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Original Paper

Low-temperature oxidation of light crude oil: Molecular composition and deposition characteristics of oxidation products

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ABSTRACT

Air flooding is an important enhanced oil recovery technology for light crude oil development. Low temperature oxidation (LTO) occurs when air is injected into light crude oil, a large number of active substances are generated, which can enhance emulsification between crude oil and water. At the same time, the formation of the deposit may block high-permeability gas channels, improve sweep efficiency, and thereby further enhance oil recovery. In this study, LTO experiments were conducted on light crude oil to investigate the change of molecular composition associated to deposition. The oxidation degree increases significantly with the increase in temperature in LTO. Molecular-scale differentiation of nitrogen and oxygen compounds is characterized in relative abundance and double bond equivalent (DBE) versus carbon number distribution of compound classes using multi-mode ionization Orbitrap MS. Oxygenation and cracking reactions occur simultaneously, with their competitive interplay collectively determining the deposit architecture. The oxygenation reaction results in the emergence of more oxygen compounds containing multiple oxygen atoms in oxidized oil, which are absent in crude oil. The cracking reaction produces small molecular compounds with low carbon numbers and low DBE values, which are adsorbed onto the coke surface of the deposit. The reaction pathways of several typical nitrogen compounds and oxygen compounds are also inferred in this study. This work provides molecular level insights into the mechanisms of LTO in enhancing oil recovery.

1. Introduction

As a new development technology, air injection has been widely used in the development of light crude oil and in situ combustion of heavy oil because of its sufficient resource and low cost advantage (Yuan et al., 2024). Many field implementation experiences have proven that air injection in light crude oil can significantly improve oil recovery by 10%–20% (Liu et al., 2023). The crude oil will occur oxidation reaction when contact air in the reservoir. According to the temperature range, it can be divided into low-temperature oxidation (LTO), medium-temperature oxidation (MTO), fuel deposition (FD), and high-temperature oxidation (HTO) (Qi et al., 2021; Yatimi et al., 2024). In recent years, LTO has been fully investigated by many researchers as an important mechanism of enhanced oil recovery, including composition analysis, oxidation properties, reaction pathways, and kinetic characteristics. LTO could increase viscosity and density of crude oil. These increases are minor and should have an insignificant effect on light crude oil (Fasslhl et al., 1990). However, molecular composition changes a lot because of oxidation reaction and thermal cracking reaction. The products before and after LTO have always been the focus of research and were studied by various analytical instruments using TG/DSC, SARA, GC-MS/GC, FT-ICR MS/Orbitrap MS.

TG and DSC methods have been used to analyze the combustion behavior of the oxidized oils, revealing their thermodynamic characteristics (Qi et al., 2021; Wang et al., 2018; Zhao et al., 2020,

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2021). At the same time, the contents of different fractions in a temperature range can be also characterized. TG/DTG curves show mass loss, which reflects the relative abundance of different fractions in oxidized oils. It was inferred that the oxidizing reaction below 120 °C could not significantly change the contents of light fractions in light crude oil (Qi et al., 2021; Zhao et al., 2021). DSC curves show the heat change. Zhao et al. (2021) found that the peak heat flow mainly occurred at temperature above 350 °C and the thermal effect was notably increased with temperature. This means that the contents of heavy fractions in oxidized oils increase with increasing temperature.

The oxidation behavior was different between light crude oil and heavy oil. Saturates exhibited the highest reactivity in LTO, followed by aromatics, and resins and asphaltenes basically had no loss (Zhao et al., 2020). Therefore, light crude oil oxidized more rapidly, while heavy oil required higher temperatures for oxidation process. Heavy components such as resins and asphaltenes were generated and polymerized, making deposition more likely to occur. Saturates and aromatics were oxidized into resins and asphaltenes continuously with increasing temperature (Liu et al., 2023). However, the influence of oxygen concentration on SARA fractions is different in some studies. Qi et al. (2021) found that when the oxygen concentration increased from 5% to 21% (126 °C, 33 MPa), the relative contents of saturates and aromatics decreased, while those of resins and asphaltenes increased. However, other studies have come to a different conclusion. As the oxygen concentration increased from 6% to 21% (150 °C, 30 MPa), the relative contents of aromatics and asphaltenes decreased, while those of saturates and resins increased (Wang and Wei, 2023).

GC methods have been used to analyze the gas composition and carbon number distribution of oxidized oils. O_2 in the gas is consumed, and CO_2 and H_2 are produced because of cracking reaction during LTO (Hu et al., 2024; Ikpeka and Ugwu, 2023; Okere and Sheng, 2024; Okere et al., 2024a, 2024b, 2025). The content of C_1–C_6 increased due to distillation and thermal cracking reaction (Liu et al., 2023; Xiao et al., 2024). Some studies concluded that LTO did not significantly affect carbon number distributions of either the light or heavy oil (Adegbesan et al., 1987; Fasslhl et al., 1990). Li et al. (2022) used GC-MS to analyze the distribution of ketones and fatty acids. The results indicated that cracking and oxidation reaction occurred in LTO, which tended to produce small molecules.

The characterization of polar compounds in oxidized oils goes beyond the scope of GC. FT-ICR MS/Orbitrap MS is necessary to analyze oxygen-containing compounds such as O1, O2, N1O1, and N1O2 classes (Yan et al., 2024). Liu et al. (2020) found that the nitrogen compounds were relatively stable and the relative abundance of phenolic compounds (O1 class) increased sharply when the temperature increased to 400 °C. Zhao et al. (2021) found that oxidized oils had high relative abundances of fatty acids and 1–3 ring naphthenic acids (O2 class), which decreased when the temperature increased from 40 to 200 °C. Zhao et al. (2025) illustrated the reaction pathways of LTO when considering temperature effect. Qi et al. (2021) detected more polar components containing multiple oxygen atoms in oxidized oils at 126 °C.

In situ combustion causes part of residue components to undergo complex dehydrogenation, cracking, and condensation, resulting in the generation of coke in FD and HTO (Zhao et al., 2020). It may influence oil recovery by partially plugging pore throats. XRD and HRTEM analyses showed that coke mainly consisted of highly disorder amorphous structures and poorly order “onion-like” structures with numerous oxygen functionalities and highly-substituted aromatic rings (Xu et al., 2017). However, some components of light crude oil may be more prone to deposition in LTO, which lead to thermal stability problems. Yet this issue has not been received attention in the development of light crude oil (Jia et al., 2021). The polar compounds produced during the LTO will be deposited due to the similarity and compatibility principle. The oxidation stability of *n*-alkanes decreases with the chain length (Chatelain et al., 2016). Aromatics oxidize more easily to form deposit, thus inhibiting other compounds. The increases in the size and concentration result in a higher deposition propensity because larger aromatics require fewer growth steps to produce deposit precursors than lower molecular (Jia et al., 2021).

In this paper, the molecular composition of oxidized oils and deposit is comprehensively characterized in LTO experiments. The oxidation degree is quantitatively analyzed and the reaction pathways of nitrogen and oxygen compounds are discussed. It will provide implications for optimizing air flooding in light crude oil reservoirs.

2. Experimental

2.1. Low-temperature oxidation and separation of the residue

A light crude oil was collected from a sandstone reservoir (gas measured permeability of 25 mD) in Yuguo Oilfield of Tuha Oil Company. The crude oil has a wax content of 10.4%, a viscosity of 1.1 mPa·s, and a density of 0.82 g/cm^3 (25 °C). The initial temperature of the oil reservoir is 90 °C, and the maximum temperature rises to 120 °C during 5% deoxygenated air injection (5% deoxygenated air was often employed in field operations to reduce safety risks). The experimental equipment for LTO was described previously (Qi et al., 2021).

The experimental procedures are as follows: (1) The vessel was filled with half its volume of the light crude oil, sealed, and evacuated for 3 h using a vacuum pump. (2) 5% deoxygenated air was injected, the temperature was increased to 90, 100, or 120 °C, and then the pressure was supercharged to 30 MPa. (3) The experimental equipment was kept static for 8 d until the pressure was reduced to a constant value, confirming that the reactions had proceeded to completion (Xiao et al., 2024). (4) Gas and solid particles (deposit) at the bottom of the vessel were collected. (5) The composition of the gas and oxidized oils were analyzed using gas chromatography (GC). The detailed settings and data processing procedures were described in a previous study (Zhang et al., 2023). (6) The deposit was extracted with toluene, dichloromethane (DCM), and methanol in a Soxhlet apparatus for 24 h for each solvent.

The extracts and the residue were named Extract-Toluene, Extract-DCM, Extract-Methanol, and Coke-Toluene, Coke-DCM, and Coke, respectively. The flow chart is shown in Fig. 1. Experiments were performed in duplicate, the variability in oxygen consumption and the yields of oxidized oil and deposit was within ±5%. It should be noted that the static oxidation conditions used in this study differ from dynamic oxidation conditions. Compared to dynamic oxidation experiments, the 8-d static oxidation experiments allow the reaction to proceed to a near-equilibrium state under oxygen sufficient conditions. In actual air flooding in reservoirs, the oxidation degree of crude oil is controlled by reaction kinetics, with temperature as the dominant factor.

2.2. Chemical composition analysis

The carbon, hydrogen, and oxygen contents of the crude oil and oxidized oils were measured using an elemental analyzer (Vario EL Cube, Elemental Analysis, Germany) according to the Chinese industry standard SY/T 5122 method. SARA fractionation was performed according to SY/T 5119-2016 method to separate the crude

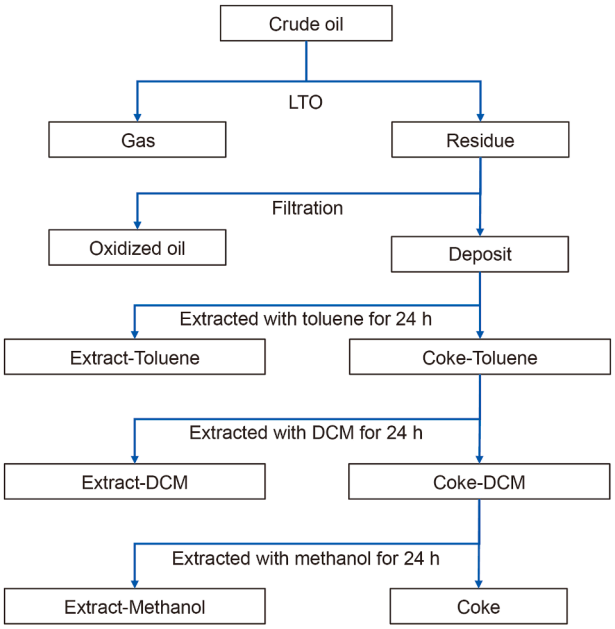

Fig. 1. Flow chart of LTO and the separation of the residue.

oil and oxidized oils into saturates, aromatics, resins, and asphaltenes.

