. Oxidation reactions started when the gas stream was switched from nitrogen to oxygen with a flow rate of 10 ml/min.

The weight loss or derivative weight loss was recorded versus time or temperature by the TGA's control and data acquisition system. The residue obtained at the end of each temperature subzone was analyzed using a CHNS (carbon, hydrogen, nitrogen, sulfur) analyzer (Perkin Elmer Model 2400, Series II). Each experiment was conducted twice to ensure reproducibility.

2.1. Thermogravimetry analysis

About 50 mg of the oil-sand mixture was put in a platinum crucible, which was then placed in the TGA. For the ramped temperature oxidation experiment, the sample was exposed to the oxygen

Table 1
Lloydminster heavy oil properties.

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