



Original Paper

Molecular composition of naphthenic acids in a Chinese heavy crude oil and their impacts on oil viscosity



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ABSTRACT

Most heavy crude oils underwent biodegradation and generated a significant amount of naphthenic acids. Naphthenic acids are polar compounds with the carboxylic group and are considered as a major factor affecting the oil viscosity. However, the relationship between the molecular composition of naphthenic acids and oil viscosity is not well understood. This study examined a “clean” heavy oil with low contents of heteroatoms but had a high content of naphthenic acids. Naphthenic acids were fractionated by distillation and caustic extraction. The molecular composition was characterized by high-resolution Orbitrap mass spectrometry. It was found that the 2- and 3-ring naphthenic monoacids with 15–35 carbon atoms are dominant components of the acid fractions; the caustic extraction is capable of isolating naphthenic acids with less than 35 carbons, which is equivalent to the upper limit of the distillable components, but not those in the residue fraction; the total acid number of the heavy distillates is higher than that of the residue fraction; the viscosity of the distillation fraction increases exponentially with an increased boiling point of the distillates. Blending experiments indicates that there is a strong correlation between the oil viscosity and acids content, although the acid content is only a few percent of the total oil.

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1. Introduction

Heavy and extra-heavy crude oils account for more than 70% of total petroleum reserves worldwide, are more energy-intensive to produce and transport due to their high viscosities (Hart, 2014; Guo et al., 2016). To be more competitive to conventional crude oil and remain viable in a low carbon economy, heavy oil producers face many urgent challenges to reduce production costs and energy used (Hart, 2014; Santos et al., 2017). Reducing oil viscosity has been a technical issue that has received tremendous attention.

China has more than 20 billion tons of heavy oil reserves located in Liaohe, Tahe, Shengli, Karamay, and Henan Oil Fields (Yang et al., 2019). Naphthenic hydrocarbons are considered as the high-quality

components of petroleum, which are raw materials used in the production of lubricating oil, extremely cold-resistant oil, high-grade transformer oil, special grade asphalt, and many high value-added products (Wang, 2013). High-quality naphthenic heavy oils are defined as heavy oils with more than 50 wt% naphthenic hydrocarbons, which account for 0.15% of total world petroleum reserves (Zheng and Qin, 2008). Xinjiang Oilfield produces a high-quality naphthenic heavy oil which has 69.7 wt% naphthenic hydrocarbons, and high viscosity, acid number, density, and resin content, but low asphaltene content (Li and Zhang, 2004). Naphthenic acids are complex mixtures of alicyclic carboxylic acids (Reinardy et al., 2013). Generally, the term of “naphthenic acids” refers all acidic compounds in crude oils (Headley et al., 2011). In this paper, naphthenic acids refer the separated acidic fractions or acidic compounds in the oils.

High oil viscosity is commonly attributed to the presence of asphaltenes (Luo and Gu, 2007; Ghanavati et al., 2013; Liu and Long,

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2018), heteroatoms (Zhu et al., 2004; Larter et al., 2008; Wang et al., 2010; Alomair and Almusallam, 2013), condensation of polycyclic arenes, and long-chain aliphatic and naphthenic hydrocarbons. Among them, the mechanism of the latter is due to the inter-twine of long-chain aliphatics and naphthenics causing high oil viscosity (Muraza, 2015). Carboxylic groups in naphthenic acids are known to cause hydrogen-bond interactions (Zhu et al., 2018). They are also interfacial active substances and have a major impact on oil-water interfacial tension (Garcia-Olvera et al., 2016).

The common separation methods of petroleum acids include acid-base extraction (Liu et al., 2015), solid phase extraction (Rowland et al., 2014), and ionic liquid extraction (Shi et al., 2008). The acid-base extraction method is simple and commonly applied in the separation of petroleum acids. However, due to the emulsification of petroleum acids, the separation yield is usually lower than the actual value. Solid phase extraction method is quick and convenient, and the recovery of petroleum acids is high. However, contacting the sample with the stationary phase may introduce impurities, and the volume of the treated sample is very small, so it is only suitable for the preparation of small amounts of petroleum acid. The ionic liquid extraction method is similar to the acid-base extraction, but without an emulsification problem. However, the acid yield is also not high and the toxicity of ionic liquid may be an eco-environmental concern (Shi et al., 2008).

Electrospray ionization source (ESI) combined with Orbitrap high-resolution mass spectrometry is one of the advanced techniques for analyzing complex polar organic compounds in heavy petroleum products (Schmidt et al., 2018; Pan et al., 2020). ESI ionization sources could selectively ionize very low concentrations of acidic compounds in complex hydrocarbon matrices (Headley et al., 2011), while Orbitrap mass spectroscopy (MS) provides high resolution and mass accuracy for accurate analysis of the molecular composition of compounds (Zubarev and Makarov, 2013).

