Sunday and Israel, 2016
J. basic appl. Res 2(4): 480-484

JBAAR
Journal of Basic And Applied Research
ISSN 2413-7014

Preliminary Assessment of the Generative Potential of Crude Oil Samples From Three (3) Offshore Exploration Oil Wells in Nigeria

Esther Sunday and A. Ubon Israel

Chemistry Department, University of Uyo, Uyo, Akwa Ibom State

*corresponding author: esthersunday403@gmail.com

Received: 18-5-2016
Revised: 22-6-2016
Published: 23-6-2016

Keywords:
Crude oil, generative potential, maturity index, hydrocarbons, kerogen

Abstract: Oil generating potential of virgin crude oil samples procured from wells within the Southern part of Nigeria was employed in this study. The work aimed at characterizing the organic matter, determining the quality, analyzing the quality status as well as highlighting the source input for the purpose of deducing the hydrocarbon potential of the crude oil sample. The crude fractions were eluted using n-hexane for Saturated Hydrocarbons (SHC), methyl-benzene for Aromatic Hydrocarbons (AHC), benzene / ethyl acetate (3:1) for Vanadyl Porphyrins (VOP), dichloromethane / n-hexane (2:3) for Nikel Porphyrins and methanol / dichloromethane (2:1) for Nitrogen, Sulphur and Oxygen compounds (NSO). The Yorla oils had the lowest VOP / NIP ratios and NSO values which ranged from 0.1 – 0.8 with an average of 0.46 ± 0.20 and 0.1 – 0.3 with an average of 0.16 ± 0.1 respectively. This indicated that the Yorla oil was more matured and has a higher quality as compared to the Usari oils and Oloibiri oils which was slightly degraded. The Total Petroleum Hydrocarbon (TPH) of the samples was relatively high, this implies that the source rocks of the oils is Type 1 Kerogen and therefore, is oil prone. The very high values of the SHC/AHC ratios of the oil showed that the oils are not degraded and have high quality. It can be concluded that the sediments of the oils posses a hydrogen rich organic matter. The source rocks of the oils have the potentials to generate oil if given sufficient maturity time.

Cite this article as: Sunday, E. and Israel, A.U. (2016). Preliminary Assessment of the Generative Potential of Crude Oil Samples From Three (3) Offshore Exploration Oil Wells in Nigeria. Journal of basic and applied Research 2(4): 480-484

1. INTRODUCTION

Crude oil or petroleum is a complex mixture of unsaturated straight chain hydrocarbons (olefins), paraffins, and aromatic hydrocarbons with small quantities of organic compounds containing oxygen, nitrogen, sulphur and trace amounts of metals such as iron, nikel, vanadium to mention but a few. The presence of these metals in crude oil does not only affect its maturity but its oil producing ability as well as the quality of the organic matter which is called kerogen. Various reports have employed different chromatographic methods to characterize crude oil fractions into acids, bases, saturates and aromatic fractions (E.O. Odebunmi, E. A. Ogunsakin, P.E.P. Ilukhor (2002). The resulting fractions were analyzed using ultraviolet and infrared spectrophotometry (E. O. Odebunmi and S. A. Adeniyi (2007), x-ray fluorescence spectrophotometry as well as proton and carbon -13- nuclear magnetic resonance spectrophotometry. The metal and non-metal contents of crude oil have also been studied using Atomic Absorption Spectroscopy methods (AAS). Elution chromatography has also been used by Karlsen(1995), to characterize the fractions of undiluted virgin crude oils. This study attempts to utilize primary chromatographic method to examine the oil generative potential and thermal maturity of crude oil samples from three offshore exploration oil wells in Nigeria (Usari, Yorla, and Oloibiri).

