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Characterization of Indian origin oil shale using advanced analytical techniques

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HIGHLIGHTS

- The paper highlights the detailed characterization of Indian origin oil shale.
- There is no work reported on detail characterization of Indian origin shale oil.
- The ICAP and XRD identify the metals and minerals in oil shale.
- The IR, NMR and MS give the information regarding hydrocarbons and structural parameters.
- Indian origin shale oil is carbon rich in nature and contains a significant component of aromatics.

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ABSTRACT

The paper highlights the detailed characterization of Indian origin oil shale using various analytical techniques viz., Elemental analysis, Induced Coupled Argon Plasma (ICAP), X-ray Diffraction (XRD), Gas Chromatography (GC), Infrared spectroscopy (IR), Nuclear Magnetic Resonance (NMR) spectroscopy and High Resolution Mass Spectrometry (HRMS). The study also focused on the molecular characterization of two shale oil samples obtained by retorting method from oil shales. A method based on NMR spectroscopy has been developed for the estimation of total aromatics, types of aromatic substituent's and average alkyl chain length of saturates in shale oil samples. Detailed hydrocarbon type analysis in terms of 22 classes has been carried out by HRMS. The results of aromatics obtained by the ^{1}H NMR method, correlated with HRMS data. The detailed analyses of Indian origin oil shale provide in depth structural information regarding the metals, minerals and hydrocarbons.

1. Introduction

Oil shale is a natural, impermeable, fine-grained, laminated black or brown combustible material, and it consists of complex organic material of high molecular weight called kerogen which is finely distributed in an inorganic matrix [1]. As a kind of fossil fuel similar to coal, oil shale has a higher mineral content. It is believed that the minerals in oil shale will affect the reaction of organic matter physically and chemically [2,3]. In the western United States, large oil shale deposits exist in Colorado, Utah, and Wyoming [4] and have been considered for utilization during periods of high crude oil prices. Patterson [5] did substantial research on Australian oil shale from different deposits. Their main focus was on the mineralogy of Australian oil shale and its effect on oil shale retorting. Jabber et al. [6] described about Jordan oil shale from different deposits and compared with Colorado oil shale. According to Jabber et al. Jordan organic matter (shale oil) contains 8.5–10.3% of sulfur. Oil shales have been divided into three categories based on mineral composition – carbonate-rich shale, siliceous shale and cannel shale. Carbonate-rich shales derive their name from the large amount of carbonate minerals such as calcite and dolomite. Siliceous oil shales are usually dark brown or black shales. Siliceous oil shales are not rich in carbonates but rather in siliceous minerals such as quartz, feldspar, clay, chert and opal. Cannel shales are usually dark brown or black shales, which consist of organic matter that completely encloses other mineral grains [7]. Wang et al. [8] identify the mineral composition of oil shale from different locations and relate it to their interval of occurrence.

The physical and chemical compositions of shale oil, a complex mixture of hydrocarbons, depend on the source of the raw shale and the type of processes used to obtain the oil. It is well-known that liquid products from petroleum, oil shale and coal are difficult to characterize in terms of chemical structure, as they consist of large numbers of structurally diverse compounds. Basically, shale oils differ from petroleum primarily in that they have higher

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nitrogen content and as shale oils are produced by pyrolysis, they also contain some concentrations of olefins, which are generally found in natural crude oils in low concentrations. Shale oil rich in alkanes, cyclanes, arenes, as well as nitrogen-, sulfur-, and oxygen-containing non-hydrocarbons; Hence, it is hard to analyze oxygen compounds in question without pretreatment of oils. Earlier traditional methods such as column chromatography and also distillation were used for the component analysis of oils. With the development of chromatographic separation methods, the molecular constitutions of shale oil and coal tar were gradually established. Zhu [9] separated two kinds of shale oils from mountainous area (land) and coastal shelf rock (sea), both China, into four fractions using silica gel column chromatography. The components of each fraction were identified by GC–MS. The results show that shale oil from land contains 269 compounds, with abundant hydrocarbon compounds (79%), and some sulfur, oxygen and nitrogen compounds. Shale oil from sea rocks contains 284 compounds with a high amount of hydrocarbon and oxygen compounds (60% and 29%, respectively), and some sulfur and nitrogen compounds. Guo and Ruan [10] analyzed by GC–MS shale oils from Fushun oil shale of Liaoning province and Maoming oil shale of Guangdong province, both China. The main oxygen-containing compounds identified are phenols, diphenols, 2-, 3- and 4-alkanones, furans and benzofurans. Among the oxygen compounds, phenols constitute 7–8 wt% of oil (<350 °C), the next most abundant being ketones. Bae et al. [11] compared the molecular compositions of two shale oils of oil shales from US Western and Russian mines, using 15 T FT-ICR MS coupled with ESI, and atmospheric pressure photoionization (APPI). Geng et al. [12] was performed, a comprehensive compositional analysis of the oxygen containing compounds present in shale oil and low temperature coal tar using FT-ICR MS and GC–MS. Due to the presence of these components, shale oils are relatively thermally unstable [13], have poor long-term storage stability and require modifications of the analytical methods used for petroleum characterization.

