Quantification of low-temperature oxidation of light oil and its SAR fractions with TG-DSC and TG-FTIR analysis

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Abstract
The oxidation reaction is the key to determining the success of air flooding. In this paper, experimental and theoretical techniques have been developed to identify the low-temperature oxidation (LTO) mechanisms for light oil during air flooding by comprehensively analyzing thermal stability and oxidation process of the crude oil and its SAR (ie, saturates, aromatics, and resins) fractions. Experimentally, both a thermogravimetric analyzer coupled with differential scanning calorimetry (TG-DSC) and a thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR) are employed to quantify the LTO process of crude oil and each SAR fraction as well as the corresponding oxidation properties. Theoretically, reaction models have been developed to reproduce the experimentally identified reactions. The results show that the oxygen addition reaction and the bond scission reaction occur simultaneously. The former can be initiated when temperature is higher than 50°C, and it is gradually shifted to the latter with the continuous increase in reservoir temperature. The LTO products of light oil include H₂O, CO₂, carboxylic acids, alcohols, phenols, and ethers. Saturates, aromatics, and resins are all the sources of H₂O, CO₂, alcohols, and carboxylic acids, whereas ethers are mainly derived from aromatics and resins. At the beginning of an air flooding process, heat is mainly generated from the oxidation of aromatics and resins. Subsequently, oxidizing saturates gradually dominates the air flooding process with an increase in the reservoir temperature.

Keywords
crude oil, LTO mechanism, oxidation process, SAR fraction, thermal stability

1 | INTRODUCTION

Due to the inherent low permeability in a tight oil reservoir, the primary recovery is still very low, though horizontal wells have been drilled and massively fractured.¹,² Numerous efforts have been directed to develop suitable enhanced oil recovery (EOR) techniques for such a tight formation due to its rapid decline of initial productions. Gas (eg, CO₂, N₂, and natural gas) flooding shows positive responses in either low permeability reservoirs or conventional reservoirs that have advanced to the late stages of waterflooding,³,⁴ though its extensive applications are still limited due mainly to the gas sources and the associated operational costs. Comparatively, air is readily available and can be compressed and injected to displace oil with relatively low cost. In 1950s, air injection was initiated in a heavy oil reservoir by means of in situ
combustion (ISC)\textsuperscript{7} and then piloted in the Sloss light oil reservoir in 1963.\textsuperscript{5} As for the latter, air is used to oxidize the light crude at reservoir temperature to generate flue gas that will displace the formation of oil to the producer under near-miscible conditions.\textsuperscript{9} This research mainly focuses on the air flooding applied in light oil reservoirs. Physically, the low-temperature oxidation (LTO) between light oil and oxygen dominates the successful application of air flooding in light oil reservoirs. Therefore, it is essential to identify the inherent reactions associated with the LTO processes prior to designing and optimizing an air flooding project in a technically feasible manner.

So far, extensive efforts have been made to quantify the LTO reaction through investigating the changes in gas composition and system pressure before and after the reaction.\textsuperscript{10,11} It is found that part components of the crude oil can be oxidized to oxygenated hydrocarbon compounds (eg, aldehydes, ketones, and alcohols) which can be further oxidized to carbon oxides such as CO\textsubscript{2}.\textsuperscript{11} However, both the main components involved in the LTO reaction and the differences associated with the oxidation characteristics among different components have not been well understood. To quantify the oxidation characteristics of crude oils, thermal analysis such as thermogravimetric analysis and differential scanning calorimetry (TG-DSC), pressure differential scanning calorimetry (PDSC), and thermogravimetric analysis coupled with Fourier transform infrared spectrometer (TG-FTIR) have been applied to investigate the oxidation properties of crude oil and its SARA fractions,\textsuperscript{10,12-32} as summarized in Table 1. Also, this table tabulates the reaction modes and characteristics during the combustion of light and heavy oils, the kinetics and thermochemical parameters of each reaction mode, the differences of oxidation characteristics between light, medium, and heavy oils, the oxidation relationship of crude oil and SARA fractions during the combustion process, and the combustion process of asphalt binder and its SARA fractions, respectively. So far, the oxidation process of light oil, especially the LTO process of light oil and its SARA fractions, has not been fully identified, and the LTO mechanisms and reaction model require a systematic and comprehensive analysis.

In this paper, experimental and theoretical techniques have been developed to identify the LTO mechanisms for light oil during air flooding by comprehensively analyzing the thermal stability and oxidation process of crude oil and its SARA fractions. Experimentally, the TG-DSC tests are conducted to determine the thermal stability by analyzing the changes of weight loss and exothermic behavior. By applying TG-FTIR tests, the real-time oxidation products of crude oil and SARA fractions are then determined to identify the key factors dominating the LTO reaction process. Theoretically, the relationship of oxidation property between crude oil and its fractions is analyzed, and then, a reaction model based on the peroxidation theory and the free radical reaction theory is developed to reproduce the LTO mechanisms.

2 EXPERIMENTAL

2.1 Materials

In this study, a light oil produced from a tight reservoir in the Changqing oilfield in China is collected and used to conduct the experiments. Physical properties of the oil and its SARA fractions are tabulated in Table 2. It is worthwhile noting that the oxidation of asphaltenes is not included in this research due to the fact that the state of asphaltenes in a crude oil is completely different from that of the asphaltenes separated from the crude oil.\textsuperscript{33,34} The air composed of 21.0 mol% oxygen and 79.0 mol% nitrogen is supplied by the Qingdao Tianyuan Gas Company. The neutral alumina, reagent-grade n-pentane, HPLC-grade toluene, HPLC-grade methanol, and HPLC-grade tetrahydrofuran used in the SARA fraction separation are all provided by the Sinopharm Chemical Reagent Co., Ltd.