Kerogen is an organic matter that is found in a sedimentary rock mixture of organic matter and is a precursor of oil and natural gas. This includes hydrogen, carbon, oxygen, nitrogen and sulphur which are formed during metagenesis by non bio-degradable macormolecules. The quality and the quantity of the kerogen formed determine the oil producing ability of a source rock. Kerogen with high hydrogen to carbon ratios (Type 2 kerogen) often produces oil while kerogen with low hydrogen to carbon ratio (Type 1 kerogen) generates gas. As the hydrogen to carbon ratio of the organic matter increases, the volume of crude oil generated and released from a source rock also increases (Hunt, 1996). Just like kerogen, sulphur contents of the crude oil reveal the type of organic matter of the source rock and its depositional environment (Moldowan, J. M., Seifert W. K., Gallegos EJ (1985). High and low sulphur content of the crude is derived from the sulphur contents of the kerogen. Source rocks that are deposited in siliciclastic environments have low sulphur contents while those in marine environments forms high sulphur crudes (Gransch and Posthuma (1974). The presence of alkanes, isoprenes, pristine and phytanes can be used to deduce the source of the organic matter (Duan and Ma, (2001). Pristine to phytane ratios shows the redox conditions in the depositional environments. High pristine to phytane ratios is an indication that the organic matter has undergone oxidation (Powell T. G and McKirdy, (1973). The objectives of this study includes: characterizing the oil samples using elution column chromatography, assessing the organic richness and maturity indices of the samples, evaluating the quality of the organic matter and deducing the oil generative potential of the oil wells.

2. **MATERIALS AND METHODS**

2.1 PROVINCE GEOLOGY OF THE SAMPLE AREA

Usari, Oloibiri and Yorla oil well all lie within Niger Delta in the South Eastern part of Nigeria. The geology of the Niger Delta Basin is the twelfth largest in the world with billions of oil and recoverable gas. The Yorla oil well lied at the boundary between Akwa Ibom and Rivers State separated from the Gulf of Guinea by the Bonny River.

EXPERIMENTAL PROCEDURE

All the reagents used in this work were of analytical grade and were used without further purification. A column utilized in the elution column chromatography was washed with detergent and distilled water and was allowed to dry. The finely divided silica gel and alumina used were activated by drying in the oven at about 300 degrees Celsius for 12 hours. A small piece of glass wool was inserted at the end of the column to filter the eluate. Silica gel and alumina in the ratio of 2:1 was loaded into the column which was periodically vibrated to remove air bubbles and ensure homogeneity in the distribution of the stationery phase. The column was then developed by wetting the stationary phase with 25 ml of n-hexane. One milligram of the crude oil sample was dissolved in 2 ml of n-hexane and was introduced into the developed column. The fractions were eluted at an approximate flow rate of 4 ml per minute with 50ml of 100% n-hexane for saturated hydrocarbons, methylbenzene for aromatic hydrocarbons, 3:1 ratio mixture of benzene/ethyl acetate for vanadyl porphyrins, 2:3 ratio mixture of dichlorometane/n-heptane for nickel prophyrins and 2:1 ratio mixture of methanol/dichloromethane for the nitrogen, oxygen and sulphur compounds. The elution of the components was completed by using only methanol to flush the column. Excess solvent was allowed to evaporate at a temperature of 30 ^{o}C to avoid denaturation of the fractions.

2.2 SAMPLE PREPARATION

Sample bottles were washed, dried and weighed using a mettle tolodo electronic weighing balance and labeled. Their weights were recorded as weights of empty bottle. The sample (1 ml) was carefully dropped into the empty bottle using a dropping burette, the bottles were reweighed and their new weights were recorded as weight of empty of bottle + 1ml of oil sample. The sample bottles were then heated using a memmmer electronic oven to allow for evaporation of lighter range hydrocarbons. After heating, the samples were weighed again before introduction into the column.

