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A comparison of the compositions of acidic and basic fractions in < 300 °C fractions from six Chinese shale oils

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ABSTRACT

Shale oil samples were obtained from the pyrolysis of six Chinese representative oil shales obtained from different locations and were divided into < 300 °C and > 300 °C fractions according to their boiling points. Chinese shale oils were similar in their high atomic H/C ratio. Huadian shale oil possessed the lowest density and viscosity. < 300 °C fractions of shale oils were subjected to acidic/basic liquid separation to prepare the acidic, basic and neutral fractions. In this paper, the acidic and basic fractions were characterized by gas chromatography-mass spectrometry. The results show that the < 300 °C fraction of shale oil had large amounts of acidic and basic components, consisting of oxygen containing compounds and nitrogen containing compounds. The intrinsic characteristics and metamorphic degree of kerogen determine the relative content of acidic and basic compounds in shale oil. The relative content of phenols was the highest in acidic compounds, and ranged from 78.24% to 86.84%. The relative content of lower phenols was significantly higher than that of the higher phenols. C_4-phenols seldom appeared in the acidic fraction of < 300 °C fraction. For the basic fractions, anilines, pyridines, quinolines and other nitrogen containing compounds with aromatic ring were identified. The relative content of pyridines in Longkou and Maoming basic fractions was obviously more than those in other samples, and was 22.2% and 22.53%, respectively. C_2-aniline, C_2-pyridine and C_1-quinoline compounds were dominant in the basic fraction of < 300 °C fraction.

1. Introduction

Oil shale is an important energy resource and belongs to the class of fossil fuels, which are matchless because of their enormous reserves [1–4]. The Chinese oil shale reserves are estimated to be 719.937 billion tons, which are equivalent to 47.644 billion tons of in-place recoverable shale oil [5]. Many studies regarding the retorting and burning of Chinese oil shales have been published [6–9]. Shale oil, combustible shale gas and semicoke can be obtained from oil shale by heat treatment [10–12]. Generally speaking, shale oil is similar to crude oil, however shale oil contains massive unsaturated hydrocarbons and hetero-atomic compounds. Although direct combustion of shale oil is the simplest and earliest utilization method, it amounts to a significant waste of energy due to a lower burning efficiency. Since a variety of chemical products separated from shale oil have uses in various industries, the identification and analysis of the structure and composition of shale oil have important significance to its comprehensive utilization [13,14]. With the rapid development of modern physical analysis techniques and analytical and testing instruments, tremendous efforts have been devoted to characterize the compositions and molecular structures of complex liquid fuels. Analytical and testing instruments such as gel permeation chromatography (GPC), gas chromatography-mass spectrometry (GC–MS), liquid chromatography-mass spectrometry (LC-MS), Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR) and electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS) have been applied to research the composition and structure of shale oil [15–17], coal tar [18–23], crude oil [24,25] and other liquid fuels. NMR and FT-IR have been used to identify the functional groups and determine the molecular structures of complicated organic compounds. GC–MS has been used to determine the molecular components of complicated organic compounds. However, because of the complexity and similar structure of various compounds in high boiling shale oil, chromatographic peaks of these compounds overlap. Hence, appropriate overall testing scheme and suitable analysis and testing technology for the analytical composition and structure of shale oil are necessary to be researched. Guo et al. [26,27] identified compounds in Chinese Fushun and Maoming shale oil (< 350 °C fraction), which was

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Nomenclature

HD	Huadian
WQ	Wangqing
FS	Fushun
LK	Longkou
MM	Maoming
YJ	Yaojie
GPC	gel permeation chromatography
GC–MS	gas chromatography-mass spectrometry
LC-MS	liquid chromatography-mass spectrometry
FT-IR	Fourier transform infrared
NMR	nuclear magnetic resonance
ESI FT-ICR-MS	electrospray ionization fourier transform ion cyclotron resonance mass spectrometry

separated by four columns packed with successively less deactivated alumina, and was analyzed by GC–MS to identify the types of compounds present in it. Structural parameters of shale oil (> 350 °C fraction) were determined by NMR. Wang et al. [28] divided the shale oil samples obtained by retorting Chinese Huadian oil shale at different final temperatures into light oil (< 300 °C fraction) and heavy oil (> 300 °C fraction). The light oil was analyzed using GC–MS and its components were classified to find a pattern to explain the variation of shale oil's chemical composition with different final retorting temperatures. ^{1}H and ^{13}C NMR were employed to analyze the chemical structures of compounds in heavy oil. Based on the above discussion, the authors have developed a series of research work about the compositions and structures of shale oils. According to the boiling temperature, shale oil was divided into < 300 °C fraction and > 300 °C fraction. The < 300 °C fraction was subdivided into acidic, basic and several neutral fractions by acidic/basic liquid separation and column chromatography. The > 300 °C fraction was characterized directly by NMR and FT-IR techniques. In this way, the < 300 °C and > 300 °C fractions were analyzed using suitable analysis and testing technologies.

