

PHYSICOCHEMICAL STUDIES OF NIGERIA'S CRUDE OIL BLENDS

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Abstract

Physicochemical parameters of crude oil blends obtained in Nigeria have been carried out. The parameters studied were: pH, temperature, viscosity, specific and API gravity, pour point, water content, Acid No, Sulphur content, salt content and heavy metals namely: Zn, Pb, Mn, Co, Cd, Fe, Ni, Cr and V. Determination of these parameters was done using standard procedures of American Society for Testing and Materials-ASTM. The result when compared to standards of the American Petroleum Institute (API) shows that crude oil blends obtained from Nigeria has low sulphur contents and are predominantly of the light crude oil category. A comparison of concentrations of heavy metals in the crude oil blends with environmental standards of the World Health Organization shows high levels of Ni and V. This indicates that, crude oil found in Nigeria could be a source of heavy metals particularly Ni and V in the environment in event of spillage. On further analysis of the results, it is concluded that crude oils found in Nigeria have a common geological and formative history.

Key Words: Crude oil; blends; Physicochemical; API gravity.

1. Introduction

Crude oil samples obtained from different oil fields vary both in physical and chemical properties. This is due to different proportions of the various molecular types, sizes of hydrocarbons and other elemental constituents in the crude mix [20,21]. Petroleum fluids are complex fluids, normally of undefined composition that require a characterization procedure to obtain relevant information [1]. According to Odebunmi and Adeniyi [18], the ever-increasing chemical utilization of crude oils and petroleum products call for a better knowledge of the composition, structure and properties of their fractions. Parameters often determined in crude oil include: Density, API gravity, Pour point, Kinematic Viscosity, Water content (%) Salt content (%) Sulphur content (%), Asphaltene (%), ASTM Distillation cracking point as well as Metal/mineral contents. These important parameters are used in specification and classification of crude oil blends [22].

In Nigeria, crude oil is produced mainly in the Niger delta region. The oil fields are characterized by multiple sand reservoirs of tertiary sedimentary deposits. Consequently, on the out fields the wells exist as pockets with each crude possessing a unique character [7]. Therefore, for convenience of commerce, economics and processing; crude oils are often blended into a mix that has a unique character. Presently, there are more than fourteen commercially available crude oil blends in Nigeria. These include: Bonny light, bonny medium Qua Iboe light, Escravos light, Brass Blend, Pennington light, Focados blends, Amenam blend, Oso condensate, Yoho light, Erha blend, Bonga blends and Agbami light [17].

This study was carried out to characterized crude oil blends obtained from Nigeria in terms of their physical and chemical parameters. The Physical parameters studied were: temperature, viscosity, specific, API gravity and pour point. The chemical parameters investigated include levels of heavy metals such as Ni, V, Pb, Zn, Fe, Mn, Co, Cd, and Cr. Other chemical parameters such as Sulphates, Nitrates, water content, acid number and salt content were also investigated. This was done as part of academic research to evaluate its commerciability and assess its potential as a source of environmental contaminants.

2. Materials and Methods

Sample collection and analysis of oil samples were carried out in line with recommended procedures of the American Society of Testing and Materials-ASTM [3]. A total of fourteen crude oil samples were collected from various Nigerian oil wells. Sample collection was done out in collaboration with field technicians from the wellheads of the various producing wells. The oil wells sampled include: Abami, Bony well 1, Bony well 2, Escravous, Pennington, Brass, Forcados, Erha, Bonga, Yoho, Qua Iboe, Oso, Asabo and Ekpe. These samples were properly labeled for easy identification. During sampling all bottles were rinsed properly with water and properly air-dried. The bottles were later rinsed with the crude oil to be sampled before the sample for analysis was collected. Samples were obtained in triplicates. The oil samples were coded samples A-O. These codes do not necessarily represent the order of oil wells/blends sampled.