2.2 Experimental setup

In this study, a vacuum oven (YZF-6032; Shanghai Yaoshi Instrument Equipment Factory), an analytical balance (AB105; Shanghai Precision Instrument Company), and an ultrasonic disperser (Scientz-2400F; SCIENTZ) are used to separate the light crudes into SARA fractions. The operating temperatures of the vacuum oven are from the room temperature to 250°C with its temperature accuracy of 0.1°C and the ultimate vacuum <133 Pa. The maximum scale of the balance is 105 g with its weighting accuracy of 0.01 mg, while the frequency of ultrasonic disperser is 19.5-20.5 kHz.

The experimental setup used in thermal analysis consists of a TG-DSC test system (STA6000; PerkinElmer) and a FTIR spectrometer (Fourier Infrared Spectrometer; PerkinElmer). As for the STA6000, its balance sensitivity is 0.1 μg with calorimetric accuracy ±2%, and temperature accuracy <±0.5%. As for the FTIR spectrometer, the scanning wavenumber precision is better than 0.008 cm\textsuperscript{-1} and the absorbance precision is better than 0.05%.

2.3 Experimental procedures

2.3.1 Separation of SARA fractions

The crude oil was separated into SARA fractions according to a modified analytical procedure used by Freitag et al.\textsuperscript{35} Asphaltenes were recovered from the oil by ultrasonic dispersion in 40 volumes of n-pentane, overnight flocculation, and filtration through 0.8-μm filter paper, while the remaining solvent was removed by evaporation in a
| Source          | Experimental type                                      | Crude oil                                               | Experimental conditions (temperature/pressure)                                                                 | Findings                                                                                                                                                                                                 |
|-----------------|-------------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Xu et al.¹²     | Thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR) | Asphalt binder obtained from Shell Bitumen Co., Ltd. in Guangdong Province, China, with viscosity of 2.6 Pa·s at 135°C | Temperature is increased to 750°C from room temperature at a rate of 5°C/min at atmospheric pressure          | The combustion process of asphalt binder consists of three main consecutive stages at a low heating rate. The release of volatiles occurs mainly at 300-570°C, and the gaseous products at each stage are different. The main products in the 1st stage are CO₂, CO, H₂O, hydrocarbons, formaldehyde, tetrahydrofuran, formic acid, and aromatic compounds. In the next stage, some new volatiles such as alcohols, phenols, and styrene are present. In the last stage, the release amount of CO₂, CO, and H₂O reaches the maximum. Among the above volatiles, CO₂ is the dominant gaseous product in the whole combustion process. |
| Shi et al.¹³    | Thermogravimetry/differential scanning calorimetry-Fourier transform infrared spectroscopy (TG/DSC-FTIR) | Asphalt binder obtained from SK Corp., Republic of Korea, with viscosity of 2.2 Pa·s at 135°C | Temperature is increased to 800°C from room temperature at a rate of 10°C/min at atmospheric pressure         | Combustion reactions of saturates, aromatics, and resins include thermal decomposition of each component and oxidation combustion of charring layer, but asphaltenes only include oxidation combustion of charring layer. Combustion reactions of aromatics are more intense than those of saturates. The total released heat of each component is increased from saturates to asphaltenes. The dynamic evolution and constituents of released volatiles from each component are different, but CO₂ and H₂O are the most important products during the combustion of each component. The morphologies of combustion residues of four components are different. Combustion residues of saturates, aromatics, and resins mainly contain C, O, and a small amount of heteroatoms, while combustion residues of asphaltenes contain less C and more O and heteroatoms. |
| Zhao et al.¹⁴   | Thermogravimetric analysis coupled with mass spectrometry (TG-MS) | Asphalt binder obtained from Lanzhou Petrochemical Company in China | Temperature is increased to 750°C from room temperature at a rate of 15°C/min at atmospheric pressure          | The activation energies of the SARA fractions during the combustion process are different, and the four components have entirely different combustion mechanisms.                                                                                                                 |
| Shi et al.¹⁵    | Thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) | Asphalt binder obtained from SK Corp., Republic of Korea, with viscosity of 2.2 Pa·s at 135°C | Temperature is increased to 800°C from 40°C at a rate of 10°C/min at atmospheric pressure                       | Volatiles released from every combustion stage of each SARA fraction are composed of different hydrocarbon compounds and gaseous products. There are differences in volatile constituents emitted from each SARA fraction at its distinct combustion stages. CO₂ and H₂O are always the two main products in different combustion stages of each SARA fraction. |
| Hao et al.¹⁶    | Thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) | Oil sand bitumen (6.13 °API) derived from Indonesia      | Temperature is increased to 820°C from 28°C at a rate of 10, 20, 50, 80, 120, 200, 500, and 800°C/min at atmospheric pressure | The asphaltenes contribute the most to coke formation of oil sand bitumen. The gaseous products in the main reaction stage predominantly consist of CO₂, CO, methane, ethylene, other light alkanes and olefins, light aromatics, and hydrogen sulfide. The release behaviors of typical gaseous products for oil sand bitumen and its SARA fractions are different due to the different composition and structure. The activation energy of oil sand bitumen ranging from 93.74 to 215.99 kJ/mol in the whole thermal cracking process falls in between that of aromatics and resins. |

