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Characterization of Petroleum Oil Seepage Using Modern Spectroscopic Techniques: In Case of Were Ilu-Legeheda, Ethiopia

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ABSTRACT

The sedimentary regions of Ethiopia cover a significant portion of the country and comprise five distinct sedimentary basins; namely, Ogaden, Abay, Mekele, Gambela and Southern Rift Basins. The Blue Nile basin is a North West-South East trending branch of the Ogaden intra continental rift basin. The presence of an oil seepage at Were Ilu and Legeheda points to the presence of an active petroleum system. The main aim of this study was to characterize the chemical nature of the seepage oil leaked out from the hard basalt rock of Mechela river. Seepage oil samples were analyzed using ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (NMR) spectroscopic methods. All the chemical analysis obtained from UV, IR and NMR showed that high contents of saturated hydrocarbons were found in the petroleum collected from the stated areas, which is the principal criterion for identification of pure petroleum oil.

Key words: Were Ilu; legeheda; petroleum; oil seepage; abay basin

INTRODUCTION

Ethiopia has five distinct sedimentary basins that cover a significant portion of the country, namely, Ogaden, Abay (Blue Nile), Mekele, Gambela and Southern Rift Basins [1] [2]. The development of most of these basins is related to the extensional tectonic events that have taken place intermittently since the Late Paleozoic and continued up to Tertiary. The former three basins are presumed to be intra continental rift basins formed as a result of extensional stresses induced by the break-up of Gondwana land in Upper Paleozoic [3], [4].

The Abay Basin covers an area of approximately 63,000km2 in the central northwestern plateau of Ethiopia. It consists of Paleozoic and Mesozoic sedimentary succession exceeding 2000 m in thickness [5], [6]. As the basin shares the same geotectonic origin as the Ogaden Basin, the different strati graphic units in the Abay are nearly similar to some of the units encountered in the Ogaden wells [7]-[9]. Beds of marl, shale and mudstone inter bedded with carbonates in the lower part of the thick limestone unit (Antalo) and upper part of the Amaba Aradom Formation (the Upper Sandstone) are potential source rocks in the Abay Basin [1], [2]. A geochemical analysis of an oil seepage from Were-Ilu locality in the northeastern margin of the basin suggests the presence of mature oil source rock of marine origin; possibly marine shale that has generated oil [10]. Oil generated from the Jurassic source rocks in the Abay Basin might be trapped by a combination of stratigraphic and structural traps [4], [8].

Crude oil is naturally occurring material that comprises various hydrocarbons including paraffins, olefins, naphthenes, aromatic and heteroatom containing compounds as well as organometallic compounds of nickel and vanadium (porphyrins) [11]. Crude oil, shale oil, and sand oil are all sources of petroleum and comprise masses of compounds whose components can be grouped into four essential instructions known as SARA: Saturated hydrocarbons (alkanes and cycloparaffins), Aromatics (with alkyl side chains), Resins (aggregates with a large number of building blocks which includes sulfoxides, amides, thiophenes, pyridines, quinolines, and carbazoles), and Asphaltenes (aggregates of prolonged polyaromatics, naphthenic acids, sulfides, polyhydric phenols, fatty acids, and metalloporphyrins) [12].

However, the presence of some compounds like polyaromatics, that are toxic or carcinogenic, sulfur and heavy metals in high concentrations, which have environmental implications and cause huge

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problems in the refining process due to the corrosion and poisoning of the catalysts, and asphaltenes which cause environmental problems as well as problems in the refining process, due to their tendency to flocculate and precipitate. Similarly, the higher concentration of these compounds leads to a greater formation of coke and increase the deactivation of catalyst sand and these also increase the risk of affecting the combustion process in various motors. In addition, the presence of conjugated dienes can bring serious problems in the industry because their presence can decrease the quality of the final products, due to their tendency to polymerize, being important to remove them from the oil fractions [13], [14].

Characterization of crude oil based on the ASTM protocol has been reported by different authors [11]. The instrumental techniques GC (Gas Chromatography), HPLC (High performance Liquid Chromatography), TLC (Thin-Layer Chromatography), UV (ultraviolent), IR (Infrared Spectroscopy) together with MS (Mass Spectrometry) and NMR (Nuclear Magnetic Resonance) facilitate knowledge of the detailed hydrocarbon type composition of the complex crude oil. Nowadays GC-MS, IR and NMR spectroscopic techniques become more useful technique for characterization of crude oil obtained from the ground [15], [16].

