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Molecular composition of low-temperature oxidation products of the heavy oil



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ABSTRACT

Low-temperature oxidation (LTO) is the main reaction that affects fuel formation in the *in-situ* combustion process, which has important significance for the subsequent combustion propulsion and the successful extraction of crude oil. In this study, heavy oil was subjected to LTO reactions at different temperatures. Three types of reaction products with varying oxidation depths were characterized in terms of the number of oxygen atoms and the polarity of the molecule to reveal the low-temperature oxidation process of the heavy oil. Ketone compounds and acid polyoxides in the oil phase and deep oxidation products with a higher number of oxygen atoms in the coke were identified with increasing oxidation depth. The experimental results showed that the oxidation reaction of the heavy oil changed from kinetic-controlled to diffusion-controlled in the open oxidation system of the heavy oil as the oxidation depth increased. The oxidation reaction of the oil phase reached a maximum and stable value in oxygen content. The molecular compositions of the ketone compound and acid polyoxide did not change significantly with further increase in reaction temperature. The molecular compositions of the deep oxidation products with a higher number of oxygen atoms in the coke phase changed significantly. The coke precursor molecules with a lower oxygen content and condensation degree participated in the coke formation, and the oxidation reaction pathway and the complexity of the oxidation product component also increased.

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1. Introduction

Recently, how to effectively and economically exploit heavy oil reservoirs has gained increasing attention due to the increasing demand for energy and the exhaustion of conventional oil (Al-Mishaal et al., 2022; Li et al., 2022; Zhao et al., 2019). Due to the sensitivity of heavy crude oil to high temperatures, researchers have conducted many laboratory and field investigations on enhanced oil recovery (EOR) technology, among which *in-situ* combustion (ISC) has been regarded as a potentially effective method of EOR so far (Castanier and Brigham, 2003; Sur, 2023; Wang et al., 1998; Xia et al., 2003; Zhao et al., 2023).

Based on the chemical reaction, the ISC process can be divided into three main phases: low-temperature oxidation (LTO), fuel deposition, and high temperature oxidation (Belgrave et al., 1993; Huang and Sheng, 2017; Kok and Gundogar, 2013; Li et al., 2017). Oxidation reactions have attracted considerable interest for thermally enhanced oil recovery applications (Ushakova et al., 2022). LTO is known to be extremely complex due to the simultaneous occurrence of many complex oxidation reactions in this phase. The oxidized distillate and its condensed mixture have a key influence on the formation of coke and directly determine the progress of the combustion and sustainability of the combustion front. For these reasons, many thermal analysis techniques, such as thermogravimetry (TG), differential scanning calorimetry (DSC), accelerated rate calorimetry, and TG coupled with Fourier transform infrared spectroscopy (TG-FTIR), have been used to extensively research the LTO characteristics of crude oils (Berna et al., 2013; Greaves et al.,

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2000; Kok and Karacan, 2000). TG and DSC curves have been used to investigate the weight loss and temperature dependence of the heat flow. Yuan et al. (2019) studied the LTO behavior of heavy crude oil via TG and DSC. TG-FTIR can be used to monitor the weight loss behavior of oxidation and to characterize the chemical composition of the gas products produced in the reactions. In recent years, Tu and Yuan (2018) and Zhang et al. (2019) used this method for investigating the oxidation behavior of crude oil. Ushakova et al. (2022) investigated the differences in the oxidation reactions between heavy and light oils at low and high temperatures, and proposed the oxidation chain reaction mechanism including the formation behavior of free radicals and hydroperoxides. Considering that coking via oxidation of heavy oil is continuous, the precursor that forms the deep oxidation products in the coke phase should exist in the polar components of the oil phase. Compared to the gas generated in oxidation, more significant information about the LTO reaction can be provided by studying the changes in the oil properties induced by LTO. Some researchers have adopted static oxidation experimental devices, such as the sequencing batch reactor (SBR) to oxidize oil samples at different temperatures. Then, the oxidized oil was subject to a series of bulk property and chemical composition analysis, including density, viscosity, acidity, coke content, and saturation-aromatic-resin-asphaltene (SARA) composition. After LTO, the saturated and aromatics hydrocarbons decreased, while the resins and asphaltenes increased (Wang et al., 2015). Although these observations increased our understanding of the properties of LTO, a better understanding in reaction mechanism requires in-depth molecular composition analysis of the complex crude oil (Orrego-Ruiz et al., 2023).

In the last 20 years, considerable researches have been conducted on the molecular composition of petroleum fractions through a combination of high-resolution mass spectrometry and various ionization technologies, which provides a series of new understanding on petroleum chemistry (Cho et al., 2015; Rodgers and McKenna, 2011; Shi et al., 2021). However, the LTO of heavy oil is a very complex reaction. It is hard to comprehensively characterize the oxidation products at the molecular level. Research has shown that the LTO of heavy oil produces a series of oxidation products, such as ketones, fatty acids, and phenolic compounds (Burger and Sahuquet, 1972). It has been found that the number of oxygen atoms in a molecule can reach 13 in the toluene extract of oxidized coke (Li et al., 2022).

