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Original Paper

Characterization of chemical composition of high viscosity heavy oils: Macroscopic properties, and semi-quantitative analysis of molecular composition using high-resolution mass spectrometry

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A B S T R A C T

Heavy oil is an important resource in current petroleum exploitation, and the chemical composition information of heavy oil is crucial for revealing its viscosity-inducing mechanism and solving practical exploitation issues. In this study, the techniques of high-temperature gas chromatography and high-resolution mass spectrometry equipped with an electrospray ionization source were applied to reveal the chemical composition of typical heavy oils from western, central, and eastern China. The results indicate that these heavy oils display significant variations in their bulk properties, with initial boiling points all above 200 °C. Utilizing pre-treatment and ESI high-resolution mass spectrometry, an analysis of the molecular composition of saturated hydrocarbons, aromatic hydrocarbons, acidic oxygen compounds, sulfur compounds, basic nitrogen compounds, and neutral nitrogen compounds within the heavy oil was conducted. Ultimately, a semi-quantitative analysis of the molecular composition of the heavy oil was achieved by integrating the elemental content. The semi-quantitative analysis results of Shengli-J8 heavy oil and a conventional Shengli crude oil show that Shengli-J8 heavy oil lacks alkanes and low molecular weight aromatic hydrocarbons, which contributes to its high viscosity. Additionally, characteristic molecular sets for different heavy oils were identified based on the semi-quantitative analysis of molecular composition. The semi-quantitative analysis of molecular composition in heavy oils may provide valuable reference data for establishing theoretical models on the viscosity-inducing mechanism in heavy oils and designing viscosity-reducing agents for heavy oil exploitation.

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1. Introduction

The world has abundant heavy oil resources (Guo et al., 2016; Huc, 2010), and high viscosity is a key factor limiting the exploitation of heavy oil (Briggs et al., 1988; Ke et al., 2020; Zhao et al., 2018). Currently, thermal methods, such as steam-assisted gravity drainage (SAGD) (Liu et al., 2018), are mainly used for heavy oil recovery. However, issues such as high-water content, low thermal efficiency, and low recovery rates arise after multiple thermal cycles (Guo et al., 2016; Pu et al., 2015), highlighting the urgent need for new viscosity reduction technologies to address late-stage production challenges in heavy oil fields. On the other hand, there are significant differences in the difficulty of heavy oil development among different oil fields (Li et al., 2017). Apart from variations in reservoir differences in their response to viscosity-reducing agents, the chemical composition of heavy oils varies (Ke et al., 2020). The development of extraction technologies and viscosity-reducing agents has created a more urgent demand for understanding the chemical composition of heavy oil.

The chemical composition of heavy oil is extremely complex, and variations in the content of different components can significantly impact its rheological properties (Delgado-Linares et al., 2022; Zadymova et al., 2017). Based on their correlation with viscosity, compounds in heavy oil can be divided into non-polar waxes and polar components (mainly resins and asphaltenes) (Xu, 2018). Non-polar waxes are primarily influenced by physical factors, such

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as temperature, that cause an increase in crude oil viscosity. High viscosity caused by such factors can be effectively managed through thermal recovery techniques (Visintin et al., 2005). On the other hand, the viscosity of heavy oil dominated by polar components is influenced by intermolecular forces and even chemical reactions, making the influencing factors more complex (Pierre et al., 2004).

Extensive research has been conducted on the impact of resins and asphaltenes on the viscosity of heavy oil (Aguiar and Mansur, 2015; Li et al., 2017; Luo and Gu, 2007). Asphaltenes are the components in heavy oil with the highest molecular weight, strongest polarity, and highest viscosity (Ortega et al., 2015). The removal of asphaltenes can significantly reduce the viscosity of heavy oil by 2–3 orders of magnitude (Ilyin et al., 2016). The presence of resins facilitates the dispersion of asphaltenes in crude oil (Anisimov et al., 2014; Franco et al., 2016). In other words, resins can act as additives to prevent the self-association and subsequent aggregation of asphaltenes (Carnahan et al., 1999; Sedghi and Goual, 2010). At the same time, resins molecules can also self-aggregate, resulting in high viscosity of crude oil (Li et al., 2017). However, the research on the relationship between the composition of heavy oil and its viscosity is macroscopic. Understanding the composition of heavy oil at the molecular level can help to further elucidate the mechanisms behind its viscosity.

The application of new soft ionization and high-resolution mass spectrometry (HRMS) techniques has greatly advanced the development of petroleum chemistry in the past few decades (Hsu et al., 2011; Palacio Lozano et al., 2020). Ionization techniques such as electrospray ionization (ESI) can ionize petroleum molecules in solution at atmospheric pressure, overcoming the problem of traditional vacuum mass spectrometry ionization techniques being unable to analyze heavy oil molecules (Marshall and Rodgers, 2008). On the other hand, HRMS has almost achieved the complete separation of petroleum molecules in the mass dimension (electron mass level), combined with ultra-high mass accuracy (Hsu, 2012). It can accurately calculate the molecular composition of compounds based on the precise mass of elements. The early application of HRMS in analyzing petroleum samples began at the National High Magnetic Field Laboratory in the United States (Rodgers et al., 2005). ExxonMobil, in collaboration with this laboratory, made significant breakthroughs in the composition of heavy oil molecules (Qian and Robbins, 2001; Qian et al., 2001). With the emergence of commercial instrumentation, many large petroleum companies and research institutions started utilizing HRMS for studying the molecular composition of petroleum after 2005 (Barrow et al., 2014; Shi et al., 2014; Wang et al., 2016b).