2.3. Molecular characterization by Orbitrap MS

Hydrocarbons in the crude oil and oxidized oils were analyzed using an Orbitrap Fusion MS (Thermo Scientific) equipped with a positive-ion APPI source. For this analysis, about 10 mg of oil sample was dissolved in 1 mL of toluene and infused into the APPI source at 20 μL/min via a syringe pump. Operational parameters were set as follows: flow rates of sheath gas, auxiliary gas, and sweep gas were 20, 5.0, and 0.1 Arb, respectively; the ion transfer tube and vaporizer temperatures were maintained at 300 and 20 °C. Heteroatoms in the crude oil, oxidized oils, and deposits were characterized using both positive-ion and negative-ion ESI sources. Approximately 10 mg of sample was dissolved in 1 mL of toluene and further diluted with toluene/methanol (1:3, v/v) to a final concentration of 20 μL/mL. The solution was introduced into the ESI source at a flow rate of 10 μL/min. The gas flow rates were set to 5.0 Arb (sheath gas), 2.0 Arb (auxiliary gas), and 0.1 Arb (sweep gas), with the ion transfer tube and vaporizer temperatures held at 300 and 20 °C, respectively. Mass spectra were acquired across an m/z range of 130–800, achieving a resolution of up to 550,000 at m/z 150. Data processing and compound identification were performed using Thermo Xcalibur Qual Browser. Although APPI enables the detection of both hydrocarbons and heteroatoms, it may exhibit lower sensitivity toward non-ionizable species. ESI primarily targets heteroatoms, and its sensitivity varies with molecular polarity. The molecular composition analysis of all oxidized oils was conducted under identical detection conditions to ensure repeatability and reproducibility.

3. Results and discussion

3.1. Molecular composition of oxidized oils characterized by GC

Fig. 2(a) shows the gas composition of the produced gas. As the temperature increased, the oxygen content gradually decreased, and the methane and CO_2 contents increased. As the temperature rose from 90 to 120 °C, the oxygen consumption was 4.72%, 4.75%, and 4.78%, respectively. These results indicate that, given sufficient reaction time, the oxygen content determines the oxidation reaction limit. Oxygen consumption significantly exceeds CO_2 generation, confirming that oxygenation reaction is the dominant reaction during LTO. Conversely, the formation of CH_4 suggests that a minor extent of cracking reaction occurs. Fig. 2(b) shows carbon number distributions of hydrocarbons in the crude oil and oxidized oils. Light crude oil contains large amounts of *n*-alkanes, which are difficult to be affected by LTO (Adegbesan et al., 1987; Fasslhl et al., 1990). The oxidation characteristic of *n*-alkanes does not depend on their carbon number (Yuan et al., 2018, 2019). The content of C_1–C_{10} hydrocarbons in oxidized oil is lower than that in the crude oil. The higher the temperature, the stronger the distillation. The volatilization of small molecule hydrocarbons leads to the increase in heavy hydrocarbons in oxidized oils.

3.2. Quantitative analysis of chemical composition of oxidized oils

Element composition of the crude oil and oxidized oils are listed in Table 1. The crude oil has a H/C ratio of 1.9068 and an oxygen content of 0.24%. Compared with the crude oil, oxidized oils have a little higher H/C ratio and a much higher oxygen content. The oxygen content increases by 53.3%, 150%, and 233.3% from 90 °C to 120 °C, respectively. It also shows that the oxidation degree of the crude oil increases significantly and there is a little bit of cracking reaction at different temperatures in LTO. The SARA composition and deposit of the crude oil and oxidized oils are listed in Table 1 based on mass balance calculations. The relative

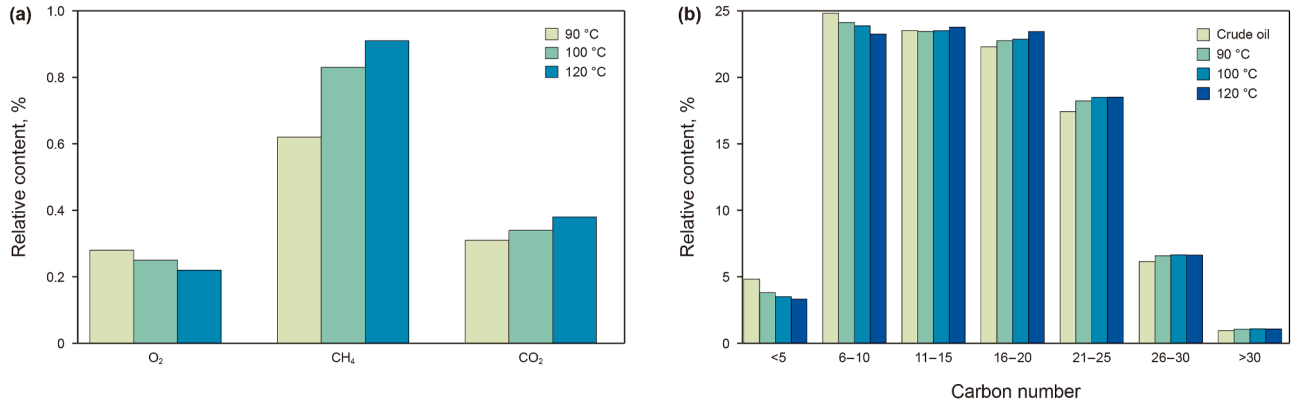

Fig. 2. (**a**) Composition of produced gases; (**b**) carbon number distributions of the crude oil and oxidized oils (oxidation temperature: 90, 100, and 120 °C).

Table 1
Element and SARA composition of the crude oil and oxidized oils.

Sample		Element content, wt%			H/C ratio	SARA analysis, wt%				Deposit, wt%	Volatilization, wt%
		C	H	O		Saturates	Aromatics	Resins	Asphaltenes		
Crude oil		86.47	13.74	0.24	1.9068	45.60	11.45	7.57	3.07	0	32.31
Oxidized oil	90 °C	86.50	13.76	0.44	1.9089	47.18	10.60	7.03	2.98	0.12	32.09
	100 °C	86.27	13.74	0.60	1.9112	48.01	8.61	6.95	2.65	0.34	33.44
	120 °C	86.09	13.78	0.80	1.9208	49.76	7.95	6.84	1.75	0.50	33.20

content of saturates in oxidized oils is higher and the relative contents of aromatics, resins, and asphaltenes are lower compared with the crude oil. When the temperature increases from 90 to 120 °C, the content of saturates in oxidized oils increases and those of the other three fractions decrease. Many studies have demonstrated that oxidation reactions generally lead to decreases in saturates and aromatics, alongside increases in resins and asphaltenes. While Niu et al. (2011) found that heavy oil components (such as resins and asphaltenes) were more easily subjected to oxidation reactions in comparison with light ones at low temperatures (75–150 °C). We hypothesize that cracking reactions may explain this phenomenon, as they typically increase saturates and aromatics while reducing asphaltenes. Furthermore, once deposition occurs, the aromatics are more likely to undergo oxygenation and polymerize with polar compounds in resins and asphaltenes (Jia et al., 2021). Therefore, the relative contents of resins and asphaltenes in oxidized oils are reduced. The molecular composition of the deposit is described in Section 3.3.

Orbitrap MS coupled with APPI ionization source was used to analyze the relative contents of hydrocarbons and nitrogen compounds, as shown in Fig. 3. The relative abundance of CH and N1 classes is lower, while that of oxygen compounds such as N1O1, N1O2, O1, O2, and O3 classes is higher compared with the crude oil. As the temperature increases, the relative abundance of CH class decreases while the oxidation degree gradually rises. Hydrocarbons are gradually oxidized to oxygen compounds such as O1 and O2 classes. This is consistent with the observed decrease in aromatics in the SARA fractions. Concurrently, the relative abundance of N1 class decreases, with progressive oxidation leading to the formation of nitrogen compounds including N1O1 and N1O2 classes.

3.3. Molecular composition of oxidized oils and deposit characterized by Orbitrap MS

The deposit is appeared in the light crude oil after LTO. The deposit after filtration accounts for approximately 0.12%, 0.34%, and 0.50% from 90 to 120 °C, respectively. The higher the temperature, the more deposit in LTO. To study the molecular composition of deposit in more detail, it is extracted successively by toluene, DCM, and methanol, which can provide a useful framework for understanding deposit formation. Yields of the extracts and coke of the deposit are shown in Fig. 4. 80.6% of the deposit is toluene soluble material. About 6.7% can be dissolved in DCM and methanol. The other insoluble material is considered as coke which accounts for 12.7% (Li et al., 2022b). The molecular composition of soluble material is characterized using Orbitrap MS with positive-ion and negative-ion ESI.

The compound classes derived from positive-ion ESI Orbitrap MS are presented in Fig. 5 (oxidized oils) and Fig. 6 (deposit). A total of 19 compound classes were identified, including basic nitrogen compounds (e.g., N1, N1O1, N1O2) and oxygen compounds (e.g., O1, O2, O1Na1, O2Na1). The N1O1, N1O2, N1O3, N1O4, and N1O5 classes were considered as basic nitrogen compounds with phenol or carboxyl groups, which makes the basic nitrogen compounds exhibit acidic property (Pan et al., 2012). Aldehydes and ketones are the major products in LTO (Khansari et al., 2014). The Na1O1, Na1O2, Na1O3, Na1O4, Na1O5, Na1O6, and Na1O7 classes were considered as ketones which have a weak molecular ion peak but a high sodium peak (Chen, 2017). The N1 class is the predominant species in the crude oil, with all other compound classes exhibiting significantly lower relative abundance. Similar to oxygen element, the content of oxygen compounds increases with the increase in temperature of LTO. The N1O3 and Na1O3 classes have a high relative abundance in all classes of oxidized oils. However, Extract-Toluene of deposit is different from oxidized oils in that it has higher relative abundance of oxygen compounds. Based on the sequential solvent extraction behavior and the distinct molecular composition of each extract, we infer a layered deposit architecture consisting of a coke core, an inner layer of adsorbed small polar molecules, and an outer layer of entrained oxidized oil. The relative abundance of nitrogen compounds in Extract-Toluene is higher than that of ketones. Extract-DCM is similar to the crude oil, which means wrapping effect may occur in deposition. Methanol can extract strong polar compounds adsorbed on the surface of coke. The N1 and N1O2 classes are dominant in Extract-Methanol, followed by the Na1O6 class. Further interpretation of the molecular composition is needed to study the reaction pathways of different compounds in LTO.