(Continues)
### TABLE 1 (Continued)

| Source               | Experimental type                                      | Crude oil                                      | Experimental conditions (temperature/pressure)                                                                 | Findings                                                                                                                                                                                                                                                                                                                                 |
|----------------------|--------------------------------------------------------|-----------------------------------------------|--------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Yuan et al<sup>17</sup> | Thermogravimetry and differential scanning calorimetry (TG-DSC) | Crude oil (29.6 °API) from Vishanskoe oilfield in Russia | Temperature is increased to 600°C from 30°C at a rate of 4, 6, and 10°C/min at atmospheric pressure               | The oxidation behavior of individual SARA component exhibits an obvious difference. Saturates show a weak high-temperature oxidation (HTO) region. Asphaltenes generate more heat in HTO than in the low-temperature oxidation (LTO) region. Aromatics show intense exothermic activity in both LTO and HTO regions. For the crude oil and each fraction, the activation energies of HTO are higher than that of LTO. The additivity of DSC data can be applied quite well in the LTO region. The total heat release of the measured and predicted values is similar, which makes it possible to predict the heat effect of crude oil from individual SARA components |
| Varfolomeev et al<sup>18</sup> | Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) | Heavy crude oil (13.9 °API) from Asha'cha field in Republic of Tatarstan | DSC: Temperature is increased to 950°C from 20°C at a rate of 10, 20, and 30°C/min at atmospheric pressure TGA: Temperature is increased to 750°C from 20°C at a rate of 20°C/min at atmospheric pressure | In DSC experiments, two main reaction regions are detected known as low- and high-temperature oxidation reactions. For all the SARA fractions studied, the highest heat of reaction is observed at lowest heating rate. Activation energy values of the crude oil sample and the fractions vary between 69.2 and 201.8 kJ/mol in LTO region and 82.9 and 182.1 kJ/mol in HTO regions, respectively |
| AlSaffar et al<sup>19</sup> | High-pressure DISC experiment | North Sea light crude oil (36 °API) | Temperature is increased to 753K from room temperature at a rate of 3 K/min at a pressure of 100 bar | The light crude oil tested is sufficiently reactive at near reservoir conditions for air injection to be feasible. The total fuel concentration burned in an air environment is predicted very accurately from the individual neat SARA components. The plot of the individual SARA fractions clearly shows a major contribution from the saturate fraction to both oxygen consumption and fuel deposition for the light oil used |
| Niu et al<sup>10</sup> | Static oxidation experiment; dynamic oxidation experiment | A light crude oil (28.2 °API) and heavy oil (7.2 °API) from the Zhongyuan oilfield in China | Static experiment: 70-150°C, 10-20 MPa; Dynamic experiment: 60°C, 16 MPa | Different oil components exhibit different reaction activities under the LTO conditions. Heavy oils can be more readily oxidized than light oils at low temperatures. Oil compounds with long hydrocarbons are more readily subjected to oxidation at relatively low temperatures than light oil compounds. Temperature, pressure, and additives of water and reservoir sands can significantly increase the LTO reaction rate |
| Kök et al<sup>20</sup> | Differential scanning calorimetry (DSC) | Two Turkish crude oils (32.8 and 31.5 °API) from southeastern part of Turkey | Temperature is increased to 600°C from 25°C at a rate of 5, 10, and 15°C/min at atmospheric pressure | Two different reaction regions are observed from the measured DSC curves due to the oxidative degradation of crude oil components. In the first reaction region, it is deduced that the free moisture and volatile hydrocarbons are evaporated from the crude oils, light hydrocarbons are burned, and fuel is formed. The second reaction region is the main combustion region where the fuel is burned. From the DSC curves, it is observed that, as the sample becomes heavier, the heat of the reaction increases. Saturates give minimum heat of reaction. As the heating rate increases, shift of peak temperatures to high values and extended reaction region intervals are observed |
### Table 1 (Continued)