The ESI ionization technique is widely used for characterizing the molecular composition of polar compounds in petroleum, such as nitrogen-containing compounds and acidic oxygen compounds (Shi et al., 2010). For nonpolar and weakly polar compounds, they can be converted into strongly polar compounds through chemical derivatization and then analyzed for their molecular composition using ESI ionization source. The State Key Laboratory for Heavy Oil Processing has developed a series of analytical methods in conjunction with ESI source to achieve HRMS analysis of difficult-to-ionize compounds. These methods include catalytic oxidation to convert saturated hydrocarbons into alcohols (Zhou et al., 2012), sulfonation to transform aromatic hydrocarbons into highly polar sulfonates (Li et al., 2022), selective oxidation to convert sulfur ethers into sulfoxides (Liu et al., 2010), and Michael addition reactions to introduce strongly polar functional groups into thiol molecules (Wang et al., 2016a). These methods are increasingly contributing to a comprehensive understanding of the molecular composition of heavy oil.

In this study, we intend to use HRMS as a platform to apply semi-quantitative methods for the molecular composition of petroleum fractions in heavy oil (Li et al., 2023). Through semi-quantitative analysis of the molecular composition of typical heavy oils in China, we aim to elucidate the viscosity-inducing mechanism of heavy oil at the molecular level. These molecular composition data can be used to build a viscosity prediction model for heavy oil, and can also provide reference for the design of viscosity-reducing agents based on the structure-effective relationship between heavy oil molecular composition and emulsification viscosity reduction.

2. Experimental section

2.1. Materials

The heavy oil samples selected are Xinjiang-P601 from the Junggar Basin in western China, Henan-L3511 from the Henan Oilfield in central China, and Shengli-J8 and Shengli-C373 from the Shengli Oilfield in eastern China. Analytical-grade toluene, *n*-heptane, *n*-hexane, methanol, ethanol, and dichloromethane were purchased from Beijing Chemical Reagent Company, and were distilled for purification before use. HPLC-grade acetonitrile, carbon tetrachloride, carbon disulfide, water, iodomethane, silver tetrafluoroborate, and sodium periodate were purchased from Aladdin Reagent. Chlorosulfonic acid was purchased from TCI Chemical Ltd.

2.2. Properties analysis

Viscosity and total acid number (TAN) were analyzed according to the Chinese industry standards SY/T 0520 and GB/T 18609, respectively. Saturates, aromatics, resins, and asphaltenes (SARA) analysis was carried out according to the Chinese industry standard NB/SH/T 0509–2010, which uses *n*-heptane as a solvent for asphaltene precipitation. The basic nitrogen content was tested by Chinese industry standards SH/T 0612. Elemental analysis of organic carbon, hydrogen, and oxygen was performed using two German Elementar instruments. The content of carbon and hydrogen was analyzed using the Vario EL cube elemental analyzer according to ASTM D5291, while the oxygen content was analyzed using the Rapid-OXY cube elemental analyzer according to ASTM D5622. The micro elemental analysis of organic sulfur and nitrogen was conducted using the multi EA3100 elemental analyzer from Analytik Jena, Germany. The analysis was performed according to the respective standard methods, ASTM D5453 for sulfur and ASTM D5762 for nitrogen.

2.3. High-temperature GC analysis

The high-temperature simulation distillation of heavy oil was performed on an Agilent 6890N equipped with an Analytical Control SIMDIS HT750 capillary column (5 m × 0.53 mm × 0.17 μm) and a programmed temperature vaporization (PTV) injector. 10 mg of heavy oil was dissolved in 1000 mg of carbon disulfide, and the injection volume was 1 μL. The PTV injector temperature program started at 100 °C, increased at a rate of 15 °C/min to 430 °C, and held for 22 min. The oven temperature program started at 40 °C, increased at a rate of 10 °C/min to 430 °C, and held for 5 min. The detector temperature was set at 430 °C. The data acquisition frequency was 50 Hz.

2.4. HRMS analysis

HRMS is performed using the Orbitrap Fusion MS instrument manufactured by Thermo Fisher Scientific in the United States. It is equipped with an ESI ion source and operated in negative-ion mode or positive-ion mode. The preparation and ionization modes for different compound categories are shown in Table 1. The sample under investigation is directly injected into the ESI source via an injection pump at a flow rate of 5 μL/min. The sheath gas flow rate is set at 5.0 Arb, the auxiliary gas flow rate is set at 2.0 Arb, and the temperature of the ion transfer tube is maintained at 300 °C. The mass range for data acquisition is *m/z* 150 to 1000, with the Automatic Gain Control (AGC) value set at 5.0×10^5, and an accumulation time of 100 ms. Data processing was described elsewhere (Shi et al., 2013).

2.5. Semi-quantitative analysis

Semi-quantitative analysis of the molecular composition of heavy oil was conducted referring to previously reported semi-quantitative methods of petroleum fractions (Li et al., 2023). The semi-quantitative analysis scheme for the molecular composition of heavy oil is shown in Fig. 1. All the molecules in the heavy oil belong to six compound categories: saturated hydrocarbons, aromatic hydrocarbons, acidic oxygen compounds, sulfur compounds, basic nitrogen compounds, and neutral nitrogen compounds. After derivatization with RICO, the saturated hydrocarbons composition is analyzed by −ESI Orbitrap MS. The aromatic hydrocarbons composition is obtained by sulfonation treatment of the heavy oil followed by −ESI Orbitrap MS analysis. The composition of acidic oxygen compounds and neutral nitrogen compounds can be directly analyzed by −ESI Orbitrap MS. The sulfur compounds composition is obtained by methylation treatment of the heavy oil followed by +ESI Orbitrap MS analysis. The composition of basic nitrogen compounds is also directly analyzed by +ESI Orbitrap MS. By following these steps, the complete molecular composition of the heavy oil can be obtained.