Estimation of oil shale reserves in India is greater than 15 billion tons. North-East India is endowed with rich deposits of coal, found in the Barail formation of tertiary age. Carbonaceous shale occurs interblended with the coal. The presence of coal and shale has been recorded in wells drilled for hydrocarbons by Indian companies. These formations outcrop on the surface towards the south of the oil fields in a region called the Belt of Schuppen. Studies have indicated that this oil shale constitute the principal source rocks that have generated the hydrocarbons produced from the region. There is no work reported on detailed characterization of Indian origin oil shale.

The present work discusses in-depth characterization of Indian origin oil shale using analytical techniques such as CHNS analyzer, Induced Coupled Argon Plasma (ICAP), Gas Chromatography (GC), Infrared spectroscopy (IR), Nuclear Magnetic Resonance (NMR) spectroscopy and High Resolution Mass Spectrometry (HRMS). The study also focused on the molecular characterization of two shale oil samples obtained by retorting method from Indian origin oil shale.

2. Experimental

2.1. Samples

Oil shale samples S1–S7 were obtained from Upper Assam Oil shale deposits and S8–S10 from neighboring area in Arunachal Pradesh shale deposits. Indian origin oil shales were dark brown or black in color. Shale oil samples are obtained by retorting method from oil shale S-7 and S-10. Retorting of oil shale has been carried out at ~500–550 °C in Retorter pilot plant using CO_2 as sweep gas. Shale oil samples were obtained by condensing the oil vapors downstream of the retorter.

2.2. CHNS Analysis

Oil shale and shale oil samples were analyzed by CHNS analyzer Vario EL-III from M/s Elementar, Germany as per ASTM D 5291 method.

2.3. ICAP Analysis

The ICAP spectrometer used in this study was radial viewing Optima 5300V from Perkin Elmer, USA. Deionized water of Millipore quality and Suprapure grades of hydrochloric acid, hydrofluoric acid, AR grade of perchloric acid and multi-element standards in water matrix from E. Merck (Germany) were used throughout this analytical work.

2.3.1. Sample and blank preparation

Sample (~0.5 g) was taken in platinum dish and ashed at 650 °C in muffle furnace to remove carbonaceous matter prior to the acid digestion. To this, 10 ml each of hydrofluoric acid and perchloric acid were added and the contents were heated on hot plate till dryness to remove silica. To the residue obtained, 20 ml of hydrochloric acid was used to get it dissolved. The solution was transferred to 100 ml volumetric flask and made up to 100 ml with water. Blank solution was also prepared by following exactly the same procedure as for the sample.

In order to maintain the same acid concentration, stock solution of multi-element standard (100 ppm) was diluted with blank to prepare 1, 5 and 10 ppm standard solutions. The peaking of ICAP spectrometer was performed with Mn line (257.61 nm) to cover all the elements.

2.3.2. Calibration and analysis

After spectral lines alignment using 10 ppm standard to cover all the elements, ICAP was calibrated using blank and 1, 5 and 10 ppm standard solutions. Blank subtraction mode was used for the sample analysis for all analytes.

2.4. X-ray diffraction (XRD)

XRD studies were carried out in an 18 KW X-ray diffractometer (Rigaku, Japan). XRD patterns were recorded at 50 kV and 250 mA, at a scan rate of 1°/min with a step size of 0.01° in the temperature range of 2–75° 2-Theta. XRD patterns were processed for smoothen, determination of inter-planner distance (*d*) of observed peaks and search match was conducted by using search match softwares to find out different compounds present in the sample.

2.5. IR Analysis

IR spectra of the oil shale samples are recorded on Perkin–Elmer BX-II FT-IR instrument. Known weight (~2 mg) of the sample is mixed with 100 mg KBr and KBr pellet is prepared using the entire sample under 5–8 kg pressure employing a Hydraulic Press. The IR Spectrum of the KBr pellet is recorded at 4 cm^{-1} resolution and 100 scans were collected. The IR spectra were corrected for baseline correction and smoothed to remove the noise and then analyzed for the presence of organic and inorganic moieties.

2.6. Open-column chromatography

The shale oil samples were fractionated into saturate and aromatic fractions as per the ASTM-2549/91 (reapproved 1995) method.