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Characterization of Niger Delta Crude Oil by Infrared Spectroscopy

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Abstract: Infrared spectroscopy was applied in characterizing crude oils from Niger Delta in terms of their source and thermal maturity. The samples were characterized based on the peak intensities of the aliphatic and the carboxyl/carbonyl groups relative to the aromatics. Using this method, the oils classified mainly as oil derived from type 1 kerogen contrary to type II/III already reported for Niger delta oil. The Vitrinite Reflectance (VR) values obtained from the VR equivalent grid ranged from 0.5 to 0.7%, indicating that the oils are of low maturity. The estimated VR determined from the IR spectra correlate favourably with available values in the literature. The results of this study showed that Infrared spectroscopy might not be a good tool for oil source characterization but can be useful in determining oil maturity.

Key words: Infrared spectroscopy, Niger-delta, kerogen, vitrinite reflectance, crude oil

INTRODUCTION

Niger Delta is one of the major hydrocarbon provinces of the world, with an estimated reserve of about 25 billion barrels of oil and 256 trillion cubic feet of natural gas. Source and thermal characterization of crude oil is a routine part of petroleum exploration programmes. Information obtained from such studies is very useful in oil-oil, oil-source rock correlation and for basin modelling. Correlations studies help in identifying the various types or families of oils in any sedimentary basin and whether they have a single or multiple origins. Oil-source rock correlation is important in determining the hydrocarbon origin and any intra-basinal facies changes in a given source rock.

Traditionally, the characterization of oils has been based on composition and distributions of biomarkers in oil by Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS)[1-3]. However, this method is time-consuming and expensive. Infra red spectroscopic technique represents another chemical approach to source and maturity determination. Instead of looking at changes in a single molecules or particular types of molecules, whole sample are characterized spectroscopically with respect to their chemical functionalities. This method has been applied successfully in the characterization of petroleum source-rock in terms of their source and thermal maturity[4-6]. Infrared spectrum helps to reflect the evolution of kerogen during its burial. With increasing maturation, the aliphatic peaks initially increase while the carboxyl/carbonyl peak decreases. As the maturity continues to increase, the aliphatic peaks decrease, while there is no apparent change in the peaks representing the aromatic C=C bands. Plotting the relative ratios of the intensities of aliphatic/aromatic bands (A-Factor) against the ratios of carboxyl and carbonyl/aromatic bands (C-Factor) in a diagram results in an excellent differentiation of the organic matter[4].

In this study, results on the attempt to apply infrared spectroscopy to crude oil characterization are presented.

Petroleum geology of the Niger Delta: The Niger Delta located in the re-entrant of the Gulf of Guinea occupies an area of about 75,000 km^2 with clastic sequence which reaches a maximum thickness of 9,000 to 12,000 m of sediments. Stratigraphically, the thick sedimentary sequence is made up of three principal lithostratigraphic units namely; the Benin, Agbada and Akata Formations[7]. The Benin Formation is the alluvial or upper coastal plain depositional environment of the Niger Delta complex. It consists of mainly fluviatile gravels and sands. It has a thickness in excess of 1820 m. The Agbada Formation underlies the Benin Formation and is made up primarily of alternating sandstones and shales and is of fluvio-marine origin. These sands, sandstones and marine shales which

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make up the Agbada Formation, attain a maximum thickness of about 4500 m. The Akata Formation is the lowest unit of the Niger delta complex. It was deposited in a typical marine environment. It consists mainly of overpressure marine.

The hydrocarbon habitat of the Niger delta is mostly within the sandstone reservoir of the Agbada Formation where they are usually trapped in the roll over anticlines associated with growth faults. The age of the reservoir sands with average thickness between 10 and 20 m ranges from Eocene to Pliocene[8]. Niger Delta produces mainly medium light oil with API gravities ranging from 30 to 450°. The lighter crude oils are volatile with GORs ranging from 180 to 1600 ft^3/bbl. The Niger delta source rock contains predominantly mixture of oil-and gas-prone type IIB and IIIA kerogen[9,10]. The oils from the basin have been grouped into three generic families based on the biomarker and isotopic distributions in the oils[11,12]. The grouping reflects the relative contribution of marine and terrestrial organic matter to the oil source rock.

MATERIALS AND METHODS

Seven crude oil samples from offshore and onshore Niger delta were analyzed. The depths of the reservoir ranged from 1571 to 3226 m. This set of crude oils and associated natural gas samples have been characterized earlier based on the biomarker (Gc-Ms) and isotope composition (Mass spectrometry)[11,13]

Infrared spectra of the crude oils were recorded between 600-4000 cm^{-1} using KBr-pellet techniques on a Buck scientific 1R-spectrophotometer M500.

