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Air Injection for Enhanced Oil Recovery: *In Situ* Monitoring the Low-Temperature Oxidation of Oil through Thermogravimetry/Differential Scanning Calorimetry and Pressure Differential Scanning Calorimetry

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Ⓢ *Supporting Information*

ABSTRACT: Low-temperature oxidation (LTO) of oil plays an important role in air-injection based oil recovery processes. Systematic investigations on the regularities of LTO reactions, especially those decoupled with the influences of mass transfer, were highly expected to improve field application and even to develop new strategies for heavy oil recovery. In this contribution, both thermogravimetry/differential scanning calorimeter and pressure differential scanning calorimeter were employed as microreactors to *in situ* monitoring the heat release and mass loss performances of the LTO process under different oxygen partial pressures. The total amount of heat resulted from LTO reactions of oil was observed in a linear relationship with oxygen partial pressure. A one-step reaction model was proposed to simulate the low-temperature mass loss behavior. The kinetic parameters were calculated based on the Arrhenius expression and the assumption of distributed activation energy. These results indicated the feasibility of *in situ* generated heat during low-temperature oxidation by the promotion of oxygen partial pressure and the contact between oil and oxygen with little loss of deposited oil.

1. INTRODUCTION

Air injection is a promising method in the field of improved oil recovery[1−3] because of its availability[4−6] and wide applications in both heavy oil[3,7,8] and light oil[9,10] recovery processes. In heavy oil reservoirs, air is employed as an oxygen donor to propagate *in situ* combustion reactions. Such *in situ* combustion generates heat to reduce oil viscosity.[11] In light oil reservoirs, oxygen in air is consumed by spontaneous low-temperature oxidation (LTO) extending from the native reservoir temperature up to a nominal limit of 300 °C.[12] The remaining nitrogen contributes most to drive oil to production wells.[13] The LTO reactions play an important role in the two applications. In the strategy of *in situ* combustion, it is the main oxidation reaction to produce fuel for the following high-temperature combustion, the amount of which is critical for the achievement of the required reaction temperature.[11,14] The success of an ignition and a stable combustion front are also strongly influenced by this group of reactions.[15] LTO consumes almost all the oxygen in the injection gas; therefore, this avoids oxygen breakthrough and consequently safety issues during the high-pressure injection process for light oil. This also results in a temperature increase leading to a reduction of oil viscosity and thus a promotion of recovery efficiency.[4,5,13] Thus, the LTO is strongly considered to fully demonstrate its potential for efficient and effective oil recovery.

The main parametric factors and their influences on oil recovery were investigated for LTO reactions. Mahinpey et al.[16] carried out combustion tube experiments and thermogravemetric analysis to explore the effect of LTO on the pyrolysis and combustion of Fosterton crude oil. The investigation reported the production of coke-like residue and a small amount of carbon oxides. A significant increase of rate constant was also observed for coke combustion after LTO, indicating an acceleration effect of LTO during *in situ* combustion. Greeves and Ren[4,5] reported the consumption rate of oxygen during high-pressure air injection, which is closely related to safety problems in operation. Most of the oils achieved complete oxygen utilization equivalent to 300−500% hydrocarbon per volume air injected over 10−20 days, and the possibility of early oxygen breakthrough was reduced to a very low order.[4,5] This finding was subsequently verified by successful oilfield applications.[17,18] Their further investigation[17] observed a significant temperature rise in a small batch reactor at the temperature of 170 °C, proving the heating effect of LTO reactions, which is considered a bonus for oil recovery. Jia et al. investigated the influence of pressure, oxidation time, water saturation, and clays on LTO behavior by both TG/DTA tests[18,19] and oxidation tube experiments.[20] An increase in the amount of small hydrocarbons in both oxidized oil and gaseous phase was observed.[21] Very recently, the exothermic catalytic LTO of heavy oil on metal oxide catalysts was detected.[22] The

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stabilization of nanometal catalysts in porous media[23] and evaluation of two self-assembly systems derived from a partially hydrolyzed polyacrylamide and xanthan gum for heavy oil recovery were established recently.[24]

