Chemical Analysis of Sara and Pona Constituents of Plain-Bitumen Seepages Deposit at Agbabu Area of Ondo State South Western Nigeria with their Correlation Matrix Properties

K.K. Bada., Leo. C. Osuji., and M.C. Onojake
Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria

ABSTRACT

*Characterization and chemical analysis is a necessary step in identifying the chemical constituents of the heavy unconventional oil (Bitumen) which will give a way forward if the production, modification and refining of the heavy oil in order to supplement and increase the life span of the present conventional natural gasoline. This study presents the (SARA) classification of the bitumen deposit at agbabu village in Ondo state Nigeria, perhaps it is highly rich in Resins, Asphaltene, Saturates or it is Aromatic compounds based oil, so as to determine the economic viability of its production, processing, modifying, refining and its upgrading as a synthetic oil as well as its other uses for engineering purposes. The data assay of these chemical components (SARA) were scrutinized by conducting a comprehensive experimental studies on four different samples of bitumen using an extraction method of column chromatography according to America society for testing and material (**ASTM D-2007)** and a detailed hydrocarbon analysis (DHA) known as PONA column chromatography; was modelled using gas chromatography flame ionization detector (GCFID) according to the (**ASTM D- 5134)**. The results obtained indicate that the bitumen samples have high content of saturates which ranges from **(36.5--- 72.6%),** low content of resins **(6.4 --- 12.5 %),** low contents of Asphaltenes **(1.8---9.5%)** and high contents of Aromatics **(16.4----54.2%)** samples. From these results, specifically the high content of saturates and aromatics, it is obvious that the bitumen sample is of good quality to be processed for synthetic oil production.*

I. INTRODUCTION

Physicochemical analysis is a good parameter while examining the details of the bitumen properties [1]. While examining the physicochemical analysis of dead oil, a lot of thermo-physical properties and chemical analyses which are not limited but includes the parafin content, the olefinic content, the napthenes content and asphaltene content are fully examined. Analysis of saturates compound, aromatics compound, resinic compound, fugacity- activity coefficient variation, isotopic analysis ratios and hydrocarbon contents are also included [2].

All these parameters have been reported to make effective classification of heavy oil with API gravity correlation [3].The nature of thermodynamic modeling regarding equilibrium of the species of bitumen samples both in liquid and gaseous phase, the peng-robinson equation of state (PR-Eos) as well as NRTL activity modeling with the integration of residual curve map are also used to evaluate the simulated distribution data and the experimental solubility of light hydrocarbon and non-hydrocarbon gases in relation to their distribution patterns and their concentrations in heavy oil [4]. This can give valuable information on the best method of production, cost of refining, environmental impact and the specification necessary to meet, regarding the upgrading of heavy conventional oil [5].

There are lots of great challenges that is related to the classification of heavy oil and source rocks using bulk parameters for heavy oil analysis. Meanwhile, with the aids of thermo-physical and chemical analysis relating to the reservoir formation using fugacity constant, such correlation can make assessment visible [6]. The molecular weight, specific gravity and SD curves can also be used with the evaluation of pseudo-components in the sample to stipulate how economical the particular bitumen sample will be prior to production, modification, upgrading, refining and optimization for other applications [7]. Carbon, hydrogen, sulphur, and nitrogen content determination are as well necessary parameters to look at. SARA contents and PONA analysis of bitumen can also be used to classify heavy oil into family [8].

The focus for this laboratory assessment is to probe into the chemical constituents of the bituminous samples and at the same time estimate the percentage composition of its (SARA) constituents such as the Saturates, Aromatics, Resins and Asphatenes contents, not limited to this but with the inclusiveness of the simulation of true atmospheric distillation of the bitumen sample and the thermo-physical parameters of seepages of plain bitumen obtained from Agbabu area in ondo state Nigeria. All these will convey a vital information regarding the method of production in situ, couple with correlation matrix index of the residual curve map in order to enhance the preliminary information concerning the economical viabilities of the upgrading, modifying, and refining of the bitumen deposit in Nigeria.