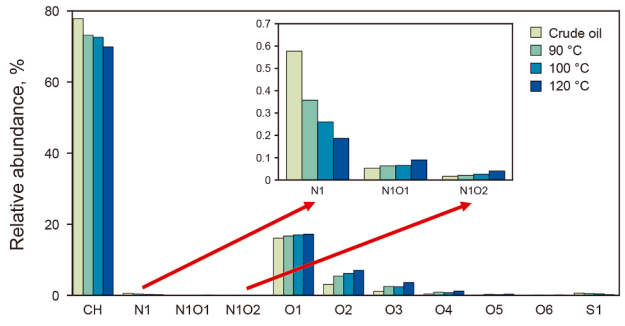

Fig. 3. Relative abundance of compound classes determined by APPI Orbitrap MS of the crude oil and oxidized oils.

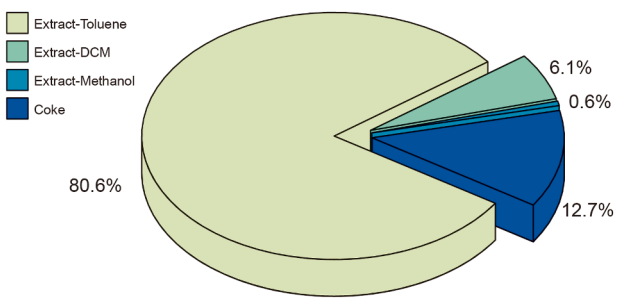

Fig. 4. Yields of the extracts and coke of the deposit.

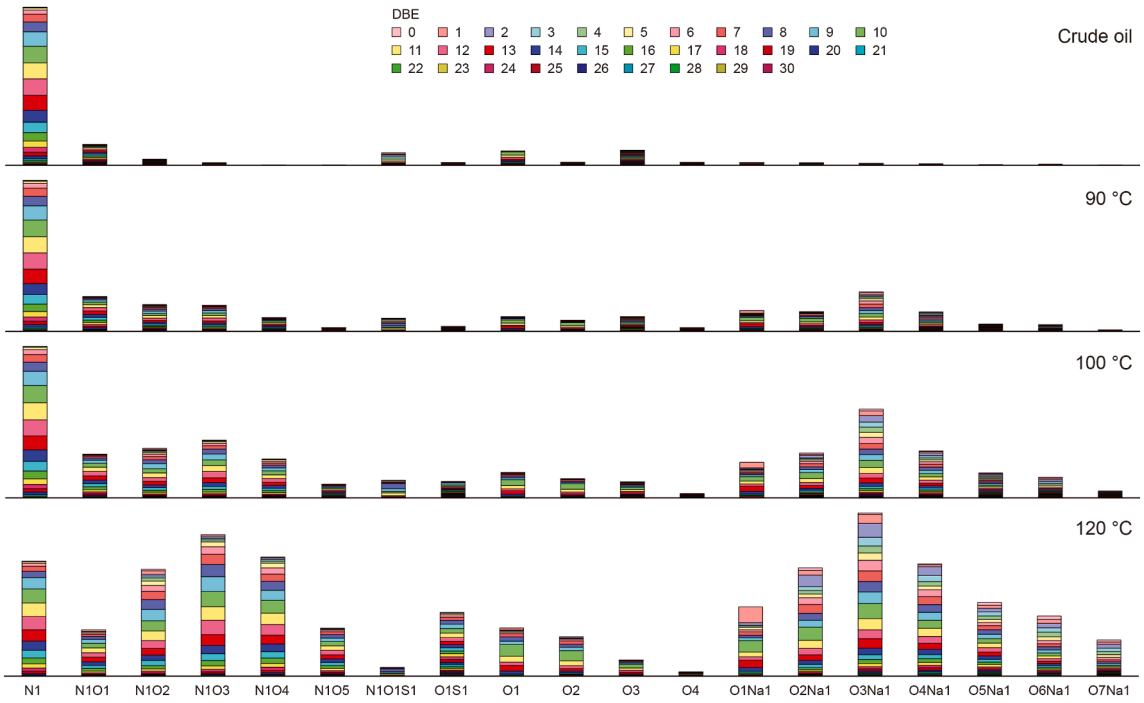

Fig. 5. Compound classes of the crude oil and oxidized oils determined by positive-ion ESI Orbitrap MS.

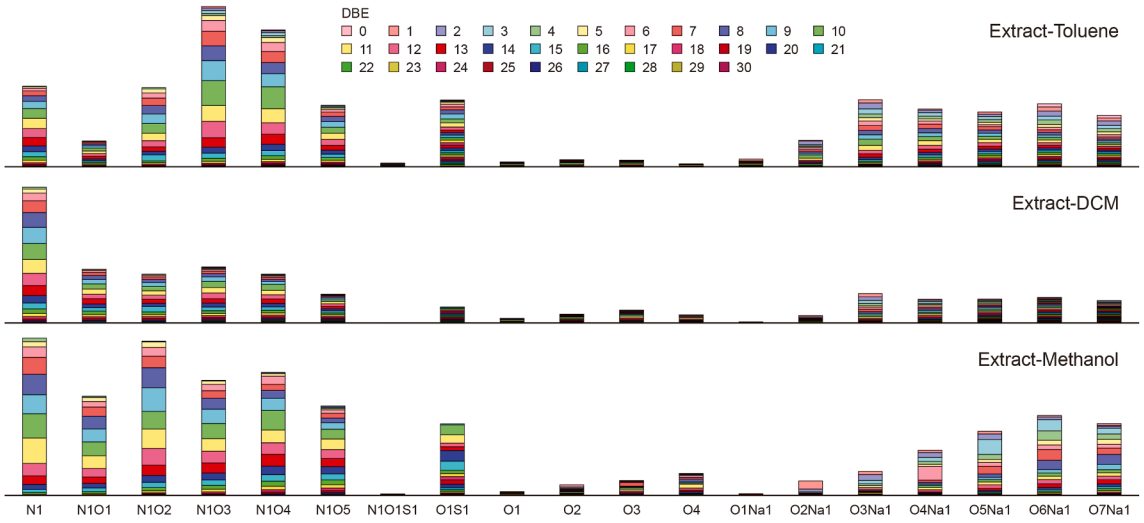

Fig. 6. Compound classes of the deposit (120 °C) determined by positive-ion ESI Orbitrap MS.

The double bond equivalent (DBE) versus carbon number distributions for N1, N1O1, N1O2, N1O3, N1O4, and N1O5 classes are illustrated in Fig. 7, comparing the crude oil, oxidized oils (120 °C), and deposit (120 °C). The molecular formula is clear and the molecular structure needs to be further confirmed. Based on established principles of petroleum chemistry, several representative molecular structures are proposed to facilitate the interpretation of the observed molecular composition. The N1 class is mainly pyridine and quinoline compounds. The N1O1, N1O2, N1O3, N1O4, and N1O5 classes are considered as oxidized products after LTO. The N1O1 class is considered as the intermediates for the oxidation of N1 class, which has phenol group. The N1O2 class is likely to be naphthenic acid compounds containing pyridine groups (Zhao et al., 2021). The N1O4 and N1O5 classes are produced in LTO, which are not detected in the crude oil.

The average carbon number and DBE of all classes are represented to show the changes caused by LTO at different temperatures in Fig. 8. The calculation method has been shown in previous studies (Zhang et al., 2024). With the increase in temperature, the average carbon number and DBE of N1, N1O1, N1O2, N1O3, N1O4 classes in oxidized oils decrease. Cracking behavior occurs in LTO, which is also the conclusion of many studies (Yan et al., 2024). However, basic nitrogen compounds with multiple oxygen atoms such as N1O5 class, require a higher reaction condition for cracking, so oxygenation is the main reaction causing the average carbon number and DBE increase. The distribution of DBE versus carbon number of basic nitrogen compounds is very similar, which may be due to the fact that the oxygenation occurs successively and simultaneously. The oxygenation occurs step by step from N1 class to N1O5 class. Additionally, cracking generates small

