

Article Ketones in Low-Temperature Oxidation Products of Crude Oil

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Abstract: Ketone compounds are oxidation products of crude oil in the in-situ combustion (ISC) process. Revealing the molecular composition of ketones can provide theoretical guidance for understanding the oxidation process of crude oil and valuable clues for studying the combustion state of crude oil in the reservoir. In this study, low-temperature oxidation (LTO) processes were simulated in thermal oxidation experiments to obtain thermally oxidized oil at different temperatures (170 °C, 220 °C, 270 °C, and 320 °C). A combination of chemical derivatization and positive-ion electrospray (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to analyze the molecular composition of different kinds of ketones (fatty ketones, naphthenic ketones, and aromatic ketones) in the oxidized oils at different temperatures. The results showed that the concentration of aliphatic ketones and aliphatic cyclic ketones in the product oils decreased with the increase in temperature, while aromatic ketones follows this order: fatty ketones < cycloalkanes < aromatic ketones. The concentrations of ketones reached their maximum value at 170 °C and decreased at high temperatures due to over-oxidation. It was also found that nitrogen-containing compounds are more easily oxidized to ketone compounds than their hydrocarbon counterparts in the LTO process.

Keywords: in-situ combustion; low-temperature oxidization; ketone; crude oil; FT-ICR MS

1. Introduction

In-situ combustion (ISC) has great potential for the recovery of heavy oil with high viscosity and density. A large amount of heat is generated by the combustion of a small fraction of heavy oil, reducing the viscosity of heavy oil and enabling in-situ upgrading [1]. For nearly 100 years, the in-situ combustion (ISC) technique has been used in the U.S. in attempts to improve recovery from oil reservoirs. Despite its long history and the commercial success of some field projects, the process has not found widespread acceptance among operators due to failures in early field trials [2]. However, the majority of these failures occurred due to a poor understanding of the physical and chemical processes involved in ISC. Successful projects indicate that the process is applicable to a wide range of reservoirs, and the chances of failure can be minimized through a detailed characterization of crude oil from oil reservoirs and the adoption of mild engineering practices [3,4]. The reactions involved in the ISC process are generally categorized into three regimes: low-temperature oxidation (LTO), fuel deposition (FD), and high-temperature oxidation (HTO) [5]. Heavy oil undergoes a series of complex physical and chemical reactions in ISC, such as distillation, pyrolysis, and oxidation, to form coke, which serves as the fuel required for combustion [6]. The LTO products are the precursors of coke produced in the FD regime, which greatly affects the sustainability and advance of the combustion front [7]. A deeper understanding



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of the LTO reactions of heavy oil is helpful for improving the process conditions of field applications of ISC [8].

For many years, due to the complexity of crude oil, studies on the changes in the chemical composition of heavy oil that result from the LTO processes focused on the use of elementary and thermal analyses [9,10]. Extensive efforts have been made to analyze the characteristics of heavy oil LTO products, such as acid value and organic element content, which can provide more information on heavy oil oxidation [11,12]. To evaluate the oxidation characteristics of heavy oils, thermal analyses such as thermogravimetric analysis and differential scanning calorimetry (TG-DSC), pressure differential scanning calorimetry (PDSC), and thermogravimetric analysis coupled with a Fourier transform infrared spectrometer (TG-FTIR) have been applied [12,13]. However, thermal analyses cannot reveal the specific reactions that occurred during the LTO process. Zhao et al. [14] characterized oxidized oil using nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), indicating that the free radicals in oxidized oil are mainly located in aromatic hydrocarbons, aliphatic hydrocarbons, and oxygen atoms. It is found that some components of crude oil can be oxidized to oxygenated hydrocarbon compounds (e.g., aldehydes, ketones, and alcohols), which can be further oxidized to carbon oxides such as CO_2 [15]. The formation of these compounds further exacerbates the complexity of LTO products. Given their reactivity, ketones should be a class of compounds of interest. The additions across the C=O double bond are numerous in organic chemistry, including those with hydroperoxides [16]. Although ketones have been considered a key component in the LTO process, little is known about their presence, likely due, at least in part, to the lack of suitable analytical methods.