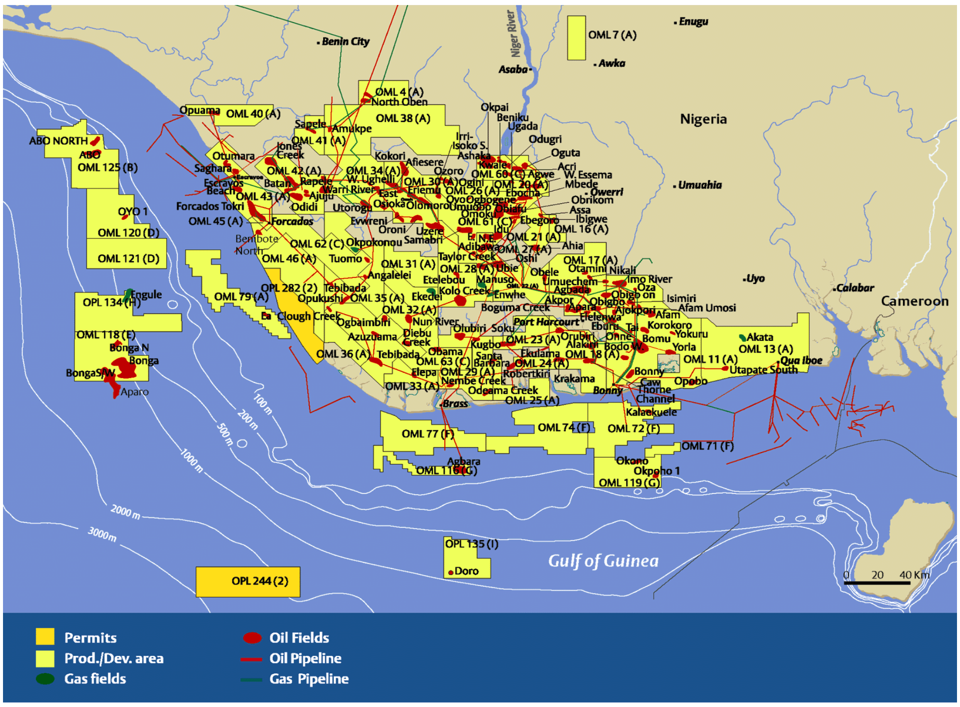

Figure 1:Map of Nigeria showing sample locations. Sample 1 =Usari, sample 2 = Oloibiri, Sample 3: Yorla(OML 11A)

2.3 CHARACTERISATION OF SAMPLES
The sample was characterized into Saturated Hydrocarbons (SHC), Aromatic Hydrocarbons (AHC), Vanadyl Porphyrins (VOP), Nikel Porphyrins (NOP), Nitrogen, Oxygen and Sulphur resin (NSO) using different solvent combinations as explained in section 2.1 above.

3 RESULTS AND DISCUSSIONS
The colors of the five fractions eluted from elution chromatography of the various samples are presented in Table 1. The table clearly shows that the color of each fraction deepens on proceeding from the yorla oil to the usari oil.

TABLE 1: Colours Of Fractions From Elution Column Chromatography Of Crude Oil Samples

Sample	(SHC)	(AHC)	(VOP)	(NIP)	(NSO)
Yorla	Golden yellow	Yellowish brown	Dark brown	Yellowish brown	Dark brown
Oloibiri	White	Deep brown	Dark brown	Yellowish brown	Dark brown
Usari	White	Dark brown	Dark brown	Carton brown	Dark brown

The colours of the five fractions (Saturated Hydrocarbons, Aromatic Hydrocarbons, Vanadyl porphyrins, Nikel porphyrins and Nitrogen/sulphur and Oxygen compounds) obtained from elution column chromatography corresponds with that of E. O. Odebunmi et al.,(2007). Table 1 clearly plainly reveals that the colour of each fraction deepens on proceeding from Yorla oil to Usari oil. Therefore, colour can be used to characterize the fractions obtained during elution column chromatography of crude oils and petroleum products (E. O. Odebunmi et al., (2002)