The kinetic modeling of LTO reactions is the first step for reservoir simulations.[25] To obtain a glance into the kinetic properties of LTO reactions with the avoidance of challenging modeling task, the kinetic parameters have been determined via thermogravimetric analysis[26−30] by the Arrhenius method,[31,32] Coats-Redfern (C-R) approximation,[18] and the distributed activation energy model (DAEM).[33] The apparent activation energy was reported to be ca. 100 kJ mol^{-1}, which was much lower than that of high-temperature oxidation (HTO).[33] Detailed kinetic models were also proposed. Ren et al.[17] performed small batch experiments to explore the heating effect of LTO reactions and proposed a two-step lumping model (an exothermic oxidation process consuming O_2 and an endothermic decarboxylation process with the production of CO_2) to explain the temperature rise and CO_2 production during the LTO process. Moore's group[12,34−37] has carried out pioneer investigations on the issue of kinetic modeling and its incorporation into field numerical simulations. Jia et al.[12,36,37] have grouped organic components in terms of four pseudocomponents (maltenes, asphaltenes, coke, and non-condensable gas) and proposed the scheme of the LTO reaction based on the assumption of first-order reactions as follows:

(1) polymerization reactions

$$Malt.(\mathrm{R}) + \mathrm{O}_2 \xrightarrow{k_1} Asp.$$

$$Malt.(\mathrm{SR}) + Malt.(\mathrm{P}) + O_2 \xrightarrow{k_2} Asp.$$

(2) asphaltene decomposition

$$Asp. \xrightarrow{k_3} Malt.(\mathrm{P}) + Coke + Gas$$

(3) burning of product maltene

$$Malt.(P) + O_2 \xrightarrow{k_4} Gas + H_2O$$

They calculated kinetic parameters through the Downhill Simplex optimization method in conjunction with the Ranga-Kutta algorithm on the basis of experimental thermal cracking and reported LTO results. This model delivered a very high accuracy in the prediction of product yields in the temperature interval from 75 to 397 °C in short-term settings and a lower accuracy in the long term data. Further investigations by Barzin et al.[34,35] incorporated vapor phase combustion reaction into the kinetic models so that precise simulations of hydrocarbon compositional change and energy generation during LTO were available. These investigations on kinetic modeling and reservoir simulation contributed much to the successful prediction of oil oxidation behavior before field applications of enhanced oil recovery strategies involving the injection of air or a gas containing oxygen as an impurity.[17,38−41] Particularly, detailed description on temperature variations and composition changes resulted from simulations and validation experiments were scarcely reported by other researchers, which might benefit the formulation of other research plans. The proposal and validation of kinetic models have been well documented. In contrast, the systematic investigations on the regularities of heat release and mass loss performances were not well-involved yet, which should be highly considered as a necessity to improve field application and even to develop new strategies. Since experiments carried out in tube and batch reactors were strongly affected by both reactions and mass transfer properties, it was very difficult to obtain intrinsic regularities only if decoupling approaches were applied. Take this work focusing on the LTO reactions for example, the microscale experiments were required to minimize the influence of mass transfer, bringing the vast challenge since LTO reactions result in only little heat, a small amount of gaseous products, and a mass loss that is very difficult to be distinguished from evaporation of light oil components.

In this contribution, both thermogravimetry/differential scanning calorimetry (TG/DSC) instrument and pressure differential scanning calorimeter (PDSC) were employed as microreactors to determine detailed heat performance and mass loss data of the LTO process under different oxygen partial pressures. To eliminate the effect of the endothermic volatilization process on measured heat derived from LTO, the light components of heavy oil were removed before oxidation experiments. Both the reaction heat and deposited compounds were concerned. The former was closely related to the oil viscosity, while the latter was relevant to recovery efficiency for high-pressure injection and the temperature of burning front for *in situ* combustion.