Gas chromatography-mass spectrometry (GC-MS), as an analytical method that can simultaneously separate and analyze complex organic substances, has been used to study the composition of crude oil during LTO [17,18]. Unfortunately, oxidized oils have higher boiling points and more complex compositions compared to crude oils, which exceed the upper limit of gas chromatography. Analytical developments have led to very powerful mass spectrometric (MS) methods for the study of fossil materials, but they have mainly been used for nitrogen, sulfur compounds, and acidic compounds, which are easily ionized when used with electrospray ionization (ESI) [19–21]. Non-polar oxygen-containing compounds, including furans and ketones, are not efficiently ionized in ESI [22,23]. In addition, MS is incapable of distinguishing compound isomers that have the same molecular formula. Therefore, in order to provide a comprehensive characterization of ketones in LTO products, the isolation of ketones from the rest of the LTO products is necessary. Ketones from fossil fuels have been traditionally separated by solid-phase extraction (SPE), liquid chromatography, and thin-layer chromatography [24-27]. However, these methods are insufficient to separate ketones from hydrocarbons, phenols, and other compounds with similar polarities to enable a definitive identification.

In recent years, a novel approach based on chemical derivatization followed by ESI high-resolution mass spectrometry has been used for the molecular characterization of ketones in fossil fuels [28–30]. The Girard-T reagent can be used to selectively create a positively charged quaternary ammonium moiety on carbonyls that can be accessed by ESI [31]. Although ketones can be ionized by positive-ion ESI [23], the derivatization largely improved the selectivity and sensitivity for the analysis of ketones in complex fossil fuels [32]. Alhassan and Andersson [28] compared two commercial derivatization reagents to selectively introduce a positive charge into the ketones for detection. It was found that the quaternary aminoxy compound was superior to Girard-T since better detectability and a larger number of ketones were found. Ketones in crude oil and coal tar were characterized by their molecular composition. Wang et al. [29] further validate that the Girard-T derivatization followed by positive-ion ESI MS analysis is suitable for the analysis of ketones in a trace amount, but it has discrimination on high double-bond equivalent (DBE) species (DBE \geq 9).

In this study, heavy crude oil from the Xinjiang oilfield in China was oxidized at different temperatures using a batch reactor. The oxidized oils were separated from the residues, and their properties were assessed, including the contents of C, H, O, and N and SARA fractions (saturates, aromatics, resins, and asphaltenes). We applied chemical derivatization with Girard-T coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to analyze ketones from the LTO products. This study will provide deep insights on the molecular composition of ketones in crude oil and their oxidation products at different reaction temperatures. The molecular composition of ketones will be helpful for the understanding of chemical reactions in the LTO's characteristics and mechanisms and will provide insights for ISC field applications.

2. Experimental Section

2.1. Samples and Regents

The heavy oil sample used in this study was collected from the Karamay Oilfield (Xinjiang, China), where in-situ combustion is being implemented. Crude oil from the same area was characterized in our previous study [33]. In general, crude oils in this oil field are biodegradable, having almost no light fraction and a boiling point lower than 200 °C.

Analytical-grade *n*-hexane, dichloromethane (DCM), chloroform, toluene, methanol, and ethanol were purchased from Beijing Chemical Reagents Company and purified by distillation with a 9600 spinning band distiller (B/R instrument, Easton Md, USA) before use. Analytical-grade Girard-T reagent and cation exchange resin (Amberlite IRC-50) were purchased from Aladdin Biochemical Technology Co., Ltd., Shanghai, China.

2.2. Oxidation Process

The oxidation experiments on the heavy oil were carried out in a batch reactor, as previously reported in [33]. A hot air flow was introduced into the reactor and bowed over the surface of the oil with a flow rate of 100 mL/min. The volatile components were flowed out of the reactor and cooled by a condenser. The reaction system was kept at a constant temperature for 2 h and then naturally cooled to room temperature. The reaction temperatures were controlled at 170, 220, 270, and 320 °C, which represented four different reaction degrees of the LTO process.