IR spectroscopy is one of the most important techniques that can provide miscellaneous information of complex mixtures of compounds, such as information about hydrocarbon skeleton and functional groups (e.g., hydroxyl and carbonyl groups) [11], [16]. NMR spectroscopy is a very important technique in the study of heavy petroleum fractions, and has been suggested as one of the most powerful techniques for laboratory and industrial analysis. The advantages are a reduction in the time taken for the analysis, and that it is a rapid and non-invasive process. Moreover, by using NMR, it is possible to analyze the chemical nature of individual types of hydrogen and carbon atoms, in various and complex mixtures of petroleum and in the final products obtained by refining processes. The limitations of IR associated with the overlap that occurs between frequency ranges which can be overcame by using NMR spectroscopy. Unusual chemical shifts in the 13C NMR spectra of the aromatic carbon between 110 and 160 ppm is the characteristic signal for asphaltenes [17]-[19].

The presence of an oil seepage at Mechela river, between Were Ilu and Legeheda woreda, points to the presence of an active petroleum system. Therefore, the main aim of this study was to characterize the chemical nature of the seepage oil leaked out from the hard basalt rock of Mechela river using modern spectroscopic instruments.

MATERIALS AND METHODS

Materials

The crude oil sample analyzed in this work is obtained from Amhara region, South Wollo administrative zone, Legeheda woreda, Kebele 010, Mechela river (the boundary between Were Ilu and Legeheda, Figure 1). In this work geological data have been taken from filed observation and interview from the community who live-in.

The method we used for the chemical analysis of crude sample is UV, IR and NMR. The measurements of ^{1}H and ^{13}C NMR spectra were performed with instruments Bruker ACQ 400 AVANCE spectrometer operating at 400 MHz The IR spectrum was recorded using a Perkin-Elmer BX Spectrometer (400-4000 cm^{-1}) in KBr. The UV spectrum was measured in a T60 UV-VS spectrophotometer in 190-600 nm region in $CHCl_3$ solution.

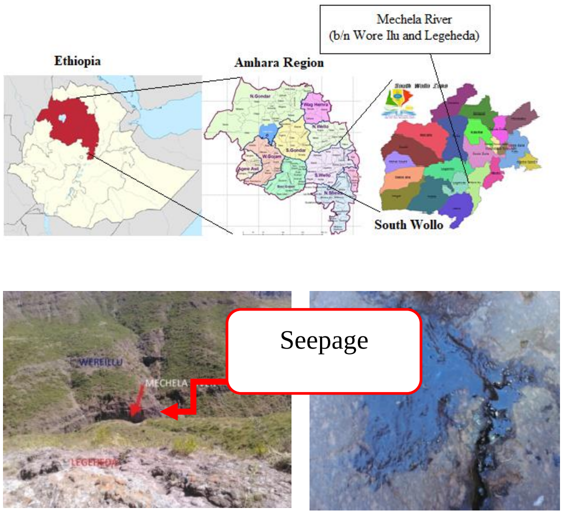

***Fig1*. Mechela river valley, the place where seepage oil sample is taken (*Photo Sisay A.*)**

RESULTS AND DISCUSSIONS

Geological findings

The result obtained from the geological survey was consistence with the information gathered from a literature. The Blue Nile Basin is a NW-SE trending branch of the Ogaden intracontinental rift basin. Thick Permo-Triassic sediments, ranging from continental alluvial fan, fluviatile and deltaic clastics to lacustrine argillaceous types, were deposited in the Ogaden region in the Karoo rifting stage. Equivalent sediments are also represented in the Blue Nile and Mekele basins. The presence of an oil seepage at Mechela, between Were Ilu and Legeheda, points out the presence of an active petroleum system [4]. Based on the geological information in the area, the presence of petroleum oil was confirmed in addition to the seepage convey from the hard rock ground.

Characterization of crude oil:

Physical properties

It is well documented elsewhere that the physical and chemical characteristics of a crude oil vary considerably with its composition [11]. Some of the physical properties of oil seepage under study were carried out. It was highly soluble in non-polar solvents such as petroleum ether, pentane, hexane and cyclohexane, slightly soluble in chloroform and insoluble in polar solvents such as methanol, ethanol, butanol and water. The flammability test of the oil was done and the result showed in the figure below. One of the physical properties of petroleum oil is its flammability [11].

Fig 2. Seepage oil burning for test at Were Ilu/Legeheda, Mechelariver (Photo Sisay A.)