2. EXPERIMENTAL SECTION

2.1. Materials. A heavy crude oil from the Xinjiang oilfield in China was applied as the oil sample. The density, viscosity, main elemental components, and the result of saturate-aromatic-resin-asphaltene (SARA) analysis are listed in Table 1. The SARA analysis was carried out by the traditional eluting chromatography (EC) method. An elementary analyzer (Elementar, Vario EL III) was employed to obtain the elemental composition.

Table 1. Physical Properties, Elemental, and SARA Analysis of the Pristine and Devolatilizated Oil Samples

		pristine oil	devolatilized oil
density (g cm^{-3}, 25 °C)		0.96	0.98
API gravity (60/60 °F)		15.5	13.8
relative molecular weight		609	764
viscosity (mm^2 s^{-1}, 50 °C)		14340.0	18428.4
elemental analysis	C (wt %)	85.18	85.98
	H (wt %)	12.45	12.08
	N (wt %)	0.83	1.10
	S (wt %)	0.39	0.28
	O (wt %)	1.14	0.56
	H/C	1.75	1.69
SARA analysis	saturates (wt %)	41.19	37.02
	aromatics (wt %)	18.18	13.27
	resins (wt %)	20.92	31.19
	asphaltenes (wt %)	0.56	2.86
	mass loss (wt %)	19.15	15.66

The oil sample was separated from oil sand to eliminate the catalytic effects induced by the residual metal oxides and was subsequently devolatilized under Ar atmosphere at 300 °C for 3.0 h to eliminate the influence of light component volatilization on thermal gravity and calorimetric measures prior to experiments. The reason that we selected a temperature of 300 °C was attributed from the fact that the upper limit of low-temperature range is around 350 °C, and the operation temperature of atmospheric distillation unit in petroleum refining is about 398 °C. Such temperature was lower than the two temperatures above to avoid the risk of overheating by the furnace. The heavy oil lost 33% of the original weight after devolatilization. A significant increase in its viscosity was observed (Table 1). However, there is little change in the shape of the heat release curve except for the lower peak and the disappearance of the endothermic peak at a temperature lower than 200 °C (Figure S1).

2.2. LTO Experiments. A sensitive thermobalance (Mettler Toledo, TGA/DSC 1) was performed as a microreactor to carry out the nonisothermal and isothermal oxidation of heavy oil. Both the mass loss and heat release behavior were *in situ* monitored. Such a TG reactor is very efficient to record the mass and reaction heat during reaction, which has been well applied for carbon nanotube growth[42,43] and oil oxidation.[2,40,44,45] A schematic illustration of the thermobalance structure is presented as Figure 1. The oxidizing gas was introduced from the upper part, across the chamber, and then onto the heavy oil sample. Since the height of the pan was only around 1.0 mm, the exhaust gas was easily derived out of the pan and then toward the outlet. This ensured the full contact between the heavy oil and the reaction gas. Aluminum pans were selected to provide an accurate measurement of heat. The TG/DSC experiments recorded the percentage of remaining weight and the value of heat flow every 5 s.