The chemical analysis in this write-up details the experimental procedures used for this study and a concise analysis of the results obtained are made on each of the sample. Prefatory conclusion regarding the technological involvement in the course of bitumen production are drawn with reference to the environmental safety concern of the area where the deposit is found for further and robust future research focal point on Nigeria bitumen deposit as a whole.

II. EXPERIMENTAL

1. Materials studied

Chemical analysis was investigated on the plain bitumen samples which were obtained as a result of outcropping of the bitumen in form of seepages from four different locations that are named as follows, Agbabu, Loda, Ilubinrin and Ode-Irele in the area of afowo formation along the Benin basin southern west of Nigeria. A sample was collected from a drilled hole as a result of exploration of bitumen in Agbabu village (AB), another sampling was collected from the outcropping of plain bitumen at Ode- Irele village (OI), seepages of bitumen deposit at Ilubinrin was also sampled. Finally, the sediment of bitumen sludge in Loda was sampled and a clean bitumen sample was collected on the surface water as a result of waterlogged in the location. The samples were kept in a small-mouthed glass container using a dry glass rod and the containers were marked and labeled for the purpose of identification. The containers were not fully filled so as to create space for the expansion and to prevent sticking of the bitumen samples with the container. In addition, all were kept in sack bag and brought into the LAB for immediate analysis in order to avoid air oxidation as a form contamination.

2. PROCEDURE

2.1 ASTMD-2007: solvent extraction of bitumen into asphaltenes and maltenes was carried out in this analysis by using 40 times the bitumen volume of *n*-pentane as solvent. The mixture was shaken for 2 hours in an ultrasonic bath and it was then filtered to recover the residual fraction of solid asphaltene fraction. The (rafinates) fraction which is known as Maltene was then recovered by evaporation of the solvent. The maltene fraction was further

separated into resin and oil using column chromatography, with a standard reference in accordance to the procedure outlined in ASTM D-2007.

The clay column is first eluted by *n*-pentane to recover the oil and the resin fraction was retained in the column. The same clay column was then eluted with methyl ethyl ketone (MEK) to extract a dark-colored oily liquid, which is low-density resin. A further elution was done with tetrahydrofuran (THF) which recovered a dark-colored crystalline semisolid, which is high-density resin. The pentane-soluble oil fraction obtained earlier was further separated into saturated and aromatic fractions using an activated silica-alumina column. The saturated fraction was the run and eluted with *n*-pentane as a colorless liquid. The adsorbed aromatic portion in the column was then eluted using toluene as an eluent solvent (9).

A double- sealed adsorption column (silica gel) was employed in this analysis, the length and inner diameter of the column is 60cm by 1.5cm respectively, 100ml burrette packed with cotton wool was inserted above the stop cock while the bottom was actually packed with 80 grams of activated brockman, and the top of the burrete was equally packed with 60 grams of activated of 60—120 mesh (250—125mm) silica gel with the enhancement of a vibrator and the top of the column was fitted with 500ml reservoir of eluents. The stepwise procedure of the extraction is illustrated bellow diagrammatically with the details of its chemistry according to the ASTMD-2007 method of (SARA) analysis (10).

3.2 **3.6 Agilent 6890**

Determination of PONA components distribution using gas chromatography flame ionization detection Agilent 6890 model with GSBP PONA COLUMN and HP PONA COLUMN.

