ANALYSIS AND IDENTIFICATION OF OXYGEN COMPOUNDS IN LONGKOU SHALE OIL AND SHENMU COAL TAR

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Abstract. *Methods of acid-base separation and extrography were used to decompose shale oil of Longkou oil shale (LSO), Shandong province, and coal tar of Shenmu coal (SCT), Shanxi province, both China, into acid, base and neutral fractions. The molecular structure and mass distribution of the oxygen compounds present in LSO and SCT were investigated using gas chromatography-mass spectrometry (GC-MS) and negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). The results of GC-MS showed that oxygen compounds in the acid fractions of LSO and SCT were phenols, indanols, naphthols, phenylphenols, fluorenols and phenanthrenols, and their derivatives, while oxygen compounds in neutral fractions 4 and 5 were aliphatic ketones, esters and minor aromatic ketones. The results of ESI FT-ICR MS demonstrated that in LSO, O_1, O_2, O_3, N_1O_1, N_1O_2, N_1 and N_2 compounds were determined with O_1 and O_2 compounds as the most abundant. SCT contained O_1, O_2, O_3, O_4, O_5 and O_6 compounds, while O_2 and O_3 compounds dominated.*

Keywords: *oxygen compound, shale oil, coal tar, GC-MS, FT-ICR MS.*

1. Introduction

In the time of high crude oil prices, oil shale mining and retorting for producing shale oil have become profitable in some countries. Especially in China, but also elsewhere in the world, the production of domestic crude oil is unable to meet the ever-growing demand for this resource, and a substantial amount of crude oil is imported [1–3].

Shale oil (SO) is produced from the organic matter contained in oil shale by pyrolysis [1], while low-temperature coal tar (LTCT) is a by-product of the low-temperature carbonization of coal. SO and LTCT contain compounds, such as α- and β-methylnaphthalenes, biphenyl, phenol, indole, fluorine, etc., which are valuable chemical raw materials for various applications. It is unreasonable to take SO and LTCT just for fuels. The oxygen compounds of shale oil and coal tar can be used to produce plastics, fibers, dyes, rubbers, pesticides, pharmaceuticals, high temperature resistant materials, etc. Therefore, analysis of the oxygen compounds contained in SO and LTCT is useful from the viewpoint of a comprehensive utilization of these products [4].

Shale oil and low-temperature coal tar are complex compounds, both being rich in alkanes, cyclanes, arenes, as well as nitrogen-, sulfur-, and oxygen-containing non-hydrocarbons, Hence, it is hard to analyze oxygen compounds in question without pretreatment of oils. Earlier traditional methods such as column chromatography and also distillation were used for the component analysis of oils [5, 6]. With the development of chromatographic separation methods, the molecular constitutions of shale oil and coal tar were gradually established. Zhu *et al.* [7] separated two kinds of shale oils from mountainous area (land) and coastal shelf rock (sea), both China, into four fractions using silica gel column chromatography. The components of each fraction were identified by GC-MS. The results show that shale oil from land contains 269 compounds, with abundant hydrocarbon compounds (79%), and some sulfur, oxygen and nitrogen compounds. Shale oil from sea rocks contains 284 compounds with a high amount of hydrocarbon and oxygen compounds (60 and 29%, respectively), and some sulfur and nitrogen compounds. Guo *et al.* [8] analyzed by GC-MS shale oils from Fushun oil shale of Liaoning province and Maoming oil shale of Guangdong province, both China. The main oxygen-containing compounds identified are phenols, diphenols, 2-, 3- and 4-alkanones, furans and benzofurans. Among the oxygen compounds, phenols constitute 7–8 wt% of oil (<350 $^{\circ}$C), the next most abundant being ketones. Zhou *et al.* [9] analyzed phenolic compounds in LTCT, using the reversed-phase high-performance liquid chromatography (HPLC). Of phenolic compounds, eight were determined, including phenols, cresols, xylenols, trimethylphenols and naphthols. The low-temperature tar obtained at 550 $^{\circ}$C by means of the GrayKing test was examined by Maria *et al.* [10] using GC-MS. The tar is made up mainly of mono- and di-aromatic compounds with a preponderance of phenolics. William *et al.* [11] identified C_0-C_6 methyl phenols and C_0-C_3 indanol phenols in the coal-derived liquids by GC-MS.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has become a promising tool for analyzing the composition of complex mixtures. This technique offers the highest available broadband mass resolution, mass resolving power and mass accuracy, which allows the assignment of a unique elemental composition to each peak in a mass spectrum. The