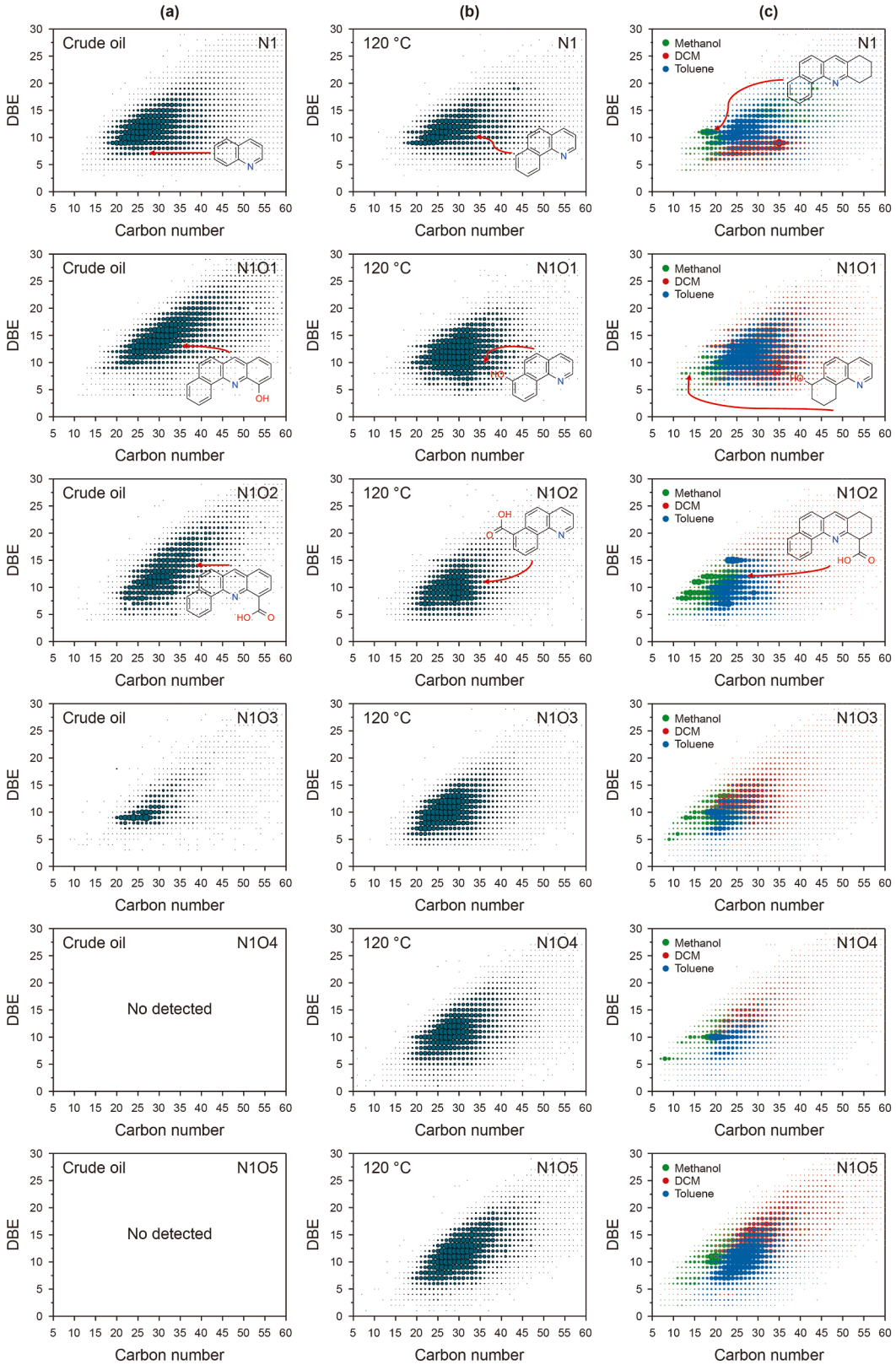

Fig. 7. DBE versus carbon number distributions of basic nitrogen compounds in the crude oil (**a**), oxidized oil (**b**), and deposit (**c**).

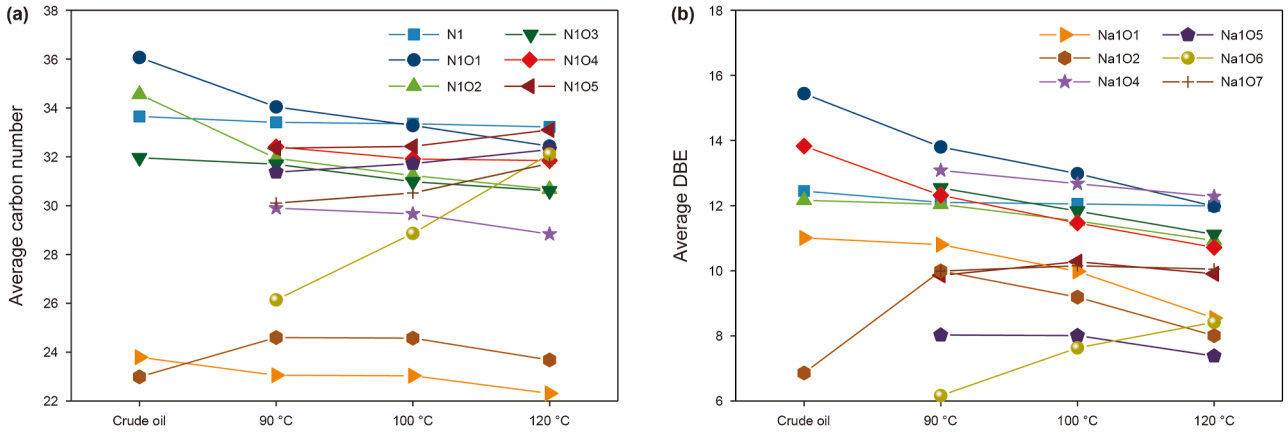

Fig. 8. Average carbon number (**a**) and DBE (**b**) of basic nitrogen and ketone compounds in the crude oil and oxidized oils.

molecular weight nitrogen compounds. Neither the crude oil nor the oxidized oils contain significant amounts of compounds with carbon number below 15. By the separate extraction of toluene, DCM, and methanol, basic nitrogen compounds with small average carbon number and DBE are observed in deposit. Extract-Toluene and Extract-DCM are basically the same as oxidized oils, but Extract-DCM has a higher distribution of carbon number versus DBE than Extract-Toluene. A large number of small molecule compounds with DBE less than 12 and carbon number less than 15 are found in the Extract-Methanol. These small polar compounds may be produced by cracking during LTO and adsorbed on the surface of coke. Based on the observed DBE versus carbon number distributions and established knowledge of petroleum chemistry, we propose plausible reaction pathways of some basic nitrogen compounds (Fig. 9). Oxygenation occurs mainly in the aromatic ring adjacent to the pyridine ring, where a hydroxyl group is introduced and further oxidized to a carboxyl group.

Fig. 10 displays DBE versus carbon number distributions for Na1O1, Na1O2, Na1O4, Na1O5, Na1O6, and Na1O7 classes across the crude oil, oxidized oils (120 °C), deposit (120 °C). Ketones are all considered as oxidized products in LTO because there is none in the crude oil. The corresponding structure of compound with different DBE values are as follows: a DBE of 1 corresponds to aliphatic ketone, a DBE of 2 corresponds to alkyl cyclo-cycloanketone, and a DBE of 10 corresponds to fluorenone, anthrone, and phenanthone (Chen, 2017). Structures of other ketones with different DBE have also been speculated to be on display. The average carbon number and DBE of all classes are represented to show the changes caused by LTO at different temperatures in Fig. 8(b). With the increase in temperature, the average carbon number and DBE of Na1O1, Na1O2, Na1O4 classes in oxidized oils decrease because of cracking occurs in LTO. However, ketones with multiple oxygen atoms (Na1O5, Na1O6, and Na1O7 classes) change different. The average carbon number of Na1O5 increases, while the average DBE decreases. Both of the average carbon number and DBE of Na1O6 and Na1O7 classes increase. These opposing trends are attributed to the competitive effects of concurrent oxygenation and cracking on ketone structures. Oxygenation generally increases the average carbon number, whereas cracking reduces both the average carbon number and DBE. It is noted that this conclusion is true for all classes in oxidized oils. Ketones are unstable and prone to free radical reactions, which can lead to a series of oxidation and eventually form insoluble deposits (Hudzik and Bozzelli, 2012). By the separate extraction of toluene, DCM, and methanol, ketones with small average carbon number and DBE are observed in deposit. Extract-DCM contain more compounds with higher carbon number than Extract-Toluene. Ketones with DBE less than 8 and carbon number less than 15 are observed in Extract-Methanol. These small polar compounds, which have almost the same carbon number and DBE, are produced by cracking during LTO and adsorbed on the surface of coke. Based on compositional trends and literature analogies, the proposed reaction pathways of ketones can be inferred from classical chain reaction theory of free radicals, as shown in Fig. 11. Hydrogen peroxide is the primary product of LTO, which generates peroxy alkyl radicals and hydroxyl radicals due to the low energy of O–O bond (Zhao et al., 2025). The peroxy alkyl radicals undergo further decomposition and isomerization to produce ketones directly, or alcohol phenols are further oxidized to produce ketones.

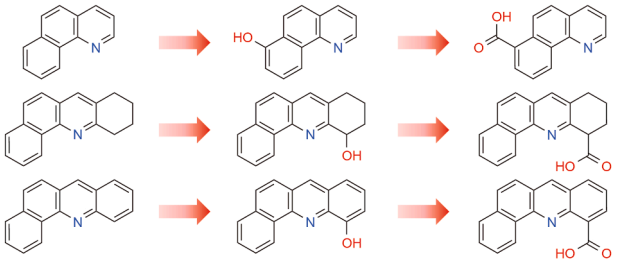

Fig. 9. Reaction pathways of some typical basic nitrogen compounds.

The compound classes obtained from negative-ion ESI Orbitrap MS are shown in Fig. 12 (oxidized oils) and Fig. 13 (deposit). 21 compound classes were detected, including non-basic nitrogen compounds (e.g., N1, N1O1, N1O2) and oxygen compounds (e.g., O1, O2). The N1O1, N1O2, N1O3, N1O4, N1O5, and N1O6 classes were considered as basic or non-basic nitrogen compounds with phenol or carboxyl groups (Shi et al., 2010). The O1, O2, O3, O4, O5, O6, O7, O8, O9, and O10 classes were considered as phenols and carboxylic acids, which contain multiple hydroxyl and carboxyl groups (Shi et al., 2013). In the crude oil, the O1 class constituted the dominant species. Both the crude oil and oxidized oils exhibited high relative abundances of oxygen compounds. As the temperature increased, the relative abundances of N1 and O1 classes declined in oxidized oils, while the compounds containing multiple oxygen atoms became more prominent. Although the O2 class showed the highest relative abundance in oxidized oils, the deposit was primarily composed of poly-oxygenated species. Notably, the N1 and N1O1 classes were nearly absent in extracts of deposit. The content of oxygen compounds containing multiple