ASTM D- 5445

Procedure: 0.1µL of a distillate sample of bitumen using true boiling point atmospheric distillation unit which was diluted in a solvent, was injected into the GC column Agilent 6890 model equipped with flame ionization detector, using a GSBP column, where the main separation is taking place, an hypodermal stringe, is used to inject the sample through the injector septum, nitrogen were used as a carrier gas with a pressure of 30 psi, hydrogen and air were also supplied at 25 and 30 psi respectively. And then the column temperature is programmed initially at 60 min, held isothermally for 2min, and then increased to 250 min, at the heating rate of 9^0C/min for 18 minutes. It was held at this temperature for 2 min, thereafter increases to a temperature of 320^0C at the heating rate of 13^0C/min for 5min and held at that temperature for 2min (11). The injector and detector were maintained at 250^0C and 350^0C respectively. As the temperature of the column increases, a part of the hydrocarbon of the crude gradually vaporizes and elutes out of the GC column into the detector. Then, the GC detector records the amount of hydrocarbon that vaporized at a particular time of elution, based on the corresponding column temperature. Elution time is also known as *retention time* and is calibrated against the boiling point of *n*-paraffin hydrocarbons. Hence, this is plotted as a weight percentage of the sample eluted against the corresponding boiling point equivalent of *n*-paraffin (12). A PONA module is the core software where parameters dealings with PONA analysis percentage distribution were calibrated, defined and set. Hence this module was used to set the calculation parameters for setting the base line, determine the start elute SE and end elute EE for calculation, elimination solvent effect and removing extraneous peaks. A reference sample was run first to establish appropriate parameters, this set-up was saved and it is used to make the algorithms interpretation index (13).

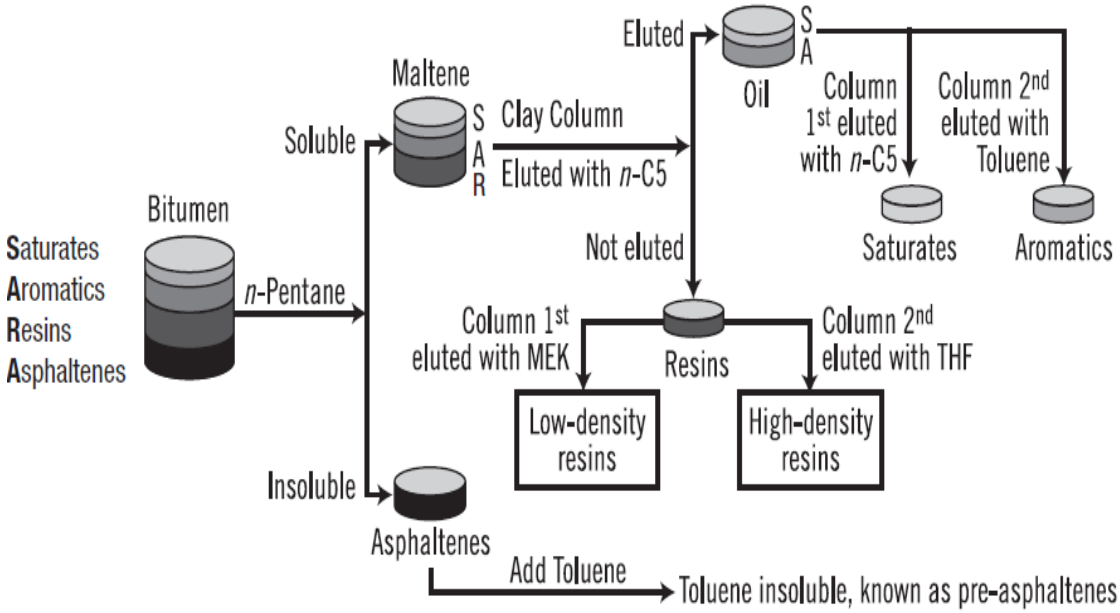


Figure 2: shows the required step in the extraction of bitumen
Source: Dwijen, 2012.

III. RESULTS AND DISCUSSION

Table 1: Result showing the (SARA) Contents of the bitumen samples

SARA	LD1	AB	OI	IL1	IL2	OI2	LD2
Saturates	55.2	40.5	72.6	54.6	53.1	36.5	63.1
Aromatics	28.2	39.4	16.4	30.2	23.5	54.2	17.5
Resins	12.1	14.7	9.4	6.7	14.1	6.4	12.5
Asphaltenes	3.2	5.5	1.8	3.6	9.5	2.0	6.8

KEYS:
LD- LODA: AB—AGBABU: OI---ODE IRELE: IL----ILUBINRIN

TABLE 2. SHOWING THE KINEMATIC VISCOSITY OF THE BITUMEN SAMPLE.