The spectra were interpreted using Ganz and Kalkreuth method[4]. The height of the peaks at approximately 1705 and 1605 cm^{-1} (corresponding to 1710 and 1630 cm^{-1} in spectra of kerogen concentrate) and at 2930 and 2860 cm^{-1} were measured. The A-Factor and C-Factor were calculated from the peak heights using the equation:

$$\text{A-Factor} = \frac{(2860+2930\ cm^{-1})}{(2860+2930+1630\ cm^{-1})}$$

$$\text{C-Factor} = \frac{(1705\ cm^{-1})}{(1705+1630\ cm^{-1})}$$

RESULTS AND DISCUSSION

Source characterization of the oils: A typical IR spectrum of one of the oils is shown in Fig. 1. Prominent functional groups present in the oils are given in Table 1. Major functional groups identified on the IR spectral of the oils include; C-H stretching of saturate (2931 and 2860 cm^{-1}), C-H deformation of saturate (1460 cm^{-1}) and C-H symmetric deformation of saturate (1374 cm^{-1}), C=O stretching of carboxyl/carboxylic acid (1705 cm^{-1}), C=C stretching of aromatics (1605 cm^{-1}) and C-H bending of substituted benzene ring (748-876 cm^{-1}). The peak heights of the four major peaks used in calculating the A and C-Factors as well as the values of the factors are given in Table 2. Figure 2 shows the plots of A-Factor against C-Factor on vitrinite reflectance grid diagram. With the exception of NDE-3, all the samples plotted along the type I evolution pathway, indicating that they were formed from source rock of algal materials. This observation contradicts the type II/III already inferred for Niger delta oil and gas using universally accepted techniques for oil and source rock characterization (biomarker and isotopic composition)[11,12].

Thermal characterization of the crude oil: The thermal maturity of the crude oils was estimated based on the calibrated Vitrinite Reflectance Equivalent (VRE%) grid on

Table 1: Functional group in the IR spectra of the crude oils

Peak	Wavelength of absorption (cm^{-1})	Mode of vibration	Functional group
P_1	2928-2931	C-H stretching	-CH_2 and -CH_3 of saturate
P_2	2850-2860	C-H stretching	-CH_2 and -CH_3 of saturate
P_3	1703-1709	C=O stretching	-C=O of carbonyl/carboxylic
P_4	1599-1606	C-C stretching	-C=C of aromatics
P_5	1460	C-H deformation	-CH_2 and -CH_3 of saturate
P_6	1374-1380	C-H sym. deformation	-CH_2 of sature
P_7 P_8 P_9	748-876	C-H bending	-C-H of substituted benzene

Table 2: A and C-Factors determined from the IR spectra of the crude oils

		Peak heights (cm)				Parameters	
Well	Depth (m)	2930	2860	1705	1606	A	B
NDE-2	2871-2874	11.5	11.3	1.6	10	0.96	0.62
NDE-3	1571-1572	10.0	3.3	8.2	6.4	0.68	0.56
NDE-4	2407-2409	10.8	3.9	4.6	3.4	0.81	0.56
OSW-3	1640-1642	11.2	9.2	2.3	1.1	0.95	0.68
OSW-4	3009-3011	11.5	10.6	2.0	1.3	0.94	0.61
OSW-5	2031-2032	11.5	10.7	0.8	0.6	0.97	0.57
OSW-6	3223-3226	10.5	10.0	2.0	1.1	0.95	0.65

Table 3: Source rock type and Vitrinite Reflectance (VR%) of the crude oil determined from the plot of A-factor against C-factor

Well	Depth (m)	Source rock type (kerogen)	Vitrinite reflectance (VR%)
NDE-2	2871-2874	Type-1	0.6
NDE-3	1571-1572	Type-2	0.6
NDE-4	2407-2409	Type-1	0.5
OSW-3	1640-1642	Type-1	0.7
OSW-4	3009-3011	Type-1	0.6
OSW-5	2031-2032	Type-1	0.6
OSW-6	3223-3226	Type-1	0.7