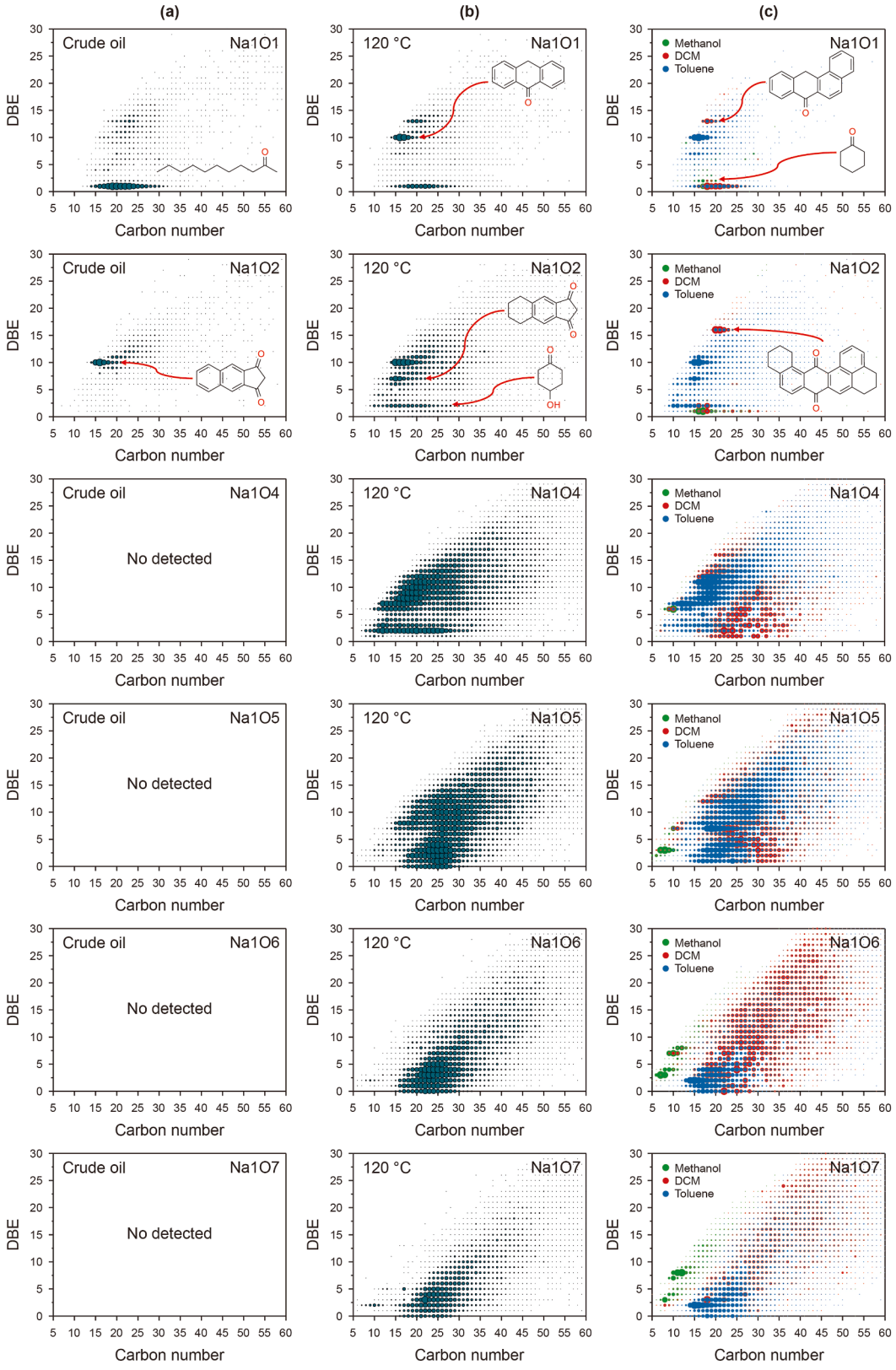

Fig. 10. DBE versus carbon number distributions of ketone compounds in the crude oil (**a**), oxidized oil (**b**), and deposit (**c**).

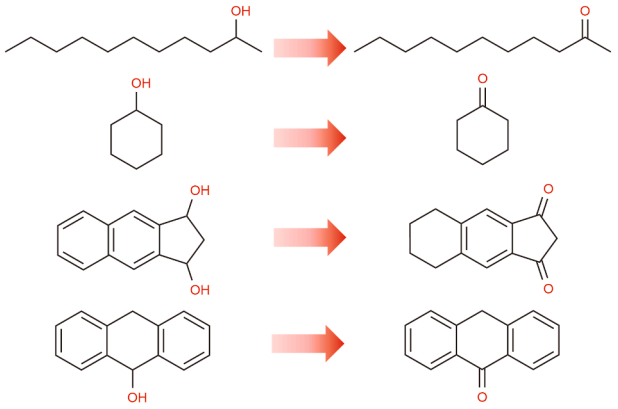

Fig. 11. Reaction pathways of some typical ketone compounds.

oxygen atoms increased from Extract-Toluene to Extract-Methanol. The O6 class was dominant in Extract-Methanol of deposit.

The DBE versus carbon number distributions for N1, N1O1, N1O2, N1O3, N1O4, and N1O5 classes in the crude oil, oxidized oils (120 °C), and deposit (120 °C) are presented in Fig. 14. The N1 class was primarily composed of carbazole and benzocarbazole compounds. The N1O1, N1O2, N1O3, N1O4, and N1O5 classes were also considered as oxidized products in LTO. The N1O1 class was considered as the intermediates for the oxidation of the N1 class, which has phenol group. The N1O1 class with DBE of 8 may be the oxidized product of carbazole due to ring opening reaction in LTO (Pan et al., 2013). The N1O2 class is likely to be phenolic compounds containing basic nitrogen-pyridine groups or naphthenic acid compounds containing non-basic nitrogen-pyrrole groups (Zhao et al., 2021). The N1O2 class with a DBE of 11 may be the

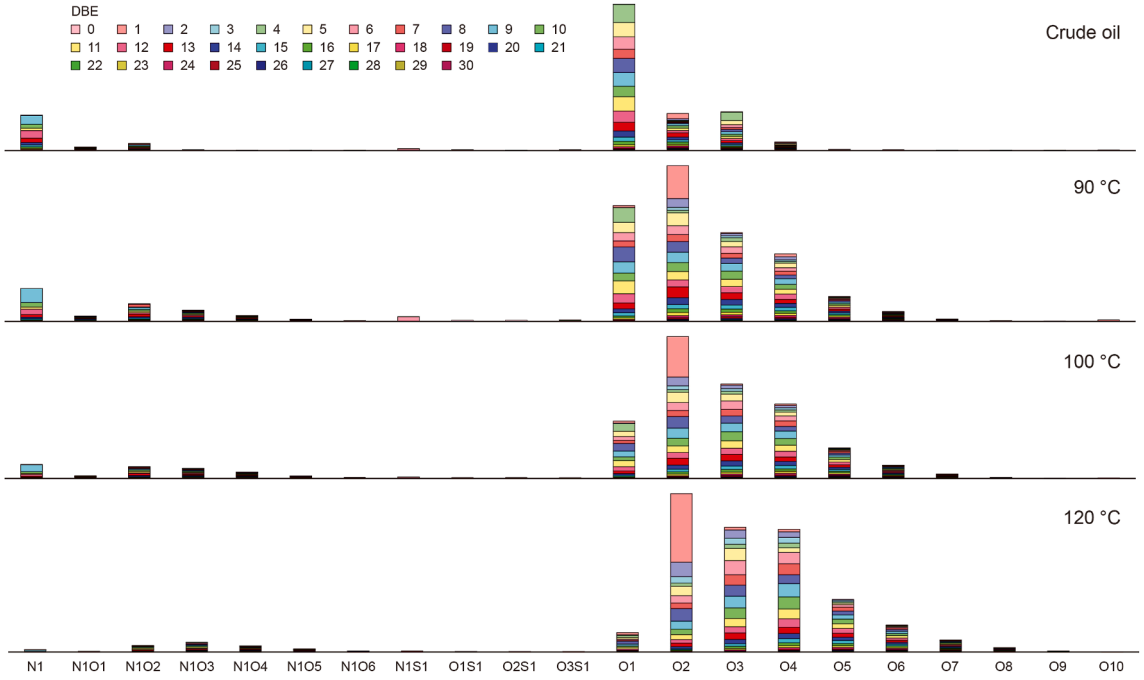

Fig. 12. Compound classes of the crude oil and oxidized oils determined by negative-ion ESI Orbitrap MS.

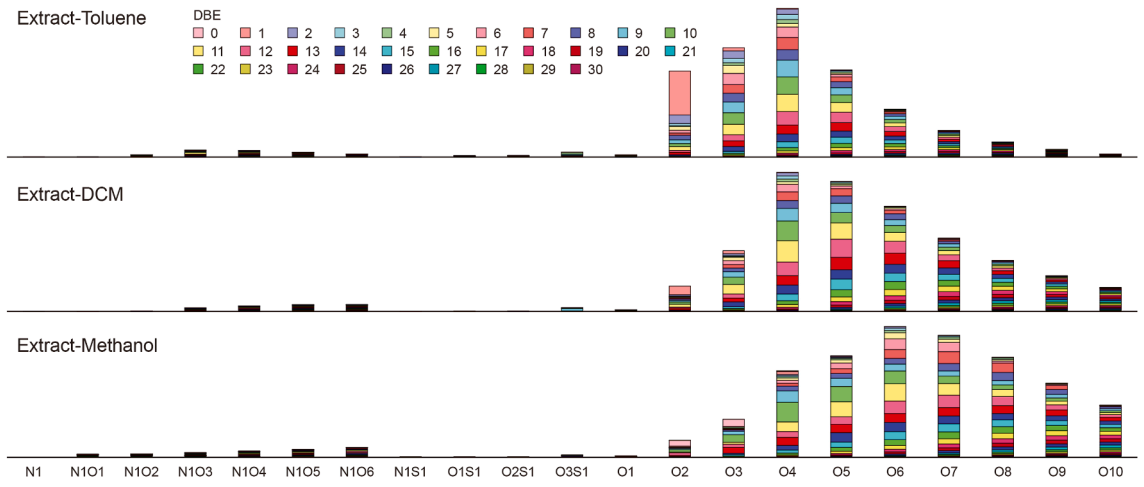

Fig. 13. Compound classes of the deposit (120 °C) determined by negative-ion ESI Orbitrap MS.