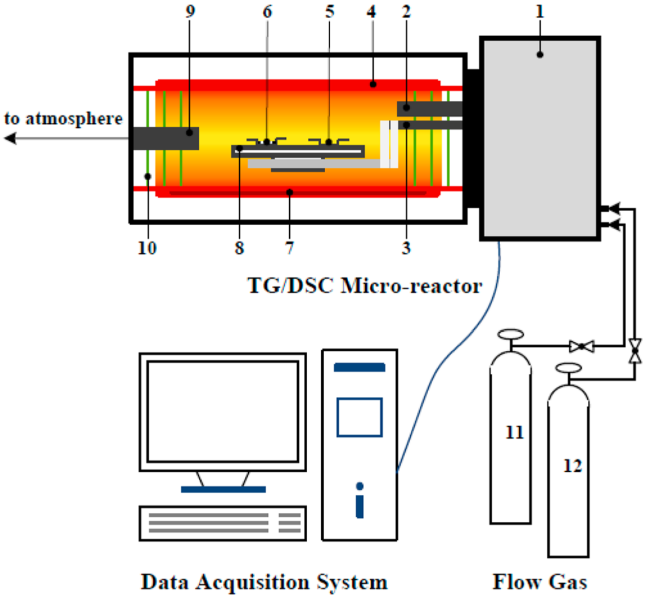

Figure 1. Schematic diagram of TG/DSC microreaction system for *in situ* monitoring the LTO of oil: 1, system controller and gas-mixing chamber; 2, inlet tube; 3, balance system; 4, furnace heater; 5, shallow aluminum crucible; 6, oil sample; 7, furnace temperature sensor; 8, sample temperature sensor; 9, outlet tube; 10, baffles; 11, an oxygen cylinder; 12, an nitrogen cylinder.

Three groups of oxidation experiments were conducted from 30 to 550 °C under a mixed gas flow of oxygen and nitrogen with a constant flow rate of 100 mL min^{-1}. To reveal the effect of oxygen partial pressure on heavy oil oxidation, the first group of nonisothermal oxidation experiments was executed with different oxygen and nitrogen ratios (1/9, 3/7, 5/5, 7/3, and 9/1) at a heating rate of 5 °C min^{-1}. The second group of nonisothermal oxidation experiments was carried out with an O_2/N_2 ratio of 9/1 at different heating rates (1, 3, 5, 10, and 20 °C min^{-1}) to determine kinetic parameters of heavy oil oxidation. The third group of oxidation experiments was completed at a family of reaction temperatures (150, 200, and 250 °C) with an O_2/N_2 ratio of 9/1. The isothermal experiments were carried out to check the validation of the developed reaction model and its kinetic parameters.

PDSC was also employed to investigate the heat generation performance of low-temperature oil oxidation under synthetic air flow at pressures of 1.0 to 3.0 MPa, which approximated to the actual pressure in the reservoir. The experiment under 100 kPa was also conducted as a comparison. The outlet of the system stayed open with a constant flow of 20 Ncm^3 min^{-1} at the required pressure to ensure the safety. Since thermobalances are only available for tests under close to atmospheric pressure, weight performances cannot be evaluated synchronously in these conditions. Each experiment was repeated at least twice to ensure the repeatability and the accuracy of the test data.

3. RESULTS AND DISCUSSION

3.1. Mass Loss and Heat Generation Performances under Atmospheric Pressure. The thermal gravimetric (TG) analysis was performed in conjunction with different scanning calorimeter (DSC) to collect the mass loss and heat release behavior of heavy oil during oxidation at atmospheric pressure. The comparison of TG and DSC profiles under different oxygen partial pressures is shown in Figure 2. Two districts with different characteristics were easily distinguished in each TG/DSC profile. The small mass loss and low heat release rate below 350 °C were ascribed to the LTO of heavy oil, while the stage above 350 °C with large mass loss and high heat release rate was assigned to HTO (Figure S2). The overlapped strong peaks in heat flow curves were detected at high temperatures which were significantly larger than those at low temperatures (Figure S2). The plateau region between the two demonstrated an outstanding increase of activation energies from LTO to HTO reactions.[33]

Benefited from the devolatilization of heavy oil before experiments, detailed analysis on the LTO performances was obtained. First, the value of significant mass loss (15 wt %) observed at the end of LTO did not vary with oxygen partial pressure (Figure 2(a)). It was speculated that LTO reactions were kinetic controlled, and only certain kinds of components or groups with a limited amount contributed to the total mass loss. This allowed the evaluation of the weight of remaining oil by a simple kinetic model, which was essential to estimate the recovery efficiency of the high-pressure injection process and the amount of fuel deposition for the *in situ* combustion process. The detailed description of the kinetic model was shown in section 3.3. Second, the phenomenon that obvious mass loss was initialized only from ca. 200 °C while the observation of exothermic behavior was almost from the starting temperature, indicating the occurrence of exothermic oxidative addition reactions from the beginning and subsequently oxidative decomposition reactions at about 200 °C. Particularly, direct observation of the heat release behavior enabled one to obtain a further investigation into heat generation performance of LTO reactions.