SARA	KINEMATIC VISCOSITY (cSt)	
@	40^0C	100^0C
SATURATES	0.21	0.08
AROMATICS	0.42	0.17
RESINS	0.62	0.36
ASPHALTENES	1.21	0.89

Table 2: Variation in the % Weight and % Volume of PONA/HP COLUMN

PONA Columns	GsBP	HP	GsBP	HP
Compositions	Wt.%	Wt.%	V %	V %
P(Normal Paraffin)	3.39	3.36	3.77	3.56
I (Iso Paraffin)	24.71	25.57	27.46	26.30
O (Olefin)	9.25	9.31	10.14	10.33
N (Naphtha)	15.62	15.51	14.31	15.26
A (Aromatic)	37.04	34.61	31.57	31.43

Table 4.5.Pearson's correlation matrix of SARA--PONA and API gravity

	S	A	R	As	P	I	O	N	API
S	1.01	1.01							
A	1.02								
R	1.01	1.01	1.01						
As	0.12	-0.27	0.06	1.01					
P	0.58	0.86	0.66	-0.72	1.01				
I	-0.84	-0.75	-0.84	-0.04	-0.42	1.01			
O	0.25	-0.08	0.22	0.76	-0.58	-0.56	1.01		
N	1.01	0.92	1.03	0.14	0.58	-0.87	0.32	1.01	
API	0.22	0.12	0.22	-0.03	-0.04	-0.73	0.62	0.25	1.01

Table 4.6: Comparison of the Average of SARA--PONA

SARA/PONA	Adebayo Omole (2007)	Ipinmoroti and Adesanmi (2001)	Obiajunwa and Ukechukwu (2000)	Present study
S	12.51	12.63	12.56	5.75
A	7	14	12	7.5
R	58.49	80.00	69.00	53.75
As	36	75	72.00	33.25
P	3.39	5.6	4.5	3.525
I	20.22	21.00	20.34	25.02
O	7.59	37.00	36.00	9.347
N	15.62	14.54	16.72	15.76

KEYS: S= Saturates: A= Aromatics: R= Resins: As= Asphaltenes: P= Paraffin: I= Isoparafin: O= Olefin: N=Napthenes