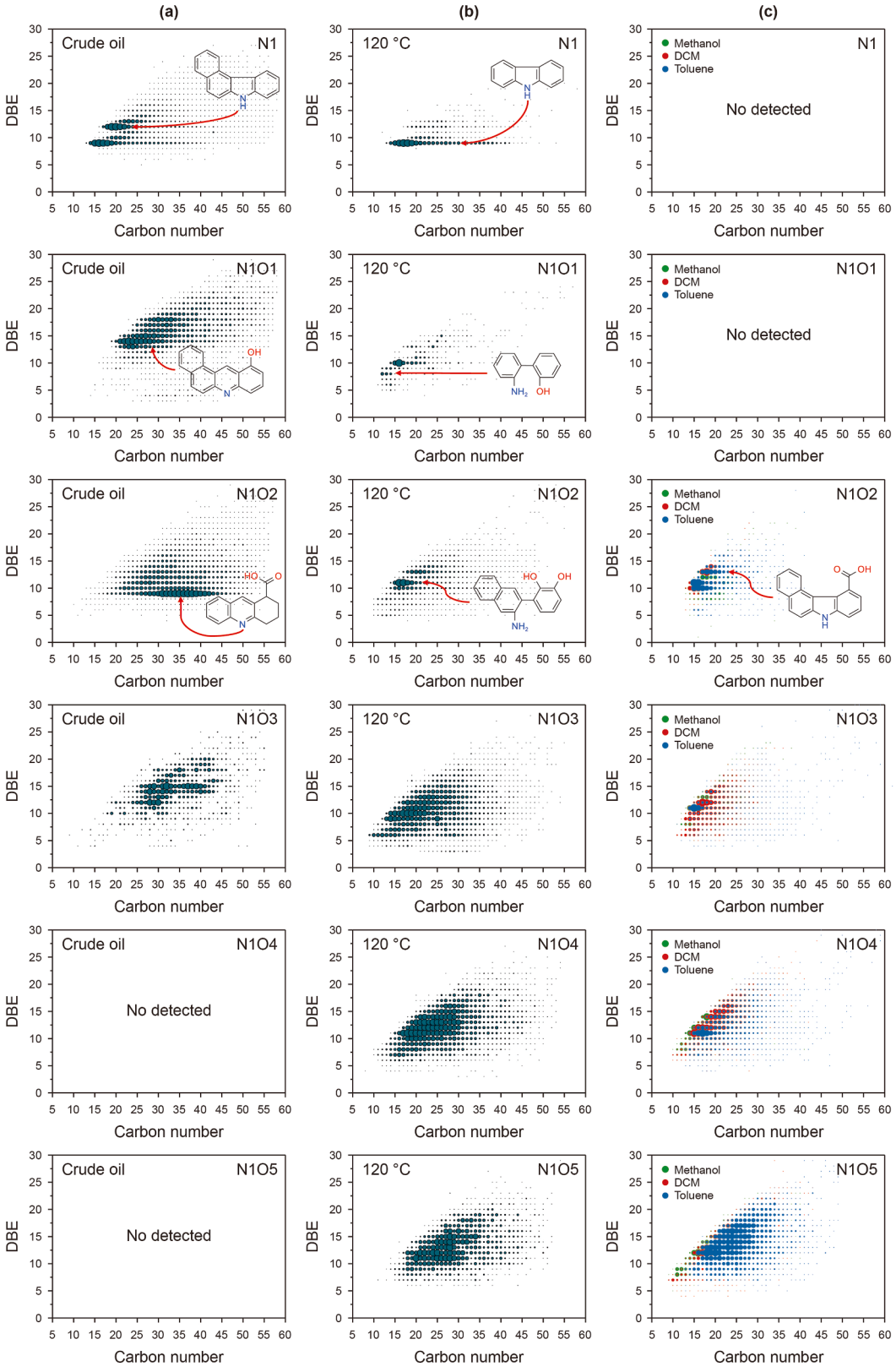

Fig. 14. DBE versus carbon number distributions of non-basic nitrogen compounds in the crude oil (**a**), oxidized oil (**b**), and deposit (**c**).

oxidized product of benzocarbazole due to angular deoxygenation catalyzed by carbazole dioxygenase (CARDO) (Pan et al., 2013). The N1O4 and N1O5 classes were produced in LTO, which were not detected in the crude oil.

The average carbon number and DBE of all classes are represented to show the changes caused by LTO at different temperatures in Fig. 15. With the increase in temperature, the average carbon numbers of N1, N1O1, N1O2, N1O3, and N1O4 classes in oxidized oils decreased and that of the N1O5 class was basically unchanged. And the average DBE values of all classes in oxidized oils decreased significantly because of cracking (Yan et al., 2024). However, through the separate extraction with toluene, DCM, and methanol, the oxidation characteristics of non-basic nitrogen compounds in the deposit were found to differ from those of basic nitrogen compounds. Both of Extract-Toluene and Extract-DCM contained more small compounds with lower carbon number and DBE compared with oxidized oils. The N1O2, N1O3, and N1O4 classes with carbon number less than 15 were observed in oxidized oils, not in Extract-Methanol. This may be due to that many intermediates such as ketones have not continued to be oxidized. Non-basic nitrogen compounds containing multiple oxygen atoms were more likely to cracking. The small polar compounds of N1O5 class with carbon number less than 15 and DBE less than 10 were produced during LTO and adsorbed on the surface of coke. Several possible reaction pathways of non-basic nitrogen compounds are proposed in Fig. 16 based on DBE versus carbon number distributions and literature analogies. In the ring-opening reaction of pyrrolic ring, one case is that the pyridine ring is replaced by hydroxyl group, and the other case is that the adjacent aromatic ring introduces hydroxyl group, and finally produces a biphenyl compound containing an amino group and two hydroxyl groups. In the oxygenation reaction, which is the same as basic nitrogen compounds, the aromatic ring introduces a hydroxyl group and is further oxidized to the carboxyl group.

Fig. 17 illustrates the DBE versus carbon number distributions for O1, O2, O4, O5, O6, and O7 classes in the crude oil, oxidized oils (120 °C), and deposit (120 °C). The O1 class was dominated by phenolic compounds (i.e. mainly phenols). For this case, a DBE of 1 corresponded to cyclohexanol, a DBE of 4 to alkylphenols, a DBE of 9 to 2-phenylcyclohexanol, and a DBE of 13 to 3-phenylcyclohexanol. Other phenols with DBE higher than 4 correspond to alkylphenols with different numbers of rings according to Pan et al. (2013). The O2 class was mainly composed of carboxylic acids. A DBE of 1 corresponded to fatty acid, a DBE higher than 2 to naphthenic acid, and a DBE higher than 4 to arylcarboxylic acid (Duan, 2016). The O4, O5, O6, and O7 classes were considered as oxidized products in LTO, which were not detected in the crude oil. It is worth noting that

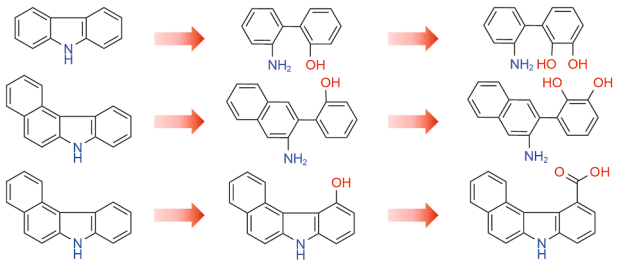

Fig. 16. Reaction pathways of some typical non-basic nitrogen compounds.

based on hydrogen/deuterium exchange experiments on oxidized oils and the deposit, the O2 class with DBE of 8 corresponded to a phenol containing two hydroxyl groups, and the O4 class with DBE of 9 corresponded to a phenylcyclohexane containing four hydroxyl groups (Kong et al., 2025).

The changes in average carbon number and DBE of all classes caused by LTO at different temperatures are shown in Fig. 15. With the increase in temperature, the average carbon numbers of the O1, O2, O4, O5 classes in oxidized oils decreased, but those of the O6 and O7 classes increased because oxygenation and cracking occurred simultaneously. And the average DBE of all classes in oxidized oils decreased significantly because of cracking (Yan et al., 2024). This trend is consistent with that observed for non-basic nitrogen compounds in oxidized oils. Through separate extraction with toluene, DCM, and methanol, both the Extract-Toluene and Extract-DCM contain more small compounds with lower carbon numbers and DBE values compared with oxidized oils. The O1, O2, O4, and O5 classes with carbon numbers less than 15 were observed in oxidized oils, but not in Extract-Methanol. The small polar compounds of the O6 and O7 classes with carbon numbers less than 15 and DBE values less than 10 were produced during LTO and adsorbed on the surface of coke. This behavior aligns with that observed for ketones in both oxidized oils and deposit. Fig. 18 illustrates proposed reaction pathways of acidic oxides based on classical chain reaction theory of free radicals. Peroxy alkyl radicals and hydroxyl radicals are generated during LTO due to the low energy of O–O bond (Zhao et al., 2025). Either peroxy alkyl radicals undergo hydrogen-abstraction reactions to form alcohols and phenols, or hydroxyl radicals initiate C–H bond cleavage in hydrocarbons to generate the same alcohol and phenol products. Some can decompose to produce CO, and some can further oxidize into carboxylic acids, which ultimately decompose into CO_2.

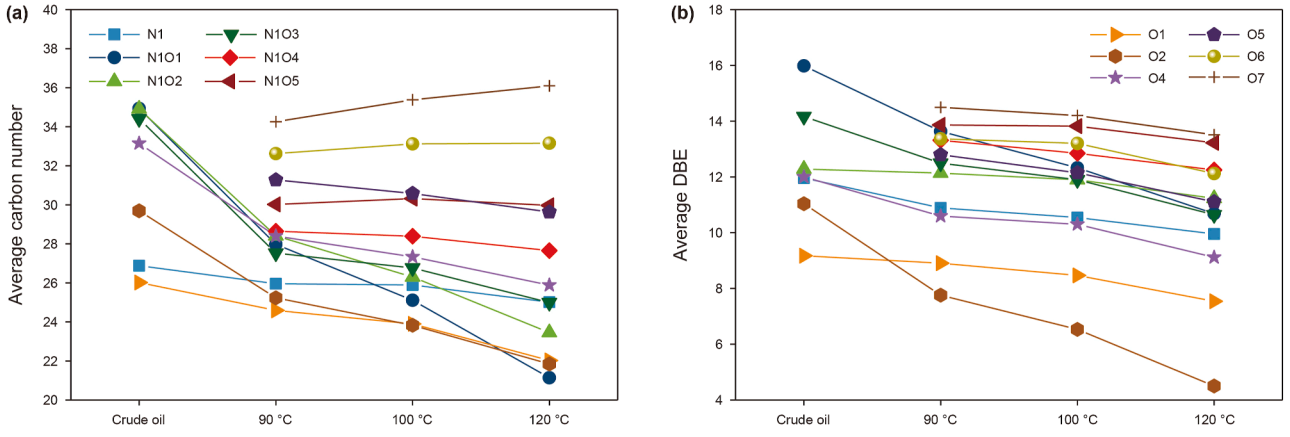

Fig. 15. Average carbon number (**a**) and DBE (**b**) of non-basic nitrogen compounds and acidic oxides in the crude oil and oxidized oils.