In this study, the crude oil was fractionated into various narrow fractions by true boiling point distillation. Petroleum acids were separated by acid-base extraction and characterized by high resolution mass spectrometry. The contribution of petroleum acids on the oil viscosity of various distillation fractions of a high naphthenic heavy oil will be investigated.

2. Experimental

2.1. Samples and reagents

The heavy crude oil sample was obtained from Fengcheng area of Karamay Oilfield in Xinjiang province, China. Ten kilograms of crude oil were distilled by atmospheric and vacuum distillation in a true boiling point distillation apparatus (i-Fisher, Germany) according to ASTM D2892 and D5236 methods. A total of eight distillate fractions (< 110 °C, 110–220 °C, 220–260 °C, 260–300 °C, 300–340 °C, 340–380 °C, 380–460 °C, 460–500 °C) and a 500 °C⁺ residue fraction were obtained.

The chemicals used in this study, the analytical (AR) grade sodium hydroxide, potassium hydroxide (KOH), aqueous solution 37 wt% hydrochloric acid, 25 wt% ammonia, and HPLC grade organic chemicals ethanol, n-hexane, dichloromethane (DCM), and toluene were purchased from Beijing Chemical Reagents Company. The solvents were purified by distillation before use.

2.2. Acidic component extraction

Acidic components in distillate fractions greater than 200 °C were separated by liquid extraction using sodium hydroxide, as shown in the separation process flow scheme in Fig. 1. The distillate

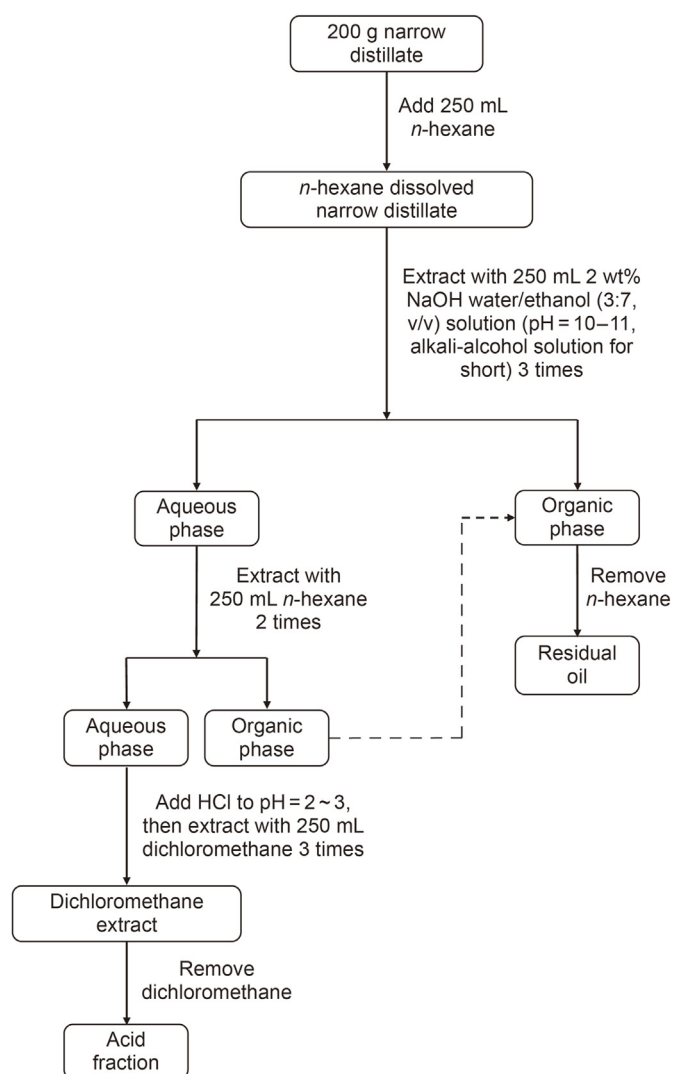


Fig. 1. Extraction procedure for acidic component separation. For the residue, n-hexane solvent was replaced by dichloromethane.

fractions were diluted by hexane, except for the residue fraction which was dissolved in dichloromethane before the extraction. Total acid numbers (TAN) of the crude oil sample, distillate fractions, their acidic components, and acid-free fractions were determined according to the Chinese GB/T 7304 standard method using KOH potentiometric titration.

Table 1
Yields and the cumulative yield of distillate fraction of Fengcheng heavy crude oil.