To further obtain quantitative results of the heavy oil molecules, a quantitative process begins with nitrogen compounds with complex elemental compositions. According to the content of neutral nitrogen and basic nitrogen, the content of element N is respectively allocated to each compound molecule containing neutral nitrogen and basic nitrogen, using the relative abundance from HRMS. Once the composition of nitrogen compounds is quantitatively analyzed, the total mass of elements C, H, O, and S in these compounds can be determined. Next, quantitative analysis of sulfur compounds is carried out. It involves subtracting the sulfur content in nitrogen compounds from the total sulfur content, followed by distribution based on the relative abundance from HRMS of sulfur compounds. This process yields the quantitative composition of sulfur compounds. Subsequently, the molecular composition of acidic oxygen compounds is quantitatively analyzed. By subtracting the oxygen content in nitrogen compounds and sulfur compounds from the total oxygen content, and using the same distribution method, the quantitative results of the molecular composition of acidic oxygen compounds can be obtained. Finally, for saturated hydrocarbons and aromatic hydrocarbons, their molecular compositions cannot be determined directly through elemental allocations as they consist only of elements C and H. However, based on the results of quantitative analysis of heteroatomic compounds, the proportions of saturated hydrocarbons and aromatic hydrocarbons in the heavy oil can be determined. With knowledge of the mass ratio between saturated hydrocarbons and aromatic hydrocarbons, quantitative analysis of their molecular compositions can be achieved based on their relative abundance from HRMS. Here, the mass ratio of saturates and aromatics in the SARA separation is approximated as the mass ratio of saturated hydrocarbons and aromatic hydrocarbons in heavy oil. This is then used in the quantitative analysis system to calculate and ultimately obtain the quantitative results of the molecular composition of heavy oil.

The semi-quantitative results of the molecular composition of heavy oils obtained from the aforementioned method are not accurate quantitative results. The following points need to be explained.

(1) This method involves multiple preprocessing steps, and oil samples with a high content of light fractions may experience significant mass loss during the processing, making it unsuitable for quantitative analysis using this method.
(2) This method equates the HRMS intensity of different molecules within the same compound type to their true abundance. This means that the response of mass spectrometry to different molecules within the same compound type is not taken into consideration.
(3) For compounds with multiple heteroatoms, such as N2 and N1O2 species, they may undergo ionization in both positive ESI and negative ESI modes, resulting in repetitive quantification calculations for these compound species.

3. Results and discussion

3.1. Bulk properties

Table 2 presents the macroscopic properties of the four heavy oils: Xinjiang-P601, Henan-L3511, Shengli-J8, and Shengli-C373. The viscosity of these heavy oils at 50 °C is above 1500 mPa•s, and their TAN values exceed 3 mgKOH/g, indicating that they are all high TAN value heavy oils. Xinjiang-P601 even has a TAN value as high as 11.77 mgKOH/g. High viscosity and high TAN value are common characteristics of these heavy oils. However, there are significant differences in the distribution of the SARA and elemental composition among them. The saturates content of Xinjiang-P601 is close to 60 wt%, while Shengli-C373 only has slightly over 25 wt%. Both Xinjiang-P601 and Henan-L3511 have low asphaltene contents, below 0.2 wt%, whereas Shengli-C373 has a high asphaltene content of 7.69 wt%. The H/C ratio of Xinjiang-P601 exceeds 1.7, while the H/C ratio of Shengli-C373 in the eastern region is around 1.6, consistent with previous reports (Zhang et al., 2020). Shengli-C373 has a sulfur content of nearly 5 wt%, while the sulfur content of other heavy oils is below 0.5 wt%. The oxygen content of these heavy oils is all above 0.5 wt%, with Xinjiang-P601 having a high oxygen content of 1.91 wt%. This may be related to their high acid values.

Table 1
The preparation and ionization modes of different compound categories.

Category	Pretreatment method	Diluent solvent (Toluene: Methanol, V:V)	Concentration, mg/mL	ESI mode
saturated hydrocarbons	RICO	1:3	0.40	negative
aromatic hydrocarbons	sulfonation	4:1	0.04	negative
acidic oxygen compounds	needless	1:3	0.20	negative
sulfur compounds	methylation	1:1	0.01	positive
basic nitrogen compounds	needless	1:1	0.20	positive
neutral nitrogen compounds	needless	1:3	0.20	negative