2.3. Bulk Property and Chemical Composition Analysis

The organic elemental composition of the heavy oil and its oxidation products was analyzed according to the Chinese standard method GB/T 19143-2017. The contents of carbon, hydrogen, and nitrogen were analyzed by a Vario EL Cube elemental analyzer (Elementar, Germany). The samples were decomposed by combustion at 950 °C, adsorbed and desorbed by a CO₂ and H₂O adsorption column, and detected by a thermal conductivity detector (TCD). The content of oxygen was analyzed by a Rapid OXY Cube elemental analyzer (Elementar, Germany). The samples were decomposed at 1450 °C, adsorbed analyzer (Elementar, Germany). The samples were decomposed at 1450 °C, adsorbed analyzer (Elementar, Germany).

The saturates, aromatics, resins, and asphaltenes (SARA) composition of the heavy oil and its oxidation products was analyzed according to the Chinese industry standard method SY/T 5119-2016. Briefly, 30 mg sample was dissolved in 30 mL *n*-hexane, and the asphaltenes were separated by filtration after sufficient precipitation. A total of 3 g of silica gel and 2 g of alumina were added sequentially to the chromatographic column. The *n*-hexane solution was concentrated and added to the chromatographic column. The saturates, aromatics, and resins were sequentially eluted using 30 mL *n*-hexane, 20 mL DCM/*n*-hexane (2/1, v/v), 10 mL ethanol, and 10 mL chloroform as eluents. The solvent of each fraction was volatilized at low temperature and weighed until it reached a constant weight.

2.4. Derivatization and Separation of Ketones

To analyze the composition of ketones in the oils by using -ESI FT-ICR MS, the ketones were derived into strongly polar compounds. The derivation of the ketones in the heavy oil

and its oxidation products was carried out by a chemical derivatization process with Girard-T reagent, which can introduce a charged quaternary ammonium moiety on carbonyl. The derivatization and separation procedures were based on previous work [31] with slight modifications, as shown in Figure 1. Briefly, 300 mg oil was dissolved in 2 mL DCM/methanol (1/1, v/v). The solution was stirred with 200 mg Girard-T reagent and 40 mg cation exchange resin at 40 °C for 14 h.



Figure 1. Sketch map of the separation of ketones and reaction schemes of ketones with Girard-T reagent.

After the reaction, the product was separated and purified by a chromatographic column composed of 2 g silica gel and 0.5 g KOH-modified silica gel. The unconverted oil matrixes were eluted with 30 mL *n*-hexane, 30 mL toluene, 40 mL DCM, and 40 mL DCM/methanol (37/3, v/v). The target derivatization products of the ketones were then eluted using 30 mL DCM/methanol (3/1, v/v) and 30 mL DCM/methanol (1/2, v/v) as eluents. The eluted solution was concentrated to 4 mL for analysis.

2.5. FT-ICR MS Analysis and Data Processing

The molecular composition of the ketones in the oils was obtained by analyzing the Girard-T reagent derivatives using an Apex-Ultra FT-ICR MS (Bruker, Germany) equipped with a 9.4 T magnet. The derivatives were diluted with toluene/methanol (1/1, v/v) to an appropriate concentration and directly pumped into the ESI source using a syringe pump at 180 µL/h. The ESI source was in positive-ion mode, and the key operating parameters were as follows: spray shielding voltage, -4500 V; front and terminal voltages of the capillary column, -4500 V and 320 V, respectively. The ions accumulated in the collision cell for 0.6 s and were transferred into the analysis cell for an ion injection time of 0.9 ms. The mass range was set to m/z 100–800. A total of 64 consecutive scans were accumulated for each analysis to improve the signal-to-noise ratio (S/N) of the mass spectrum.