3.2 OIL GEOCHEMISTRY AND MATURITY INDEX
NSO VALUES
The NSO values (Table 2) of the Usari oil ranged from 1.0 – 2.3 with an average of 1.23 ± 0.4. The values for the Oloibiri oil ranged from 1.2 – 1.4 with an average of 1.32 ± 0.9. The values for the Yorla oil ranged from 0.1 – 0.3 with an average of 0.16 ± 0.1.
Figure 2 shows that Yorla oil have low values of NSO which is a suggestion that the Yorla oil is more matured and has a high quality while the Usari and Oloibiri oils are slightly degraded as biodegradation increases the sulphur contents of an oil. Various researchers have confirmed that as oil is heated underground, the weak sulphur carbon bonds breaks and produces hydrogen sulphide gas. Therefore, crude oils with lower NSO contents will have high quality while those with high NSO contents will have low quality. The low values of the Yorla oil also reveals that the oil was derived from sediment containing low organo sulphur kerogen.

VOP/NIP RATIOS
The ratios of Vanadyl and Nikel porphyrins (metals) in crude oils are beneficial in the determination of source rock type and maturity because they tend to be unchanged irrespective of alteration effects (Lewan, M. D., (1984). The VOP/NIP ratios (Table 3) for Usari oil ranged from 4.2 – 6.5 with an average of 5.2 ± 0.35. The values for Oloibiri oil ranged from 4.4 – 6.8 with an average of 6 ± 1.7. The values for Yorla oil ranged from 0.1 – 0.8 with an average of 0.46 ± 0.20. Figure 3 shows that the Yorla oil had the lowest value of VOP to NOP ratio. This suggests that the Yorla oil is more mature than the Usari and Oloibiri oil. According to findings made by Barwise (1990) and Udo O. T and Ekwere S. Abrakasa (1992), the maturity of an oil increases as VOP to NIP ratio decreases. Nevertheless, the mean values of Usari oil and Oloibiri oils are quite close, this is an indication that the oils are generated from similar source rocks. This could mean that the source rocks of the both oils were deposited where Vanadyl and Nikel cations were available for absorption into the sediments (Lewan M. D, (1984).

AHC/SHC RATIOS
The ratios of Aromatics to Saturated Hydrocarbons are always used for oil maturation and biodegradation findings. As compared to the pristine/phytane ratio in gas chromatography, AHC/SHC ratio can be used as an indicator of depositional environments. The samples had low AHC/SHC ratios (Table 3) which ranged from 01-0.5 with an average of 0.28 for the Usari oli, 0.3-0.4 with an average of 0.38 for the Oloibiri oil and 0.4-1.1 with an average of 0.62 for the Yorla oil. Various researchers have suggested that a high AHC/SHC value is an indication of high maturity level. From Table 3, Yorla oil had AHC/SHC values greater than the other samples. This is a sign that Yorla oil is more matured that the other crude samples.

TABLE 2: Column Chromatography Data.

SAMPLE CODE	SHC	AHC	VOP	NIP	NSO	%SHC	%ACH	%NSO	STARTING WEIGHT
	Mg X 10^{-1}	Mg X10^{-1}	Mg X 10^{-1}	Mg X 10^{1}	Mg X 10^{-1}				Mg X 10^{-1}
Usari	2.8	1.0	1.5	0.3	1.4	55.6	18.5	25.9	7.0
U2	2.7	0.6	0.1	0.4	2.3	48.2	11.7	40.1	6.1
U3	3.0	0.4	1.2	0.2	1.2	65.2	8.7	26.1	6.0
U4	2.8	0.5	1.3	0.3	1.3	60.9	10.8	28.3	6.2
U5	3.7	1.7	1.3	0.2	1.0	57.8	26.6	15.6	7.9
Oloibiri	4.1	1.6	2.5	0.4	1.3	58.6	20.0	18.6	9.9
O2	4.3	1.4	2.4	0.2	1.4	60.6	19.7	19.7	9.7
O3	3.7	1.6	2.2	0.5	1.4	55.2	18.4	16.1	9.4
O4	3.8	1.7	2.4	0.4	1.2	56.7	25.4	17.9	9.5
O5	3.9	1.6	2.4	0.3	1.3	57.4	23.5	19.1	9.5
Yorla	2.3	2.5	0.4	1.4	0.3	45.1	49.0	5.9	6.9
Y2	2.0	1.3	0.1	1.3	0.2	57.1	37.1	5.7	4.9
Y3	1.4	0.7	0.8	1.0	0.1	63.6	31.8	4.5	4.0
Y4	2.2	0.9	0.1	1.2	0.1	68.6	28.1	3.1	3.3
Y5	2.8	1.0	1.0	1.0	0.1	71.8	25.6	2.6	5.9