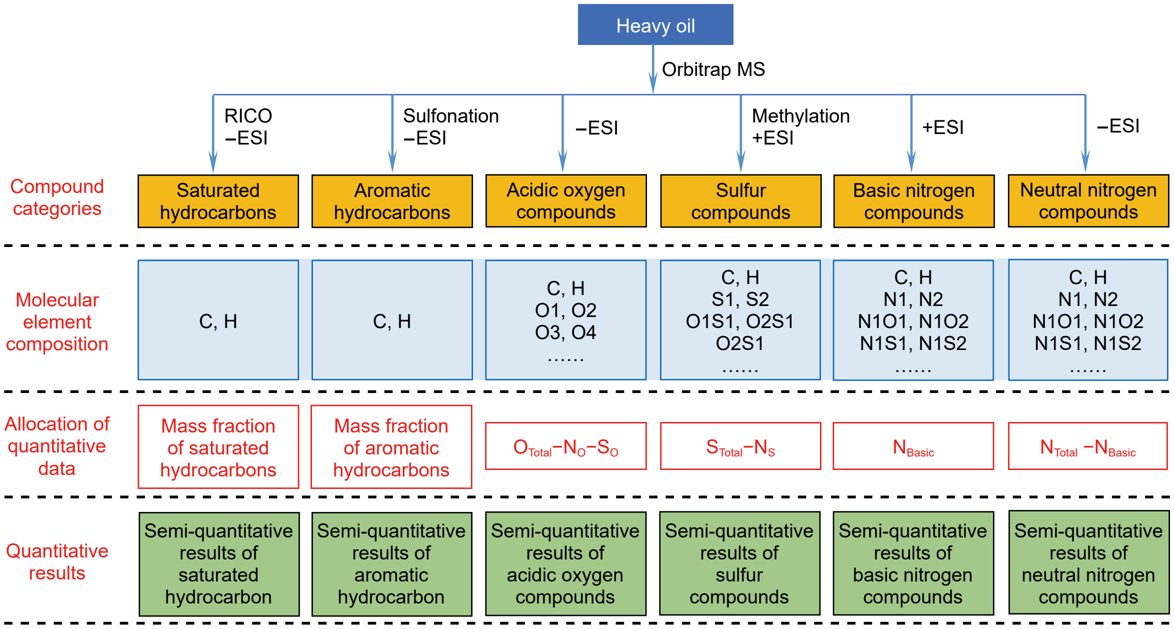

Fig. 1. Semi-quantitative analysis scheme of molecular composition of heavy oil based on compound categories.

Table 2
Bulk properties of the four heavy oils.

	Xinjiang-P601	Henan-L3511	Shengli-J8	Shengli-C373
Viscosity, 50 °C mPa•s	3033	1665	1864	6883
TAN, mgKOH/g	11.77	4.91	3.87	3.11
Saturates, wt%	58.20	45.79	44.86	25.28
Aromatics, wt%	19.73	22.91	24.85	39.68
Resins, wt%	20.31	31.19	28.17	29.00
Alsphaltens, wt%	0.19	<0.05	1.32	7.69
H/C	1.72	1.68	1.65	1.57
S, wt%	0.22	0.27	0.31	4.98
N, wt%	0.25	0.64	0.75	0.73
O, wt%	1.91	1.31	0.57	0.98

The simulated distillation analysis based on high-temperature gas chromatography provides the relationship between boiling point and yield for heavy oils. Fig. 2 shows the distillation curve distribution of the four heavy oils. At the same boiling point temperature, Xinjiang-P601 oil has the highest yield. Henan-L3511 shows a significant increase in yield around 430 °C, while Shengli heavy oils have the lowest yield. It is evident that the initial boiling points of these heavy oils are all above 200 °C. Comparing with the boiling point information of normal paraffins, it can be inferred that these heavy oils contain almost no compounds with carbon numbers below C11. This characteristic allows us to conduct molecular composition analysis of the heavy oils without having to overly consider the uncertainty interference caused by easily volatile light components on the semi-quantitative results.

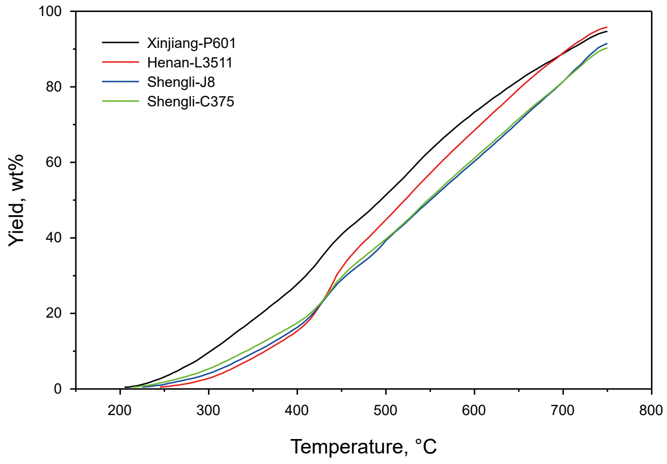

Fig. 2. Boiling point-yield curves of the heavy oils by simulated distillation.

3.2. Semi-quantitative molecular composition

Fig. 3 shows the molecular composition analysis results of Shengli-J8 heavy oil based on compound categories. HRMS provides the accurate elemental composition information (i.e., molecular formula) of compounds. Additionally, the analysis results of molecular composition based on compound categories inherently carry structural information about functional groups. Accordingly, we can determine the main structural information of different category of compounds based on the HRMS analysis results. For example, saturated hydrocarbons with double bond equivalence (DBE) $= 0$ correspond to linear alkanes, and other DBE values correspond to cycloalkanes with different naphthenic ring numbers. The DBE value of aromatic hydrocarbons starts from 4, corresponding to alkylbenzenes. In acidic oxygen compounds, the