high selectivity of electrospray ionization (ESI) improves identification of trace polar compounds found in petroleum systems [12]. By ESI coupled to high-field (9.4 T) FT-ICR MS tens of thousands of compounds observed as positive or negative molecular ions from basic or acidic species, respectively, have been resolved and their elemental compositions (CcHhNnOoSs) as well as the degree of saturation (number of rings plus double bonds) in crude oil, shale oil and coal tar and their distillates determined [12–14]. Bae *et al*. [15] compared the molecular compositions of two shale oils of oil shales from U. S. Western and Russian mines, using 15 T FT-ICR MS coupled with ESI, and atmospheric pressure photoionization (APPI). The class and double-bond equivalence (DBE) distributions of shale oils were compared with those of conventional oil. Wu *et al*. [14, 16, 17] resolved and identified several thousand polar compounds in coal extracts of two geochemical origins, and examined their class, type and alkylation distributions by negative-ion ESI FT-ICR MS.

In this paper, a comprehensive compositional analysis of the oxygen-containing compounds present in LSO and SLTCT was performed using FT-ICR MS and GC-MS. This effort lays the groundwork for a better under-standing of the heteroatom-containing species present in shale oil and coal tar.

2. Experimental

2.1. Materials

Shale oil was obtained from Longkou oil shale (Shandong province, China) by pyrolysis at 600 $^{\circ}$C. Low-temperature coal tar was obtained from the Sanjiang Coal Chemical Company, Shenmu, Shanxi province, China. The properties of LSO and SLTCT are presented in Table 1.

Table 1. Properties of LSO and SLTCT

Sample	Oxygen, m%	Viscosity (50 °C), mm^2/s^{-1}	Ash, %	Carbon residue, %	Freezing point, °C	Moisture, %	Density (20 °C), g/mL^{-1}	Flash point, °C
LSO	3.68	19.01	0.58	3.42	32	1.26	0.9047	132
SLTCT	6.07	16.83	0.085	6.89	27	2.89	1.02	125

2.2. Separation methods for GC-MS analysis

Methods of acid-base separation [18] and extrography [19] were used to decompose LSO and SLTCT into acid, base and five neutral fractions. Neutral fractions 1, 2 and 3 (Table 3) in the oils were mainly saturates, aromatics and nitrogen-containing compounds, respectively. The oxygen-containing compounds analyzed in this article are acid fractions and neutral fractions 4 and 5.

As seen from Table 2, the acid fraction content in LSO is much higher than in SLTCT, which is consistent with the oxygen content of the oils (Table 1).

Table 2. Acid-base extraction of LSO and SLTCT

Sample	Acid component, m%	Basic component, m%	Neutral component, m%	Recovery, m%
LSO	8.02	3.58	83.54	95.14
SLTCT	37.60	3.04	53.72	94.36

Table 3. Chromatographic separation of neutral fractions

Sample	Neutral component 1, m%	Neutral component 2, m%	Neutral component 3, m%	Neutral component 4, m%	Neutral component 5, m%	Recovery, m%
LSO	44.72	24.35	1.15	18.60	0.20	89.02
SLTCT	22.12	35.15	2.54	18.00	10.84	88.65

It is clear from Table 3 that the content of neutral component 5 in LSO is lower than in SLTCT, while the contents of neutral component 4 in the oils are almost similar.

2.3. GC-MS analysis

A Thermo-Finnigan Trace DSQ GC-MS coupled with an HP-5MS (30 m × 0.25 mm × 0.25 μm) fused silica capillary column was used to analyze the composition of shale oil and coal tar samples. The mass spectrometer was operated with an electron impact (EI) source at a 70 eV ionization energy. The mass range was set to 35–500 Da at 1-s scanning intervals. The oven temperature was maintained at 50 °C for 1 min, then increased to 300 °C at 4 °C/min and held constant at 300 °C for 30 min. The sample was injected at 300 °C. The amount of the injected sample was 1 μL at a concentration of 8 mg/mL. Helium was used as a carrier gas at a flow rate of 1 mL/min.