Boiling point, °C	Yield, wt%	Cumulative yield, wt%
IBP–110	0.63	0.63
110–220	1.46	2.09
220–260	1.86	3.95
260–300	3.53	7.48
300–340	3.73	11.21
340–380	3.35	14.56
380–420	0.49	15.05
420–460	9.81	24.86
460–500	10.49	35.36
> 500	63.75	99.11

Table 2
Yields of acid-free oil and acids of distillate fractions and their TANs.

Distillate fraction, °C	Acid-free oil, %	Acids, %	Yield, %	TAN of fraction, mg KOH/g	TAN of acid-free oil, mg KOH/g	Acids-removal*, %
220–260	94.62	0.10	94.73	0.63	0.06	90.99
260–300	97.03	0.47	97.50	1.25	0.08	93.79
300–340	94.77	1.64	96.41	3.36	0.44	87.58
340–380	91.59	2.77	94.36	6.65	0.09	98.76
380–420	90.52	3.45	93.96	4.60	0.09	98.23
380–460	91.18	2.81	93.99	4.98	0.09	98.35
460–500	91.63	2.35	93.97	5.61	0.09	98.53
> 500	93.93	0.09	94.02	3.98	0.21	95.04

* Acids removal = $(1 - \text{Yield of acid-free oil} \times \frac{\text{TAN}_f}{\text{TAN}}) \times 100\%$, where TAN_f and TAN were the TAN of the acid-free oil and the distillate fraction, respectively.

2.3. Orbitrap MS analysis

The test samples, including the crude oil sample, narrow distillate fractions, residue fraction, and their acid fractions, were dissolved in toluene at 10 mg/mL, and then diluted with toluene/methanol (1:3, v/v) to 0.02 mg/mL (equivalent to 0.005 mg/mL for acid fractions). Ammonium hydroxide (NH₄OH, 15 mL) was added into one 1 mL sample solution to enhance the negative ion ESI ionization efficiency (Lu et al., 2016). The MS characterization was carried out using an Orbitrap mass spectrometer (Orbitrap Fusion, Thermo Scientific, USA). The test samples were injected directly into the ESI source at 12 μL/min through an injection pump. The sheath, auxiliary, and sweep gas flow rates were 8.0, 3.0, 0.1 arbitrary units, respectively. The ion transfer tube temperature was at 300 °C. The mass resolution was 500,000 at *m/z* 200. The ions in the range from *m/z* 150 to *m/z* 1000 were recorded in a 1 min detection period. The MS data analysis was carried out using Qual Browser of the Thermo Xcalibur software, which has been reported elsewhere (Chen et al., 2018; Pan et al., 2020).

2.4. Mixing experiment of petroleum acids with acid-free oil

To examine the effect of petroleum acids on oil viscosity, the acid fraction separated from the 380–460 °C distillate fraction was added into the acid-free oil at various concentrations: 0.29, 0.59,

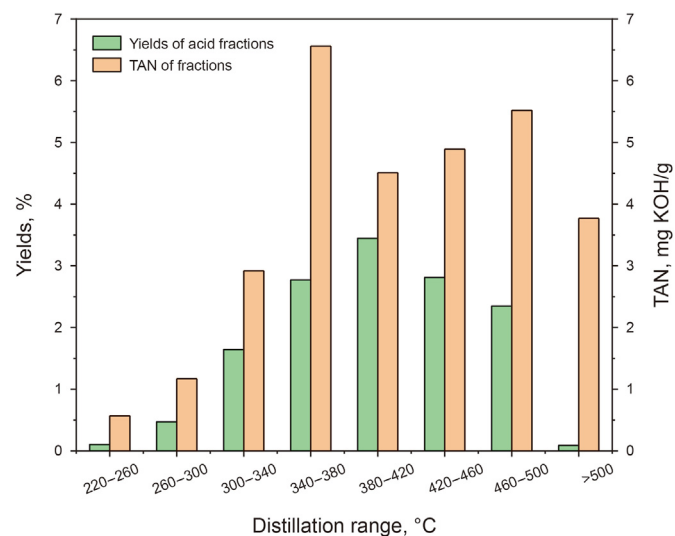
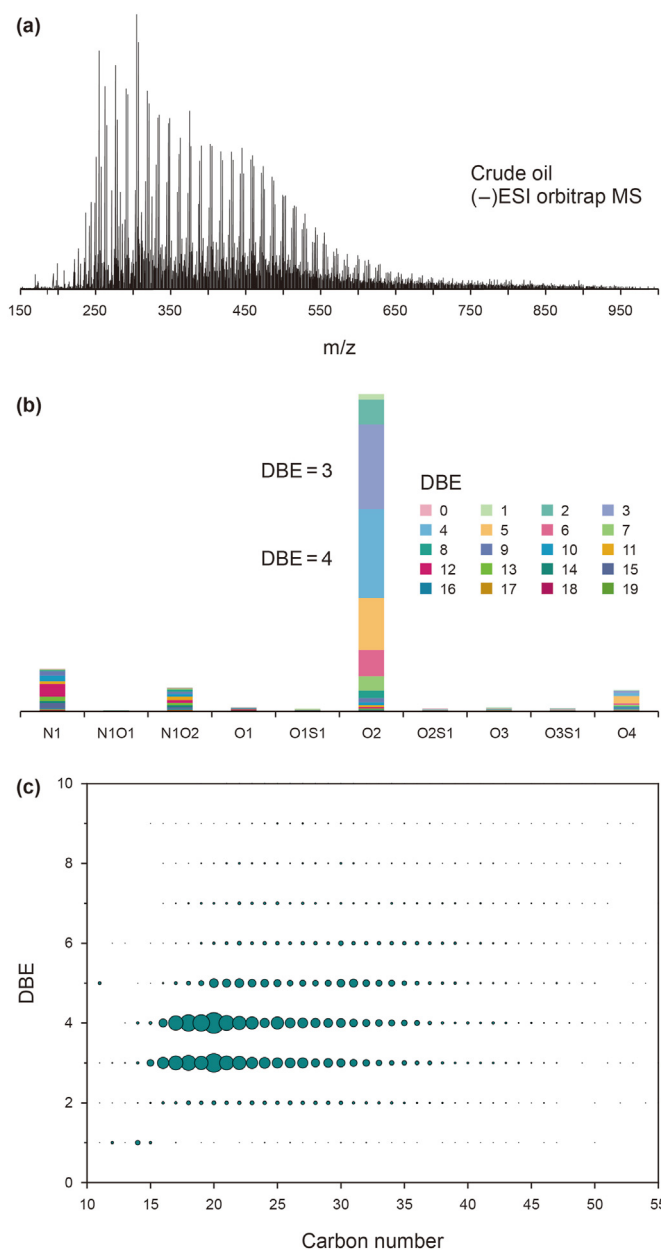