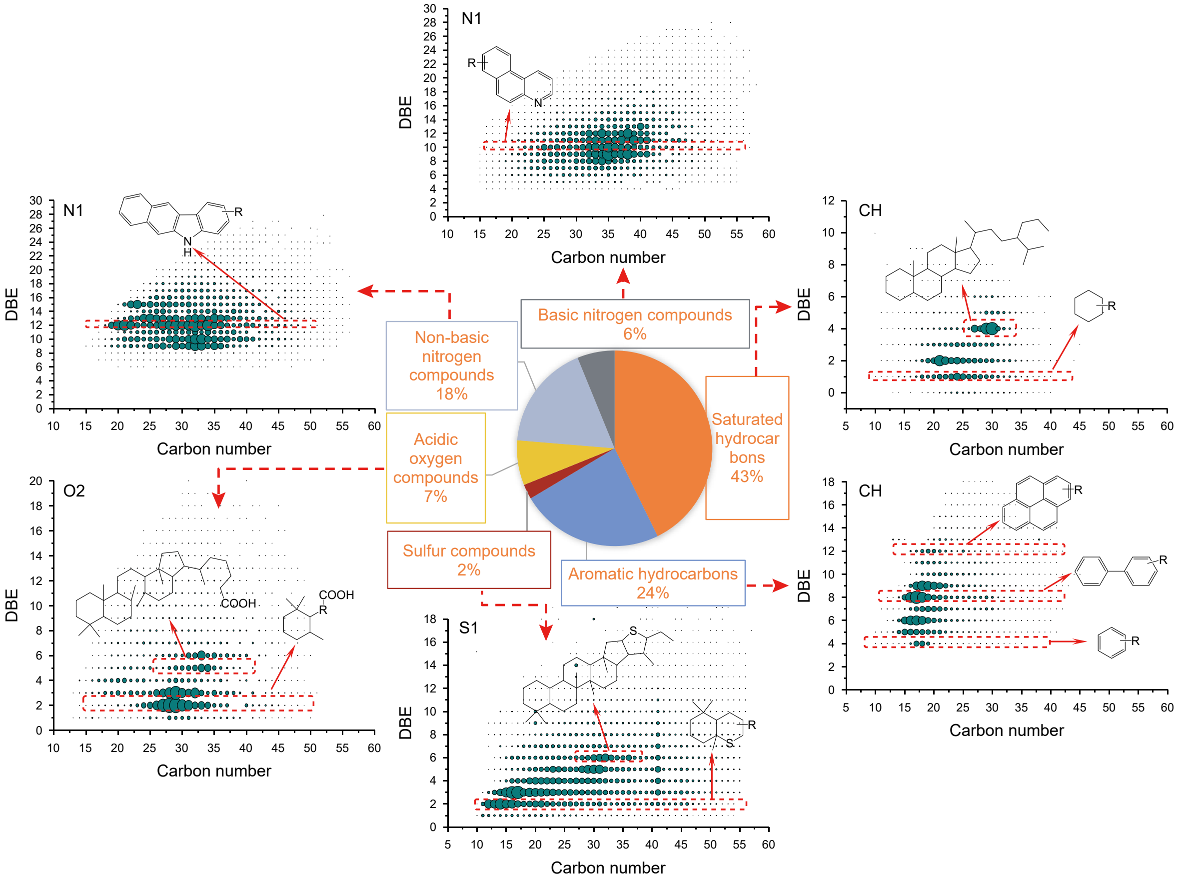

Fig. 3. The comprehensive molecular composition distribution of six categories (saturated hydrocarbons, aromatic hydrocarbons, acid oxygen compounds, sulfides, basic nitrogen compounds, and neutral nitrogen compounds) of Shengli-J8 heavy oil. For each category, carbon number-DBE distribution dot plot and typical molecular structures of the major compounds are provided.

DBE value of O2 compounds starts from 1, generally corresponding to chain carboxylic acids, whereas higher DBE values represent monocarboxylic acids with different naphthenic ring numbers.

The independent characterization of different categories greatly eliminates the ionization suppression effects between them. A semi-quantitative analysis of the molecular composition of heavy oil has been achieved through the rational allocation of organic element content and macroscopic component content in the molecular composition analysis results (Li et al., 2023). This provides a quantitative representation of thousands of molecules in heavy oil, and each molecule in different categories undergoes semi-quantitative analysis. The enormous number of molecules detected in each heavy oil makes it challenging for us to directly understand the molecular composition characteristics of the heavy oil. This requires statistical analysis of the semi-quantitative data on the molecular composition of the heavy oil. The analysis data of the molecular composition of heavy oil consists of six categories. The sum of the contents of all the molecules within each category represents the proportion of different categories in the heavy oil. A pie chart depicting the mass proportion of the six categories in Shengli-J8 heavy oil is also displayed in Fig. 3.

The category attribution of each molecule in the semi-quantitative results of heavy oil molecular composition is clear. This allows us to separately analyze the distribution of the content of different categories based on the carbon number and DBE values, giving rise to the carbon number-category abundance diagram and the DBE-category abundance diagram for heavy oil. These statistical diagrams can help us better understand the molecular composition characteristics of heavy oil. Fig. 4 illustrates the aforementioned three types of statistical diagrams for different semi-quantitative data of heavy oil. Saturated hydrocarbons are the main compounds in Xinjiang-P601, Henan-L3511, and Shengli-J8, with saturated hydrocarbons accounting for nearly 50 wt% of Xinjiang-P601. The content distribution of saturated hydrocarbons in Xinjiang and Henan heavy oils is more evenly distributed across carbon numbers, with Xinjiang heavy oil exhibiting a wider distribution range at higher carbon numbers. On the other hand, the carbon number distribution range of saturated hydrocarbons in Shengli-J8 is narrower and primarily concentrated around C30. Xinjiang-P601 and Shengli-J8 have higher content of aromatic hydrocarbons before C30, while the content range of aromatic hydrocarbons in Henan-L3511 heavy oil is broader and can reach above C40. Xinjiang-P601 has the highest acid value and oxygen content, with acidic oxygen compounds accounting for up to 23 wt%, primarily composed of naphthenic acids with 2–4 rings. Shengli-C373 has an extremely high sulfur content, with sulfur compounds accounting for nearly 50 wt% of the total heavy oil mass. Both Shengli-C373 and Shengli-J8 show high compound abundances around C30, exhibiting typical structure characteristics of steroids and hopanes. The high abundance of sulfur compounds in Shengli-C373 seems to be the product of sulfur elements combining with these special hydrocarbon skeletons in the form of thiolane (Wu et al., 2019).