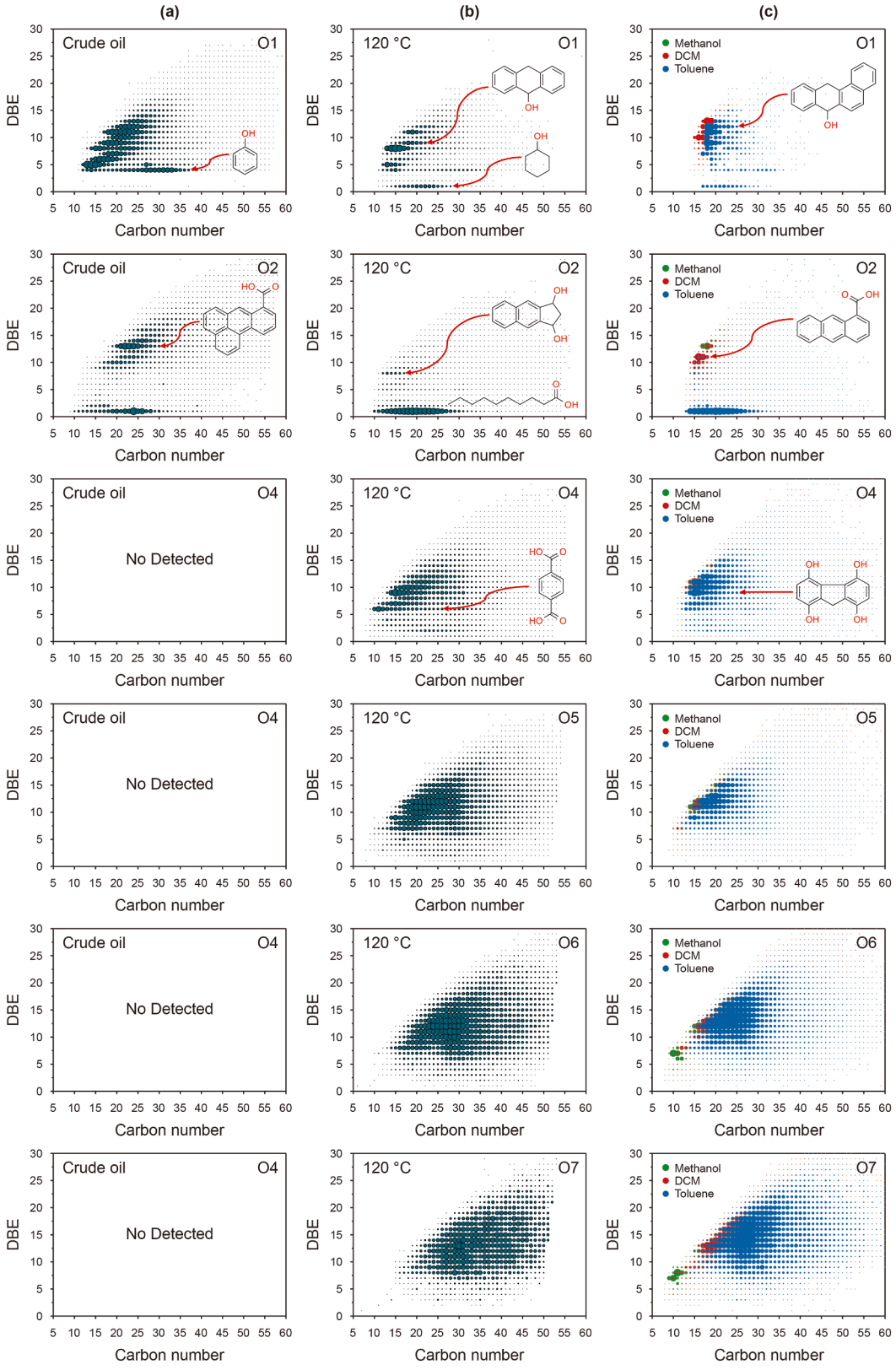

Fig. 17. DBE versus carbon number distributions of acidic oxides in the crude oil (**a**), oxidized oils (**b**), and deposit (**c**).

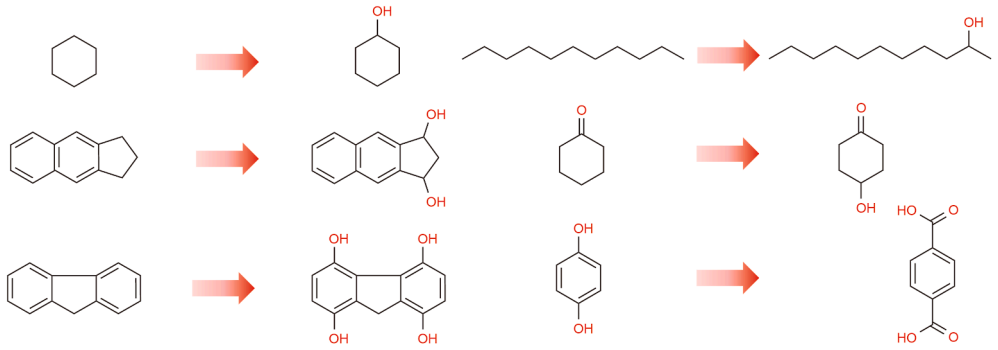

Fig. 18. Reaction pathways of some typical acidic oxides.

3.4. Prospects for practical air flooding in light crude oil reservoirs

In the actual air flooding in light crude oil reservoirs, the oxygen content varies in different pores, leading to differences in the duration of air exposure for the crude oil. The oxidation reaction also releases heat, resulting in varying temperature accumulation across different pores. As a result, the molecular composition and the deposit distribution differ due to convective mass transfer and moving reaction fronts, ultimately leading to variations in the oxidation products. Generally, air preferentially enters high-permeability channels as air injection continues. Therefore, the crude oil in these channels is exposed to air most thoroughly and undergoes the most complete oxidation reaction, making it most prone to deposition. The deposit subsequently aggregates and causes plugging, diverting the air into other low-permeability channels, thereby expanding the sweep volume. To further EOR of air flooding in light crude oil reservoirs, chemical-assisted methods are now being developed to delay gas channeling. However, the oxidation of crude oil generates numerous active substances that significantly affect oil–water emulsification. Preliminary interfacial tension experiments revealed that oxidized oils can change the oil–water interfacial tension which depends on the surfactant structure and its compatibility with the crude oil components. Taking a specific surfactant and formation water as an example (as shown in Fig. 19), the interfacial tensions of oxidized oils are lower than that of the crude oil at low concentration of 0.001%, Moreover, the interfacial tension of oxidized oil decreases as the temperature increases, making emulsification more likely to occur. However, when the concentration increases to 0.05%, the interfacial tensions become higher than that of the crude oil. The interfacial tension of oxidized oil increases further with the increasing temperature, making emulsification more difficult. This reversal phenomenon indicates that in regions of the reservoir with higher temperatures, lower surfactant concentrations are required, which can significantly reduce surfactant usage. Therefore, molecular composition and deposition characteristics in this study provides fundamental support and optimization guidance for the application of air flooding in actual reservoirs.

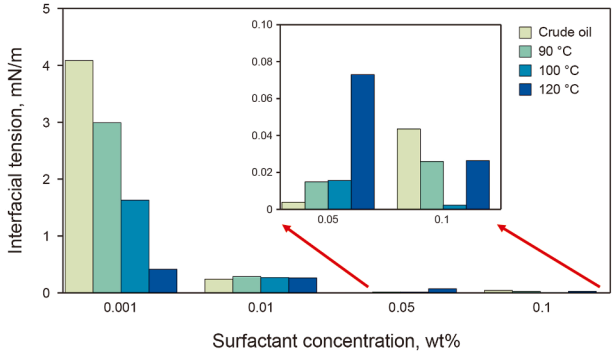

Fig. 19. Interfacial tension of the crude oil/oxidized oils and a specific surfactant.

4. Conclusions

Three low-temperature oxidation (LTO) experiments of light crude oil were carried out at 90, 100, and 120 °C. Molecular-scale differentiation of nitrogen and oxygen compounds in the crude oil, oxidized oils, and deposit was characterized comprehensively in relative abundance and DBE versus carbon number distribution of compound classes using multi-mode ionization Orbitrap MS. The possible reaction pathways of nitrogen and oxygen compounds were proposed according to the observed results and established knowledge of petroleum chemistry.

(1) A variety of oxygen compounds are found in oxidized oil that are absent in the crude oil. The oxidation degree of the crude oil increases significantly with the increase in temperature in LTO.
(2) When deposition occurs in LTO, aromatics are more prone to oxygenation reaction and tend to polymerize with polar compounds in resins and asphaltenes.
(3) Oxygenation and cracking reactions occur successively and simultaneously during LTO, with their competitive interplay collectively determining the deposit architecture. The oxygenation reaction results in the emergence of more oxygen compounds containing multiple oxygen atoms, and the cracking mainly produces some small molecular compounds with low carbon numbers and low DBE values.
(4) Based on solvent extraction and molecular composition analysis, the deposit is inferred to possess a layered structure, which consists of a coke core, an inner layer of adsorbed small molecular compounds, and an outer layer of oxidized oils.
(5) The proposed reaction pathways and deposit architecture provide implications for optimizing air flooding in light crude oil reservoirs.

CRediT authorship contribution statement

Bo Zhang: Writing – original draft, Investigation, Data curation. **Jing-Hua Wang:** Resources. **Qi-Hang Li:** Methodology, Investigation. **Yang-Nan Shangguan:** Data curation. **Zhao-Hui Zhou:** Funding acquisition, Formal analysis. **Quan Shi:** Writing – review & editing, Supervision, Formal analysis, Data curation. **Yi-Qiang Li:** Writing – review & editing, Methodology, Investigation,

Conceptualization. **Qun Zhang:** Project administration, Funding acquisition. **Chun-Ming Xu:** Resources, Project administration, Funding acquisition.

