



Full Length Article

A comparison of the structures of > 300 °C fractions in six Chinese shale oils obtained from different locations using ¹H NMR, ¹³C NMR and FT-IR analyses



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ABSTRACT

Structural features of > 300 °C fractions of six Chinese shale oils, namely the Huadian, Wangqing, Fushun, Longkou, Maoming and Yaojie oil, have been characterized using ¹H nuclear magnetic resonance, ¹³C nuclear magnetic resonance and Fourier transform infrared techniques. Based upon the results obtained from ¹H nuclear magnetic resonance and ¹³C nuclear magnetic resonance, the distribution of various types of hydrogen and carbon atoms, and related structural parameters in > 300 °C fractions were determined. Different types of functional groups were studied based on the curve-fitting analysis of Fourier transform infrared spectra with Gaussian function. The results showed that the > 300 °C fraction of Huadian shale oil had the highest ratio of aliphatic carbon among the six samples. Meanwhile, the average carbon number of substituents in Huadian oil's > 300 °C fraction was the highest, and had the value of 8.98. Moreover, the Huadian sample owned the lowest degree of branching of aliphatic chain, whereas it had the highest ratios of –CH₂– and –CH₃–. These results indicated that, in Huadian oil's > 300 °C fraction, the alkyl carbon chains were longer, whereas the branched chains were less (in number) compared to other samples. Furthermore, the curve-fitting analysis indicated that 2 and 3 adjacent H deformations were dominant in aromatic structures. The oxygen-containing groups in > 300 °C fraction of Chinese shale oil were mainly the C–O groups, followed by the C–OH groups, O=C=O groups and conjugated C=O groups. In summary, > 300 °C fractions of Chinese shale oils showed similar differences with regards to the elemental compositions and functional groups.

1. Introduction

Shale oil, which is produced by pyrolysis of oil shale, is an important alternate energy resource to crude oil [1]. Chinese oil shale reserves rank fourth in the world after those of USA, Brazil and Estonia. Shale oil has a broad application prospect in China [2,3]. In recent years, attention has been gradually transferred to the comprehensive utilization of shale oil. Therefore, in order to make better use of shale oil, studies on the composition and structure of shale oil are necessary to be conducted. The structures and properties of shale oil are quite complicated. Moreover, the development of modern analytical technology provides more foundations for the study of composition and structure of shale oil, as well as other liquid fossil fuels.

Generally speaking, Chinese shale oil is similar to crude oil, though it contains massive amounts of unsaturated hydrocarbons and heteroatomic compounds. For the compositional analysis of multicomponent

mixture, gas chromatography (GC) [4–6] and gas chromatography-mass spectrometry (GC-MS) [7,8] provide detailed composition of the compounds, which are undoubtedly the most suitable analytical methods. However, the critical temperature of common chromatographic column is about 350 °C. This not only makes it impossible for the high boiling compounds to be separated in the chromatographic column, but also causes contamination of the chromatographic column. In spite of using the high temperature chromatographic column, the column temperature can reach values of 450 °C [9]. However, this method is still unable to detect the full spectrum of distillate products of shale oil. Therefore, the microscopic study of high boiling heavy oil could only be started from its structure. In early 1960 s, nuclear magnetic resonance (NMR) technology was used for structural characterization of heavy oil [10,11]. Under the premise of not damaging the sample structure, NMR provides information on the atomic distribution of various types of hydrogen and carbon species, which is different from

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Nomenclature

HD	Huadian
WQ	Wangqing
FS	Fushun
LK	Longkou
MM	Maoming
YJ	Yaojie
GC	gas chromatography

GC-MS	gas chromatography-mass spectrometry
NMR	nuclear magnetic resonance
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
ESI-MS	electrospray ionization mass spectrometry
FT-IR	Fourier transform infrared
CP/MAS	cross polarization-magic angle spinning
CDCl ₃	deuteriochloroform
TMS	Tetramethylsilane

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), electrospray ionization mass spectrometry (ESI-MS) and other mass spectrometry techniques [12,13]. In addition, average structural parameters of heavy oil can be calculated using experimental results of NMR and elemental analysis [14–16]. Fourier transform infrared (FT-IR) technology, having features of high sensitivity and good reproducibility, is used for the qualitative and quantitative analysis of complex functional groups [17–19]. Guo *et al.* [20] determined the structure parameters and concentrations of functional groups in > 350 °C fraction of shale oil by using NMR and FT-IR. Wang *et al.* [21,22] obtained the atomic distribution information of various types of hydrogen and carbon species in > 300 °C fraction of Huadian and Wangqing shale oils in China. Furthermore, ¹H and ¹³C NMR were employed to find the regular pattern of chemical structure of compounds in > 300 °C fraction of Huadian shale oil with final retorting temperature.