Fig. 2. Distribution of TAN in the distillate fractions and the acids yield of the extraction.

Fig. 3. (a) Negative-ion ESI Orbitrap mass spectrum of the crude oil sample, (b) relative abundance of assigned class species assigned from the mass spectrum, and (c) ion relative abundance plot of double bond equivalent versus carbon number of O2 class species.

0.92, 1.24, 1.57, 1.82, 2.01, 2.11, 2.39, 2.67, and 2.72 wt% acids in the oil, respectively. The viscosities of the mixed oil samples were determined using a rotary viscometer according to the Chinese SY/T 0520–2008 standard method at 50 °C and 20 °C at 100 s⁻¹ shear rate.

3. Results and discussion

3.1. Characterization of petroleum acids in various distillate fractions of Fengcheng crude oil

The sulfur content and TAN of Fengcheng crude oil were 0.28 wt%

and 5.46 mg KOH/g, respectively, which were similar to other heavy oils from Karamay Oil field (Zhang et al., 2021). The yields of distillate fractions were shown in Table 1, indicating it was a heavy oil with 64 wt% 500 °C⁺ residues. The yield of 380–420 °C distillate fraction was abruptly decreased, due to switching from atmospheric to vacuum mode distillation operation.

Table 2 shows the yields of acid-free oil and acids of distillate fractions and their TANs. Fig. 2 shows the distributions of TAN and acids yield of distillate fraction, indicating the TAN exhibited a bimodal distribution with two peak TAN values of 6.65 and 5.61 at 340–380 °C and 460–500 °C fractions, respectively. The finding was consistent with those reported by Tian (2005), indicating the