The data processing has been described elsewhere [34]. Briefly, the data were calibrated using a known series, and the mass peak with S/N over 6 was exported by the Bruker DataAnalysis software (Version 3.4). A window of two nominal mass units chosen among the abundant peaks was randomly selected for manual assignment of the elemental composition of the peaks. For fast and reasonable calculation, the calculated molecular formula results were constrained by a range of double-bond equivalent (DBE) of less than 30. Once a peak was assigned to a molecular formula, it was used as a reference for assignment for other peaks with consecutive DBE values (with a mass interval of 2 Da) and/or carbon numbers (with a mass interval of 14 Da). The calculated results were further confirmed by the isotopic abundance. The Kendrick mass defect (KMD) plot of the uncalculated peaks was checked to make sure no classes were left out, which can be easily found as a row and/or consecutive rows [35].

3. Results and Discussion

3.1. Properties of Crude Oil

Table 1 lists the contents of C, H, O, and N and O/C and H/C in the crude oil and its oxidization products. The H/C ratio and the oxygen content imply that the crude oil dominates saturated moieties and has a high total acid number value [36]. It can be seen from the table that the contents of oxygen in the four oxidized oils are significantly higher than those of the crude oil. Therefore, it can be inferred that some oxygenates were generated during LTO. The O/C of crude oil is 0.012. Similarly, the O/C values of the oxidation products, from 0.012 to 0.018, are significantly higher compared to the crude oil, which was apparently caused by the introduction of oxygen atoms during the oxidation process. The H/C values are an important indicator of the degree of molecular condensation in fossil fuels. As the oxidation temperature increases, the H/C values of the oxidation products decrease gradually, indicating that the oxidation process promotes intramolecular condensation reactions such as cyclization and aromatization.

Sample	C, wt%	H, wt%	O , wt%	N, wt%	O/C	H/C
Crude oil	85.91	12.38	1.42	0.28	0.012	1.73
170 °C	85.72	12.58	2.03	0.28	0.018	1.76
220 °C	86.42	12.18	1.87	0.28	0.016	1.69
270 °C	86.22	11.81	2.10	0.24	0.018	1.64
320 °C	86.68	11.45	2.12	0.21	0.018	1.58

Table 1. Elemental contents of the crude oil and the oxidized oils.

The SARA composition of the crude oil and its oxidation products is listed in Table 2. Apparently, the content of saturates in the oxidation products gradually decreased with the increase in oxidation temperature, from an initial value of 53.21% to a final value of 30.18%. The content of aromatics showed a trend of first decreasing and then slightly increasing with the increase in oxidation temperature. The content of both resins and asphaltenes increased with the increase in oxidation temperature, with the asphaltic value showing the most significant increasing trend from 0.55% in the crude oil to 18.94% in the 320 °C product. It is well known that compounds in the saturates are dominated by chain and cyclic hydrocarbons; compounds in the aromatic fraction are mainly aromatic hydrocarbons and some weakly polar heteroatomic compounds (e.g., thiophenic compounds); and compounds in resins and asphaltenes are dominated by high condensation and/or strong polarity ones. The elemental compositions are consistent with the SARA compositions: on the one hand, the increase in O/C improves the polarity of the oxidation products, and on the other hand, the decrease in H/C increases the degree of condensation of the oxidation products. Both of these can lead to a decrease in the content of non-polar components (saturated and aromatic fractions) and an increase in the content of polar components (resins and asphaltenes) in the products.

Sample	Saturates (wt%)	Aromatics (wt%)	Resins (wt%)	Asphaltenes (wt%)	Yield (wt%)
Crude oil	53.21	22.20	12.81	0.55	88.78
170 °C	53.02	21.69	13.82	3.46	91.98
220 °C	45.68	17.26	15.87	13.08	91.90
270 °C	43.42	17.95	18.64	11.93	91.95
320 °C	40.18	18.07	20.61	18.94	97.80

Table 2. SARA composition of the crude oil and the oxidized oils.

The distribution of the elemental and SARA compositions shows the macroscopic properties of crude oil during the LTO process. Combined with high-resolution mass spectrometry, the molecular composition changes in crude oil during low-temperature oxidation can be discussed at the molecular level.