| Source | Experimental type | Crude oil | Experimental conditions (temperature/pressure) | Findings |
|--------|-------------------|-----------|-----------------------------------------------|----------|
| Li et al\(^{21}\) | Thermogravimetric and differential thermal analysis (TG/DTA) | Eight pure paraffin hydrocarbon samples; Two light crude oil (38 and 30 °API) | Temperature is increased to 650°C from 15°C at a rate of 5°C/min at atmospheric pressure | Each paraffin sample shows different oxidation behaviors at different temperatures. The fractions lighter than C\(_{16}\) are distilled before they reach a temperature where oxidation reactions are significant. Only low-temperature exothermic activities are apparent for the fractions between C\(_{16}\) and C\(_{36}\). The heavier fractions show both low- and high-temperature exothermic activities. The lower molecular weight samples show lower onset temperatures for oxidation reactions. With increasing molecular weight, the exothermic peak temperatures both in the low- and high-temperature regions shift to higher temperatures and increased energy release. The addition of heavier paraffins offers the potential to accelerate reactions and improve ignition of light crude oil. |
| Freitag et al\(^{22}\) | Pressure differential scanning calorimetry (PDSC); tubular flow reactor experiment | A heavy oil (15.8 °API) from the Neilburg field in the Lloydminster region of Saskatchewan; a bitumen (8.3 °API) drawn from the Grand Rapids Formation of the Wolf Lake field in the Cold Lake region of Alberta. | PDSC: Temperature is increased to 580°C from 40°C at a rate of 10°C/min at a pressure of 232 kPa; Reactor experiment: 130-230°C, 30-1300 kPa | For aromatics, resins, and asphaltenes, their pure form can be used to gather LTO reaction rate data for use in modeling. The LTO rate increases in the order of aromatics, resins, and asphaltenes. The LTO rates of the SARA fractions separated from both Wolf Lake bitumen and Neilburg heavy oil are almost the same. |
| Li et al\(^{23}\) | Pressure differential scanning calorimetry (PDSC) | A light oil (42.2 °API), a medium oil (27.9 °API), and an Athabasca bitumen (8.5 °API) | Temperature is increased to 600°C from 20°C at a rate of 5°C/min at pressures from 110 to 6,894 kPa | The increase in pressure promotes oxidations of all crude oils, but the impact is different for light oil and heavy oil. The effect of chemical structure of the samples on their oxidation behavior is significant. The extent of oxidation of hydrocarbon samples is strongly dependent on the nature of the hydrocarbon. The oxidation behavior of a crude oil strongly depends on its composition. |
| Verkoczy et al\(^{24}\) | Thermogravimetric (TG) analysis; pressure differential scanning calorimetry (PDSC); low-temperature oxidation experiment | Tangleflags North oil (12.1 °API), Tangleflags oil (13.0 °API), and the Wolf Lake Grand Rapids Formation oil (9.0 °API) | TG: Temperature is increased to 800°C from 40°C at a rate of 10°C/min at atmospheric pressure PDSC: Temperature is increased to 580°C from 40°C at a rate of 10°C/min at pressures of 233 and 2853 kPa LTO experiment: 225°C, 430-1500 kPa | Low-temperature oxidation has significant effects on the amount of coke formation. Asphaltenes apparently undergo the low-temperature oxidation more rapidly than the other fraction. All the SARA fractions are susceptible to LTO reactions, and saturates display the lowest reaction rate with a broad range of products, while asphaltenes are the most reactive. |
| Source       | Experimental type                                      | Crude oil                                         | Experimental conditions (temperature/pressure)                                           | Findings                                                                                                                                 |
|--------------|-------------------------------------------------------|---------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Kök et al25  | Thermogravimetric analyzer (TG/DTG) and differential scanning calorimeter (DSC) | Garzan crude oil (26.1 °API) and B. Raman crude oil (14.9 °API) from Turkish | Temperature is increased to 600°C from 20°C at a rate of 10°C/min at atmospheric pressure | Saturates do not contribute too much to the HTO reaction. In LTO, asphaltenes are almost negligible as a reactant, and resins and aromatics are moderate in terms of heat release. In MTO, however, the contribution of saturates to the total heat decreases and heavier components such as asphaltenes and aromatics dominate at higher temperatures. In HTO, asphaltenes give a great amount of heat and dominate the process in terms of heat flow. The oxidation of single constituents in combustion is almost independent of the presence of other constituents and they follow their own oxidation pathway. |
| Huang et al26 | Thermogravimetry analysis (TGA)                       | A pure hydrocarbon C20, a Wolfcamp crude oil (40 °API) | Temperature is increased to 400°C from 25°C at a rate of 3, 5, and 10°C/min at atmospheric pressure | The kinetic data obtained from the TGA experiments have no physical meaning, and the practical kinetic data can be obtained by matching the air injection model with the air purging TGA experiments. The light oil air injection process in a low-temperature region can be well defined through the combination of the isomerization reactions and the oxygen addition reactions. |
| Wang et al27  | Thermogravimetry and differential scanning calorimetry (TG-DSC) | Q-131 crude oil (9.0 °API) and D-80 crude oil (9.0 °API) from Liaohe oilfield in China | Temperature is increased to 700°C from 35°C at a rate of 10°C/min at atmospheric pressure | The reaction enthalpy of LTO reactions of heavy oil is comparable to that of the light oil, while the enthalpy of HTO reactions is about 2.5 times that of the light oil. The LTO mechanism can also be applied for heavy oils to utilize the thermal effect, and air injection process in terms of HTO for heavy oils can be more pronounced in comparison with that for light oils. Although the activation energy of HTO reactions is much higher than that of LTO reactions, the reaction rate of HTO can be much larger than that of LTO as a result of the relatively higher frequency factor and reaction temperature. |
| Jia et al28   | Thermogravimetry/derivative thermogravimetry (TG/DTG), differential thermal analysis (DTA) | A light crude oil (44.3 °API) from Keke Ya oilfield in China | Temperature is increased to 650°C from 25°C at a rate of 10°C/min at atmospheric pressure | Keke Ya oil has a favorable exothermic behavior, exhibiting apparent LTO, fuel deposition, and HTO stages. An extended fuel deposition stage is observed by addition of cuttings. Smeecte present in illite/smectite plays a positive role of catalyzing effects for oil oxidation in different reaction regions. Smeecte is ranked first, and illite or chlorite is ranked second, followed by kaolinite, in the aspect of catalytic ability for crude oil oxidation. |
| Pu et al29    | Static oxidation tube experiment; thermogravimetry/differential thermal analysis (TG/DTA) | A light crude oil (33.3 °API) and a heavy crude oil (18.7 °API) from different reservoirs | Static experiment: 90°C, 14-15 MPa; TG/DTA: Temperature is increased to 650°C from 25°C at a rate of 10°C/min at atmospheric pressure | High-content heavy components benefit LTO performance, and heavy oil has better oxidation activity at low temperature and is more easily oxidized. All samples undergo an endothermic reaction during the LTO stage and the faster the LTO rate is, a larger amount of energy is absorbed by oil, and more heat is released in the high-temperature oxidation stage. An excellent consistency is found between thermokinetic analysis and oxidation tube experiment results. |
| Source      | Experimental type                      | Crude oil                                      | Experimental conditions (temperature/pressure)                                                                 | Findings                                                                                                                                 |
|------------|----------------------------------------|------------------------------------------------|---------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| Pu et al   | Isothermal oxidation reactor; thermo-gravimetry (TG-DTG) experiment | Heavy crude oil (17.9 °API) from Tahe oilfield in China |Isothermal oxidation experiment: 120°C, 14-15 MPa; TG/DTG: Temperature is increased to 700°C from 32°C at a rate of 10°C/min at atmospheric pressure | Reservoir core, formation water, and catalyst have important influences on LTO. The upgrading of heavy oil occurs in the presence of catalyst. The inflammable coke is formed, and combustion reaction happens at 40 MPa and 120°C after oxidation for 7 days, which implies heavy oils have a spontaneous combustion potential for HPAI without ignition process in Tahe heavy oil reservoir. Simultaneously, the heavy oil upgrading indicates that HPAI without ignition process in the presence of catalyst is a promising and potential air injection-based IOR technique for deep, high-pressure, heavy oil reservoirs such as the Tahe oilfield |
| Xia et al  | Thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) tests | Asphalt binder obtained from Refinery of Nanjing Petrochemical Co., Ltd., China | Temperature is increased to 800°C from room temperature at a rate of 5, 10, and 15°C/min at atmospheric pressure | Combustion processes of SARA components include the volatilization of light components and the combustion of a charring layer. Thermal stability of SARA components is successively increased from saturates to aromatics, resins, and asphaltenes. There is a lag of combustion processes due to more incomplete decomposition of each component at a higher heating rate. Thermal decompositions of resins and asphaltenes are less affected by the heating rate than those of saturates and aromatics. The release rate and amount of gaseous products are increased at a higher heating rate |
| Xia et al  | Thermogravimetry (TG) and differential scanning calorimetry (DSC) coupled with mass spectrometer (MS) tests | Asphalt binder obtained from Refinery of Nanjing Petrochemical Co., Ltd., China | Temperature is increased to 800°C from room temperature at a rate of 5, 10, and 15°C/min at atmospheric pressure | Combustion processes of resins and asphaltenes only show single-stage exothermic reactions, but other two fractions present obvious multistage combustion reactions. As the heating rate is increased, the incomplete combustion of SARA fractions is increased and more volatiles are released. Main volatiles released from SARA fractions are inflammable, toxic, corrosive, or explosive compounds, and such common volatiles as acetaldehyde and propane are released from each SARA fraction. Volatile release behaviors of saturates and aromatics are more obviously affected by the heating rate. Combustion residues show more intact morphologies from saturates to asphaltenes and mainly contain C, O, and S elements. Asphalt binder is a hazardous material at high temperature |
vacuum oven. The fractions of saturates, aromatics, and resins were subsequently separated from the maltenes (ie, the residual oil after removal of asphaltenes) by a modified liquid chromatography procedure on an alumina packing. The saturates were eluted from the alumina column using n-pentane, the aromatics were separated using toluene, and the resins were eluted out with a mixture of 12.5 vol% methanol and 87.5 vol% tetrahydrofuran. Any remaining solvents were removed from the isolated fractions by evaporation in a vacuum oven. During the fraction purification and cooling process, nitrogen was used to prevent the oxidation of SARA fractions.