TABLE 3: Data For TPH, %TPH, VOP/NIP, VOP/(NIP + VOP), SHC/AHC RATIO,

Sample code	TPH	%TPH	VOP/NIP	VOP/(NIP+VOP)	SHC/AHC	AHC/SHC
	Mg X 10^{-1}		PPM	PPM	PPM	PPM
USARI	3.8	67.8	5.0	0.8	2.8	0.4
U2	3.3	86.8	4.2	0.8	4.5	0.2
U3	3.4	70.8	6.0	0.9	5.2	0.1
U4	3.3	67.3	4.3	0.8	5.6	0.2
U5	4.4	74.6	6.5	0.9	2.2	0.5
Oloibiri	5.7	66.3	6.3	0.9	2.6	0.4
O2	5.7	68.7	6.7	0.9	3.1	0.3
O3	5.3	66.3	4.4	0.8	2.3	0.4
O4	5.5	66.5	6.0	0.9	2.2	0.4
O5	5.5	66.3	6.8	0.9	2.4	0.4
Yorla	4.8	72.7	0.3	0.2	0.9	1.1
Y2	3.3	70.2	0.1	0.3	0.8	0.7
Y3	2.1	53.8	0.8	0.4	2.0	0.5
Y4	3.1	70.5	0.1	0.1	2.4	0.4
Y5	3.8	65.5	1.0	0.5	2.8	0.4

3.3 QUALITY AND TYPE OF ORGANIC MATTER

The differences in the mean values of VOP to NIP ratio suggests that the crude oils were generated from different sources of organic matter. The high values of VOP/(NIP + VOP) ratio reveals the reducing condition of the source rock (Lewan M. D., (1984). Type 2 kerogen is deposited in a reducing environment,. It is very rich in Hydrogen and low in oxygen as it is derived primarily from the remains of planktons which have been reworked by bacterial activities. The oils had very high values of TPH, this shows that the source rock is a Type 2 kerogen and is therefore oil-prone.

3.4 OIL GENERATIVE POTENTIAL OF THE OILS

The quality and quantity of kerogen gives the generative potentials of any oil. Kerogens with high hydrocarbon ratio greater than 2 tends to generate oil while kerogens with lower hydrocarbon ratio between 0.2 – 1.8 tend to generate gas. In this study, the oils have high hydrocarbon ratio, this suggests that the oils are oil-prone (high generative potential).

4 CONCLUSION

The experimental data revealed that although the oils are derived from type 2 kerogen which is oil-prone, the Usari and Oloibiri oils are yet to be matured while the Yorla oil is matured and ready for exploration. The Usari and Oloibiri oils are derived from an organic matter that is deposited in a relatively high reducing depositional environment. From the parameters analyzed, it is concluded that the oil sample form the Yorla oil well is mature and has a very high productivity potential as compared to other samples.

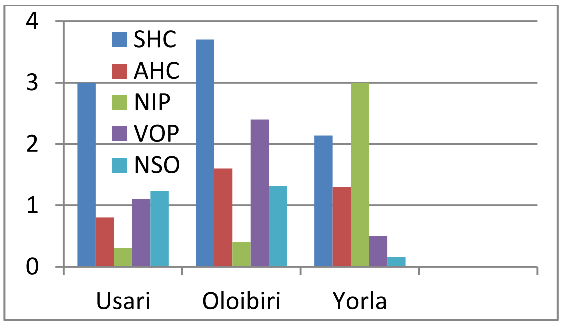

Figure 2: chart showing the distribution of SHC, AHC, NIP, VOP and NSO of the 3 samples