3.2. Molecular Composition of Ketones in the Oxidation Products

After Girard-T reagent derivatization, the molecular composition of ketones in petroleum can be characterized by high-resolution mass spectrometry equipped with an ESI source. The results of the high-resolution mass spectrometry analysis of ketones in crude oil and its products at different oxidation temperatures are shown in Figure 2. The two most abundant mass peaks in the left area are contaminants induced in the derivatization process. The inserts are mass spectra segments at around m/z 406, which illustrate the high mass resolution (about 500 K) of the mass spectra. High mass resolution and mass accuracy enable the unambiguous molecular assignments of these mass peaks. During the derivatization process, the mono-ketones of the O1 class (compounds with one oxygen atom in the molecules) are derivatized to produce N3O1 class species. It should be emphasized that previous studies have proven that only one carbonyl group of the diketone participates in the derivatization reaction, and the efficiency and conversion of both of its carbonyl groups participating in the reaction at the same time are very low [37]. The magnified plot of the mass point m/z 406 shows that significant N3O2, N3O3, and N3O4 classes appear in the oxidation products as the oxidation temperature increases. According to the present results, it can be confirmed that the oxygen atom in N3O1 is carbonyl oxygen; however, it is not sure that the oxygen atoms in the N3O2, N3O3, and N3O4 classes are all present in the form of carbonyl groups. In addition, the N3O1 class dominates the abundance distribution of both crude oil and oxidation product compound types. Therefore, the subsequent discussion in this study will mainly focus on the N3O1 class.

Figure 3 shows a histogram of the ion intensity of the N3O1 and N4O1 class species of the Girard-T derivatization products of the crude oil and its thermal oxidation products at different temperatures (170 °C, 220 °C, 270 °C, and 320 °C). The N4O1 class species should be nitrogen-containing ketones because compounds with four nitrogen atoms are rarely detected in crude oils without a separation for the enrichment of porphins and/or porphyrins [22]. As shown in Figure 3, the ketones of N3O1 in the oxidation products are more abundant than those in the crude oil. Meanwhile, the ketones of N4O1 reach their maximum intensity at 170 °C.

In order to quantitatively describe the composition changes in the ketones, an indicator of oxidation rate was defined according to Equation (1):

Oxidation rate =
$$(I_{\text{product}} - I_{\text{crude oil}})/I_{\text{crude oil}} \times 100\%$$
 (1)

where I_{product} and $I_{\text{crude oil}}$ are the total ion intensities of the product and the crude oil, respectively. The calculated oxidation rates are listed in Table 3. Apparently, the oxidation rate of the N3O1 class tended to increase with the increase in oxidation temperature, from 9.22% at 170 °C to 44.94% at 320 °C, almost doubling. In contrast, the oxidation rate of the N4O1 class showed a decreasing trend with the increase in oxidation temperature and even



decreased to -63.98% at 320 °C. This may be caused by the increasing instability of the nitrogen-containing ketones at higher oxidation temperatures.

Figure 2. +ESI FT-ICR MS mass spectra (**left**) and compound-type abundance histograms (**right**) of the Gerard-T reagent derivatization products of crude oil and its oxidation products at 170 °C, 220 °C, 270 °C, and 320 °C. The legend in various colors corresponds to different DBE values, which are shown more clearly in Figure 4.



Figure 3. Ion intensities of N3O1 and N4O1 class species in the mass spectra. These compound classes correspond to ketones and nitrogen-containing ketones in oils.

Table 3. Oxidation rates of N3O1 and N4O1 classes at different oxidation temperatures.

Oxidation Temperature	ΔN3O1 (%)	ΔΝ4Ο1 (%)
170 °C	9.22	93.65
220 °C	28.69	-1.59
270 °C	24.03	-55.77
320 °C	44.94	-63.98