2.3.2 | TG-DSC tests

Thermal stability of crude oil and each fraction was examined by using the TG-DSC test. In this work, 12 mg oil or its fraction sample was placed in the alumina crucible prior to the TG-DSC analysis. The input gas was composed of 21.0 mol% oxygen and 79.0 mol% nitrogen at a flow rate of 30 mL/min. The samples were then heated from 40°C to 600°C at a heating rate of 4°C/min to examine the changes of weight loss and heat flow.

2.3.3 | TG-FTIR tests

The TG-FTIR tests were conducted to quantify the oxidation process of the crude oil and its SAR fractions. 12 mg oil or its fraction sample was placed in the alumina crucible of the thermogravimetric analyzer, while air with a flow rate of 30 mL/min was used to ensure an oxidation environment. The sample was first heated to 180°C at a heating rate of 50°C/min and then kept at 180°C for 120 min. By using air as a carrier gas, the oxidized volatiles were directly introduced to the IR gas cell of the FTIR spectrometer for online analysis. The gas cell temperature was kept at 180°C, the resolution was set at 1 cm⁻¹, and the scanning range was 500-4000 cm⁻¹. The transfer line between the thermal analyzer and the infrared spectrometer was maintained at 180°C to avoid any condensation of the released gaseous products.

### Table 2: Physical properties of the crude oil sample

| Properties          | Value   | Appearance          |
|---------------------|---------|---------------------|
| Density (g/cm³)     | 0.850   | N/A                 |
| Viscosity at 70°C (mPa.s) | 2.14    | N/A                 |
| SARA composition (wt%) |         |                     |
| Saturates           | 70.91   | Colorless liquid    |
| Aromatics           | 16.07   | Yellow or red sticky liquid |
| Resins              | 9.78    | Brown viscous liquid |
| Asphaltenes         | 3.24    | Black fragile powder solid |

3 | RESULTS AND DISCUSSION

3.1 | Thermal stability

The TG, DTG, and DSC curves of crude oil and its fractions are plotted in Figure 1. The thermal stability can be characterized by the weight loss and heat flow changes at different temperatures, while the temperature ranges of each phase are summarized in Table 3.

During the heating process, the TG curves show a continuous decline (see Figure 1A), while the DTG and DSC curves are fluctuated (see Figure 1B, C). The peaks of the DTG and DSC curves correspond to the rapid weight loss and rapid exothermic stages, respectively. The heating process of crude oil and SAR fractions consists of three main consecutive stages, that is, LTO phase, fuel deposition (FD) phase, and high-temperature oxidation (HTO) phase. This finding is consistent with those documented elsewhere.

The LTO phase mainly occurs distillation and LTO reactions. Due to distillation, the weight loss of saturates reaches 90.9% at the end of the LTO phase. LTO reactions, typically occurring at temperatures below 350°C, consist of oxygen addition reaction and bond scission reaction, and the rate of heat generation and weight loss of the latter is much higher than the former. During the heating process, the oxidation peak first appears in saturates at 339°C, indicating that the reaction mode of saturates is the most prone to change from oxygen addition reaction to bond scission reaction with an increase in temperature. The FD reaction involves the oxidation of pyrolysis products where coke and light hydrocarbons with low molecular weight are generated, accompanied by heat absorption. The FD reaction temperatures of aromatics and resins are higher than that of saturates, and their weight losses and exothermic peaks in FD stage are obviously larger. Combustion is the main reaction at the HTO phase which consumes the coke generated from the FD stage and produces large heat and carbon oxides. At the HTO phase, the starting and peak temperatures of aromatics and resins are higher than those of saturates, and their combustion reaction intensity is much greater than saturates. Resins have the highest heat production at the HTO phase.