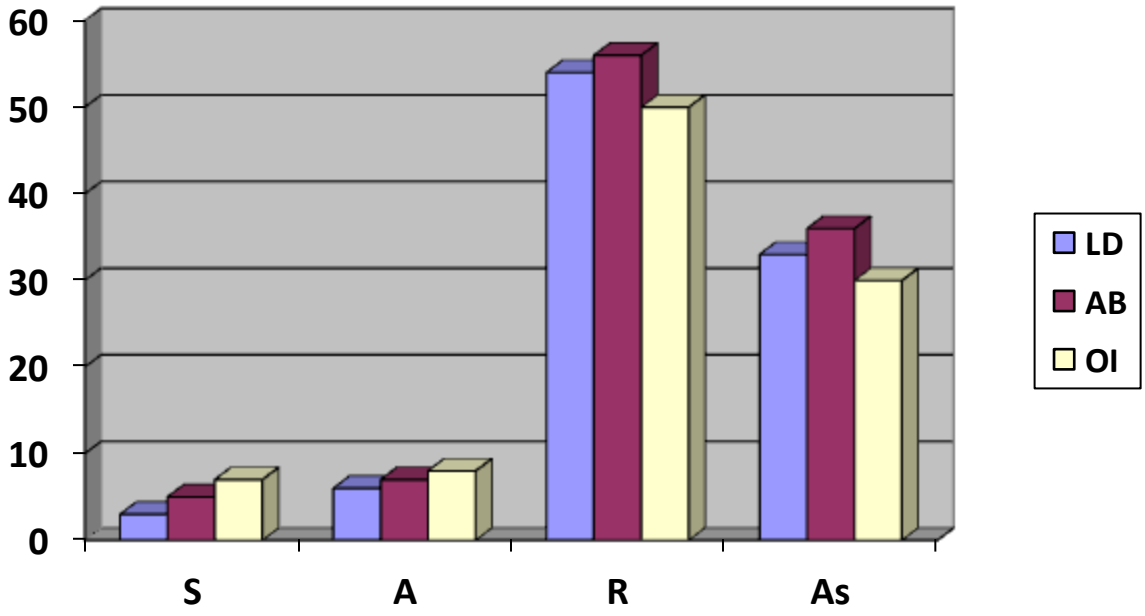


Figure3: showing the chart distribution of (SARA) compnents.

4.2.2 SARA AND PONA Analysis.

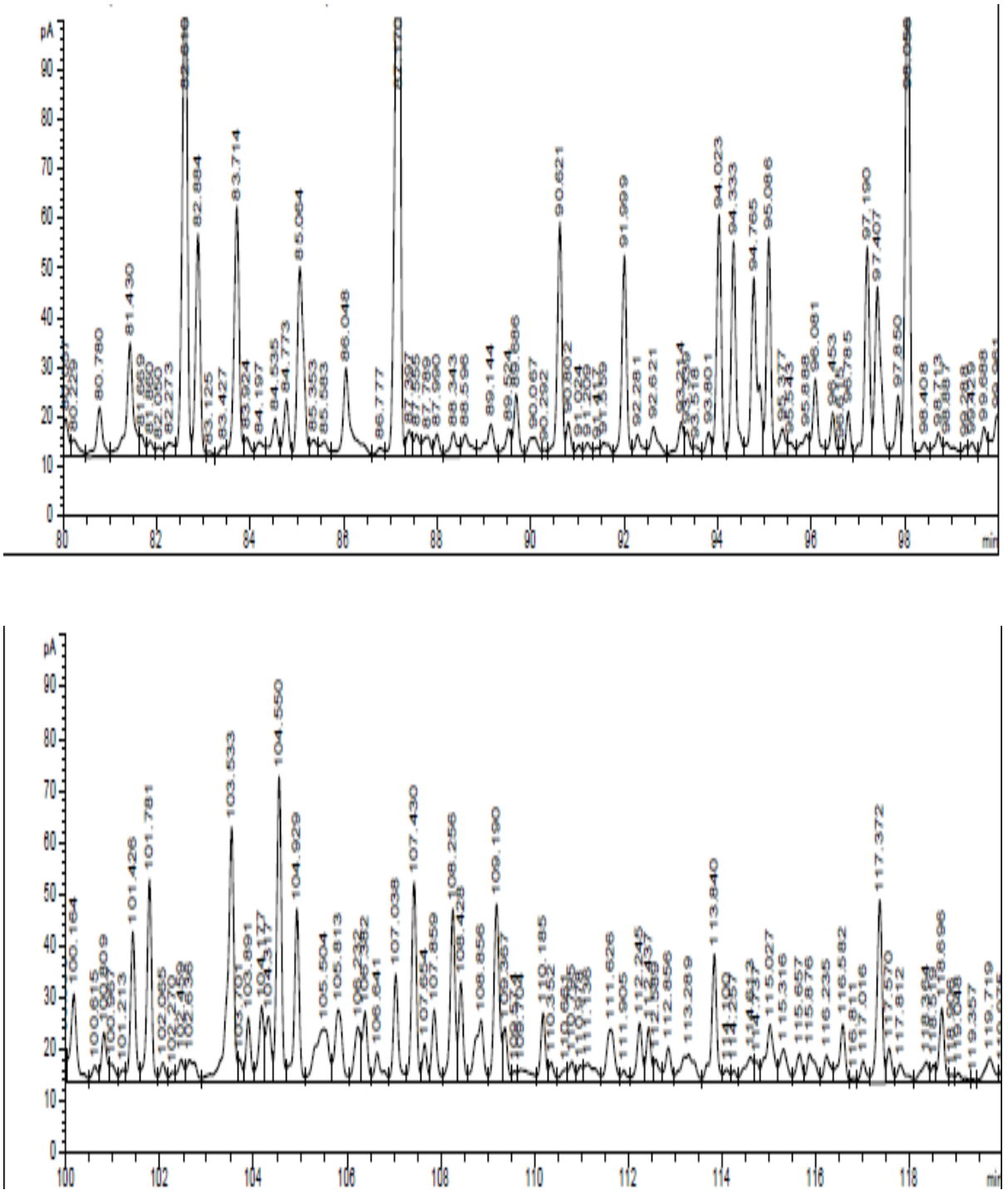
The SARA and PONA analysis have been studied due to its usefulness to make chemical classification of crude oil, especially when it comes to refining operation [31]. The levels of most of the SARA and PONA obtained in this study were generally considered to be low, although special attention is paid on the PONA content of the bitumen sample obtained in one of the location, at Ode-Irele.