Different from mass loss, the heat flow at low temperatures exhibited a positive dependence on oxygen partial pressure (Figure 2(b)). The peaks at oxygen partial pressures of 10, 30, 50, 70, and 90 kPa were 1.56, 1.87, 2.35, 2.99, and 3.40 kJ g^{-1},

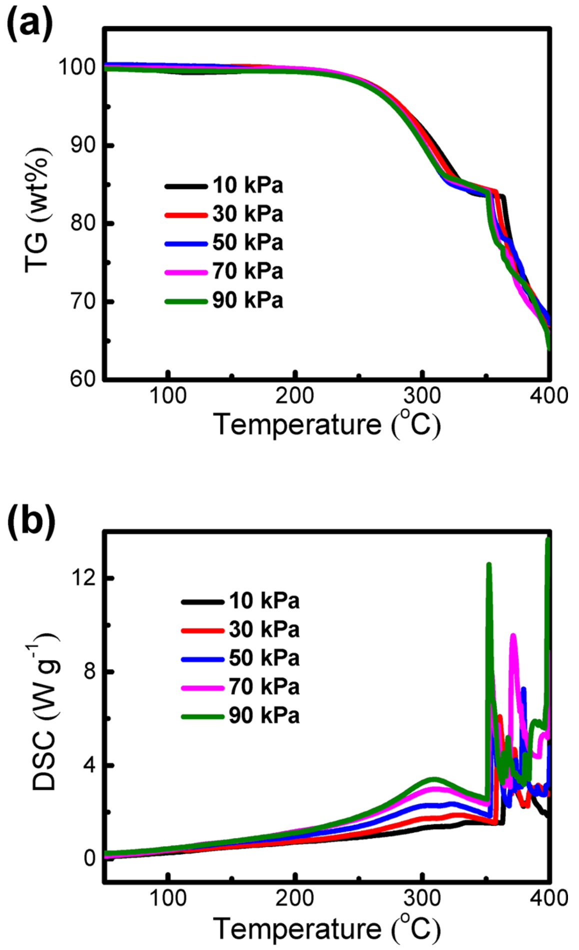

Figure 2. (a) Mass loss and (b) heat release performances of heavy oil oxidation in the low-temperature interval with different oxygen partial pressures.

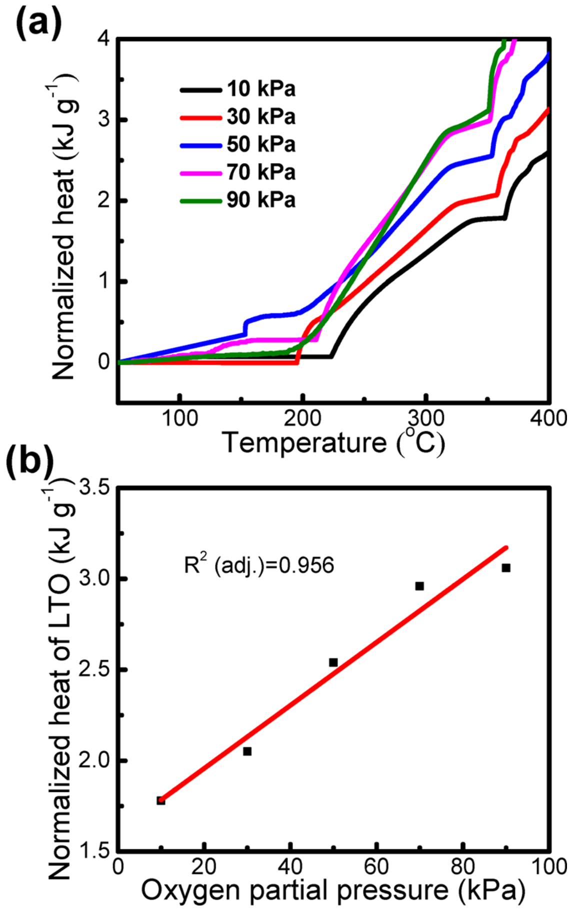

Figure 3. (a) Cumulative heat generated with different oxygen partial pressures and (b) the relationship of the total heat generated in the low-temperature oxidation vs the oxygen partial pressure at atmospheric pressure during the heavy oil oxidation process.