The weight loss pattern of crude oil is similar to that of saturates, that is, both weight losses at the LTO phase are above 80%, and the weight loss patterns are similar at both FD and HTO phases. However, the weight loss of crude oil is greater than that of saturates at T < 200°C due to the inherent deviation associated with the separation of SARA fractions. Such hydrocarbon loss occurs the most frequently with saturates because the initial boiling points of the aromatics and resins are much higher. In addition, the heat production of crude oil at the LTO and FD phases is in a good agreement with that of saturates in the DSC tests, though the heat release
Crude oil and its fractions have a measurable heat production at a temperature higher than 50°C, that is, the LTO reactions can occur at \( T > 50°C \). The increase of sample weight at the initial of the TG tests (see Figure 1A) also confirms the existence of the oxygen addition reaction. The peak weight of saturates, aromatics, and resins reaches 100.18, 100.28, and 100.32 wt% at a temperature below 200°C. In addition, the heat release intensity sequence is found to be resins > aromatics > saturates at \( T < 200°C \). Therefore, the oxidation activity of SAR fractions is resins > aromatics > saturates when temperature is lower than 200°C. This finding is consistent with those documented elsewhere. The differences in oxidation activity of SAR fractions are due to the different molecular structures: Resins are a heavy fraction of crude oil, which contains a large number of aromatic rings, alicyclic rings, and kinds of short- and long-chain branches, resulting in a strong polarity and can react with oxygen more easily than light fractions. In addition, resins contain a large number of heteroatoms, such as S and N atoms, and the bond energy of the C-S and C-N bonds is significantly lower than the C-C bond, so the resins are more susceptible to the attack of oxygen. When the temperature is above 200°C, the heat production rate and weight loss rate are both increased dramatically, especially for saturates. This is because the bond scission reactions with higher heat generation efficiency gradually become dominant with an increase in temperature. Therefore, at the initial stage of LTO, aromatics and resins are the important sources for oxygen consumption and heat generation. After the reservoir temperature is increased due to the heat production, the oxidation of saturates is enhanced and gradually dominates the LTO. The content of saturates in a light crude oil is dominant and ensures the stable oxygen consumption during air flooding.

As for a reservoir with good insulation, the reservoir temperature will increase continuously due to the heat generated from LTO reactions. Then, the spontaneous combustion can occur with the reaction mode spontaneously changed to the FD and HTO reactions, during which aromatics and resins dominate the stability of the combustion front.

### 3.2 Oxidation relationship between crude oil and fractions

The additivity rule is used to quantify the connection of oxidation behavior between the crude oil and its fractions. The weight loss of each fraction is summed according to its content in crude oil to obtain the cumulated weight loss, and the same method is used to obtain the cumulated heat flow. The same calculation method is applied in reference. The relationship between the cumulated and measured weight loss and heat flow is illustrated in Figure 2. Obviously, there exists a similar pattern between the cumulated and measured weight loss, though differences remain when temperature is
lower than 200°C (see Figure 2A). This is mainly due to the loss of the light hydrocarbons during the SARA separation. As for the heat flow (see Figure 2B), the cumulated values are close to the measured ones within the test temperature range except those at 130-240°C (loss of light hydrocarbons) and 480-560°C (excluding asphaltene). Asphaltene is the heaviest fraction in crude oil and important source of combustion fuel at the HTO phase.\textsuperscript{16,44} In addition, the interaction between SARA fractions during the reaction is also an important reason for the differences between the cumulated and measured values.\textsuperscript{22}

In general, the cumulated weight loss and heat flow of crude oil based on the oxidation properties of SAR fractions are qualitatively similar with their measured values. As such, it is an effective method to quantify the oxidation characteristics of crude oil by analyzing that of its individual fraction. This finding is consistent with those documented elsewhere.\textsuperscript{19,22}
3.3 | LTO reaction process

The TG-FTIR tests are conducted to quantify the LTO reaction process by describing the dynamic evolution of gaseous products during each fraction oxidation. The TG curves, 3D FTIR, and FTIR spectra of the released volatiles during the oxidation of crude and fractions are analyzed and discussed, respectively.

3.3.1 | Weight loss

The weight loss of crude oil and each fraction at 180°C is depicted in Figure 3. As can be seen, the weight losses of crude oil and saturates are large at the beginning and reach 47.96 wt% and 30.11 wt% at \( t = 10 \) min, respectively. Then, their weight losses slow down, and the residual weights are 38.49 and 40.21 wt% at the end of the test (ie, \( t = 120 \) min). The weight loss at the initial stage is mainly attributed to the distillation of hydrocarbons with low boiling points. The weight losses of aromatics and resins are significantly lower due to their high boiling points. The weight losses of aromatics and resins are only 19.85 and 6.92 wt% at the end of the test. The evaporation of water, carbon oxides, and light oxygenated hydrocarbons produced during the LTO are the contributor for the continued weight loss, especially at \( t > 20 \) min when the evaporation of low-molecular-weight hydrocarbons is terminated. This finding is also supported by the spectra changes of the released volatiles (see Figure 4 and Figure 5). In addition, the sample weight is increased significantly in the first three minutes of the tests (see Figure 3), indicating the existence of oxygen addition reactions at the LTO stage.