2.4. FT-ICR MS analysis

The samples of shale oil and coal tar to be analyzed by ESI FT-ICR MS were dissolved with a 3:1 solvent mixture of toluene and dichloromethane to 10 mg/mL. A total of 20 mL of the sample solution was further diluted with 1 mL of a 1:1 toluene/methanol solution. The resulting sample solutions were subjected to ESI FT-ICR MS analysis without further treatment. All the solvents used were analytical reagent grade and were distilled twice. Glassware was used for solvent handling and transfer, except for the steel pistons of 10 μL Hamilton syringes. The samples were analyzed using a Bruker Apex ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. The sample solutions were infused at a flow rate of 180 μL/h. Typical conditions

for negative ion formation were the following: emitter voltage 4.0 kV, the voltage introduced to the capillary column 4.5 kV, capillary column end voltage -320 V. The ions were accumulated for 0.1 s in an argon-filled collision cell and transferred to the ICR cell with a 1.2 ms time-of-flight window. The ions were trapped with a sidekick voltage of 6 V. At least 200 scans were accumulated and averaged to improve the signal-to-noise ratio of the obtained spectra. The mass range was set at 100–800 m/z. The size of the data set was adjusted to 2 M words.

3. Results and discussion

3.1. ESI FT-ICR MS analysis of shale oil and coal tar

Figure 1 illustrates negative-ion ESI FT-ICR MS spectrums of LSO and SLTCT. It is clearly seen that the molecular weight range of LSO is wider than that of SLTCT. The peaks with masses of LSO are within the molecular weight range of 150−600 Da, while the m/z values of SLTCT are from 100 to 350. Being lower than 600, these m/z values indicate that LSO and SLTCT are composed mainly of low molecular compounds, and the latter are polymerized by the van der Waals force and hydrogen bonding. So, the properties of shale oil and coal tar, such as fluidity and viscosity, are similar to those of macromolecular compounds.

Figure 2 depicts the heteroatom class and type distribution of LSO and SLTCT derived from a negative-ion ESI FT-ICR MS spectrum. The relative abundance of the peaks of O_1, O_2, O_3, N_1O_1, N_1O_2, N_1 and N_2 compounds in shale oil is 36.25, 35.35, 3.05, 4.38, 7.47, 6.37 and 7.12, respectively. The oxygen compounds O_1 and O_2 are prevailing in LSO, while in SLTCT, O_2 and O_3 compounds are dominant species with the respective abundances of 58.98 and 24.05%. In SLTCT, the other oxygen compounds are less abundant: O_1 1.79%, O_4 8.24%, O_5 5.58% and O_6 1.35%. N_1O_1 and N_1O_2 compounds were determined in shale oil only, while O_4, O_5 and O_6 compounds were detected only in coal tar.
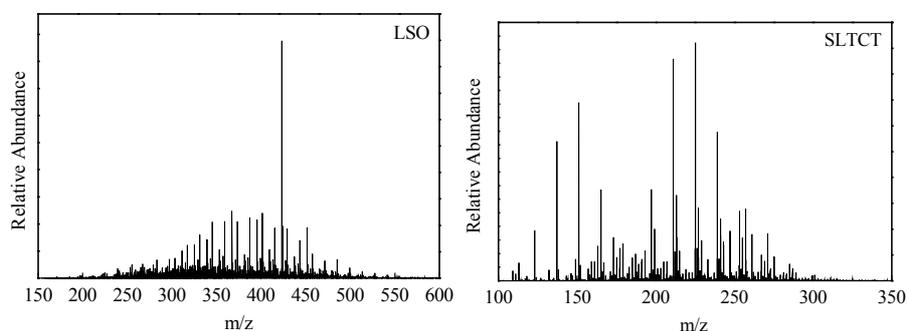

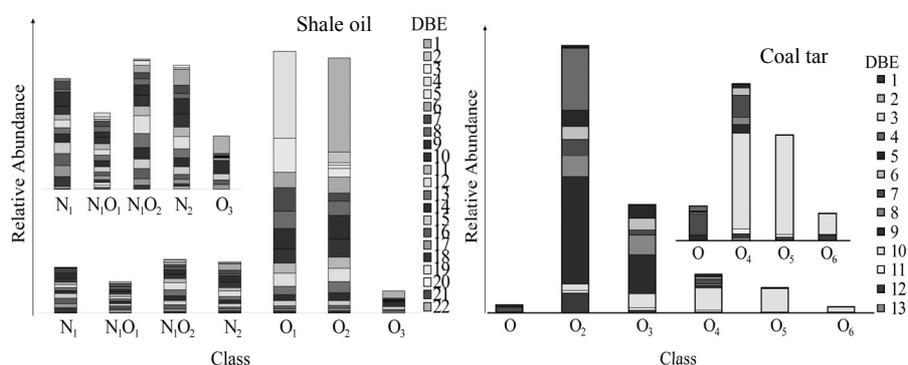Fig. 1. Negative-ion ESI FT-ICR MS spectrums of LSO and SLTCT.