In this study, the molecular composition was characterized by using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to reveal the chemical changes in the oxidation process. The mechanism of LTO reactions was discussed according to the molecular composition.

2. Experiments

2.1. Samples

The crude oil was obtained from the Hongqian area of the Karamay Oil Field (Xinjiang, China). The crude oil was numbered as #1, and the remaining solid residues in the tank were collected as the final product. The LTO products obtained temperatures of 170, 220, 270, and 320 °C were numbered as #2, #3, #4, and #5, respectively. The crude oil from this oil field has been well characterized in previous studies (Li et al., 2022; Ma et al., 2023; Zhang et al., 2021).

2.2. Oxidation process

The tank reactor shown in Fig. 1 was used to research the LTO process of the crude oil, and its specifications have been reported in

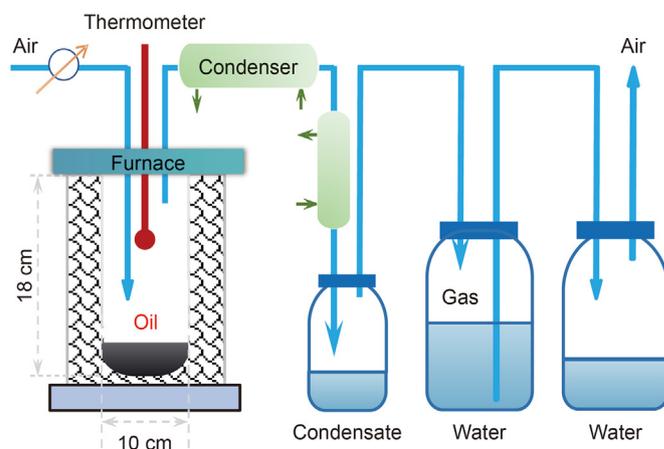


Fig. 1. Schematic diagram of the instrument used to conduct the low-temperature oxidation experiments.

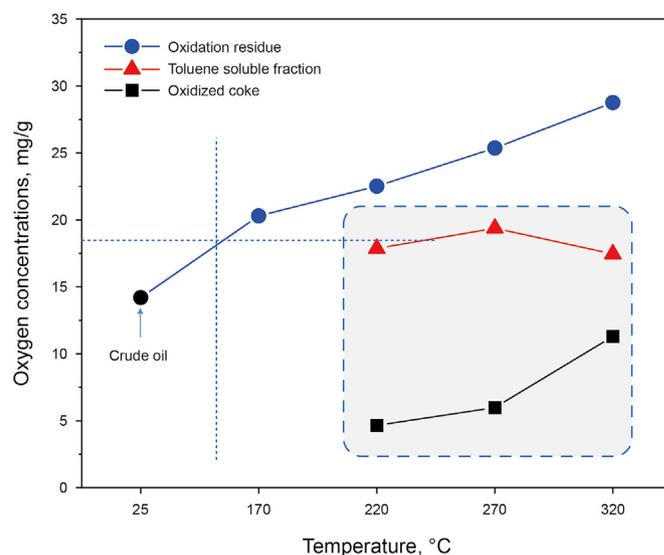


Fig. 2. Oxygen concentrations in the oxidized residues. The values of the 220, 270, and 320 °C products were calculated by the total oxygen in the toluene soluble fraction and the coke. The values in the dotted box refer the mass ratio of oxygen in the subfractions (toluene soluble and insoluble) accounts for the mass concentration of the total oxidation residue.

a previous study (Li et al., 2022). The reaction unit was an open system, the atmosphere was air, the gas injection rate was 100 mL/min, and the reaction time was 2 h. During the experiment, the samples were heated from room temperature to the target temperature. The gas phase temperatures controlling the reaction were 170, 220, 270, and 320 °C, representing the four different stages of the LTO reaction.

2.3. Separation of polar fractions from the asphaltenes and oxidation products

Oxidation products were extracted by Soxhlet extraction with toluene. The toluene insoluble fractions were defined as oxidation coke. *n*-Heptane asphaltenes of the crude oil were separated according to the standard method of ASTM D3279. The asphaltenes and the oxidation cokes were extracted by methanol by microwave enhancement. The extracts were further purified by PPL solid phase extraction (SPE) to remove inorganic salts from the polar fractions

Table 1
Element contents of the crude oil and its oxidation products.

No.	Samples	C, wt%	H, wt%	O, wt%	N, wt%	H/C	O/C
#1	Crude Oil	85.91	12.38	1.42	0.28	1.73	0.012
#2	170 °C Oil	85.72	12.58	2.03	0.28	1.76	0.018
#3	220 °C Oil	86.42	12.18	1.87	0.28	1.69	0.016
#4	270 °C Oil	86.22	11.81	2.10	0.24	1.64	0.018
#5	320 °C Oil	86.68	11.45	2.12	0.21	1.58	0.018
#6	220 °C Coke	79.52	7.65	10.55	0.81	1.15	0.100
#7	270 °C Coke	83.59	7.78	7.57	0.46	1.12	0.068
#8	320 °C Coke	85.45	7.67	6.03	0.28	1.08	0.053

Note: #3 oil refers to the oil-phase component acquired from sample #3 through dissolution with toluene, and #6 coke refers to the oxidized coke in sample #3 that insoluble in toluene.

of the asphaltenes and the oxidation products (Li et al., 2020). Molecular compositions of the separated polar fractions were characterized by negative-ion ESI high-resolution mass spectrometry.