3.3. Particularity of the heavy oil on molecular composition

The semi-quantitative analysis of molecular composition of

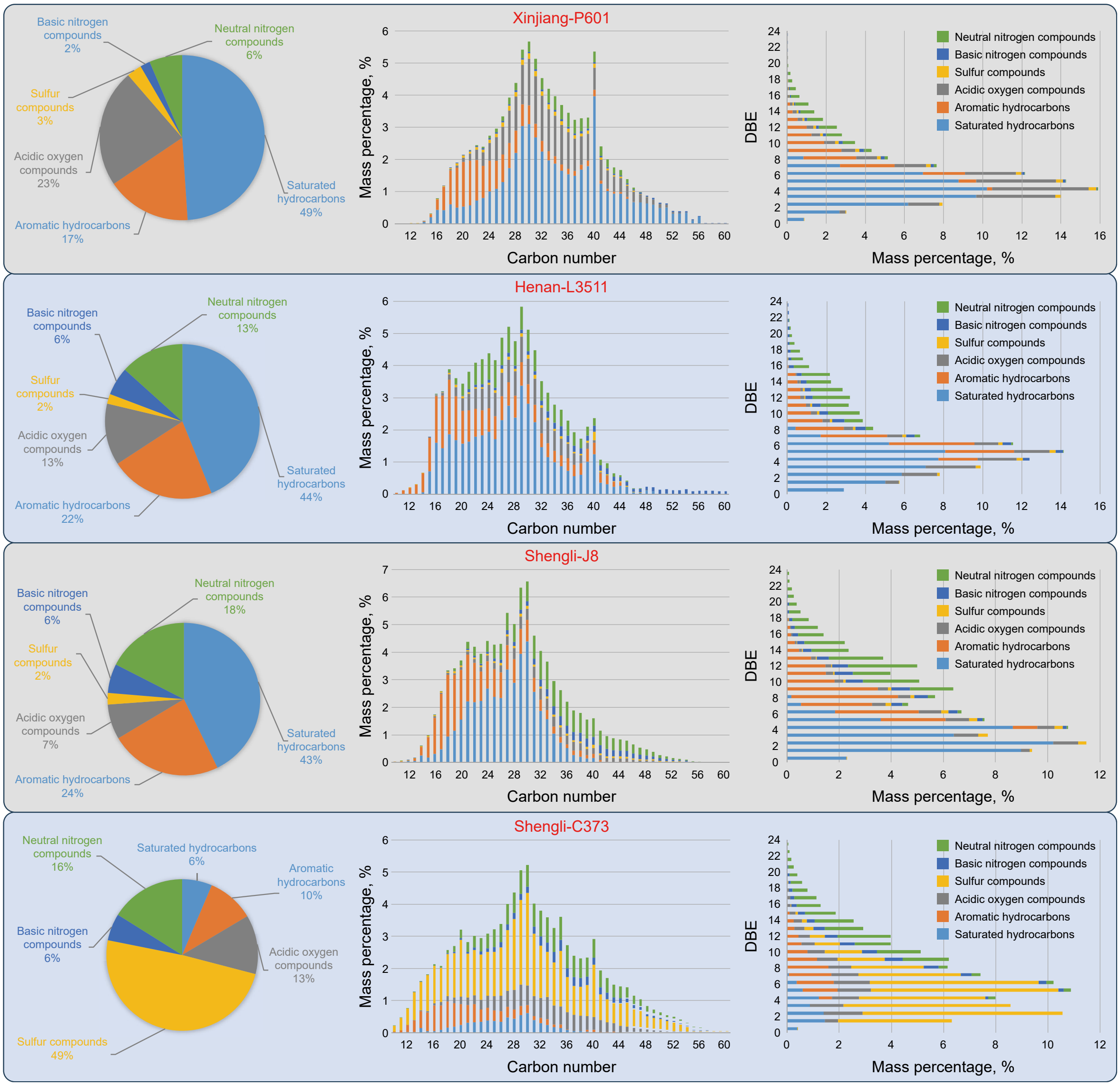

Fig. 4. Statistical plots of semi-quantitative analysis of the molecular compositions of Xinjing-P601, Henan-L3511, Shengli-J8 and Shengli-C373: pie chart of the mass proportion of different compound categories (left); bar chart of carbon number-category abundance (center); bar chart of DBE-category abundance (right).

heavy oil enables the revelation of its chemical composition characteristics that contribute to its viscosity at the molecular level. Fig. 5 compares the semi-quantitative analysis results of the molecular composition between Shengli-J8 and a conventional Shengli crude oil. While both these two oil samples are extracted from the Shengli oilfield, the differences in their molecular composition are quite significant. Shengli-J8 has alkanes (DBE = 0) content slightly above 2 wt%, with the saturated hydrocarbons primarily composed of steranes near C30. In contrast, the conventional Shengli crude oil has alkanes content of over 15 wt%, exhibiting an absolute dominance in its saturated hydrocarbons. The aromatics in Shengli-J8 are predominantly distributed in the high carbon number range of C15–C30 and high DBE range of 5–14. Conversely, the aromatics in the conventional Shengli crude oil are mainly distributed in the low carbon number range of C8–C15 and low DBE range of 4–8.