Fig. 2. Heteroatom class and type distribution of LSO and SLTCT derived from a negative-ion ESI FT-ICR MS spectrum.

The number of rings plus double bonds is usually expressed by a double bond equivalent value (DBE) [20]. DBE indicates hydrogen deficiency of a given molecular formula and is commonly used to investigate the high-resolution mass spectra of crude oil [15]. The DBE values of the compounds identified in LSO are chiefly 1 and 4. The DBE values of O_1 compounds are mostly 4 and 5, indicating that of these compounds, phenols and indanols are present in LSO. DBE of O_2 compounds is mainly 1, suggesting that of the latter compounds, acids or lipids occur in LSO. Abundant O_3 compounds have DBE of 1 or 14, while those values of N_1O_1, N_1O_2, N_1 and N_2 compounds are similar. The DBE values of the compounds identified in SLTCT are mainly 4 and 9, being a little different from those of LSO's. DBE of O_1 compounds is mostly 7. Of oxygen compounds, chiefly phenols occur in coal tar, implying that naphthols may exist as O_1 compounds. The occurrence of O_2 compounds with DBE of 4 and 9 suggests that mostly diphenols are present in SLTCT. O_3 compounds with DBE of 9 are abundant in shale oil, while O_4, O_5 and O_6 compounds with DBE of 10 predominate in SLTCT.

Figure 3 compares plots of DBE versus the carbon number of heteroatom compounds in LSO and SLTCT. In LSO, O_1 compounds have DBE of 4–16 and carbon number of 12–41, the most abundant being those with DBE of 4 and carbon number of 28. When DBE is 4, 7 or 9, among these compounds, probably phenols, naphthols and fluorenols, respectively, predominate. The O_1 compounds contained in SLTCT have DBE of 4–9 and carbon number of 10–22. DBE of the most abundant O_1 compounds in SLTCT is 7 and carbon number 11. So, the range of DBE values and carbon numbers for O_1 compounds in LSO is wider than that in SLTCT. The O_2 compounds present in LSO have DBE of 1–16 and carbon number of 14–33, while the respective values in SLTCT are 4–12 and 8–21. Thus, the range of DBE values and carbon numbers for O_2 compounds in LSO is also wider than that in SLTCT. The most abundant O_2 compounds in LSO are those whose DBE is 1 and carbon number 28. In SLTCT, O_2 compounds with DBE of 4 and 9 and carbon number of 14 and 15 are prevailing. In LSO, O_2 compounds with