2.4. Chemical composition analysis

Two elemental analyzers (Vario EL Cube, Elemental Analysis, Germany) were used to measure the contents of the C, H, and O according to Chinese industrial standard SY/T 5122 (Analytical Method for Carbon, Hydrogen, and Oxygen Elements in Rock Organic Matter). The total nitrogen content was measured according to Chinese industrial standard NB/SH/T 0704-2010 (Standard Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-inlet Chemiluminescence). Saturates, aromatics, resins, and asphaltenes (SARA) analysis was conducted according to Chinese industrial standard SY/T 0509–2010 (Measurement Method for Four Components of Petroleum Asphalt). The acidity of the crude oil was determined via the potentiometric titration method in accordance with standard GB/T 18609-2011 (Determination of the Acidity of Crude Oil). The viscosity of the crude oil was determined according to the standard method SY/T 0520–2008.

2.5. Molecular characterization by FT-ICR MS

Molecular characterization of the crude oil and its oxidation products was carried out by a Bruker Apex-Ultra FT-ICR MS equipped with a 9.4 T magnet. The operation and data processing

have been described elsewhere (Shi et al., 2013). Briefly, the oil was diluted with toluene to a concentration of about 10 mg/mL and further diluted with toluene/methanol (3:1) to a concentration of about 0.2 mg/mL for electrospray ionization (ESI) analysis. For +ESI, 10 μ L of formic acid was added in one mL sample solution to facilitate the ionization and eliminate the formation of sodium ion adducts. The solution was pumped into the ionization source using an injection pump at 180 μ L/h. The operating conditions of positive-/negative-ion ESI analysis were as follows: spray shield voltage, -4.0 kV/ $+3.0$ kV; capillary entrance voltage, -4.0 kV/ $+2.5$ kV; capillary column end voltage, -280 V/ $+280$ V. The quadrupole (Q1) was optimized at 180 Da to obtain a broad range for ion transfers. The ions accumulated in the collision cell for 0.6 s and were transferred into the analysis cell for an ion injection time of 1.0 ms. The recorded mass range was m/z 200–800. A total of 128 consecutive scans were accumulated for each spectrum to improve the signal-to-noise ratio (S/N).

3. Results and discussion

3.1. Properties of the sample

The crude oil has a viscosity of 1650 mPa·s (50 °C) and an acidity of 5.63 mg KOH/g. The SARA composition of the crude oil is as follows: 53.21 wt% saturates; 22.20 wt% aromatics; 24.04 wt% resins; and 0.50 wt% asphaltenes.

The oxygen concentration in the crude oil and its oxidation products (residue in the reactor, include the oil and coke) are presented in Fig. 2. The oxidized cokes deposited from the oil phase were separated from samples #3–5, and the yield coefficients increased with increasing reaction temperature, namely, by 4.5, 7.7, and 17.6, respectively. Sample #2 remained an oxidized oil with all of the toluene dissolved and no oxidized coke formed. The compositional analysis results of the crude oil, toluene soluble fraction, and oxidized coke are presented in Table 1. With further oxidation, the unsaturation degree of the oil phase products continued to increase, and the hydrogen-to-carbon ratio decreased from 1.76 to 1.58, which was mainly the result of the distillation loss of the light components and the oxidation reaction. It should be noted that the oxygen content of sample #2 was the highest (2.03%). With increasing temperature, oxidized coke formed in sample #3, and the oxygen concentration reached 10.55%. At this condition, the oxygen concentration of the oil phase decreased to 1.87%. This indicates that the oxygen in the product was transferred from the oil phase to the coke phase as the degree of oxidation increased. A mass balance of the total oxygen concentration in the reactor was conducted, and the results are shown in Fig. 2. With increasing reaction temperature, the mass fraction of the total oxygen in the reactor continued to increase. When the reaction temperature was greater than 170 °C, the oxygen in the product in the reactor was enriched in the coke phase, and the mass fraction of the oxygen in the toluene soluble fraction stabilized at around 19 mg/g oxidation residue. The absolute mass fraction of the oxygen in the oxidized coke increased as the temperature increased. This indicates that the low-temperature oxidation reaction of heavy oil in an open system can be divided into two parts according to the different phase states, namely, the soluble oil phase oxidation reaction and the coke phase oxidation reaction. The upper limit of the oil phase oxidation reaction should correspond to the saturation of the surface oxidation of oil phase, which is controlled by the solubility of oxygen in the oil. At this point, the reaction may transition from being controlled by reaction dynamics and thermodynamic control to being controlled by diffusion. The oxidation reaction of the coke phase was completely different from the oxidation reaction of the oil phase. The oxygen concentration decreased as the