The cyclic structure serves as a carrier for viscosity. The absence of alkanes leads to the saturated hydrocarbons, which are the most abundant compound category in Shengli-J8, are predominated by multi-ring structures with short side chains, such as steranes. This results in an increase in viscosity. In addition, aromatic hydrocarbons, as the secondary major compound category in Shengli-J8, are dominated by high molecular weight and highly condensed structures. This further increases the viscosity of Shengli-J8. The differences in molecular composition effectively reveal the reasons that contribute to the high viscosity of heavy oil from a chemical composition perspective.

The semi-quantitative analysis of the molecular composition reveals that the mass fraction of non-polar categories, such as hydrocarbons and sulfur compounds, in heavy oil is all above 60%. This obscures the molecular composition characteristics of polar heteroatomic categories. Fig. 6 illustrates the variation of the content of major polar species with carbon number and DBE in Shengli-J8 and a conventional Shengli crude oil. The highest mass distribution of polar species in Shengli crude oil is around C25, while in Shengli-J8, it is around C32. In terms of DBE, the mass fraction of polar species in Shengli-J8 is higher in the high DBE range (DBE≥9), while in Shengli crude oil, it is higher in the low DBE range (DBE<9). Higher carbon numbers and DBE values are the molecular

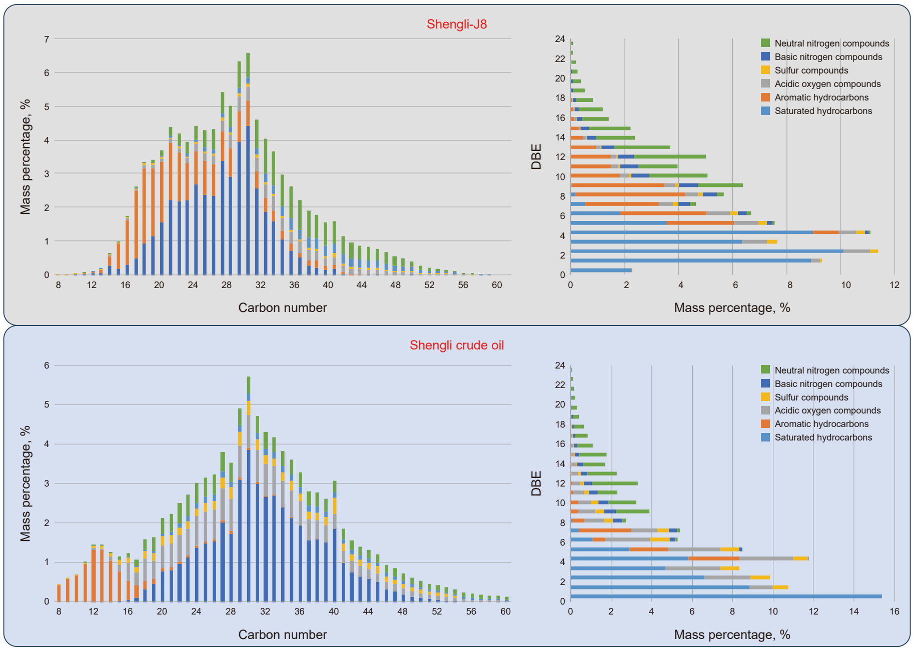

Fig. 5. Histograms of carbon number-category abundance (left) and DBE-category abundance (right) for Shengli-J8 and a conventional Shengli crude oil.

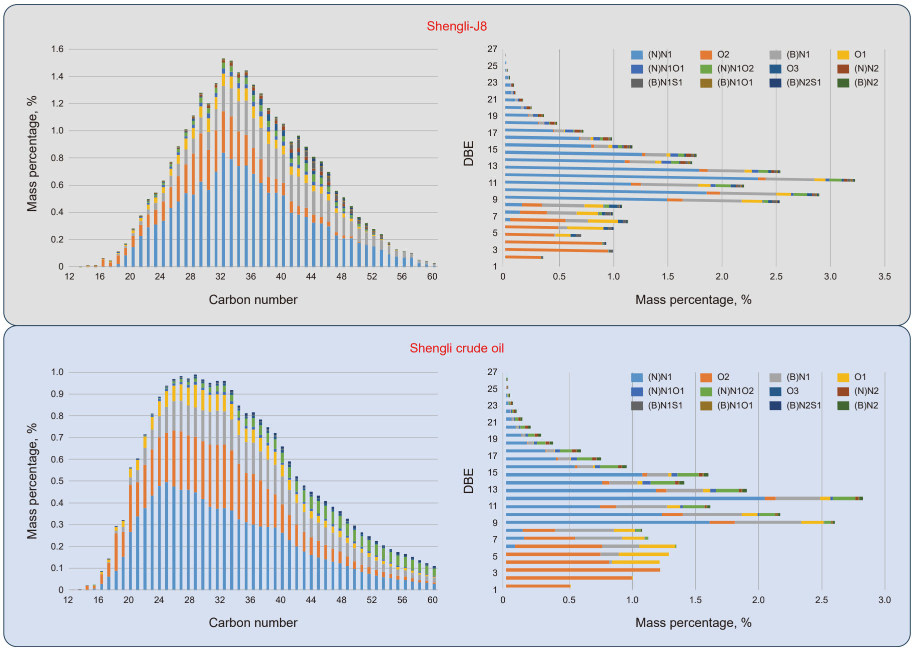

Fig. 6. Histograms of carbon number-polar species abundance (left) and DBE polar species abundance (right) for Shengli-J8 and a conventional Shengli crude oil. (“(N)” instead of Neutral nitrogen compounds, “(B)” instead of Basic nitrogen compounds.).

composition characteristics of polar species in Shengli-J8, and also the factors contributing to its high viscosity.