In this paper, experimental results of ¹H and ¹³C NMR and elemental analysis were used to determine the structural parameters of > 300 °C fractions of six different Chinese shale oils. The > 300 °C fractions were also subjected to FT-IR analysis for the identification of major functional groups.

2. Experimental

2.1. Materials

Full fractions of six Chinese shale oil samples were obtained using the retorting method from oil shales from Huadian (HD), Wangqing (WQ), Fushun (FS), Longkou (LK), Maoming (MM) and Yaojie (YJ) areas. The pyrolysis experiments of oil shales were conducted at the final temperature of 520 °C and heating rates of 10 °C·min⁻¹ by an in-house experimental device having a temperature controller. These liquid products were centrifuged using a centrifugal machine to achieve oil-water separation. Furthermore, > 300 °C fractions of shale oils were obtained by using the distillation method by employing a petroleum-products' distillation range determinator. The results of elemental analysis are shown in Table 1.

2.2. NMR analysis

NMR analysis for > 300 °C fractions was carried out on a Bruker Avance III spectrometer with cross polarization-magic angle spinning (CP/MAS). The samples were dissolved in deuteriochloroform (CDCl₃), whereas the test temperature was set to be 25 °C. Tetramethylsilane (TMS) was used as the internal standard, and added to the dissolved sample. Resonance frequencies of ¹H NMR and ¹³C NMR were 500 MHz and 125 MHz (respectively), whereas the spectral widths were 10 KHz and 25 KHz, respectively. Delay times of ¹H NMR and ¹³C NMR were 5 s and 6 s, respectively. Both ¹H NMR and ¹³C NMR spectra were studied using the MestReNova 9.0 software.

2.3. FT-IR analysis

The FT-IR experiments of > 300 °C fractions were performed using a PerkinElmer Spectrum Two portable Fourier transform infrared

spectrometer. The spectral measurement range was 4000–450 cm⁻¹, with the resolution and scanning times of 4 cm⁻¹ and 4, respectively. Since > 300 °C fractions of shale oils were sticky and semi-solid at room temperature, samples were heated in a water bath to liquid state, and then rapidly processed under infrared baking light to ensure that high quality spectra of the liquid states of > 300 °C fractions shall be obtained. FT-IR spectra were studied using the curve-fitting analysis in OMNIC Quantpad 8.2 software.

3. Results and discussion

3.1. ¹H NMR analysis of > 300 °C shale oils

Fig. 1 shows the ¹H NMR spectra of > 300 °C fractions of shale oils from different locations. Moreover, Fig. 1 was enlarged to ensure a clear view of the region of resonance peaks. The ¹H NMR spectra of six samples were similar. The chemical shift around 7.25 ppm was the obvious resonance peak of CDCl₃. According to the results of elemental analysis presented in Table 1, it was found that the content of hydrogen was less than that of carbon in > 300 °C fractions. Due to the different chemical environments of the diverse hydrogen atoms, their chemical shifts were observed at slightly different locations in the spectra. The distribution information of hydrogen atoms in the > 300 °C fractions was calculated based on the attribution of the chemical shift summarized by other researchers [23,24]. Fig. 2 shows the assignments of various types of hydrogen in molecular structure model. The resonance regions of internal standard and CDCl₃ were not integrally calculated. The results for the integral calculations are presented in Table 2.

The chemical shift ranged from 0.4 to 1.9 ppm in ¹H NMR, and was the resonance region of methyl hydrogen γ and aliphatic hydrogen β or futher from the aromatic ring. Moreover, H γ represented the hydrogen atoms on terminal methyl groups with three or more bonds from the aromatic rings. In this study, the relative content of H γ in > 300 °C fractions of six Chinese shale oils ranged from 10.55% to 14.63%. Furthermore, H β indicated the methylene hydrogen atoms attached to carbon atoms with at least two bonds from the aromatic rings. The relative content of H β in > 300 °C fractions was very high, and was around 71.67% in HD sample. The chemical shift ranging from 1.9 to 4.5 ppm was aliphatic hydrogen α to aromatic ring, which was α -CH₂- and α -CH₃ linked with the aromatic ring side chain. The relative contents of H α and H β would obviously change with temperature during the process of pyrolysis. With regards to the reaction mechanism, it was found that the C–C bond of saturated hydrocarbon groups, attached to

Table 1
Elemental contents of > 300 °C fractions of six different Chinese oil shales.

Shale oil	C/wt %	H/wt %	O/wt %	N/wt %	S/wt %	H/C	O/C
HD	83.75	11.36	2.65	1.51	0.75	1.63	0.023
WQ	84.59	11.31	1.58	1.88	0.81	1.60	0.014
FS	85.66	11.48	1.03	1.61	0.51	1.61	0.009
LK	85.36	10.83	2.24	1.33	0.34	1.52	0.020
MM	85.32	10.88	2.48	1.16	0.42	1.53	0.022
YJ	84.96	10.35	2.97	0.95	0.91	1.46	0.026

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