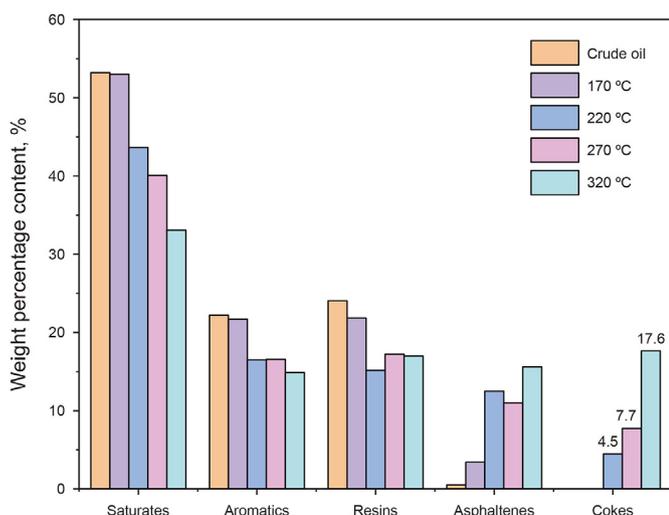


Fig. 3. Diagram showing the changes in the group composition of the crude oil and its oxidation products with temperature.

temperature increased, indicating that the oxidation path of the heavy oil increased and the composition of the coke precursor changed. Although no repeated experiments were conducted to verify this data due to the limitations of the instrumental conditions, the overall variation trend of the results should be credible.

The group composition of saturates, aromatics, resins, asphaltenes, and coke in the crude oil and the oxidation residues are shown in Fig. 3. With increasing reaction temperature and increasing oxidation degree, the contents of the saturates and aromatics in the reactor decreased continuously, and the contents of the asphaltenes and oxidized coke increased continuously. The new resins generated by the oxidation of the hydrocarbons can make up for the loss of the original (#1) resin components in the oxidation process to a certain extent. Thus, the total amount of resins increased slightly within the temperature range of 170–270 °C. It should be noted that the resin content decreased significantly within the temperature range of 270–320 °C, and the contents of the asphaltene and oxidized coke increased significantly. In particular, the content of the oxidized coke doubled from 7.7% to

17.6%. This indicates that the oxidation reaction of the heavy oil changed greatly within this temperature range, which is consistent with the conclusion based on the mass balance of the oxygen.

3.2. Molecular composition of the crude oil and its oxidation products characterized by +ESI FT-ICR MS

The crude oil and the oxidation products in the reactor were analyzed via +ESI FT-ICR MS and the results are shown in Fig. 4. Positive-ion ESI selectively ionize basic nitrogen compounds and ketones in the oil (Shi et al., 2021). N1 (compounds have one nitrogen atom in each molecule), N1O1, N1O2, O1, O2, O3, O1S1 compound classes were assigned from the mass spectra according to the accurate mass values. The N1 compound class is corresponding basic nitrogen compound, which is usually the most abundant compound class in +ESI analysis; the O1 compounds should be ketones because ketones are respond to positive-ion ESI. It should be noted that the O2 and O3 compound also could be acids and/or alcohols/phenols, but at least one oxygen should be in