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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References

Adegbesan, K.O., Donnelly, J.K., Moore, R.G., et al., 1987. Low-temperature-oxidation kinetic parameters for in-situ combustion: Numerical simulation. SPE Reserv. Eng. 2 (4), 573–582. https://doi.org/10.2118/12004-PA.

Chatelain, K., Nicolle, A., Ben Amara, A., et al., 2016. Wide range experimental and kinetic modeling study of chain length impact on *n*-alkanes autoxidation. Energy Fuels 30, 1294–1303. https://doi.org/10.1021/acs.energyfuels.5b02470.

Chen, X., 2017. Separation and Molecular Characterization of Ketones in a Low Temperature Coal Tar. MS Thesis. China University of Petroleum (Beijing) (in Chinese).

Duan, S.S., 2016. Separation and Molecular Composition of Naphthenic and Aromatic Carboxylic Acids. MS Thesis. China University of Petroleum (Beijing) (in Chinese).

Fasslhl, M.R., Meyers, K.O., Baslle, P.F., 1990. Low-temperature oxidation of viscous crude oils. SPE Reserv. Eng. 5 (4), 609–616. https://doi.org/10.2118/15648-PA.

Hu, Q., Yan, L., Cheng, Y.F., 2024. *In-situ* hydrogen production from petroleum reservoirs and the associated high temperature hydrogen attack: A review. Int. J. Hydrogen Energy 95, 1038–1051. https://doi.org/10.1016/j.ijhydene.2024.11.280.

Hudzik, J.M., Bozzelli, J.W., 2012. Thermochemistry and bond dissociation energies of ketones. J. Phys. Chem. A 116 (23), 5707–5722. https://doi.org/10.1021/jp302830c.

Ikpeka, P.M., Ugwu, J.O., 2023. *In situ* hydrogen production from hydrocarbon reservoirs–modelling study. RSC Adv. 13 (18), 12100–12113. https://doi.org/10.1039/d3ra01762a.

Jia, T., Pan, L., Wang, X., et al., 2021. Mechanistic insights into the thermal oxidative deposition of C10 hydrocarbon fuels. Fuel 285, 119136. https://doi.org/10.1016/j.fuel.2020.119136.

Khansari, Z., Gates, I.D., Mahinpey, N., 2014. Low-temperature oxidation of Lloydminster heavy oil: Kinetic study and product sequence estimation. Fuel 115, 534–538. https://doi.org/10.1016/j.fuel.2013.07.071.

Kong, F., Zhang, Y., Liu, Y., et al., 2025. Structural speciation of oxygen-containing compounds in fossil fuels using hydrogen/deuterium exchange ESI high-resolution mass spectrometry. Fuel 392, 134888. https://doi.org/10.1016/j.fuel.2025.134888.

Li, Y., Liao, G., Wang, Z., et al., 2022. Molecular composition of low-temperature oxidation products in a simulated crude oil in-situ combustion. Fuel 316, 123297. https://doi.org/10.1016/j.fuel.2022.123297.

Liu, Y., Huang, H., Liu, Q., et al., 2020. The acid and neutral nitrogen compounds characterized by negative ESI Orbitrap MS in a heavy oil before and after oxidation. Fuel 277, 118085. https://doi.org/10.1016/j.fuel.2020.118085.

Liu, Z., Pu, W., Huang, B., et al., 2023. New insights on low temperature oxidation characteristics and possibility of auto-ignition in light oil reservoir. Geoenergy Sci. Eng. 223, 211583. https://doi.org/10.1016/j.geoen.2023.211583.

Niu, B., Ren, S., Liu, Y., et al., 2011. Low-temperature oxidation of oil components in an air injection process for improved oil recovery. Energy Fuels 25 (10), 4299–4304. https://doi.org/10.1021/ef200891u.

Okere, C.J., Sheng, J.J., 2024. Probing the mechanism and impact of light oil oxidation on in situ hydrogen production from petroleum reservoirs: A combined SARA-based experimental and numerical investigation. Energy Fuels 38 (18), 17649–17661. https://doi.org/10.1021/acs.energyfuels.4c03325.

Okere, C.J., Sheng, J.J., Ikpeka, P.M., 2024a. Comparative numerical study on the optimization of double-simultaneous gas injection techniques for enhanced hydrogen production from depleted light oil reservoirs. Energy Fuels 38 (17), 16358–16370. https://doi.org/10.1021/acs.energyfuels.4c02792.

Okere, C.J., Sheng, J.J., Ikpeka, P.M., 2024b. Maximizing hydrogen yield: Pioneering gas injection for enhanced light oil reservoir utilization. In: SPE Western Regional Meeting. https://doi.org/10.2118/218948-MS.

Okere, C.J., Sheng, J.J., Ikpeka, P.M., 2025. Which offers greater techno-economic potential: Oil or hydrogen production from light oil reservoirs? Geosciences 15 (6), 214. https://doi.org/10.3390/geosciences15060214.

Pan, N., Cui, D., Li, R., et al., 2012. Characterization of middle-temperature gasification coal tar. Part 1: Bulk properties and molecular compositions of distillates and basic fractions. Energy Fuels 26 (9), 5719–5728. https://doi.org/10.1021/ef3007323.

Pan, Y., Liao, Y., Shi, Q., et al., 2013. Acidic and neutral polar NSO compounds in heavily biodegraded oils characterized by negative-ion ESI FT-ICR MS. Energy Fuels 27 (6), 2960–2973. https://doi.org/10.1021/ef400191h.

Qi, H., Li, Y., Chen, X., et al., 2021. Low-temperature oxidation of light crude oil in oxygen-reduced air flooding. Petrol. Explor. Dev. 48 (6), 1393–1402. https://doi.org/10.1016/S1876-3804(21)60295-1.

Shi, Q., Hou, D., Chung, K.H., et al., 2010. Characterization of heteroatom compounds in a crude oil and its saturates, aromatics, resins, and asphaltenes (SARA) and non-basic nitrogen fractions analyzed by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 24 (4), 2545–2553. https://doi.org/10.1021/ef901564e.

Shi, Q., Pan, N., Long, H., et al., 2013. Characterization of middle-temperature gasification coal tar. Part 3: Molecular composition of acidic compounds. Energy Fuels 27 (1), 108–117. https://doi.org/10.1021/ef301431y.

Wang, Y.F., Wei, J.G., 2023. Reaction characteristics of low temperature oxidation of light crude oil with disoxidation air. Bulletin of Geological Science and Technology 42 (2), 207–213. https://doi.org/10.19509/j.cnki.dzkq.2022.0181 (in Chinese).

Wang, Z.M., Liao, G.Z., Pu, W.F., et al., 2018. Oxidation reaction features of formation crude oil in air injection development. Acta Peteolei Sinica 39 (3), 314–319. https://doi.org/10.7623/syxb201803006 (in Chinese).

Xu, Q., Liu, Z., Jiang, H., et al., 2017. Chemical-structural properties of the coke produced by low temperature oxidation reactions during crude oil in-situ combustion. Fuel 207, 179–188. https://doi.org/10.1016/j.fuel.2017.06.026.

Xiao, Z.P., Zhang, Y.B., Li, Q.H., et al., 2024. Influences of low-temperature oxidation on oil recovery during oxygen-reduced air flooding in Guo-8 block of Yuguo oilfield. Xinjiang Petroleum Geology 45 (3), 334–339. https://doi.org/10.7657/XJPG20240310 (in Chinese).

Yan, H.X., Xu, J.B., Tao, S., et al., 2024. Application of fourier transform ion cyclotron resonance mass spectrometry in assessing high- and low-temperature oxidation of heavy crude oil. Sci. Technol. Eng. 24 (18), 7615–7622. https://doi.org/10.12404/j.issn.1671-1815.2304963 (in Chinese).

Yatimi, Y., Mendil, J., Marafi, M., et al., 2024. Advancement in heavy oil upgrading and sustainable exploration emerging technologies. Arab. J. Chem. 17 (3), 105610. https://doi.org/10.1016/j.arabjc.2024.105610.

Yuan, C., Emelianov, D.A., Varfolomeev, M.A., et al., 2018. Oxidation behavior and kinetics of eight C_{20}–C_{54} *n*-alkanes by high pressure differential scanning calorimetry (HP-DSC). Energy Fuels 32 (7), 7933–7942. https://doi.org/10.1021/acs.energyfuels.8b01401.

Yuan, C., Emelianov, D.A., Varfolomeev, M.A., et al., 2019. Comparison of oxidation behavior of linear and branched alkanes. Fuel Process. Technol. 188, 203–211. https://doi.org/10.1016/j.fuproc.2019.02.025.

Yuan, S.Y., Han, H.S., Wang, H.Z., et al., 2024. Research progress and potential of new enhanced oil recovery methods in oilfield development. Petrol. Explor. Dev. 51 (4), 841–854. https://doi.org/10.11698/PED.20240198 (in Chinese).

Zhang, B., Xu, C.-M., Liu, Z.-Y., et al., 2023. Mechanism investigation of steam flooding heavy oil by comprehensive molecular characterization. Pet. Sci. 20 (4), 2554–2563. https://doi.org/10.1016/j.petsci.2023.03.018.

Zhang, B., Xu, C., Shi, Q., et al., 2024. Wettability of different mineral surfaces in supercritical CO_2 extraction: Interpretations from the molecular composition of crude oil. Energy Fuels 38 (10), 8589–8597. https://doi.org/10.1021/acs.energyfuels.4c00808.

Zhao, S., Pu, W., Varfolomeev, M.A., et al., 2020. Oxidation characteristics of heavy oil and its SARA fractions during combustion using TG-FTIR. J. Pet. Sci. Eng. 192, 107331. https://doi.org/10.1016/j.petrol.2020.107331.

Zhao, S., Pu, W., Peng, X., et al., 2021. Low-temperature oxidation of heavy crude oil characterized by TG, DSC, GC-MS, and negative ion ESI FT-ICR MS. Energy 214, 119004. https://doi.org/10.1016/j.energy.2020.119004.

Zhao, S., Pu, W., Li, Y., et al., 2025. Low-temperature oxidation characteristics and reaction pathways of crude oil within tight shale during air injection. Petroleum 11 (1), 84–93. https://doi.org/10.1016/j.petlm.2023.12.005.