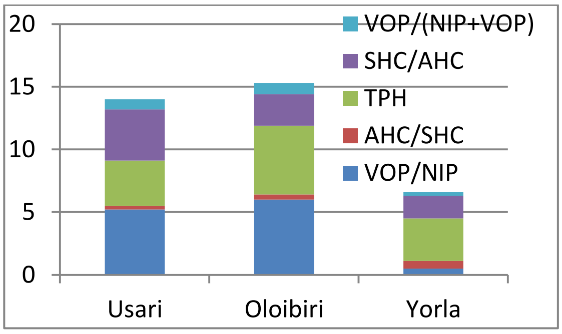

Figure 3: vop/(nip+vop), shc/ahc, tph, ahc/shc,vop/nip ratios. (parameters for determining oil maturity

ABBREVIATIONS

AHC- Aromatic Hydrocarbons
NIP - Nikel Porphyrins
NSO - Nitrogen, Sulphur and Oxygen compounds
SHC - Saturated Hydrocarbons
VOP - Vanadyl Porphyrins
TPH - Total Petroleum Hydrocarbon

ACKNOWLEDGEMENT

The authors wish to thank Dr. P. Neji for many fruitful discussions, critical and helpful comments and reviewing an earlier draft of manuscript. We also wish to thank Mobil and NNPC Oil Company, for providing the oil samples and support provided by Cross River University of Technology. The work depended on support provided by technical staff at the University of Uyo, and Cross River University of Technology. The work was much improved by reviews and comments provided by anonymous reviewers.

REFERENCES

Barwise, AJG.(1990),Role of nickel and vanadium in petroleum classification. Energy Fuels 4: 647 – 652.

Duan and Ma,(2001). Source rocks, Geochemical journal, v. 272, p. 216-222.

E. O. Odebunmi, E. A. Ogunsakin and P.E.P. Ilukhor (2002). Characterization of Crude Oils and Petroleum Products: (1)Elution Liuid Chromatographic Seperation and Gas Chromatographic Analysis of Crude oils and Petroleum products. Bulletin of Chemical Soicety of Ethopia, 16(2), 115-132.

E. O. Odebunmi and S. A. Adeniyi (2007). Infrared and Ultraviolet Spectrophotometric Analysis oc Chromatographic Fractions of Crude oils and Petroleum Products. Bulletin of Chemical Society of Ethopia, 21(1), 135-140.

Gransch and Posthuma(1974), Sulphur geochemistry, Edu. Publications, v. 113p. 27-33.

Hunt, J. M. (1996). Petroleum Geochemistry and Geology, second ed., W.H. freeman and company, New York.

Karlsen DA, Nyland B, Flood B, Ohm SE, Brekke T, Olsen S, Backerowe K (1995), Petroluem geochemistry of the Haltenbanken, Norwegian Continental Shelf. In: Cubitt JM, England WA(eds), The geochemistry of reservoirs. Geological Society Special Publication 86, London, pp 203-256.

Lewan, M. D., Factors controlling the proportionality of Vanadium to Nikel in crude oils, Geochimca et Cosmochimca Acta, 1984, v. 48, p. 2231-2238.

Moldowan, J.M., Seifert W.K., Gallegos EJ (1985), Relationship between petroleum composition and depositional environment of petroleum source rocks, American Association of Petroleum Geologist Bulletin, v. 48, p. 1255-1268.

Powell, T.G and McKirdy, Relationship between ratio of pristine to phytane, crude oil composition and geological environment in Australia, Nature, (1973), v. 243, p. 37-39.

Shashi Chawla, Petroluem and Petrochemicals (2003), in: Taruna Chawla (Ed.), A Textbook of Engineering Chemistry, third ed., Dhanpat Rai & Co. (P) LTD., India. P . AC.130 – AC.137.

Udo O.T, Ekwere S, Abrakasa S (1992), Some trace metal in selected Niger Delta Crude oil: application in oil-oil correlation studies. Journal of Mineral Geology. 28(2): 289-291.