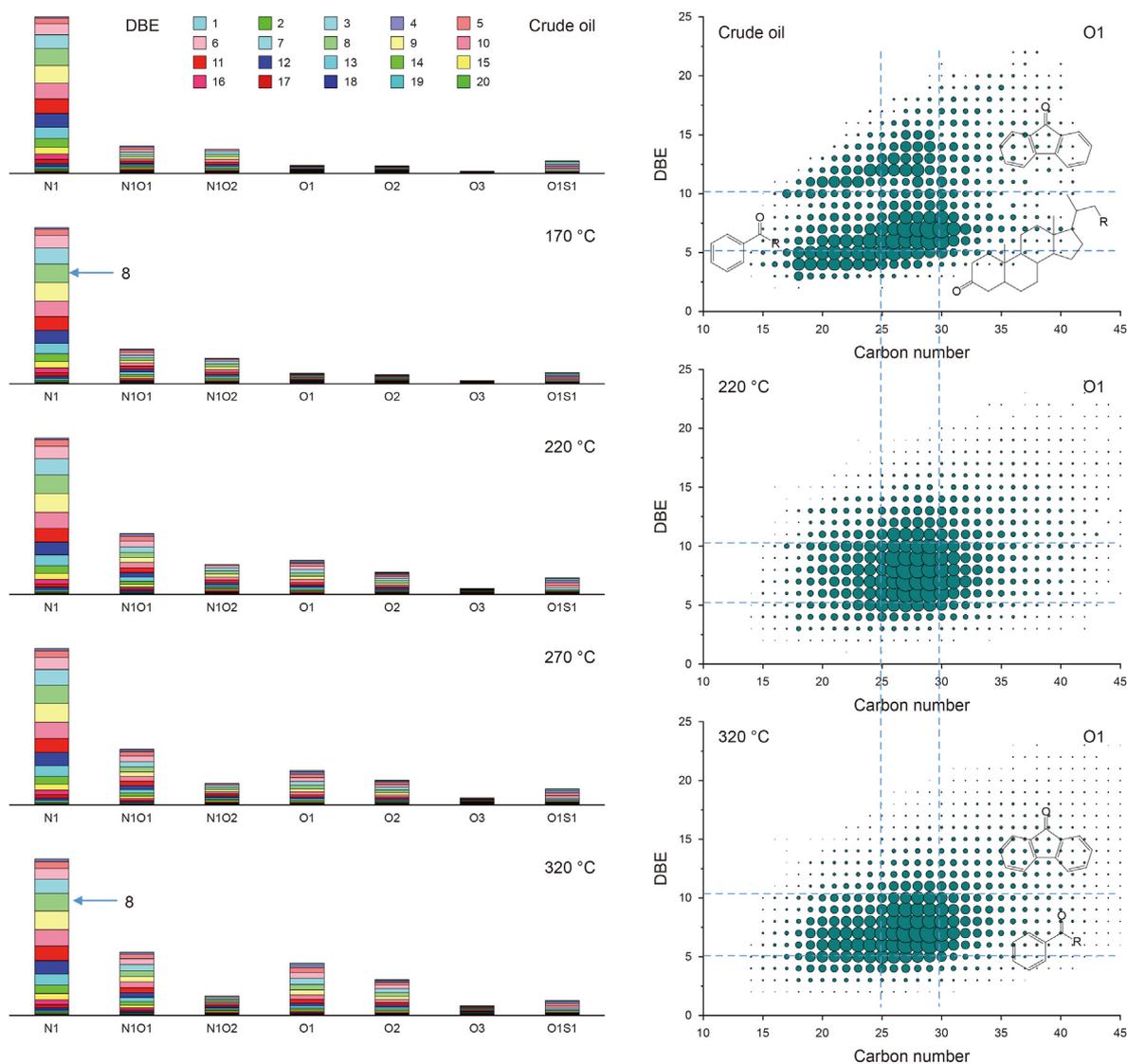


Fig. 4. Relative abundance of heteroatom compound classes of the crude oil and its oxidation products assigned from the positive-ion ESI mass spectra (left), and relative abundance plots of DBE versus carbon number of the O1 compound class species of the crude oil and its 220 and 320 °C toluene soluble oxidation products (right). Molecular structures are suppossed by DBE values.