3. Results

Table 1: gives the physicochemical parameters of the crude oil blends. Table 2: shows levels of heavy metals present in the blends. Coefficient of variation for API gravity and sulphur contents of the crude oil samples are given in table 3, while correlation matrix for the heavy metal contents of the blends is given in table 4. Figures 1 and 2 respectively shows a comparison of the API gravity and sulphur contents of Nigerian crude oil with that of American Petroleum Institute –API (2005) standard. The results showed range of values for physicochemical parameters obtained for the oil samples as follows: specific gravity ($0.46 \pm 0.06 - 0.90 \pm 0.07$); API gravity ($24.2 \pm 0.17 - 48.5 \pm 1.11$); viscosity ($1.35 \pm 0.03 - 11.05 \pm 0.78$); temperature ($22.3 \pm 0.23 - 26.7 \pm 1.11$); % sulphur content ($0.02 \pm 0.00 - 0.25 \pm 0.05$); % water content ($0.01 \pm 0.00 - 0.09 \pm 0.01$); % salt content ($0.10 \pm 0.00 - 0.50 \pm 0.01$); acid No ($0.05 \pm 0.01 - 0.58 \pm 0.22$); pour point ($-53.5^{\circ}\text{C} - 11.78 \pm 1.30$) and % Nitrogen ($0.03 \pm 0.00 - 0.12 \pm 0.00$). For heavy metals, the range of values were: Zn (Not Detected-ND to 5.32 ± 0.33); Cu (ND- 3.6 ± 0.55); Pb (ND- 0.005 ± 0.00); Fe ($0.04 \pm 0.01 - 0.5 \pm 0.01$); Mn (ND- 0.41 ± 0.01); Co (ND- 0.27 ± 0.05); Cd (ND- 0.01 ± 0.00); Cr ($0.01 \pm 0.00 - 0.05 \pm 0.01$); Ni ($1.98 \pm 0.03 - 28.00 \pm 0.02$) and V ($0.13 \pm 0.03 - 06.3 \pm 0.98$). The range of Ni/ V ratio was found to be 3.83 – 7.56. Negative correlation was observed between specific gravity and API gravity (- 0.51) as well as API gravity and % sulphur (-0.850) contents of the blends. Negative correlation was also observed between viscosity and temperature (-0.66). On the other hand, positive correlation was observed for specific gravity and % sulphur contents (0.56).

Table 3 Coefficient of variation for API gravity and % Sulphur contents of Nigeria's crude oil blends.

	Light crude oil samples		Heavy crude oil samples	
	API Gravity	% sulphur content	API Gravity	% sulphur content
Max	48.5	0.18	29.85	0.25
Min	33.69	0.11	24.6	0.18
Mean	39.55	0.13	26.22	0.20
SD	1.19	0.023	3.52	0.04
CV	3.00%	17.50%	13.40%	19.87%

For the heavy metals, positive correlations were observed between Ni and V (1.00); Zn and Cu (0.84); Pb and Fe (0.17); Cd and Cr (0.15); Pb and Cr (0.16); Zn and Co (0.94); Zn and Cr (0.38); Zn and Ni (0.43); Zn and V (0.44); Cu and Fe (0.21); Cu and Co (0.91); Cu and Cr (0.49); Cu and Ni (0.39); Cu and V (0.37); Mn and Ni (0.28); Mn and V (0.26); Fe and Cd (0.29); Fe and Cr (0.17); Fe and Ni (0.11); Fe and V (0.094); Co and Cr (0.30); Co and Ni (0.54) and Co and V (0.54). Negative correlations were observed for parameters

such as: Fe and Mn (-0.11); Zn and Pb (-0.31); Zn and Fe (-0.03); Zn and Mn (-0.56); Zn and Cd (-0.2); Cu and Pb (-0.31); Cu and Mn (-0.36); Cu and Cd (-0.20); Mn and Co (-0.43); Mn and Cd (-0.21); Pb and Mn (-0.21); Pb and Co (-0.23); Pb and Cd (0.79); Pb and Ni (-0.10); Pb and V (-0.06); Fe and Mn (-0.11) and Co and Cd (-0.15).

Table 4 Correlation matrix for heavy metals in Nigeria’s crude oil blends.

	Zn	Cu	Pb	Fe	Mn	Co	Cd	Cr	Ni	V
Zn	1									
Cu	0.84	1								
Pb	-0.31	-0.31	1							
Fe	-0.03	0.21	0.17	1						
Mn	-0.56	-0.36	-0.21	-0.11	1					
Co	0.94	0.91	0.23	0.17	-0.21	1				
Cd	-0.20	-0.20	0.79	0.29	-0.21	-0.15	1			
Cr	0.38	0.49	0.16	0.17	-0.43	0.30	0.15	1		
Ni	0.43	0.39	-0.1	0.11	0.28	0.54	-0.26	-0.23	1	
V	0.44	0.37	-0.06	0.094	0.26	0.54	0.51	0.27	1	1