UV-Vis spectroscopy:

UV-Vis spectroscopic technique is one of a vital technique for the determination of conjugated dienes, aromatics and asphaltenes in petroleum seepage oil [20]. The UV-Vis spectrum didn't show an absorption maximum in between 190nm to 700 nm. The common chromophores in petroleum products are aromatics, unsaturation, carbonyls and asphaltenes. For example, in the UV spectra of two absorption regions appear, a para band (200 nm) and an □ band (260-270 nm) are the general shape of the spectrum which is characteristic for hydrocarbons with a single benzene ring. The presence of naphthalenoid hydrocarbons will show up in the spectrum and can be judged qualitatively only in the 320 nm region. The two principal bands that are characteristics for the naphthalene ring system (220 and 280 nm) are masked by the absorption region of monoaromatic rings [16]. However, the lack of all these bands in the data generated from UV-V is spectrophotometer indicated that the oil seepage is free of aromatics, conjugated dienes, carbonyls and asphaltenes or with very small ratio indicate the purity of petroleum oil.

Characterization of petroleum using IR spectroscopy

In order to check the reliability of the IR technique for the determination of aromatic hydrocarbons in mixtures of different groups of hydrocarbons, the IR spectra of the crude sample was recorded at 4000-200 cm^{-1}. It has been reported elsewhere that crude oils which have similar physical properties but possess widely varying chemical compositions [11]. The absorption bands of aliphatic C−H bonds, with additional bands originating from groups containing aromatics, oxygen, sulfur, and nitrogen, usually dominate the spectra of crude oils [11].

The FTIR of the oil seepage obtained from Legeheda was carried out and the data is given in Figure 3. The clear larger size absorption peaks were observed at 2952 and 2864 cm^{-1} corresponded to the CH and CH_2 stretching vibrations. The other well-developed bands centered at 1463 and 1375 cm^{-1} corresponded to the CH, CH_3 bending vibrations were also observed. A medium intensity peak appeared at 1162 cm^{-}1 and band between 690 and 727 cm^{-1} observed evident for the CH and CH_2 bending vibrations, respectively [20]. The appearance of these peaks reveals the paraffins characterized by CH, CH_2 and CH_3 vibrations.

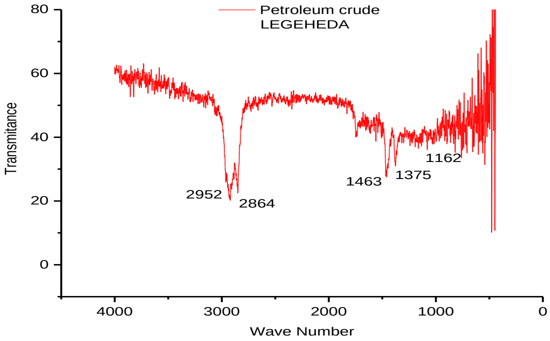

Fig. 3: IR spectral data

However, the characteristic bands between 1500-1800 cm-1 designated for olefins, aromatics (1650-1550 cm-1 [20]), aldehydes, ketones, carbonyl derivatives with oxygen and sulfur function are not detected in this spectrum. And also, absence of broad intense band between 3300-3550 cm^{-1} which is a characteristic band for O-H and N-H stretching was indicative for the absence of alcohol, amine, and acid in the oil. Moreover, the absence of intense strong signal between 2750-2810 cm^{-1} is also suggestive for the absence of aldehyde. Similarly, a typical signal for alkyne C-H stretching is not observed between 2100-2200 cm^{-1} which is indicative for the absence of alkyne in the crude oil.

It is clear from the results that the intensities of the bands appeared for paraffins were found to be high which reveals its high concentration and the peaks for aromatics/ olefins and oxygenated compounds is not observed which indicate their absence or their presence may be very low in concentrations. From the result it is concluded that the sample obtained from the research area possess long chain paraffins as the major constituents which is indicative that the material is as pure petroleum.

Characterization of petroleum using NMR spectroscopy

NMR has been used in the analysis of heavy petroleum fractions in many researches. The SARA fractions of crude petroleum oil (saturated, aromatics, resins, and asphaltenes) were characterized by using NMR spectroscopic technique [12], [18]. It was reported from the assignment of different types of proton and carbon atoms in the ^{1}H and ^{13}C NMR spectra of SARA fractions that the aromaticity region (110 -150 ppm) increased from saturated to asphaltenes fractions. This was confirmed by the hydrogen-carbon ratio decreasing with the increasing of aromaticity. On the other hand, the saturated fraction was characterized by an aliphatic nature represented with a high hydrogen-carbon.