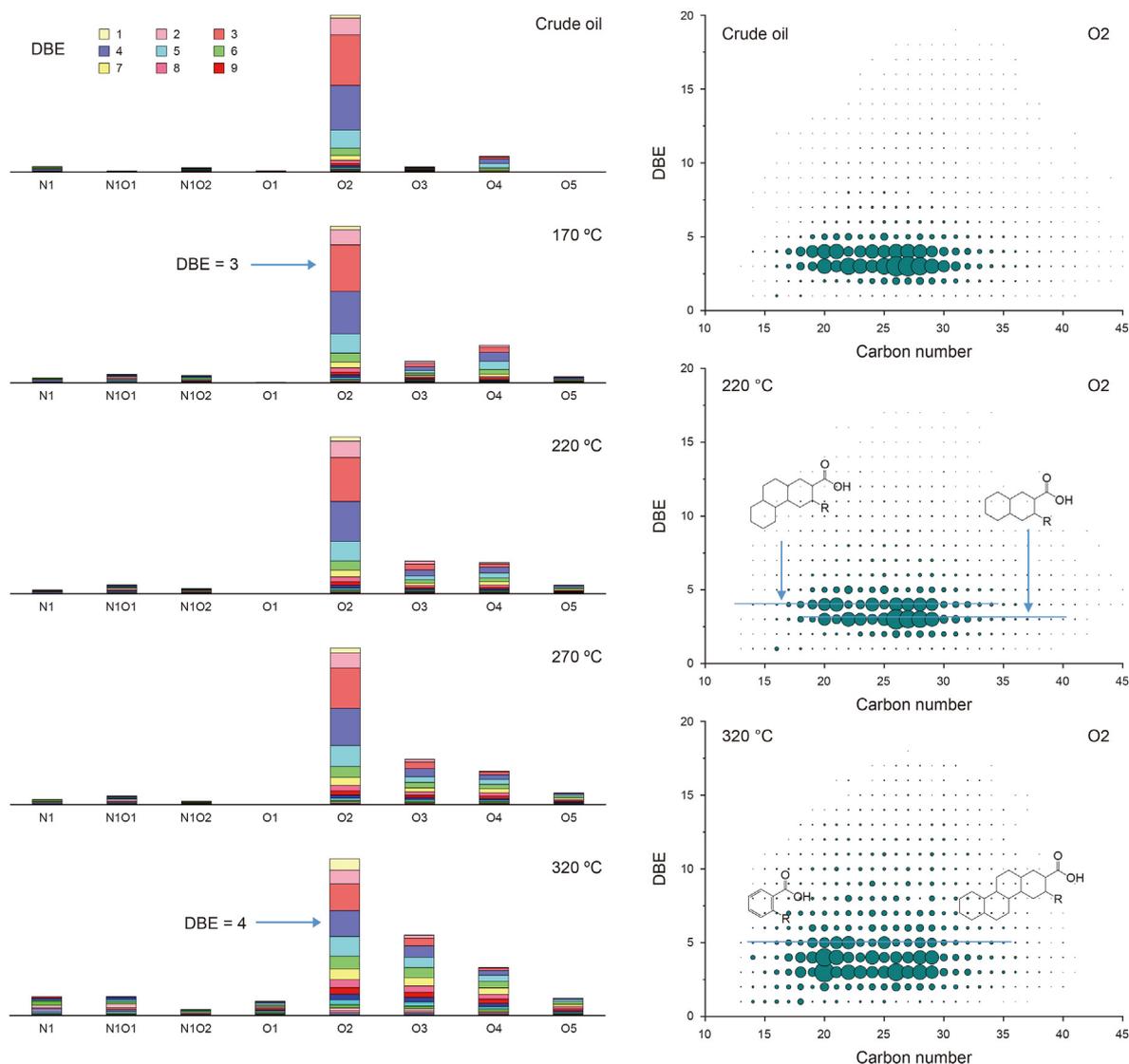


Fig. 5. Relative abundance of heteroatom compound classes of the crude oil and its oxidation products assigned from the negative-ion ESI mass spectra (left), and relative abundance plots of DBE versus carbon number of the O2 compound class species of the crude oil and its 220 and 320 °C toluene soluble oxidation products (right). Molecular structures are supposed by DBE values.

carbonyl. Considering that the N1 compounds only likely to be oxidized into other compound classes but not increased in the oil, the changes in relative abundance of O1 to N1, or N1O1 to N1 can be used as indicators of oxidation degree. The abundance of O1–O3 compounds increased gradually as the reaction temperature increased. Among them, the O1 compounds were the most abundant. Through comparison of the molecular compositions of the O1 compounds in the samples, it was found that the thermal oxidation of the heavy oil produces new ketone compounds. As shown in Fig. 5, O1 compounds in the crude oil distributes in two areas, one is in a DBE range of 3–8 and another is having DBE values of 10+. The O1 compounds with lower DBE values are more like naphthenones, while those with high DBE values should be aromatic ketones. The proposed structures of the O1 compounds are shown in Fig. 5. In the 220 and 320 °C products, the most abundant compounds are concentrated in an area of 25–30 carbon atoms and 5–10 DBEs. Clearly, these compounds should be mainly aromatic ketones oxidized from aromatic hydrocarbons in the heavy oil. The molecular composition of the O1 compounds did not change significantly as the oxidation temperature increased. The composition of

ketones in the crude oil and its oxidation products has been characterized by the Girard-T reagent derivatization and the orbitrap MS in another paper (Ma et al., 2023). The derivatization largely improved the selectivity and sensitivity in positive-ion ESI for the analysis of ketones in the complex matrix but it had discrimination on high DBE species (DBE \geq 9) (Wang et al., 2018).

3.3. Molecular composition of the crude oil and its oxidation products characterized by -ESI FT-ICR MS

Fig. 5 shows the molecular composition of the crude oil and its oxidation products characterized by -ESI MS. It is known that -ESI is the best ionization technique for the selective analysis of acidic oxygen compounds and neutral nitrogen compounds in petroleum fractions (Shi et al., 2021). Eight compound classes, namely N1, N1O1, N1O2, O1, O2, O3, O4, and O5 were assigned from the mass spectra, in which the O2 class is the most abundant. The O2 class species have DBE values of mainly 3 and 4, which are corresponding to naphthenic acids with 2 and 3 rings, respectively. The significant relative abundance predominance of O2 to N1 indicates high