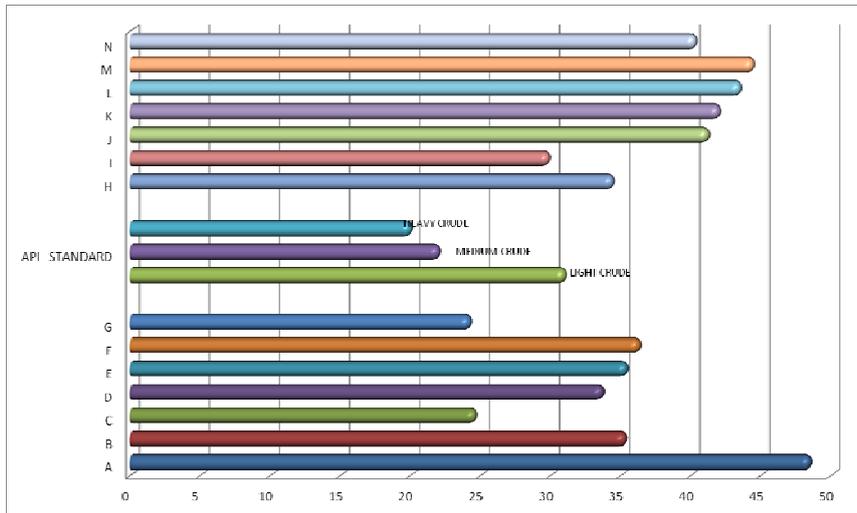
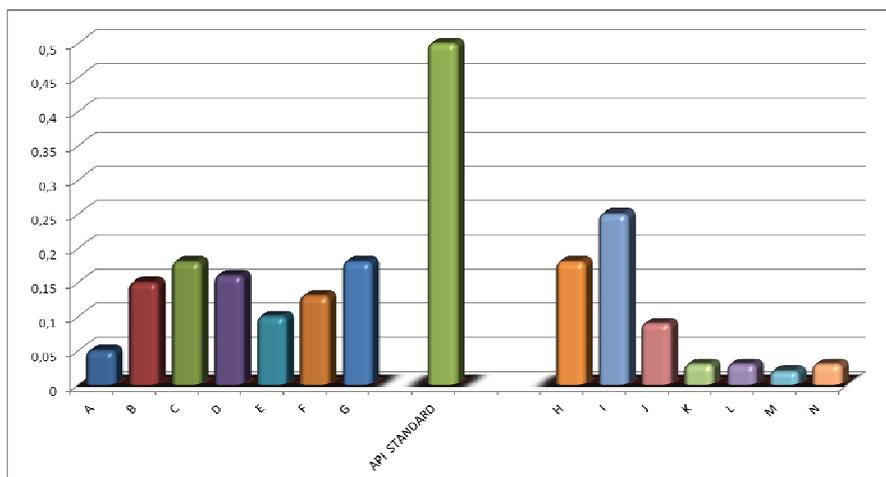


Figure 1 Comparison of API Gravity of Nigerian Crude Oil with that of API Standard.



Note: Crude oil with sulphur content greater 0.5% is referred to as sour crude while that of less than 0.5% is Crude.

Figure 2 Comparison of Sulphur Content of Nigerian Crude Oil with that of API Standard.

Table 1 Physicochemical parameters of Nigerian crude oil samples

Samples	Temp. °C	Viscosity at 40 °C	Specific gravity	API Gravity	Parameters							Pour Point °C	% Nitrogen
					% Sulphur Content	% water Content	% Salt Content	Acid No Mg, KOH/g	% Nitrogen	% Sulphur Content	% water Content		
A	29.5±1.33	1.61±0.33	0.79±0.3	48.5±1.1	0.11±0.0	0.02±0.0	0.5±0.01	0.05±0.00	5.76±0.6	0.08±0.00	7	0.08±0.00	
B	26.4±1.1	3.28±0.17	0.85±0.5	35.3±1.2	0.13±0.0	0.02±0.0	0.39±0.01	0.23±0.03	-11.56	0.11±0.02		0.11±0.02	
C	24.6±0.6	5.01±0.07	0.90±0.0	24.6±2.0	0.18±0.0	0.01±0.0	0.37±0.01	0.52±0.02	-2.88	0.12±0.00		0.12±0.00	
D	25.8±1.2	4.17±0.03	0.86±0.0	33.69±1.0	0.16±0.0	0.08±0.0	0.5±0.01	0.23±0.00	-1.43	0.09±0.01		0.09±0.01	
E	24.4±0.5	2.85±0.50	0.86±0.0	35.42±0.5	0.1±0.01	0.06±0.0	0.33±0.01	0.21±0.01	1.41	0.11±0.03		0.11±0.03	
F	26.4±1.5	2.89±0.13	0.84±0.0	36.3±0.6	0.13±0.0	0.01±0.0	0.42±0.01	0.29±0.03	-11.98	0.05±0.00		0.05±0.00	
G	24.6±0.5	11.05±0.7	0.90±0.0	24.2±0.1	0.18±0.0	0.09±0.0	0.31±0.00	0.55±0.05	-38	0.1±0.05		0.1±0.05	
H	26.7±0.6	3.77±0.50	0.85±0.1	34.4±1.0	0.18±0.0	0.05±0.0	0.10±0.00	0.37±0.01	-13.33	0.08±0.00		0.08±0.00	
I	25.3±0.2	5.4±0.50	0.87±0.2	29.85±0.7	0.25±0.0	0.05±0.0	0.5±0.01	0.58±0.22	-53.55	0.06±0.01		0.06±0.01	
J	25.4±0.9	5.1±0.03	0.82±0.0	41.2±2.0	0.11±0.0	0.01±0.0	0.45±0.02	0.28±0.01	1.67±0.6	0.05±0.00		0.05±0.00	
K	25.5±1.0	4.92±0.33	0.46±0.0	42.0±1.1	0.13±0.0	0.01±0.0	0.30±0.00	0.37±0.03	11.78±1.3	0.03±0.00		0.03±0.00	
L	24.3±0.6	5.23±0.03	0.80±0.0	43.5±0.7	0.12±0.0	0.01±0.0	0.44±0.01	0.33±0.03	9.78±0.5	0.04±0.00		0.04±0.00	
M	28.4±0.5	1.46±0.07	0.80±0.0	44.4±1.5	0.13±0.0	0.01±0.0	0.39±0.01	0.36±0.04	5.6±0.50	0.04±0.00		0.04±0.00	
N	27.4±0.5	2.3±0.16	0.82±0.0	40.3±0.3	0.13±0.0	0.01±0.0	0.41±0.03	0.4±0.01	2.3±0.33	0.03±0.00		0.03±0.00	