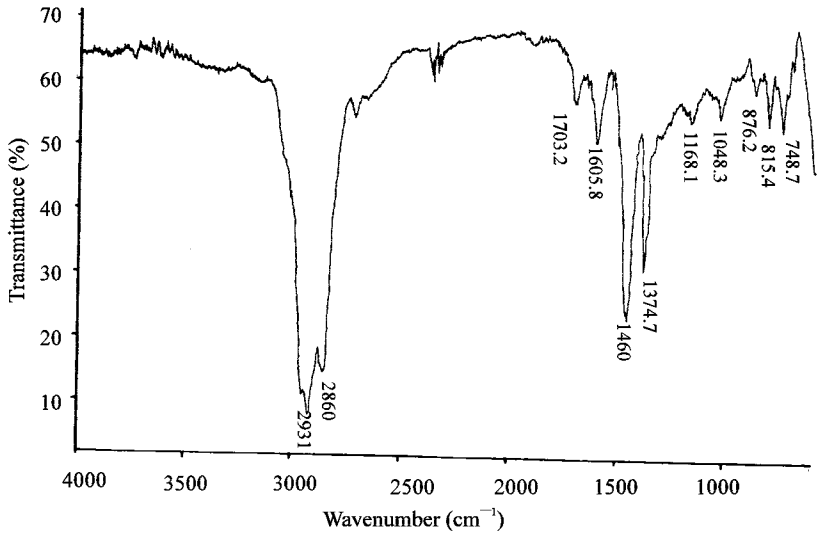

Fig.1: IR spectrum of Nigar Delta crude oil (OSW-3)

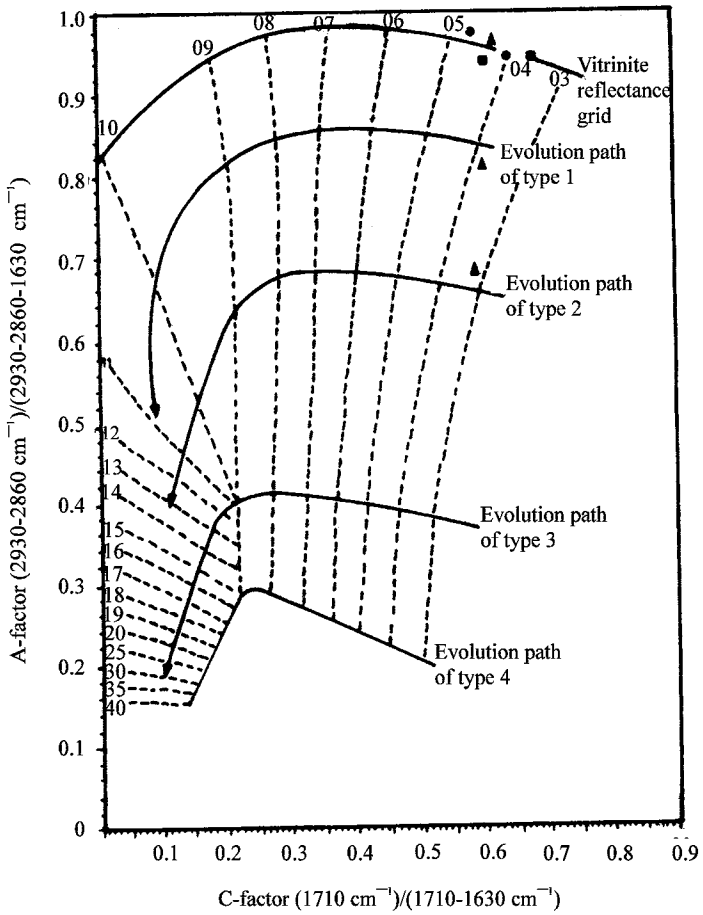

Fig. 2: Classification of Niger Delta crude oil source and maturity according to plots of A and C-Factor and the vitrinite reflectance equivalent grid obtained from the IR spectral (▲ NDE-1 and 2; ■ OSW-3 and 4; • OSW-5 and 6)

the plot of A-Factor against C-Factor (Fig. 2). The virtrinite reflectance values ranged from 0.5 to 0.7 VR%. Vitrinite reflectance values for kerogen in the main zone of oil generation typically ranged from about 0.5 to 1.3% Ro with light liquid and gas generation continuing on to about 2.0% Ro. Reflectance above 2.0% Ro indicates metagenesis (last stage in the process of petroleum generation). The VR values recorded for the studied samples suggest low maturity level i.e. oils formed at the early stage of petroleum formation. Similar observation has been reported for the same set of samples based on their biomarker distributions[11,12].

CONCLUSIONS

The IR analysis showed that most of the oils are of type I kerogen origin. This observation contradicts the earlier works done on Nigeria crude oil and source rock which classified Niger Delta oil and source rock as type II/III. This implies that infrared spectroscopy might not be a suitable tool for crude oil characterization in terms of origin.

The vitrinite reflectance obtained for the crude oil ranged from 0.5-0.7%, indicating low maturity as earlier reported for Niger delta oils. Infrared spectroscopy technique may be useful in characterizing crude oil as regard thermal maturity.

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