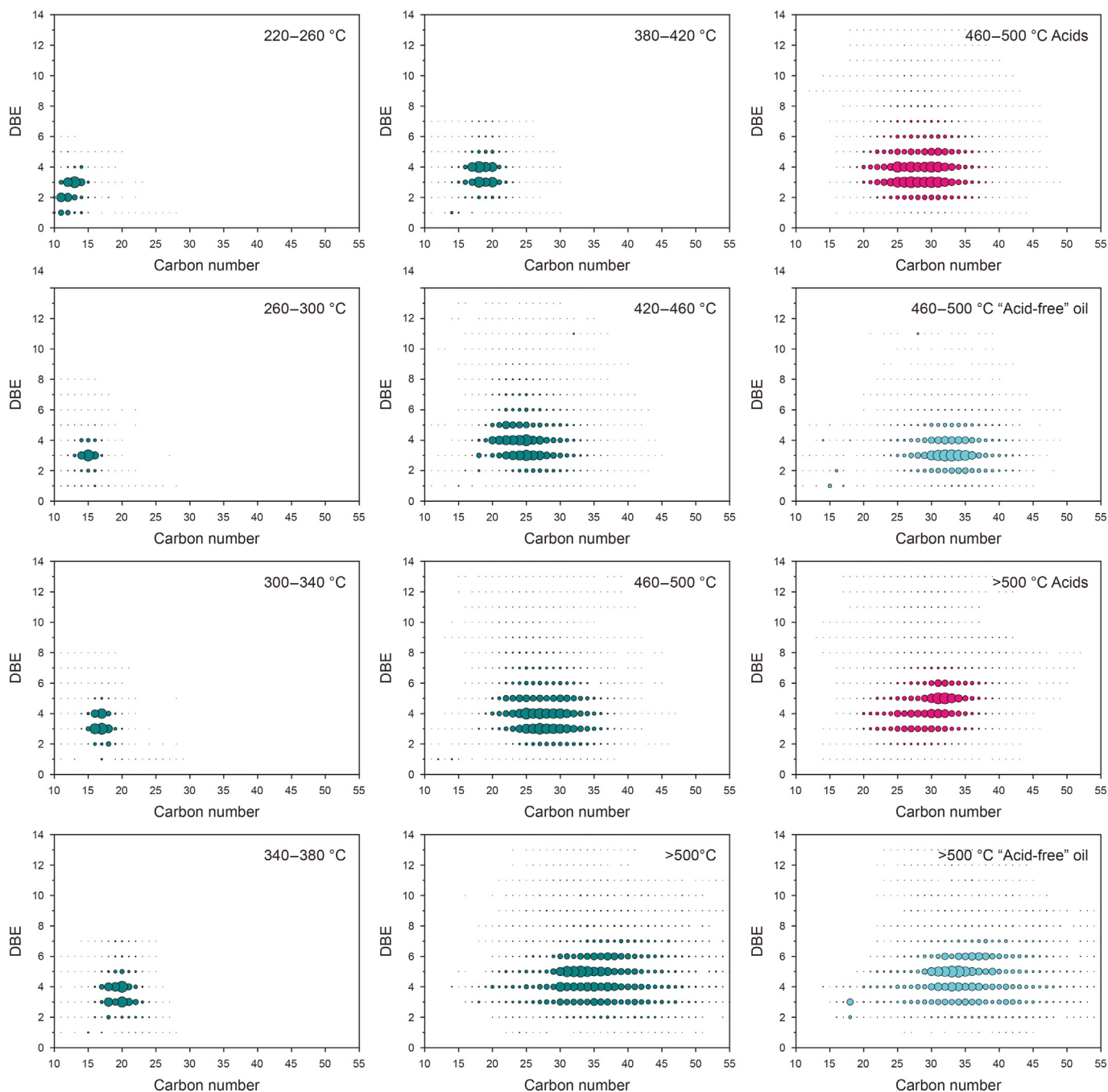


Fig. 4. Ion relative abundance plots of DBE as a function of carbon number of O₂ class species assigned from the negative-ion Orbitrap mass spectra of the distillates and the residue (dark cyan), acids (pink) and “acid-free” oils (light cyan) of the 460–500 °C distillates and the residue.

bimodal TAN distribution was common among 13 high-TAN heavy oils from various geological origins. Whereas, the distribution of acids yields of distillate fraction exhibited a normal distribution with a wide range of yield from 0.10% to 3.45%. The distribution of TAN of distillate fraction was not correlated to that of acids yield of distillate fraction. Theoretically, the acids yield of an oil sample is expected to be correlated to its TAN from the calculation of TAN based on the average molecular weight and molecular composition of naphthenic acids in the oil. Clearly, the acids yields of distillate fractions shown in Fig. 2 were much lower compared to the TAN values. This could be attributed to the oil loss in the extraction and the low recovery of large molecular acids. To obtain a high purity of the acid fraction, a proportion of the oil which attached on the glass wall of the extraction apparatus was not recovered in the operation. This also led to a low extraction yield, as shown in Table 2. Another reason for the low yield of acids was the molecular selectivity in the extraction. Lu et al. (2008) reported that the base extraction was effective only for low molecular acids; large molecular naphthenic acids, especially those in the residue, cannot be extracted from the oil. This is consistent with the results in Table 2, indicating a very low yield of acids (0.09%) for the 500 °C⁺ residues, although it had a high TAN value of 3.98.

The data in the last column of Table 2 showed that the caustic extraction method was effective in removing acid compounds from the oil samples (90% acids removal). Emulsification during the separation process results in partial loss of acids.