The appearance of signals at δ 0.93 ppm in the ^{1}H NMR is suggestive for the presence of terminal methyl (CH_3) group. The most intense signal observed at δ 1.32 ppm which was integrated as many protons revealed that the methylene (CH_2) protons. The broad and intense characteristic multiple signals resonated at δ 2.35 to 2.59 ppm showed that the presence of branched side chains in petroleum oil. From the ^{1}H and ^{13}C NMR spectra, it was possible to determine the average number of specific CH_m groups (-CH, -CH_2 and -CH_3) per molecule. The ratio of CH: CH_2: CH_3 was calculated as 1.0:5.0:2.5 from the peak integration of proton signals, respectively. From ^{1}H NMR, there is no olefinic as well as oxymethine proton signals in the respective regions. That narrates the absence of aromatic protons that indicates the presence of aromatic and asphaltenes and also indicative the absence of alcohol containing hydrocarbons in the analyzed crude oil. The weak signal observed at δ 7.26 is the solvent $CHCl_3$.

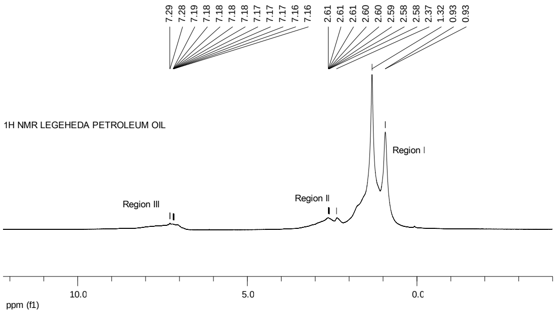

Fig. 4: ^{1}H NMR spectra of crude oil

The data generated from ^{13}C NMR and DEPT-135 of analyzed sample indicated that the presence of isolated methyl carbon at δ 14.23 ppm which is a characteristic signal for terminal methyl carbons. The remaining carbon signals at δ 19.81 and 22.80. Intense and many overlapping carbon signals are observed at δ 27.19-30.14 ppm which are the characteristic peaks for methylene carbons of aliphatic compounds. The signals assigned for methine carbons are visible in the δ 32.04-37.14 ppm that confirms the presence of branched aliphatic carbons as a mixture of crude oil.

However, as indicated in the spectra, no signals are appeared in the downfield regions. For example, the presence of aromatic or asphaltenes components can be confirmed by looking the presence of characteristic signals such as signals at The signals assigned for methine carbons are visible in the δ 132.5-137.2 ppm were due to substituted aromatic carbons bonded to methyl groups or to cycloparaffinic methylene (CH2). The signals at δ 137.2-149.2 ppm corresponded to the resonance of substituted aromatic carbons bonded to some alkyl groups and that at δ 149.2 -158 ppm to C-OH groups. However, oxymethine, unsaturated, aromatic and carbonyl carbons are not visible in the spectra that support the conclusion made above in ^{1}H NMR, absence of unsaturated, aromatic, asphaltene and oxygenated components in the crude oil.

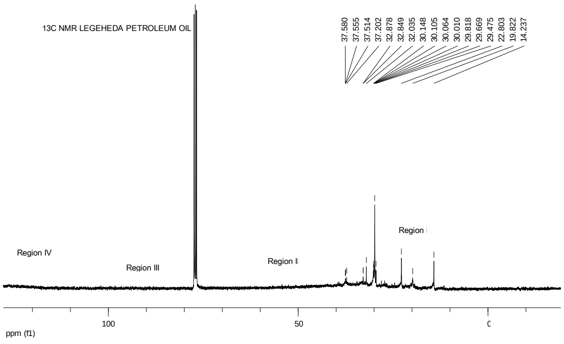

Fig. 5: ^{13}CNMR spectra of crude oil

CONCLUSION

The chemical nature of crude oil seepage obtained from Mechela river between Legeheda and Were Ilu Woreda, South Wollo Administrative Zone, was studied using spectroscopic techniques to analyze the quality or SARA content. Based on the geological information in the area, the presence of petroleum oil was confirmed in addition to the seepage convey from the hard rock ground. All the spectroscopic data obtained from UV, IR and NMR showed high content of saturated petroleum constituents, which is the principal criterion for pure petroleum. The seepage found under strong basalt rock, so, to determine the coverage and amount of this oil in the reservoirs needs more sophisticated instruments.

Conflict of Interest

The authors hereby declare there is no conflict of interests.

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