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Compositional characterization of neutral fractions in < 300 °C distillates of six shale oils using extrography followed by GC-TOF/MS analysis

Qing Wang[a,*], Da Cui[a], Shuo Pan[a], Zhichao Wang[a], Qi Liu[a], Bin Liu[b]

[a] Engineering Research Centre of Oil Shale Comprehensive Utilization, Ministry of Education, Northeast Electric Power University, Jilin City, Jilin 132012, China
[b] Jishun Oil Shale Development Co. Ltd., Jilin City, Jilin 132013, China

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ABSTRACT

The neutral fractions of < 300 °C fractions of six Chinese shale oils obtained from different locations of Huadian, Wangqing, Fushun, Longkou, Maoming and Yaojie were eluted to six sub-fractions using extrography method. The compositions of sub-fractions were determined using gas chromatography-time of flight mass spectrometer (GC-TOF/MS). The results showed that F1 sub-fractions contained aliphatic hydrocarbons, such as alkanes, alkenes and cycloalkanes. In addition, HD F1 sub-fraction had the highest content of aliphatic hydrocarbons. The F2 sub-fractions contained aromatic hydrocarbons with 1–4-ring. Furthermore, a small amount of heteroatom compounds with aromatic rings (such as, dibenzofurans and carbazols) were also detected. The F3 sub-fractions contained aliphatic ketones and aliphatic nitriles ranging from C_7-C_{25} and C_9-C_{24}, respectively. The F4 sub-fractions contained aliphatic ketones. However, the aliphatic ketones in F3 sub-fractions were 4-, 5-, 6-, 7- and 9-ketones, whereas those in F4 sub-fractions were all 2-ketones. The F5 sub-fractions contained nine kinds of compounds. Moreover, 2,5-hexanedione was dominant in all the samples except for MM F5 sub-fraction, whereas only two compounds were detected in MM F5 sub-fraction. Moreover, the F6 sub-fractions with less than 1 wt% in neutral fractions contained the unresolved complex matter (UCM), which cannot be eluted through gas chromatography (GC). Compared with the distribution of compounds in sub-fractions, the compounds of different samples consisted of similar species and slightly different contents. It indicates that the formation of compounds in the neutral fraction follows the same reaction pathways during kerogen pyrolysis.

1. Introduction

Oil shale is a kind of sedimentary rock with solid combustible organic matter in the mineral skeleton, and belongs to the category of unconventional petroleum resources. Oil shale is recognized as an important future global petroleum supplement for its abundant reserves and the feasibility of its exploitation and utilization [1,2]. Low temperature pyrolysis of oil shale plays an important role in Chinese oil shale industry [3]. Shale oil is the major product from low temperature retorting of oil shale, which is different from coal tar that is a byproduct produced during the coal carbonization and gasification [4]. Both the composition and structure of shale oil are similar to petroleum and coal tar. However, the contents of unsaturated hydrocarbons and heteroatom compounds are relatively high, which makes the processing and utilization of shale oil very difficult [5–10]. Furthermore, shale oil contains a large number of aromatic hydrocarbons, which are not good for complete combustion. In addition, shale oil contains nitrogen compounds, which produce NOx and other harmful gases while burning [1]. Therefore, the direct combustion of shale oil will result in waste of resources, while on the other hand, it will inevitably cause serious environmental pollution. However, shale oil can be fractionated and purified using high-value chemicals, and then, processed and utilized. The laboratory separation and the analysis of organic chemicals in shale oil are not only prerequisites to the extraction and utilization of high-value chemicals, but also provide theoretical guidance for industrial production. They also help researchers to further understand the properties of shale oil and to make the better use of oil shale resources.

The composition of shale oil is very complex. With the development of modern physical analysis techniques and instruments, researchers have begun using various techniques, such as gas chromatography-mass spectrometry (GC–MS) [11], nuclear magnetic resonance (NMR) [12,13], Fourier transform infrared (FT-IR) spectroscopy [14,15], and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) to study the composition and chemical structure of shale oil and other liquid fuels. The average structural parameters and functional group information of organic compounds could be determined using NMR and FT-IR. However, ESI FT-ICR MS is widely applied to study the molecular structure of complex organic

* Corresponding author.
E-mail address: rlx888@126.com (Q. Wang).

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compounds, such as crude oil, coal tar, shale oil and bio-oil, and has more advantages in the analysis of molecular structure of heavy oil [16–20]. In addition, GC and GC–MS can also be used to obtain information on molecular compositions. The components in samples could be separated using GC, and then, qualitatively analyzed using mass spectrometers (MS) or other detectors. However, due to the complexity and similarity in structures of various complex high-boiling organic compounds in shale oil, chromatographic peaks of similar compounds are difficult to be separated. Therefore, shale oil should be separated as carefully as possible to alleviate the problem of overlapping of chromatographic peaks and limited peak capacity prior to the GC analysis [21]. Common methods employed to separate shale oil include rectification, crystallization, solvent extraction and column chromatography. The acidic, basic, and neutral fractions in the sample could be separated using acidic/basic solvent extraction. The column chromatography separation is driven by the continuous mobile phase, and the components in the sample are redistributed repeatedly between the mobile phase and the stationary phase. Finally, the components are separated according to their different partition coefficients between the two phases [22–27]. Shi et al. [21] applied acidic/basic solvent extraction and column chromatography to study the composition of medium-temperature coal tar. Moreover, the neutral sub-fractions were subjected to GC–MS and FT-ICR MS analyses for neutral nitrogen compounds.