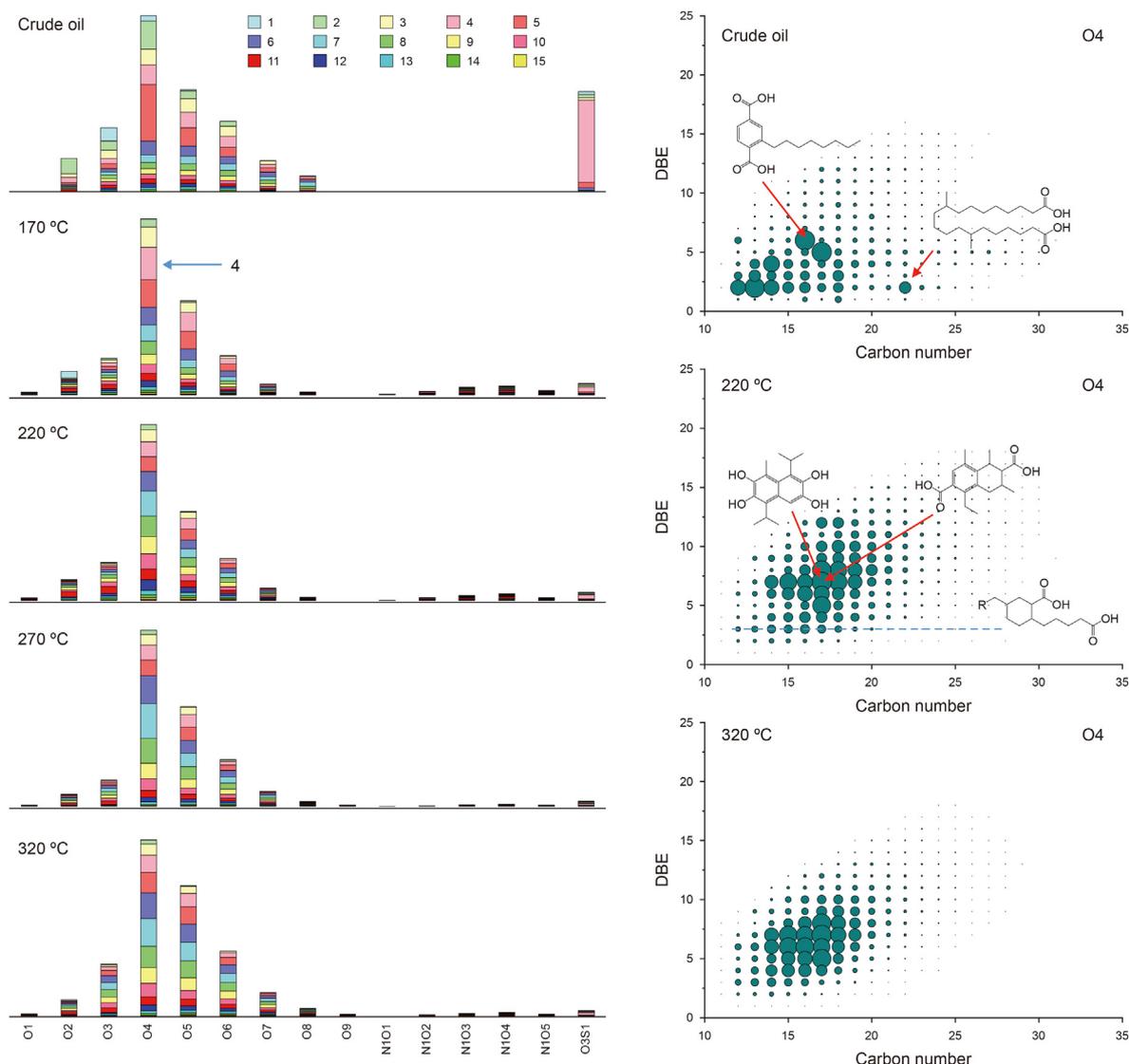


Fig. 6. Relative abundance of heteroatom compound classes assigned from the negative-ion ESI mass spectra of polar fractions extracted from the crude oil asphaltenes and the oxidation products (left), and relative abundance plots of DBE versus carbon number of the O4 compound class species in the polar fractions of the crude oil asphaltenes and its 220 and 320 °C oxidation products (right). Molecular structures are supposed by DBE values.

naphthenic acids in the oil and is consistent with bulk property of high TAN value of the crude oil. The O4 compound class has higher relative abundance than O3 and O5, implies these compounds are dicarboxylic acids, which has been discussed in previous studies.

The major changes in the relative abundance of compounds with the increase of the oxidation temperature are the increase of relative abundance of O3 and O5 compound classes. These compounds should be the oxidation products of the hydrocarbons and the inherent naphthenic acids. As long as a carboxylic or a hydroxyl group exists in the molecule, the additional oxygen atoms could be any other forms such as ketone, aldehyde, ether, alcohol, phenol, acid, and ester. The increase in relative abundance of O3 and O5 compounds classes indicates the oxidation of the oil, however the molecular composition of O2 compound class seems not changed significantly. For the 320 °C product, the predominance of 3 and 4 DBE series is decreased. This could be explained as that some of these compounds were oxidized into hyperoxic compounds because the total relative abundance of O2 is decreased comparing with the N1 compound class.

The polar fraction can be considered as the coke precursor of the

oxidation coke (Li et al., 2022). Polar fractions extracted from the asphaltenes and the oxidized cokes were analyzed by negative-ion ESI FT-ICR MS, the results are shown in Fig. 6. The O2 to O8 compound class species show a high relative abundance in the polar fractions of both crude oil and oxidation cokes, with no significant difference in relative abundance between the crude oil asphaltenes and cokes. Among them, the O4 compounds were the most abundant. As shown in Fig. 6, the molecular composition of O4 compounds is largely different according to the DBE and carbon number distribution between the crude oil asphaltenes and the cokes. Aromatic compounds with multi oxygen atoms are generated in the oxidation. However, the molecular composition of the O4 compounds did not change significantly as the oxidation temperature increased.