3.2. Molecular composition of naphthenic acids

Fig. 3 (a) shows the negative-ion ESI Orbitrap mass spectrum of the crude oil. Ten class species, such as N1 (molecule has one nitrogen atom), N1O1, N1O2, O1, O2, O3, O4, O1S1, O2S1, and O3S1 were assigned from the mass spectrum based on the exact mass values. Among them, the O2 class species have the highest relative abundance, as shown in Fig. 3 (b). Fig. 3 (c) shows the ion relative abundance plot of double-bound equivalent (DBE) as a function of the carbon number of O2 class species. The high relative abundance O2 class species with 3, 4 and 5 DBEs are corresponding to 2, 3, and 4 ring naphthenic acids, respectively. These abundant O2 class species were distributed in a carbon number range of 15–35, in which C₂₀ was the maximum.

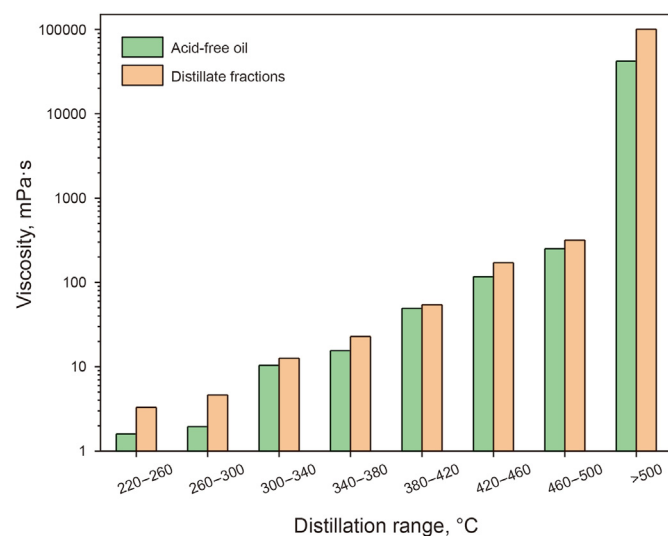


Fig. 5. Viscosity of the distillate fractions with and without naphthenic acids.

Fig. 4 shows relative abundance plots of DBE as a function of carbon number of O2 class species assigned from the negative-ion Orbitrap mass spectra of the distillates. The ranges of carbon number of O2 class species in the atmospheric distillates (left column) were narrow, whereas those in the vacuum distillate fractions (middle column) were wider. This is expected, since operating the laboratory distillation unit at the vacuum mode has fewer theoretical plates than at the atmospheric mode, and the heavy fractions have more complex molecular composition. The upper boundary of high relative abundance O2 class species was around C₃₅ for the distillates.

The extracted acids from 460 to 500 °C distillate and residue fractions were subjected to negative ESI Orbitrap MS analysis. The results showed that the O2 class species in 460–500 °C distillate were the same as those in the extracted acids from 460 to 500 °C distillate; similar range of carbon numbers. As for the residue fraction, the O2 class species in the extracted acids were different with the O2 class species in the residue (in Fig. 4, > 500 °C acids and > 500 °C “acid-free” oil have different range of carbon numbers). The results suggested that naphthenic acids with more the 35 carbons are not readily separated from the heavy oils by the extraction method.

3.3. Viscosity contribution of the naphthenic acids

Fig. 5 shows the viscosities of oil fractions at 50 °C before and after naphthenic acids removal. As expected, oil viscosity increased dramatically with its boiling point. In order to describe the viscosity reduction after the removal of acids, we defined the viscosity reduction parameter as the ratio of viscosity reduction to acids yield. The viscosity decreased 35% on average after acids were removed, even though the acids accounted for less than 3.5 wt% in each oil fraction. The acids enhance hydrogen bonding and acid-base interactions, making molecules more likely to polymerize, thus increasing viscosity.

To examine the effect of acids content on oil viscosity, the extracted acids from the 420–460 °C distillate fraction were blended in various concentrations with their acid-free oil fraction. Fig. 6 shows the oil viscosity as a function of acids content in 420–460 °C fraction. The viscosities of the initial and endpoints (0 and 2.82 wt%) were acid-free oil and distillate fractions, respectively. The results indicated that oil viscosity was strongly

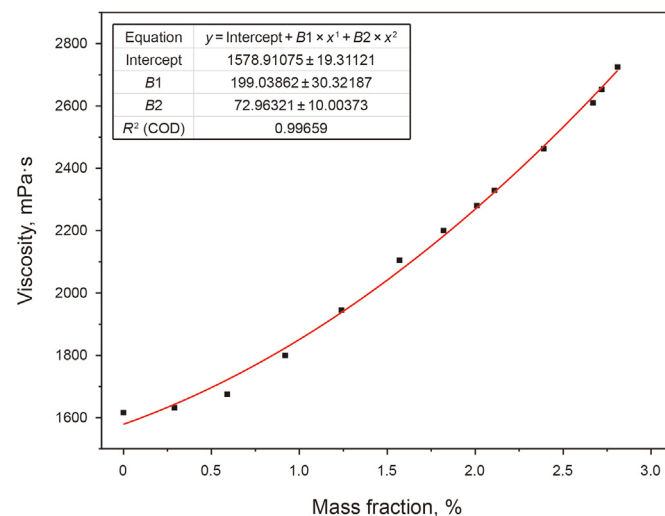


Fig. 6. Viscosity as a function of the mass fraction of naphthenic acids in the 420–460 °C distillate.

correlated with the acids content, as shown by the goodness of fit of oil viscosity-acids content correlation equation.