Figure 4 shows the ion relative abundance plots of DBE versus carbon number of the N3O1 and N4O1 class species assigned from the mass spectra of the Girard-T derivatives of crude oil and its thermal oxidation products. According to the derivatization mechanism, the N3O1 compounds correspond to ketones with five fewer carbon atoms and one fewer DBE. The distributions of the N3O1 class species shown in Figure 4 indicate that the ketones in the crude oil mainly have DBE values (one fewer than in the N3O1 class species) of 1, 2, 4, and 4, which correspond to acyclic, one-ring naphthenic, two-ring naphthenic, and three-ring naphthenic ketones, respectively. The carbon numbers of the ketones (five fewer than in the N3O1 class species) with high relative abundance in the crude oil are mainly in a range of about 15–30. With the increase in temperature, the relative abundance of ketones with DBE = 1 and 5–13 in the oxidized oils is significantly increased. It can be speculated that ketones (fatty ketones, alicyclic ketones, and aromatic ketones) were generated during LTO, and aromatic ketones are dominant. It can also be seen from Figure 3 that the compositional change is not continuous with the increase in temperature; this should be due to the continuous oxidation of the generated ketones, which converts ketones into acidic compounds or peroxides [38].



Figure 4. Ion relative abundance plots of DBE versus carbon number for N3O1 and N4O1 class species at different temperatures. Top: N3O1, corresponding to ketones; bottom: N4O1, corresponding to nitrogen-containing ketones.

Figure 4 and Table 3 show that nitrogen-containing compounds seem to be more easily oxidized to ketone compounds than hydrocarbons. This can be explained by the fact that the nitrogen atom in the hydrocarbon increases the molecular polarity, resulting in the

formation of carbocation intermediates in the oxidation process. However, with increasing temperature, ketones are over-oxidized at temperatures higher than 170 °C, resulting in lower contents of ketones compared to crude oil [39].

The ketones detected in the oils can be classified into some groups according to their DBE values. Compounds with DBE values of 1, 2–4, and 5+ correspond to aliphatic ketones, alicyclic ketones, and aromatic ketones, respectively. Figure 5 shows the composition and classification of ketones in crude oil and its oxidation products. Aliphatic ketones and alicyclic ketones gradually decrease with an increase in temperature, while aromatic ketones gradually increase. This trend shows that aliphatic ketones, alicyclic ketones, and aromatic ketones have different transformation rules, indicating that aliphatic ketones and alicyclic ketones have a tendency to transform to aromatic ketones in the process of LTO. The decreasing trend of H/C with the increase in temperature in the preceding part of the text also confirms this conclusion. In addition, with the increase in oxidation temperature and the deepening of the oxidation degree, more aromatic ketones with a high condensation degree are generated, resulting in an O/C increase in oxidation products. High condensation and O/C can result in an increase in polar components (resins and asphaltenes), which corresponds well with the analysis results of the SARA composition. Crude oil is naphthenic in nature, so it is not surprising that cyclic ketones are the dominant ones in it. The increase in relative abundance of aromatic ketones could be caused by the oxidation of aromatic hydrocarbons or by the aromatization of cyclic ketones.



Figure 5. Relative abundance of different ketones. Aliphatic ketones, alicyclic ketones, and aromatic ketones are classified by DBE values of 1, 2–4, and 5+, respectively.

4. Conclusions

Low-temperature oxidation of crude oil was performed at four reaction temperatures. The chemical transformation of the crude oil during the oxidation process was revealed by the characterization of its bulk properties and molecular composition. With the increase in oxidation temperature, the O/C values of the products increased, the H/C values decreased gradually, and the content of polar components increased significantly. It was found that the oxidation rate of mono-ketones, which dominated the absolute abundance, tended to increase with the increase in oxidation temperature and was up to nearly 45% at 320 °C. In addition, both aliphatic and cyclic ketones tended to convert to aromatic ketones as the oxidation degree deepened. During oxidation, the oxygen content of the products increases with deeper oxidation, and mono-ketones are important carriers of these introduced oxygen elements. The conversion of aliphatic and cycloalkanones to aromatic ketones is an important reason for the decrease in H/C and the increase in condensation of

the products. Ultimately, these intramolecular conversions containing the introduction of

oxygen elements and the increase in condensation lead to an increase in polar components (resins and asphaltenes). Since the composition and abundance of ketones (especially monoketones) are closely related to the degree of oxidation, they have potential for applications in determining the different stages of the LTO process.

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