respectively. The cumulative heat in the low-temperature range at different oxygen partial pressures exhibited a similar tendency. To provide a quantitative relationship between the two, normalized heat was calculated from TG and DSC profiles. The equation for the calculation was listed in eq 1.

$$H_{mass} = \frac{\iint H_{heatflow}\, dt\, d\Delta w}{\int d\Delta w} \tag{1}$$

where t is time, Δw is the percent of mass loss, $H_{heatflow}$ (unit: W g^{-1}) is the heat flow detected by DSC instrument, and H_{mass} (unit: J g^{-1}) is the heat of oil oxidation normalized by mass loss. Ignoring the oxidation degree of the residue, the normalized heat (H_{mass}) represents the absolute enthalpy value of the oil components that converted to gaseous products. The plots of normalized heat against temperature and oxygen partial pressure were displayed in Figure 3.

The normalized heat in the low-temperature range was no more than 3.0 kJ g^{-1} (Figure 3(a)). A linear relationship with oxygen partial pressure was determined (Figure 3(b)). The maximum value (3.0 kJ g^{-1}) of normalized heat at the end of low-temperature interval under experimental oxygen partial pressures was much lower than both the minimum value of normalized heat at the end of high-temperature interval (5.0 kJ g^{-1}, Figure S3) and the theoretical value of oil combustion enthalpy (41.8 kJ g^{-1}). This indicated the formation of a large amount of incomplete oxidation products in the gaseous phase. This inference coincided with the previous literature[20] that light hydrocarbon compounds (C1−C6), CO, and CO_2 were detected by gas chromatography (GC) as LTO products of Keke Ya light crude oil. The linear dependence of heat generation and independence of mass loss on oxygen partial pressure at low temperatures also indicated a significant heating effect of low-temperature oxidation with little loss of oil residue when oxygen partial pressure was increased. Further investigations at high pressures were performed by PDSC tests.

3.2. Heat Generation Performances under Reservoir Pressures.

Compared with TG/DSC experiments carried out under atmospheric pressure, PDSC tests operated at pressures up to several MPa were much closer to the real process occurring under reservoir pressure. The variation of heat flow under different oxygen partial pressures (20, 200, and 600 kPa) resulted from LTO reactions of heavy oil was illustrated in Figure 4(a). Three peaks were easily distinguished in the interval of 200−400 °C with values of 4.4, 9.0, and 16.9 mW, respectively, exhibiting a positive correlation with oxygen partial pressure. It was speculated that the promoted oxidation degree of products resulted from the higher oxygen concentration contributed to the more rapid heat release at high pressures, considering the mass loss and heat release performances at atmospheric pressure.

Integrating the heat flow versus time, the total heat generated from the oxidation of 1.0 mg oil sample was obtained. The