3.3.2 | 3D FTIR

The 3D FTIR of crude oil and its fractions can provide the overall information of dynamic evolution of gaseous products in the LTO process (see Figure 4). The absorption peaks in the spectrum represent different functional groups. The 3D FTIR of fractions are obviously different, indicating obvious differences between the LTO processes of each fraction (see Figure 4A-D).

3.3.3 | Gaseous products

FTIR spectra of the emitted volatiles of crude oil and its fractions at different times are selected to analyze the LTO process (see Figure 5A-D).

**Crude oil**

As shown in Figure 5A, in the first 10 min of the test, the released volatiles are mainly hydrocarbons (corresponding to wavenumber 2800-3000 cm\(^{-1}\)) with low boiling points, but the LTO reaction has already occurred at this time. The wavenumber 3400-4000 cm\(^{-1}\) in the spectra at \( t = 2.5 \) min corresponds to the stretching vibration of the O-H bond, which is indicative of H\(_2\)O, phenol, or alcohol. In the fingerprint spectrum region, H\(_2\)O, phenol, and alcohols can be distinguished by the bending vibration of the hydroxyl group. Wavenumbers 1518 and 1701 cm\(^{-1}\) absorption peaks correspond to H\(_2\)O, while the peaks at 650-770 and 1330-1430 cm\(^{-1}\) correspond to phenols and alcohols, respectively.\(^{51}\) Both fingerprints appear in the FTIR spectra of crude oil, but the absorption peaks at 650-770 cm\(^{-1}\) and 1330-1430 cm\(^{-1}\) are weak, indicating a low concentration of alcohol and phenols in the evolved gas. The intensity of the hydroxyl bond is decreased greatly after \( t = 4.1 \) min. Later, the free water in the sample is evaporated completely and the detected water is the product of oxidation reaction. Meanwhile, there exist obvious absorption peaks at 2900 and 1729 cm\(^{-1}\) in the spectra, confirming the presence of carboxylic acid.\(^{51}\) This is also supported by the follow-up tests of the crude oil acidity and the oxygen element content. The acidity is increased from 0.04 mg KOH/g of the original oil to 0.12 mg KOH/g after its oxidation at 120°C for 6 hours, and the oxygen element content is increased from 0.32 wt% to 0.48 wt%. In addition, the weak absorption peak at 1000-1300 cm\(^{-1}\) indicates the presence of a small amount of ether in the evolved gas.

Asymmetrical stretching and bending vibrations of CO\(_2\) occur at 2360 and 670 cm\(^{-1}\), respectively,\(^{42}\) and both absorption peaks are found in the FTIR spectra. CO\(_2\) is originated from decarboxylation of carboxylic acids generated by oxygen addition reaction.\(^{10,51}\) The concentration of CO\(_2\) is increased as the test progresses. Accordingly, the bond scission reactions are intensified. After \( t = 30 \) min, CO\(_2\) becomes the main component of the gaseous products.

The LTO products of crude oil include H\(_2\)O, CO\(_2\), and oxygenated hydrocarbons (eg, carboxylic acids, alcohols, phenols, and ethers). The oxygenated hydrocarbons are the main products at the early stages; however, CO\(_2\) is increased with time and becomes the main gaseous product at the later
stages of the test. Therefore, both oxygen addition reaction and bond scission reaction occur, but the former is dominant at the beginning of the reaction and the latter is gradually enhanced and dominated as time proceeds.

**Saturates**
Similar to crude oil, the main released volatiles of saturates in the first 10 min are hydrocarbons with low boiling points (see Figure 5B). The oxygenated hydrocarbons produced in the LTO of saturates include carboxylic acids and alcohols, but phenols cannot be detected. CO₂ production is significant later of the test. During the LTO of saturates, the oxygen addition reaction and the bond scission reaction also occur simultaneously, and the products consist of H₂O, CO₂, alcohols, and carboxylic acids. Saturates are an important source of carboxylic acid and CO₂ in the LTO of crude oil.

**Aromatics**
Different from saturates, the main gaseous products of aromatics at the initial stage are H₂O and oxygenated hydrocarbons rather than light hydrocarbons (see Figure 5C). Another notable difference is the obvious adsorption peaks at 970-1080 and 1120-1270 cm⁻¹, indicating the presence of aromatic ether in LTO products of aromatics. The products of aromatics during LTO include H₂O, CO₂, phenols, alcohols, carboxylic acids, and ethers. The oxygen addition reaction is prominent at the beginning of LTO, while the bond scission reaction is dominant at later stages. The aromatic ethers produced are an important source of ethers in the LTO of crude oil.

**Resins**
The gaseous LTO products of resins include H₂O, CO₂, phenols, alcohols, carboxylic acids, and ethers, among which H₂O, CO₂, and ethers are the main components (see Figure 5D). Different from saturates and aromatics, both oxygen addition reaction and bond scission reaction are obvious in the entire process of the resins test, and the LTO intensity of resins is higher than that of saturates and aromatics. The ethers produced in the LTO of resins are another major source of ethers in the LTO of crude oil.

In summary, the oxidation characteristics of SAR fractions are the intrinsic determinants of the crude oil oxidation. Saturates, aromatics, and resins are all the sources of the produced H₂O, CO₂, alcohols, and carboxylic acids, whereas ethers are mainly derived from aromatics and resins. CO₂ gradually becomes the main gaseous product with the continuous increase of bond scission reactions.

### 3.4 LTO reaction models

Under reservoir conditions, the oxidation of crude oil and its fractions occur according to the free radical chain reaction...
FIGURE 5  FTIR spectra of released volatiles at different times during (A) crude oil, (B) saturates, (C) aromatics, and (D) resins LTO at 180°C
The LTO mechanisms of crude oil and SAR fractions are reproduced by the peroxidation theory of Bach-Engler and the free radical chain reaction theory of Semyonov, and thus, the corresponding LTO reaction model is established.