Parafins ranges from 3.39 –3.49. These values are lower compare to the values obtained by Obiajunwa and Nwachukwu (2000).

Aromatics ranges concentrations range from 24.71– 24.82, the values is as well lower than those of Obiajunwa and Nwachukwu (2000), but higher than that of Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007)

Olefin ranges concentrations range from 9.25– 9.42. These values are higher than the values obtained by Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007).

Finally, the values of napthenes range from 15.26–16.34mg. These values are considerable higher compare to that obtained by Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007). The relatively higher levels of (PNA) observed in the result is highly expected because these are compounds commonly associated with petroleum oil samples unlike that olefins [30]. Furthermore, most organic source associated with the formation, where the bitumen sample is formed are also associated with appreciable amount of the compound. The SARA separation of the heavy and light fractions of a crude oil give the composition of the crude oil from the point of view of the four basic families of compounds, namely, aromatics, resins and asphaltenes(14). Interactions among these four families of compounds has an eminent effect regarding the chemical composition of the crude oil which must be understood and modeled in the analysis of crude oils. Characterization and concentration measurement of SARA/ PONA contents can be particularly useful for petroleum reservoir fluids with high gas to oil ratios (15). The findings in this report could explain the chemical compound in a crude oil. Thus, the above results indicate that the bitumen sample is highly aromatic in nature and mostly consists of poly-condensed aromatic structures. As the boiling-point ranges of various fractions increase, the molecules become heavier , the relative concentrations of aromatics increase, and the relative concentrations of saturated hydrocarbons (e.g., naphthenes and paraffins) decrease. The above results confirm the fact that bitumen is a poor-quality feedstock for the upgraders or refiners because of its large molecular structure, high aromaticity, high deficiency in hydrogen, and high concentrations of metals and heteroatoms. However, the high-aromatic asphaltene bitumen responds better to steam-injected thermal recovery processes than high-paraffinic crude does [16]. Dead oil sample from Ilubirin and Loda villages, used for this study are water lodge based. The percentage distribution of most of the SARA/ PONA, differ from that obtained by Obiajunwa and Nwachukwu (2000), Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007). The difference is based on the fact that earlier studies of Obiajunwa and Nwachukwu (2000), Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007) were made on bituminous sand while the present study focused on bitumen obtained from clear outcrop unassociated with sand.



Appendix 2: The above two Chromatograms showing the PONA analysis distribution of two bitumen sample obtained from Ode-Irele, using the GsBP PONA column and HP PONA column. Top, GSBP, Bottom, HP.

IV.CONCLUSSION

The chemical analysis assessment that was discussed in this study presents the way forward for the estimation of the amounts and correlation matrix properties of the constituents of the bitumen samples. An extensive method for the characterization and analysis of the existing solids in the heavy oils is presented. The results of the procedure can dictate whether the asphaltene content deposition can hinder the processing of the oil sample under study. The PONA content of the heavy oil are measured using various eluents as solvent and its chemistry is actually established. This data assay along with GSBP PONA analysis may be used to estimate the peak of the theoretical models. The SARA separation of the heavy fraction of the crude oil gives the composition of the heavy oil from the point of view of the four basic families of compounds, namely saturates, aromatics, resins and asphaltenes. Interactions among these four families of compounds has a profound effect on the stability of a crude oil which must be understood and modelled in the stability analysis of crude oils. Characterization and concentration measurement of SARA compound is highly necessary in petroleum reservoir fluids with high viscosity index. The technical procedure that are discussed in this study can be used to determine the composition and nature of SARA/PONA compound present in an unconventional oil in general.