In two previous works [28,29], six Chinese shale oils were divided into < 300 °C fractions and > 300 °C fractions. The < 300 °C fractions were subjected to acidic/basic liquid separation. The acidic and basic fractions were characterized using GC–MS method. The structural parameters and functional groups of > 300 °C fractions of six Chinese shale oils were determined using NMR and FT-IR. In this paper, extrography method was used to separate the neutral fractions of < 300 °C fractions of six Chinese shale oils. Furthermore, GC-TOF/MS was used to analyze the neutral sub-fractions of < 300 °C fractions of the six Chinese shale oils.

2. Experimental

2.1. Materials

The oil shale samples were obtained from Huadian (HD), Wangqing (WQ), Fushun (FS), Longkou (LK), Maoming (MM) and Yaojie (YJ) areas of China. According to the Van Krevelan diagram with H/C as the ordinate and O/C as the abscissa [1,30], it is determined that HD kerogen and WQ kerogen belong to type I kerogen, FS kerogen and MM kerogen belong to type I-II kerogen and close to type I kerogen, LK kerogen belongs to type I-II kerogen and closes to type II kerogen, and only YJ kerogen belongs to type II kerogen [31]. In addition, the maturity of HD, WQ, FS, LK and MM kerogen is not very different from each other. Nevertheless, it is generally accepted that the maturity of YJ kerogen is much higher, which is more closer to lignite in this study. The pyrolysis experiments were conducted using an in-house retorting device equipped with a temperature controller. The final temperature of the pyrolysis was set to be 520 °C, while the heating rate was 10 °C/min. The < 300 °C fractions of six shale oils were obtained through atmospheric distillation. In order to remove acidic and basic fractions in < 300 °C fractions, 3 mol/L sodium hydroxide (NaOH) and 6 mol/L hydrochloric acid (HCl) solutions were used [21,28]. The yields of neutral fractions in < 300 °C fractions are listed in Table 1 [28].

Table 1
Yields of neutral fractions in < 300 °C fractions of shale oils.

Sample	HD	WQ	FS	LK	MM	YJ
The yields of neutral fractions w/%	86.8	85.5	84.3	84.7	83.1	84.6

2.2. Extrography

The extrography was carried out on a Bûchi preparative chromatography unit equipped with a pump module C-601. The length and inner diameter of the glass column were 230 and 15 mm, respectively. Silica gel (200–300 mesh) was purified using Soxhlet extraction with chloroform ($CHCl_3$) for 20 h, which was heated at 105 °C for 5 h as the activated silica gel. 10 g activated silica gel was mixed with 0.2 g deionized water as the deactivated silica gel, and then, a total of 0.5 g neutral fraction of the < 300 °C fraction was dissolved in 70 ml dichloromethane (CH_2Cl_2). The vacuum drying treatment was carried out on the CH_2Cl_2 solution mixed with deactivated silica gel and neutral fraction sample after stirring to ensure that the neutral component samples were evenly adsorbed on the silica gel. The silica gel with the adsorbed sample was loaded into a glass column containing 25 g of activated silica gel. Then, 2 g of activated silica gel was placed on the top of the mixture sample in order to secure the sample. The six neutral sub-fractions of < 300 °C shale oil were obtained by successively using cyclohexane (180 ml), cyclohexane/toluene (v/v = 1:1; 100 ml), toluene/dichloromethane (v/v = 1:1; 80 ml), dichloromethane (100 ml), ethyl ether/methanol (v/v = 1:1; 100 ml) and methanol (80 ml) as eluents [21]. Furthermore, the flow rate of eluent was controlled at 5 ml/min. The each extrographic sub-fraction was concentrated using a rotary evaporator to remove the eluent, and transferred to a sample bottle (Fig. 1). The yields of extrography sub-fractions are listed in Table 2.

2.3. GC-TOF/MS analysis

GC-TOF/MS was carried out using an Agilent 7890 gas chromatography (GC) unit, which was equipped with a DB-PETRO column (50 m × 0.20 mm inner diameter × 0.50 μm film thickness) and a LECO Pegasus 4D time of flight mass spectrometer (TOF/MS). The gas chromatography oven was maintained at 50 °C for 0.2 min, ramped to 100 °C at 3 °C/min, and held at 100 °C for 3 min. This was followed by ramping to 300 °C at 5 °C/min, and finally maintaining it at 300 °C for 15 min. The ion source and transfer line temperature were 250 and 300 °C, respectively. The injection volume was 1 μL, and acetone was used as the solvent for samples. The solvent delay time was 16.67 min to avoid the interference of eluents and solvent. The mass spectrometer scanned within the m/z range of 33–500, whereas the ionizing voltage was 70 eV. A blank analysis was carried out before the GC-TOF/MS experiment to make sure that the baseline is in normal condition. In addition, the qualitative and quantitative analysis was processed by LECO Pegasus 4D workstation software. Furthermore, the relative contents of different compounds were calculated by peak area normalization of the total ion chromatogram.

3. Results and discussion

3.1. Characterization of F1 sub-fraction

The F1 sub-fraction was eluted with cyclohexane. Fig. S1 presents the GC-TOF/MS total ion chromatograms of F1 sub-fractions. The aliphatic hydrocarbons were dominant in the F1 sub-fraction, and mainly consisted of n-alkanes and α-alkenes. Furthermore, a small amount of cyclanes, branched alkanes and non-α-alkenes, including isoprenoid hydrocarbons, such as pristane and phytane with obvious biological markers were present in F1 sub-fraction. The mass chromatograms of m/z = 85 and 97 are shown in Fig. 2. The carbon number distributions of n-alkanes and α-alkenes in neutral fractions of < 300 °C fractions from different locations ranged from C_9 to C_{30} and C_9 to C_{27}, respectively. Moreover, n-alkanes and α-alkenes presented obvious double-peak distribution in total ion chromatograms. Table 3 presents the relative contents of different types of compounds calculated by area normalization. In addition, n-alkanes and α-alkenes were dominant in