Fig. 7 shows the calculated O/C ratio of Ox classes as a function of carbon number of the polar fractions. As the molecule gains more oxygen atoms, the plots shift towards the upper-left corner. Comparing with ketones (oxygen containing compounds detected by +ESI), polar acidic hyperoxic compounds dissolved in toluene soluble fractions should prior to the formation of oxidation coke,

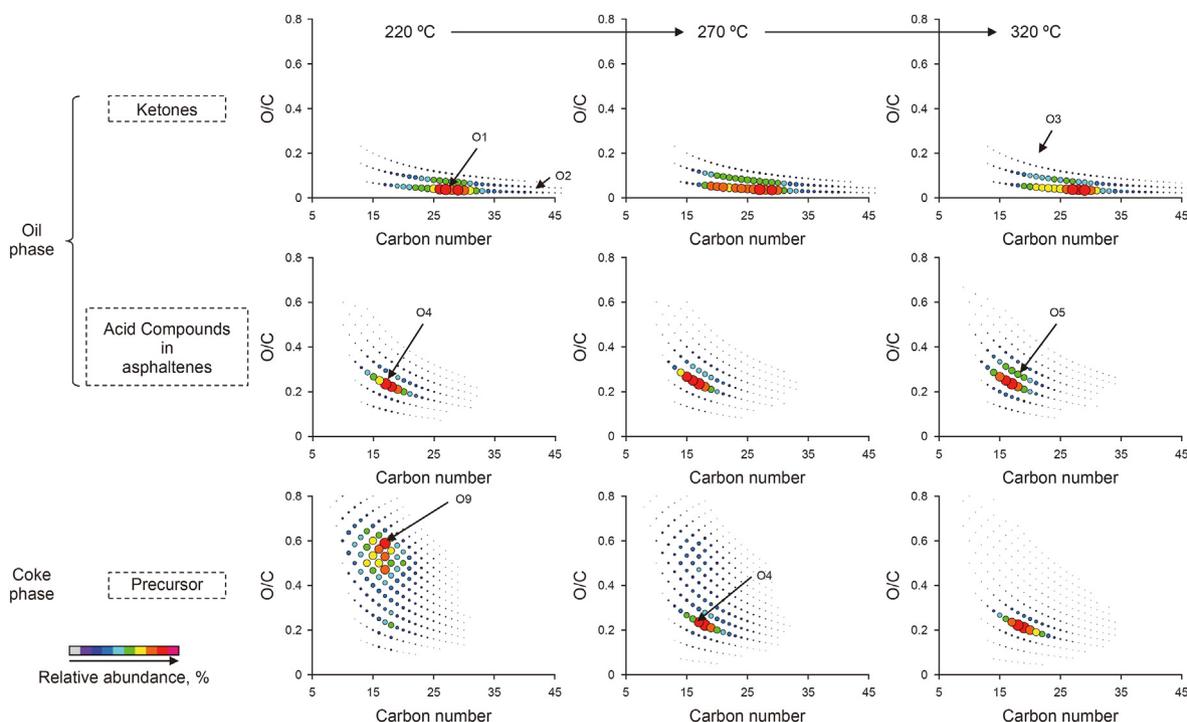


Fig. 7. Plots of the calculated O/C ratio versus carbon number of Ox compound classes in the coke-forming precursors of the crude oil and its oxidation products.

and coke-forming precursors in oxidation coke are methanol-soluble. The oxidation reaction of the heavy oil in the reactor was occurred in the oil phase and coke phase. Before 220 °C, the oil phase oxidation reaction temperature did not reach the upper limit. The molecular composition of the oil phase oxidation product was closely related to the reaction temperature. When the reaction temperature exceeded 220 °C, the oil phase oxidation reaction of the heavy oil tended to equilibrium, which represents a change from reaction dynamics-controlled to surface diffusion-controlled. At this point, the extent to which the coke phase reaction is not affected, and oxidized coke continued to form. As the reaction temperature increased further, the oil phase reaction, which tended toward oxidation saturation and was controlled by diffusion, exhibited no obvious change, while the coke phase reaction exhibited a completely different reaction pathway. The coke precursor had a lower oxygen number and longer carbon chain. The results reveal that the coke phase oxidation pathway varied with increasing reaction temperature, the coke precursor molecules with lower oxygen contents and condensation degrees participated in the coke contribution, and the complexity of the oxidation products also increased with increasing oxidation temperature.

4. Conclusions

Low-temperature oxidation of heavy crude oil was conducted in an open system and the bulk and molecular composition of the crude oil and its oxidation products were characterized to investigate the chemical reaction in the process. Hydrocarbons were oxidized into various oxygen-containing compounds which become asphaltenes and the precursor of coke. The hyperoxic compounds have low thermostability and convert into oxidation coke at higher temperature. The oxygen content in the oil kept a relative low value and had a maximum value at around 220 °C. It was also found that nitrogen compounds are more likely oxidized in the process. The coke obtained at low temperature had high oxygen content and H/C ratio, and a distinct chemical composition

from the coke generated at high temperature. The molecular composition of ketones in oxidation products was different from that of inherent ketones in crude oil, in which aromatic ketones are abundant. The naphthenic acids in the crude oil were survival even at the highest experimental temperature of 320 °C, monocarboxylic acids in the oxidation oils have similar molecular composition with the raw crude oil. Hyperoxic compounds with high condensation degree were the precursor of the oxidation coke. These compounds are mainly small molecules with high molecular polarity, which are easy to precipitate from oil phase to form coke.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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