DBE of 1 may be acids or lipids, whereas no O_2 compounds with this DBE value have been found in Shenmu low-temperature coal tar. When DBE is 4, 5 or 7, the compounds are dihydroxybenzenes, bisphenol indanes and naphthalenediols, respectively. O_3 compounds with DBE of 1 and 14 are abundant in LSO, in contrast to SLTCT, in which O_3 compounds with DBE of 9 are predominant. Overall, the ranges of both DBE values and carbon numbers of oxygen compounds in LSO are wider than those in SLTCT, indicating that oxygen compounds in LSO may have longer side chains on the core of the molecules than those in SLTCT [21]. The presence of O_1, O_2 and O_3 compounds, whose DBE is mostly 1 or 4, suggests that LSO is less biodegraded [15, 22, 23].
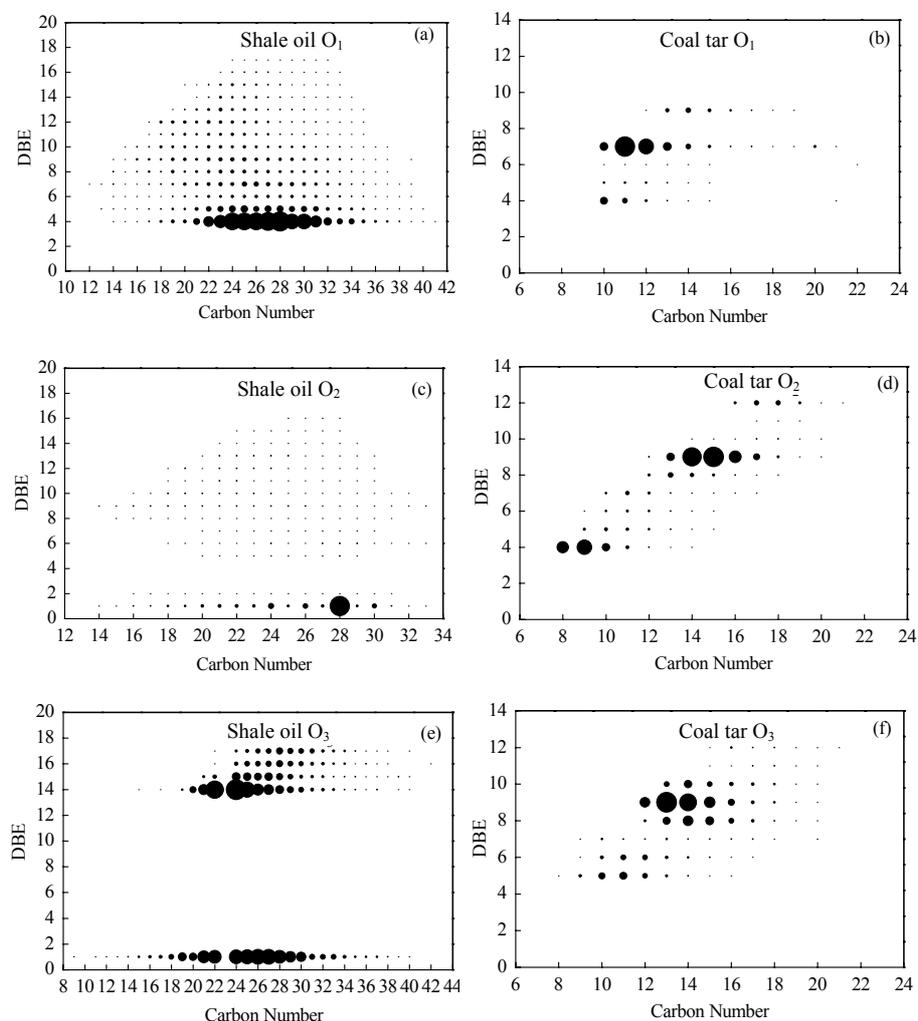
Fig. 3. Plots of DBE versus the carbon number of heteroatom compounds in LSO and SLTCT.

3.2. GC-MS analysis of the acid fractions of shale oil and coal tar

Figure 4 shows the TIC of the acid fraction from LSO and SLTCT. It is obvious that both are complex mixtures, with a wide range of components present.

Based on the results of GC-MS analysis, monohydric phenols, such as phenols, indanols, naphthols, phenylphenols, fluorenols and phenanthrenols, were identified in the two oils. From Figures 2 and 3 it is seen that O_1 compounds with DBE of 4, 5, 7, 9 or 11 were phenols, indanols, naphthols, fluorenols and phenanthrenols, respectively. In LSO, carboxylic acids ranged from C_5 to C_{16}, whereas no these acids were found in SLTCT.

O_2 compounds are usually considered as carboxylic acids in petroleum and coal liquefaction products [14, 16, 17]. However, dihydroxybenzenes have also been identified among the acid components of SLTCT. Shi *et al.*
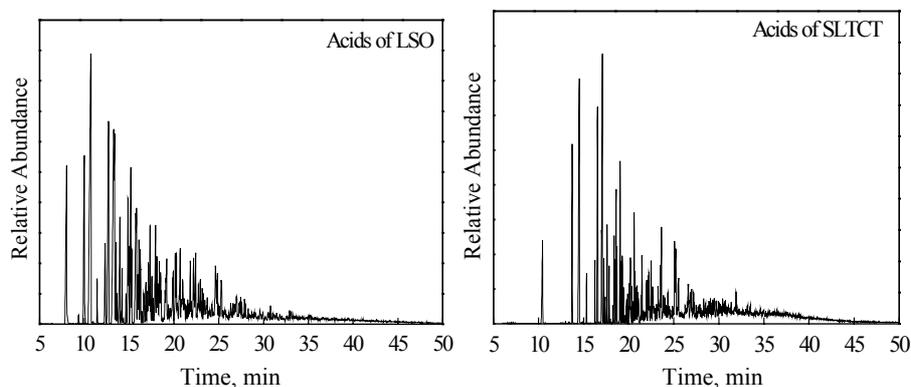