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REFERENCES

1. Abdul-Rauf, S, Muhammad, J., Muhammad, U. and Sajid, A. (2009). Assessment of
2. heavy Metals in sediments of the river Ravi. Pakistan, *International Journal of Agriculture and Biology*, 11 (2), 197–200.
3. Abubakar, F. M., Basta, J. S. and Ahmad, S. M. (2010). Genetic origin, thermal maturation, paleo-environment and classification of some crude oils from the Western Desert, Egypt, by aid of organic and inorganic geochemistry. *International Journal of Academic Research*.**2** (2), 249- 263.
4. Adebayo, E. A. (2004). Extraction and Characterization of Bitumen from Ondo State Tarsand, proceedings of the 8th National Engineering conference of Kaduna Polytechnic, Nigeria. 82-88.

5. Adebiyi, F. M., Asubiojo, O. I. and Ajayi, T. R. (2006). Multi-elemental analysis of Nigerian bitumen by TXRF spectrometry and the physical constants characterization of its hydrocarbon content. *Fuel* 85(3): 396 – 400.
6. Adebiyi, F. M. and Omode A. A. (2007). Organic, Chemical and Elemental Characterization of Components of Nigerian Bituminous Sands Bitumen. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 29(8), 669-676.
7. Adedimila, A. S. (1987). Okitipupa bituminous sands: New construction materials for flexible pavements? Nig. Eng., 22: 1- 14.
8. Adegoke, O. S. (1977). Stratigraphy and palaeontology of Ewekoro formation (Paleocene) of South Western Nigerian. Bulletin *American paleontology*. 71(295): 375.
9. Adegoke, O. S., Ako, B. D., and Enu, E. I. (1980). Geotechnical Investigations of the Ondo State bituminous sands, Geology and Reserves Estimate Geological Consultancy Unit, Department of Geology, University of Ile-Ife, 257.
10. Adegoke, O. S. and Ibe, E. C. (1981). The tar sand and heavy crude resources of Nigeria. In the proceedings of the 2nd International Conference on heavy crude and tarsands, Caracas, Venezuela, chapter (32), 280 – 285.
11. Akinlua, A., Ajayi, T. R., and Adeleke, B. B. (2007). Organic and inorganic geochemistry of northwestern Niger Delta oils. *Geochemical Journal*, 41, 271-281.
12. Akintola, J. O. (1986). Rainfall distribution in Nigeria 1982-1983. Impact Publishers Nigeria Limited, Ibadan, Nigeria. 371.
13. Ako, B. D., Adegoke, O. S. and Peter, S. W. (1980). Stratigraphy of the Oshosun Formation in Southwestern Nigeria. *Journal Mineral Geology;* 17, 9 -10.
14. Ako, B. D., Alabi, A. O., Adegoke, O. S and Enu, E. I. (1983). Application of resistivity sounding in the Exploration for Nigerian Tar sand: Energy exploration and exploitation. 2. 155-164.
15. Alberdi-Genolet, M. and Tocco, R. (1999). Trace metals and Organic geochemistry of the Machiques member (Aptian-Albian) and LaLuna Formation (Cenomanian-Campanian), Venezuela, *Chemical Geology*. 160, 19 - 37.
16. Al-Shahristani, H. and Al-Atyia, M. J. (1972). Vertical migration of oil in Iraqi oilfields. Evidence based on vanadium and nickel concentrations. 36, 929-938.
17. ASTM. (1990). Standard test method for determination of water in liquid petroleum products by Karl Fischer reagent. D1744-92.