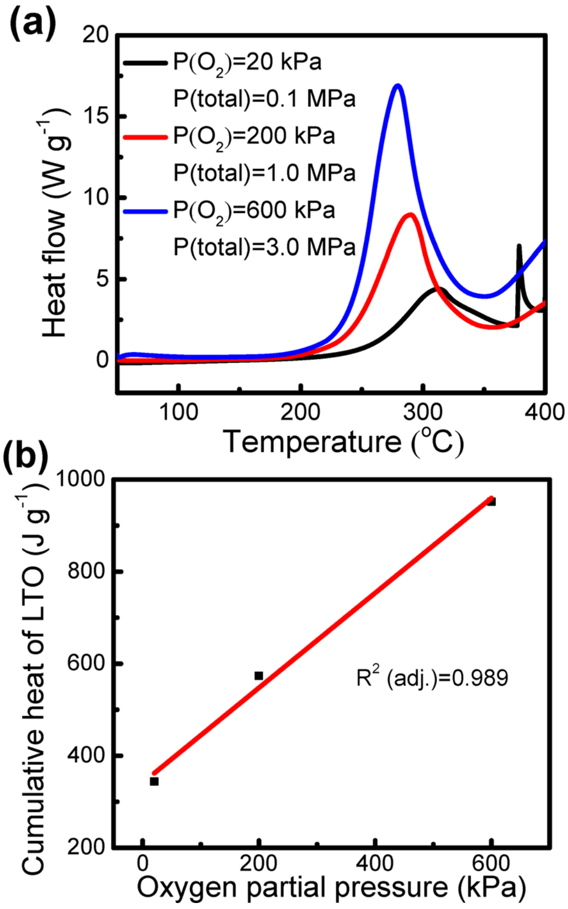

Figure 4. (a) The heat release performance and (b) the relationship of the total heat generated in the low-temperature oxidation vs the oxygen partial pressure under air pressure and high pressures during the oxidation of heavy oil.

values in low-temperature range under oxygen partial pressures of 20, 200, and 600 kPa were 344.1, 573.7, and 951.7 mJ, respectively. Its linear dependence on oxygen partial pressure was also observed in Figure 4(b), in accordance with the previous DSC results. In particular, when oxygen partial pressure was 200 kPa, the amount of heat generation at low temperatures (573.7 mJ mg^{-1}) was comparable with that detected at high temperatures (653.6 mJ mg^{-1}) (Figure S3). When oxygen partial pressure reached 600 kPa, the total heat generation in the low-temperature range (951.7 mJ mg^{-1}) was even higher than that detected in the high-temperature range (831.3 mJ mg^{-1}) (Figure S3). This finding indicated that considerable heat was available in the low-temperature oil oxidation by the promotion of the oxygen partial pressure and the contact between oil and oxygen. For the process of high-pressure air injection, this resulted in higher reservoir temperature, reduced oil viscosity, a greater amount of evaporated light components, and increased drive force for oil recovery. For the process of *in situ* combustion, it was expected to be controllable at a low operation temperature approaching the upper limit of the low-temperature range, to obtain not only sufficient evaporation of light components but also significant viscosity reduction and recovery of deposited heavy components. However, great efforts were still highly required to determine the factors resulting in this linear relationship and quantitative modeling on total heat.

3.3. Low-Temperature Oxidation Reaction Model.

Besides the heat generation during LTO, the mass loss behavior is also strongly concerned in this contribution. As mentioned in section 3.1, the low-temperature oil oxidation was kinetic-controlled, and the corresponding mass loss curve had little relevance with oxygen partial pressure at atmospheric pressure. Thus, an overall model on the low-temperature oxidation of heavy oil can be given as follows on the basis of the above analysis to achieve a quantitative analysis of mass loss performance

$$C_xH_y + O_2 \rightarrow M_{heavy} + M_{light} - \Delta H \qquad (2)$$

where M_{heavy} represents the residue which is left in a state of liquid or solid; M_{light} is the mixture of organic gaseous products, carbon oxide, and water, which are directly resulted from the reactions between oxygen and oil components or residue; ΔH is the reaction enthalpy; the front negative sign suggests it is an exothermic reaction. As discussed in sections 3.1 and 3.2, the total amount of released heat at low temperatures had a linear relationship with oxygen partial pressure at both atmospheric and reservoir pressures when oxygen was in excess and fully contacted with oil. As comparison, the corresponding weight of M_{heavy} at atmospheric pressure under the same conditions was little affected by the oxygen partial pressure but was closely related to the LTO reaction rate.