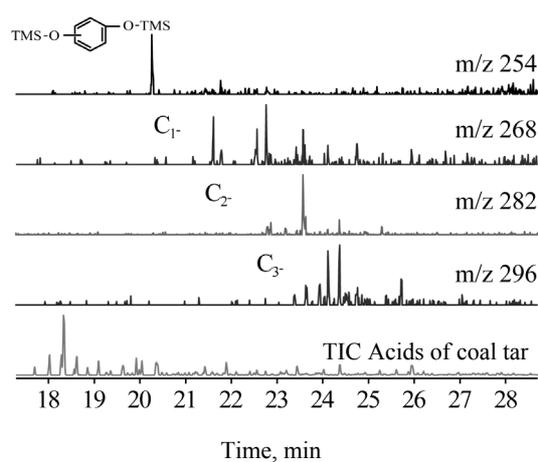Fig. 4. TIC of the acid fractions of LSO and SLTCT.

Fig. 5. Dihydroxybenzenes in the acid fraction of SLTCT.

stated that dihydroxy aromatics were dominant O_2 compounds in the coal tar distillate fraction [24].

In LSO, the content of the acid components detected accounts for 83.51%. Among them, phenol and phenol derivatives constitute 66.63%, indanol and its derivatives 7.53%, naphthol and its derivatives 8.42%, while carboxylic acids account for only 0.2%. The relative content of the acid components detected in SLTCT makes 51.20%. Of them, phenol and phenol derivatives account for 33.43%, indanol and its derivatives 5.71%, naphthol and its derivatives 8.13%, while phenanthrenol and its derivatives constitute about 1.14%. The relative content of phenol and phenol derivatives is high, which is consistent with the fact that DBE of the compounds identified in LSO and SLTCT is mainly 4.

3.3. GC-MS analysis of neutral fractions 4 and 5 of shale oil and coal tar

Neutral fraction 4 of LSO involves aliphatic ketones ranging from C_9 to C_{32}, their relative content being 22.17%, while neutral fraction 4 of SLTCT is mostly represented by aliphatic ketones ranging from C_{10} to C_{28}, with a relative content of 4.88%. Compared with SLTCT, the range of carbon numbers of the aliphatic ketones present in LSO is wider.

Neutral fraction 5 of LSO includes chiefly esters with a relative content of 5.35%. SLTCT involves aliphatic ketones ranging from C_{10} to C_{29}, and minor aromatic ketones, the relative content of neutral fraction 5 being 16.64%.

4. Conclusions

In this paper, a comprehensive compositional analysis and comparison of the oxygen compounds present in Longkou shale oil (LSO) and Shenmu low-temperature coal tar (SLTCT) were performed using FT-ICR MS and GC-MS. The following conclusions were drawn:

1. The weight-average molecular weights of LSO and SLTCT are low. It is obviously because LSO and SLTCT are composed mainly of low molecular compounds and the latter are polymerized by the van der Waals force and hydrogen bonding. So, the properties of shale oil and coal tar, such as fluidity and viscosity, are similar to those of macromolecular compounds.

2. In LSO, O_1, O_2, O_3, N_1O_1, N_1O_2, N_1 and N_2 compounds are present with O_1 and O_2 compounds as the most abundant. SLTCT includes O_1, O_2, O_3, O_4, O_5 and O_6 compounds, while O_2 and O_3 compounds are dominating.

3. The ranges of both the DBE values and carbon numbers of oxygen compounds of LSO are wider than those of SLTCT, indicating that oxygen compounds in LSO have longer side chains on the core of the molecules than those in SLTCT.

4. LSO contains O_1, O_2 and O_3 compounds whose DBE is mainly 1 and 4, implying that this oil is less biodegraded.

5. The oxygen compounds in the acid fractions of LSO and SLTCT are represented by phenols, indanols, naphthols, phenylphenols, fluorenols and phenanthrenols, and their derivatives. The relative content of phenol and phenol derivatives is high, which is consistent with the fact that DBE of the compounds identified in LSO and SLTCT is chiefly 4.

6. Neutral fraction 4 of LSO involves aliphatic ketones ranging from C_9 to C_{32}, their relative content being 22.17%, while that of SLTCT includes mainly aliphatic ketones ranging from C_{10} to C_{28}, with a relative content of 4.88%. Compared with SLTCT, the carbon number range of aliphatic ketones in LSO is wider.

7. Neutral fraction 5 of LSO contains mainly esters, with a relative content of 5.35%. Neutral fraction 5 of SLTCT involves aliphatic ketones ranging from C_{10} to C_{29}, and minor aromatic ketones, whose relative content is 16.64%.

Acknowledgements

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