4. Conclusions

Naphthenic acids in a Chinese heavy crude oil were fractionated by distillation and caustic extraction. The molecular composition was characterized by high-resolution Orbitrap MS. The 2- and 3-ring naphthenic monoacids with 15–35 carbon atoms were the dominant components of the acid fractions. The caustic extraction is capable of the separation of naphthenic acids with less than 35 carbon atoms, which is also the upper limit of the distillable component. The TAN of the distillation residue was lower than the heavy distillates but still in a high value, however, the acids in the residue cannot be extracted from the oil by the caustic extraction. The viscosity of the distillate fraction increased exponentially with the increased distillation temperature. A small amount of petroleum acid could provide a large contribution in viscosity of the oils.

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References

- Alomair, O.A., Almusallam, A.S., 2013. Heavy crude oil viscosity reduction and the impact of asphaltene precipitation. *Energy Fuels* 27 (12), 7267–7276. <https://doi.org/10.1021/ef4015636>.
- Chen, X., Xu, C., Zhang, W., et al., 2018. Separation and molecular characterization of ketones in a low-temperature coal tar. *Energy Fuels* 32 (4), 4662–4670. <https://doi.org/10.1021/acs.energyfuels.7b03630>.
- Garcia-Olvera, G., Reilly, T.M., Lehmann, T.E., et al., 2016. Effects of asphaltenes and organic acids on crude oil-brine interfacial visco-elasticity and oil recovery in low-salinity waterflooding. *Fuel* 185, 151–163. <https://doi.org/10.1016/j.fuel.2016.07.104>.
- Ghanavati, M., Shojaei, M.J., Ar, S.A., 2013. Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: experimental and modeling study. *Energy Fuels* 27 (12), 7217–7232. <https://doi.org/10.1021/ef400776h>.
- Guo, K., Li, H., Yu, Z., 2016. In-situ heavy and extra-heavy oil recovery: a review. *Fuel* 185, 886–902. <https://doi.org/10.1016/j.fuel.2016.08.047>.
- Hart, A., 2014. A review of technologies for transporting heavy crude oil and bitumen via pipelines. *J. Pet. Explor. Prod. Technol.* 4 (3), 327–336. <https://doi.org/10.1007/s13202-013-0086-6>.
- Headley, J.V., Barrow, M.P., Peru, K.M., et al., 2011. Salting-out effects on the characterization of naphthenic acids from Athabasca oil sands using electrospray ionization. *Journal of Environmental Science and Health, Part A*. 46 (8), 844–854. <https://doi.org/10.1080/10934529.2011.579857>.
- Larter, S.R., Adams, J., Gates, I.D., et al., 2008. The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoirs. *J. Can. Pet. Technol.* 47, 1–16. <https://doi.org/10.2118/08-01-52>.
- Li, J., Zhang, H., 2004. The situation about the paving bitumen produced from Xin Jiang heavy crude oil & the researching and discussion about it's processing conceptual desing. *Petroleum Asphalt* 18 (1), 55–59. <https://doi.org/10.3969/j.issn.1006-7450.2004.01.014> (in Chinese).
- Liu, B., Long, J., 2018. The mechanism of how asphaltene affects the viscosity of Tahe heavy oil. *Scientia Sinica Chimica* 48 (4), 434–441. <https://doi.org/10.1360/N032017-00171> (in Chinese).
- Liu, L., Li, W., Du, C., et al., 2015. Separation and analysis of petroleum acids in Changqing crude oil. *Petrochemical Industry Application* 34 (3), 112–115. <https://doi.org/10.3969/j.issn.1673-5285.2015.03.028> (in Chinese).
- Lu, J., Zhang, Y., Shi, Q., 2016. Ionizing aromatic compounds in petroleum by electrospray with HCOONH₄ as ionization promoter. *Anal. Chem.* 88 (7), 3471–3475. <https://doi.org/10.1021/acs.analchem.6b00022>.
- Lu, X., Shi, Q., Zhao, S., et al., 2008. Composition and distribution of acidic compounds in duba extracts: revealed by negative electrospray ionization-fourier transform ion cyclotron resonance-mass spectrometry. *Chin. J. Anal. Chem.* 36 (5), 614–618. <https://doi.org/10.3321/j.issn:0253-3820.2008.05.010> (in Chinese).