The semi-quantitative results of the molecular composition of each heavy oil include the quantity information of thousands of molecules. Constructing a representative molecule set is beneficial for further applications of the analytical results, such as simulating the interactions between heavy oil molecules and predicting the viscosity of heavy oil. Fig. 7 illustrates the characteristic molecule sets of the four heavy oils. The molecule sets contain representative molecules with the highest mass content of different compound categories. Xinjiang-P601 exhibits the highest content of long-chain cycloalkanes and dicarboxylic acids. Henan-L3511 shows a significant amount of nitrogen-containing carboxylic acids. Shengli-J8 has the highest content of C30 steranes, while Shengli-C373 has the highest content of sulfur-containing steranes and significant levels of sulfur-containing carboxylic acids. Overall, the compound molecular composition in different heavy oils is essentially the same, with the main differences lying in the varying levels of different categories of molecules.

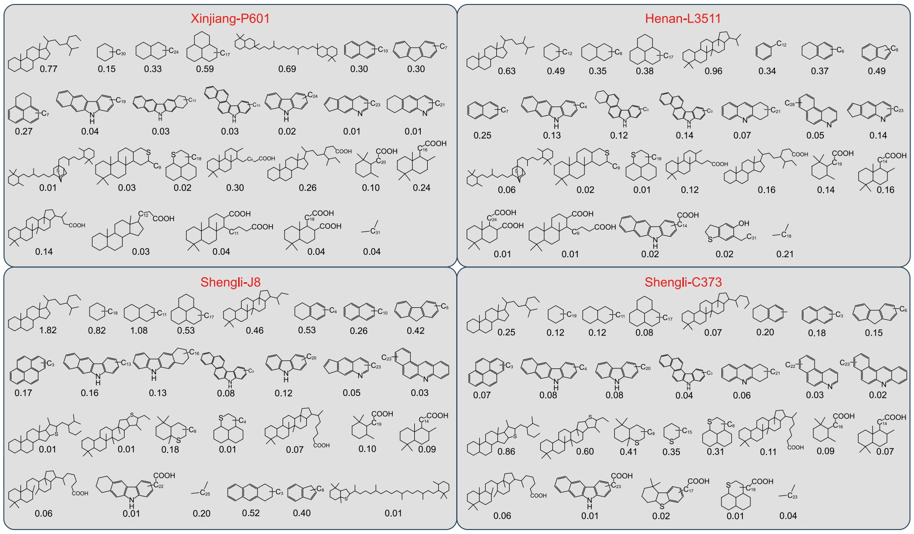

Fig. 7. Characteristic molecular sets of Xinjiang-P601, Henan-L3511, Shengli-J8, and Shengli-C373 based on semi-quantitative analysis of molecular composition. The numbers represent the mass percentage of each molecule.

4. Conclusion

This study utilizes derivative pretreatment and HRMS equipped with an ESI source to achieve the molecular composition of six compound categories in heavy oil. By incorporating macroscopic quantitative data into the quantitative process, semi-quantitative analysis of molecular composition of typical heavy oils from western, central, and eastern China has been ultimately accomplished. Saturated hydrocarbons are the dominant compound category in Xinjiang-P601, Henan-L3511, and Shengli-J8, with Xinjiang-P601 exhibiting a wide range of carbon numbers and a significant abundance of cyclic alkanes beyond C40. In contrast, Shengli-J8 has a narrow distribution of saturated hydrocarbon carbon numbers, primarily concentrated around C30. Shengli-C373 has a high sulfur content, with sulfur-containing compounds accounting for close to 50 wt% of its composition, mainly composed of cyclic sulfides.

The absence of linear alkanes and low-molecular-weight aromatics is the primary characteristic that distinguishes Shengli-J8 heavy oil from conventional Shengli crude oil in terms of molecular composition, and it is also the chemical composition responsible for the high viscosity of heavy oil. The composition of the characteristic molecular set of heavy oil indicates that the molecular types of different heavy oils are similar, and the differences in the proportions of different types of molecules are the main reasons for the variations in heavy oil properties. The semi-quantitative analysis of heavy oil molecular composition reveals the compositional characteristics of heavy oil at the molecular level, and the analysis results are expected to be used in heavy oil molecular simulation to further understand the mechanisms behind the high viscosity of the heavy oil.

Declaration of interests

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.

CRediT authorship contribution statement

Jian-Xun Wu: Writing – original draft, Visualization, Methodology, Data curation. **Shuo-Fan Li:** Investigation, Data curation. **Qi-Fu Li:** Resources, Investigation. **Feng Yan:** Resources, Investigation. **Qi-Lin Zhou:** Investigation, Data curation. **Shuai Ma:** Data curation. **Ya-He Zhang:** Investigation. **Suo-Qi Zhao:** Validation, Investigation. **Quan Shi:** Writing – review & editing, Supervision.

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