To the best of our knowledge, a comparison of various Chinese shale oils has not yet been reported in literature. From our recent analytical work on six shale oils, namely the Huadian, Wangqing and Fushun from the northeast, Maoming from the south, Longkou from the east and Yaojie from the northwest of China, a series of papers on the compositions and structures of shale oil will be presented. In this paper, six shale oils were characterized for their bulk properties. The < 300 °C fractions of shale oils originating from different locations were subjected to acidic/basic liquid separation to prepare the acidic, basic and neutral fractions. The acidic and basic fractions were characterized using the GC–MS technique. Direct combustion of shale oil can cause environmental pollution because of the high nitrogen content of shale oil. Moreover, high valuable chemicals in acidic and basic fractions can be extracted through refining. Therefore, the analysis of compositions and structures of acidic and basic fractions in shale oils is significant for understanding and mastering the characteristics of shale oil and comprehensive utilization of oil shale resources. Such an analysis can provide basic data for studying the pyrolysis mechanism and average molecular model of kerogen.

2. Experimental

2.1. Materials and methods

The Chinese oil shales used in this work for the preparation of shale oil fractions were obtained from Huadian (HD) and Wangqing (WQ) in Jilin Province, Fushun (FS) in Liaoning Province, Longkou (LK) in Shandong Province, Maoming (MM) in Guangdong Province and Yaojie (YJ) in Gansu Province. The oil shale samples were crushed and screened to the desired particle size. 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. The liquid products were collected in a condensation tank filled with a mixture of ice and water. These liquid products were centrifuged using a centrifugal machine to achieve oil-water separation. All of the shale oil samples were kept in a cooler at 4 °C. The bulk properties of shale oils are listed in Table 1.

2.2. Distillation of shale oil

Whole shale oil samples obtained from different locations were divided into < 300 °C and > 300 °C fractions according to the boiling points by using a petroleum products distillation range determinator. The weight percentages of < 300 °C fractions for whole shale oil samples are listed in Table 2.

2.3. Acidic/basic extraction

The < 300 °C fractions of shale oils obtained from different locations were subjected to acidic/basic liquid separation to prepare the acidic, basic and neutral fractions using extraction separation method [19,29,14]. The acidic/basic liquid extraction scheme is shown in Fig. 1. A total of 10 g of shale oil was dissolved in 100 mL of *n*-hexane. The diluted shale oil mixture was extracted with 50 mL of 3 mol/L sodium hydroxide (NaOH) solution until the lower layer of the mixture became colorless to yield an aqueous phase and an organic phase. 6 mol/L hydrochloric acid (HCl) solution was added dropwise to the aqueous phase. The acidity of the solution was determined by a pH paper. When the pH of the mixture solution was 1–2, the solution was extracted with dichloromethane (CH_2Cl_2), followed by solvent evaporation using a rotary evaporator to remove dichloromethane (CH_2Cl_2) and yield the acidic fraction. The previous organic phase extracted by sodium hydroxide (NaOH) solution was extracted with 50 mL of 6 mol/L hydrochloric acid (HCl) solution until the lower layer

Table 1
Properties of shale oils.

Shale oil	Density (20 °C) g/cm	Viscosity (50 °C) mm^2/s	Moisture wt%	Freezing point °C	Flash point °C	Ash wt%	C wt%	H wt%	O wt%	N wt%	S wt%	H/C
HD	0.8922	8.32	0.37	26	92	0.061	83.51	12.3	2.44	1.38	0.82	1.77
WQ	0.9249	12.33	0.25	25	121	0.044	84.32	11.76	1.45	1.71	0.92	1.67
FS	0.9032	13.94	0.89	31	132	0.053	85.27	11.99	0.91	1.58	0.55	1.69
LK	0.9118	16.73	0.46	26	72	0.031	84.85	11.45	2.28	1.21	0.33	1.62
MM	0.9088	10.07	0.64	30	103	0.104	84.67	11.37	2.26	1.18	0.48	1.61
YJ	0.9317	15.22	0.95	21	108	0.085	84.37	10.88	2.85	0.93	0.92	1.55