The LTO process mainly involves chain initiation reaction, chain propagation reaction, chain degenerate-branching reaction, and chain termination reaction, among which the chain initiation reaction that produces hydrocarbon radicals is not only the most difficult step in the whole oxidation process, but also the key factor causing the reactivity differences between SAR fractions. The radicals at the beginning of the reaction are produced by the action of external energy (e.g., heat), and the reaction formula is shown as follows:

\[ R_s \cdot R_l \rightarrow R_s \cdot + R_l \cdot \quad (1) \]

The chain propagation reactions are mainly the addition reaction and the hydrogen abstraction reaction between hydrocarbon radicals and oxygen molecules or hydrocarbon molecules, and their products are hydrocarbon peroxides and new free radicals listed as follows:

\[ R_s \cdot CH_2 \cdot + O_2 \rightarrow R_s \cdot CH_2OO \cdot \quad (2) \]
\[ R_s \cdot CH_2OO \cdot + RH \rightarrow R_s \cdot CH_2OOH + R_l \cdot \quad (3) \]

In the degenerate-branching chain reaction, the organic peroxides decompose to free radicals such as RO \( \cdot \), then, the free radicals produced can initiate new chain reactions and produce oxygenated hydrocarbons such as alcohols, aldehydes, and carboxylic acids.

\[ R_s \cdot CH_2OOH \rightarrow R_s \cdot CH_2O + OH \quad (4) \]
\[ R_s \cdot CH_2O \cdot + RH \rightarrow R_s \cdot CH_2OH + R_l \cdot \quad (5) \]

\[ R_s \cdot CH_2 + O_2 \rightarrow R_s \cdot CH_2OH \rightarrow R_s \cdot CH_2OOH + O \cdot \quad (6) \]
\[ R_s \cdot CH_2 + O_2 \rightarrow R_s \cdot CH_2OH \rightarrow R_s \cdot CH_2 + H_2O \quad (7) \]
\[ R_s \cdot CH + O_2 \rightarrow R_s \cdot C-OOH \rightarrow R_s \cdot C \cdot O \cdot + OH \quad (8) \]
\[ R_s \cdot C \cdot O \cdot + RH \rightarrow R_s \cdot C \cdot OH + R \cdot \quad (9) \]
\[ R_s \cdot C \cdot OH \rightarrow R_s \cdot H + CO_2 \quad (10) \]

The chain termination reactions are mainly the combination of free radicals, which generate oxygenated hydrocarbons (e.g., ethers and alcohols) or high-molecular-weight components, that is,

\[ R_s \cdot CH_2 \cdot + OH \rightarrow R_s \cdot CH_2OH \quad (11) \]
\[ R_s \cdot CH_2O \cdot + R \cdot \rightarrow R_s \cdot CH_2-O-R \quad (12) \]
\[ R_s \cdot + R_l \cdot \rightarrow R_s \cdot R_l \cdot \quad (13) \]

In the aforementioned reaction formulae, -Rs and -Rl can represent an alkyl group, an alkyl side chain containing an aromatic ring or a cycloalkane ring, or an alkyl side chain containing a fused aromatic ring.

With an increase in molecular weight, the C-C bond energy in hydrocarbons is decreased. Then, the C-C thermal stability sequence of SAR fractions is found to be saturates > aromatics > resins. This means that resins are more prone to initiate the chain initiation reaction [ie, Reaction (1)] under the same conditions. Saturates produce the least free radicals due to the high bond energy. Therefore, the LTO activity of the SAR fractions is in this order: resins > aromatics > saturates. The temperature rise can not only promote the chain initiation reaction and increase the initial amount of free radicals, but also accelerate the chain propagation reactions and promote the formation of hydrocarbon peroxides. Therefore, the oxidation reaction intensity increases with the increase of temperature in the DSC tests.

The production of oxygenated hydrocarbons during a LTO process can be explained by the chain degenerate-branching reactions and chain termination reactions. As found in the FTIR tests, the oxygenated hydrocarbons include alcohols, aldehydes, ethers, and carboxylic acids, and these products are related to Reactions (5), (7), (9), (11), and (12). H\( _2 \)O is a by-product of these reactions. The decarboxylation reaction (ie, Reaction (10)) is the main source of CO\( _2 \) in the LTO. As the amount of carboxylic acids formed by chain degenerate-branching reaction increases, the intensity of decarboxylation increases, and the CO\( _2 \) production increases gradually. Since resins contain a large number of aromatic rings and alicyclic rings, resulting in a strong polarity and can react with oxygen more easily, the production of oxygenated hydrocarbons and CO\( _2 \) in LTO of resins is obvious and the reaction intensity of resins is higher than that of saturates and aromatics.

The content of heavy components is increased after the LTO of crude oil, which can be explained by Reaction (13). The combination of two high-molecular-weight free radicals produces hydrocarbon with higher molecular weight, which is an important mechanism for the increase of heavy components in crude oil after the LTO reaction.

4 | CONCLUSIONS

1. Oxygen addition reaction and bond scission reaction exist simultaneously in the LTO of light oil. The former
can occur when the temperature is higher than 50°C, and it shifts to the latter as temperature rises. Saturates have a lower transition temperature than aromatics and resins.

2. The LTO products of crude oil include H₂O, CO₂, carboxylic acids, alcohols, phenols, and ethers. Saturates, aromatics, and resins are all the sources of the produced H₂O, CO₂, alcohols, and carboxylic acids, whereas ethers are mainly derived from aromatics and resins.

3. The LTO products of aromatics and resins are important ways of oxygen consumption and heat generation at the initial stage of air flooding. Subsequently, the oxidation of saturates gradually dominates the air flooding process with an increase in the reservoir temperature.

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CONFLICT OF INTEREST

The authors declare no competing financial interests.

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