- Luo, P., Gu, Y., 2007. Effects of asphaltene content on the heavy oil viscosity at different temperatures. *Fuel* 86 (7–8), 1069–1078. <https://doi.org/10.1016/j.fuel.2006.10.017>.
- Muraza, O., 2015. Hydrous pyrolysis of heavy oil using solid acid minerals for viscosity reduction. *J. Anal. Appl. Pyrol.* 114, 1–10. <https://doi.org/10.1016/j.jaap.2015.04.005>.
- Pan, Q., Zhuo, X., He, C., et al., 2020. Validation and evaluation of high-resolution Orbitrap mass spectrometry on molecular characterization of dissolved organic matter. *ACS Omega* 5 (10), 5372–5379. <https://doi.org/10.1021/acsomega.9b04411>.
- Reinardy, H.C., Scarlett, A.G., Henry, T.B., et al., 2013. Aromatic naphthenic acids in oil sands process-affected water, resolved by GCxGC-MS, only weakly induce the gene for vitellogenin production in zebrafish (*Danio rerio*) larvae. *Environ. Sci. Technol.* 47 (12), 6614–6620. <https://doi.org/10.1021/es304799m>.
- Rowland, S.M., Robbins, W.K., Corilo, Y.E., et al., 2014. Solid-phase extraction fractionation to extend the characterization of naphthenic acids in crude oil by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* 28 (8), 5043–5048. <https://doi.org/10.1021/ef5015023>.
- Santos, I.C.V.M., Oliveira, P.F., Mansur, C.R.E., 2017. Factors that affect crude oil viscosity and techniques to reduce it: a review. *Brazilian Journal of Petroleum and Gas* 11 (2), 115–130. <https://doi.org/10.5419/bjjpg2017-0010>.
- Schmidt, E.M., Pudenzi, M.A., Santos, J.M., et al., 2018. Petroleomics via Orbitrap mass spectrometry with resolving power above 1 000 000 at m/z 200. *RSC Adv.* 8 (11), 6183–6191. <https://doi.org/10.1039/c7ra12509g>.
- Shi, L.J., Shen, B.X., Wang, G.Q., 2008. Removal of Naphthenic Acids from Beijiing Crude Oil by Forming Ionic Liquids. *Energy & Fuels* 22 (6), 4177–4181. <https://doi.org/10.1021/ef800497p>.
- Tian, S., 2005. Study on the distribution of petroleum acids in crude oils. *Corrosion & Protection in Petrochemical Industry* 22 (2), 1–5. <https://doi.org/10.3969/j.issn.1007-015X.2005.02.001> (in Chinese).
- Wang, L., 2013. Distribution and characteristics of naphthenic crude oil resources. *Petroleum Products Application Research* 31 (6), 52–57. <https://doi.org/10.3969/j.issn.1006-1479.2013.06.010> (in Chinese).
- Wang, S., Shen, B., Lin, R., 2010. Correlation for the viscosity of heavy oil and its chemical composition. *Acta Pet. Sin.* 26 (5), 795–799. <https://doi.org/10.3969/j.issn.1001-8719.2010.05.023> (in Chinese).
- Yang, Y., Wang, X., Wang, T., 2019. China's heavy-oil development technology: status and recommendations. *Open J. Nat. Sci.* 7 (6), 471–477. <https://doi.org/10.12677/ojns.2019.76057> (in Chinese).
- Zhang, S., Huo, J., Sun, X., et al., 2021. Molecular composition reveals unique rheological property of Karamay heavy crude oil. *Energy Fuels* 35 (1), 473–478. <https://doi.org/10.1021/acs.energyfuels.0c03639>.
- Zheng, P., Qin, H., 2008. Properties, refining and utilization of naphthenic crude oils. *Modern Business Trade Industry* 20 (4), 267–269. <https://doi.org/10.3969/j.issn.1672-3198.2008.04.146> (in Chinese).
- Zhu, L., Wang, Y., Wang, S., et al., 2018. High viscosity-reducing performance oil-soluble viscosity reduction agents containing acrylic acid ester as monomer for heavy oil with high asphaltene content. *J. Petrol. Sci. Eng.* 163, 37–44. <https://doi.org/10.1016/j.petrol.2017.12.079>.
- Zhu, Z., Lin, R., Wang, S., 2004. The influence of heavy oil composition on its viscosity. *Xinjing Pet. Geol.* 25 (5), 512–513. <https://doi.org/10.3969/j.issn.1001-3873.2004.05.016> (in Chinese).
- Zubarev, R.A., Makarov, A., 2013. Orbitrap mass spectrometry. *Anal. Chem.* 85 (11), 5288–5296. <https://doi.org/10.1021/ac4001223>.