The classification method of the two-lumping reaction model is in accord with that of TG analysis, that is, to identify the products removed away as light chemicals and to weigh the residue left as heavy chemicals. The kinetic parameters were calculated by a nonisothermal method based on the assumption of distributed activation energy published in our previous publication.[33] Assuming first-order decomposition kinetics in consideration of the excess oxygen in the system, the relationship between the weight of residue and the LTO reaction rate was described by an Arrhenius expression (eq 3) as a function of temperature

$$r = \frac{dw_{oil}}{dt} = k_0 \exp(-E/RT)w_{oil} \qquad (3)$$

where r and w_{oil} are the overall reaction rate and the weight of residue at the time of t, k_0 is the pre-exponential factor, E is the activation energy, and T is temperature of the system. The activation energy and pre-exponential factor were 10^5 J mol^{-1} and 2×10^7 min^{-1}.

A set of isothermal gravity analysis under different temperatures (150, 200, and 250 °C) was performed to validate the reaction model and kinetic parameters. The method of isothermal gravity analysis was employed to achieve real-time data and to avoid possible systematic error induced by the ramped temperature oxidation. Herein, only one oxygen partial pressure of 90 kPa was selected since oxygen partial pressure had little effect on mass loss rate. The isothermal gravity measurements as well as modeling results were presented in Figure 5. The range of the vertical axis, representing the weight of residue compared with that of original oil sample, was displayed only from 76 to 100%, considering that the total mass loss in the low-temperature interval was no more than 20%. An inflection point was observed in Figure 5 when the heavy oil lost more than 20% of its original weight, probably due to the shift of dominant reactions to other kind of reactions. When the total mass loss was within 20%, the model predictions were in rather good agreement with experimental results, suggesting

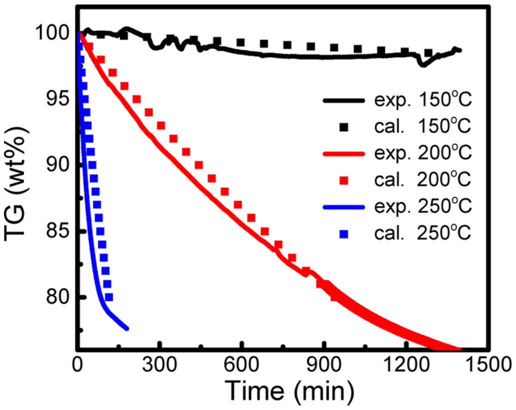

Figure 5. Experimental and calculated mass loss performances of heavy oil oxidation.

that the low-temperature oxidation of heavy oil was correctly predicted by the proposed reaction model and kinetic parameters. It should be pointed out that the model is only suitable for the conditions that oxygen is in excess. In other conditions with inadequate oxygen, there are other dominate reactions with slower rates than reaction 2, which would be uncompetitive once oxygen is available.

4. CONCLUSIONS

Both TG/DSC and PDSC instruments were employed as microreactors to investigate the low-temperature oxidative reactions of heavy oil. Significant exothermic behavior was observed from the starting temperature of oxidation, benefiting from the devolatilization of light components before experiments. The total amount of released heat in the low-temperature interval presented a linear relationship with oxygen partial pressure in atmospheric and reservoir pressures. When the oxygen partial pressure reached 600 kPa, the total heat during low-temperature oxidation was even higher than that of high-temperature oxidation. The mass loss performance had little relevant to oxygen partial pressure and was well simulated by a one-step reaction model and kinetic equation on the basis of the Arrhenius expression. These findings indicate the availability of considerable heat during low-temperature oxidation by the promotion of oxygen partial pressure and the contact between oil and oxygen with little loss of deposited oil, which are expected to afford an improved operation temperature for a high-pressure air injection process and a controllable low temperature in the low-temperature interval for the *in situ* combustion process with effective viscosity reduction and enhanced oil recovery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Comparison of the heat release behavior between oil and devolatilized oil by PDSC tests, mass loss, heat generation, and cumulative heat of heavy oil during the whole oxidation process, heat release performances of heavy oil under air pressure and high pressures, and a summary of PDSC results at pressures of 0.1, 1.0, and 3.0 MPa. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b00997.

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Notes

The authors declare no competing financial interest.

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