Table 2 Concentrations of some heavy metals in Nigerian crude oil.

Samples	Parameters (mg/L)											Ni/V ratio
	Zn	Cu	Pb	Fe	Mn	Co	Cd	Cr	Ni	V		
A	0.01±0.00	0.04±0.01	0.005±0.00	0.22±0.01	0.3±0.00	N.D	0.01±0.00	0.01±0.00	3.20±0.05	0.77±0.02		4.15
B	0.02±0.00	ND	0.005±0.00	0.25±0.01	0.4±0.05	ND	0.001±0.0	0.01±0.00	3.59±0.15	0.79±0.05		4.54
C	1.84±0.05	ND	ND	0.04±0.01	ND	ND	ND	0.04±0.01	2.23±0.03	0.31±0.06		7.19
D	5.2±0.33	3.6±0.55	ND	0.31±0.03	ND	0.27±0.05	ND	0.04±0.01	4.69±0.02	0.62±0.01		7.56
E	ND	1.6±0.03	ND	0.29±0.01	0.31±0.03	ND	ND	0.05±0.01	3.2±0.33	0.73±0.01		4.38
F	0.01±0.00	0.03±0.01	ND	0.33±0.01	0.33±0.05	ND	ND	0.03±0.00	1.99±0.03	0.49±0.05		4.06
G	ND	ND	0.005±0.00	0.51±0.01	ND	ND	0.01±0.00	0.04±0.01	2.2±0.05	0.50±0.00		4.40
H	0.02±0.00	0.04±0.01	0.005±0.00	0.18±0.00	0.41±0.01	ND	0.01±0.00	0.04±0.00	2.0±0.50	0.5±0.03		4.00
I	0.01±0.00	0.03±0.00	0.005±0.00	0.27±0.02	0.33±0.03	ND	ND	0.02±0.00	22 ±0.03	4.1±0.15		4.31
J	ND	0.08±0.03	0.005±0.00	0.20±0.00	ND	ND	ND	0.02±0.00	28±0.05	6.3±0.05		4.44
K	0.01±0.00	ND	ND	0.23±0.01	0.3±0.03	ND	ND	0.01±0.00	4.40±0.35	0.13±0.03		3.83
L	0.01±0.00	ND	ND	0.27±0.03	0.41±0.01	ND	ND	0.01±0.00	6.45±0.03	1.60±0.03		4.03
M	0.01±0.00	ND	ND	0.18±0.03	0.35±0.03	ND	ND	0.02±0.00	2.01±0.05	0.50±0.03		4.02
N	0.01±0.00	ND	ND	0.20±0.00	0.33±0.01	ND	ND	0.02±0.00	1.98±0.06	0.45±0.04		4.40

4. Discussion

4.1. Specific gravity, API gravity and sulphur content

These are important parameters commonly used for the classification of crude oil samples [18]. Generally API gravity of crude oil is known to increase as the specific gravity decreases [23]. API gravity has also been reported to have an inverse relationship with % sulphur contents of crude oil blends [8]. This is because, in calculation of API gravity from specific gravity (SG), it takes an inverse function ($API = 141.5/SG - 131.5$) which can be written in the form $API = A/SG + K$, where A and K are constants. Also, % sulphur content of crude oil is known to increase as the specific gravity increases. This can be explained in terms of the geologic composition of the areas where these crude oils are found. It has been found that, areas where heavy crude oil samples are reportedly in abundance are also associated with high deposits of sulphur rich rocks [16,23,27]. While light crude oil samples are found mostly in areas with low deposits of sulphur rocks. Furthermore, Sulphur is relatively a heavy element. Thus, its presence will therefore add to the specific gravity of oil samples. This also explains why crude oil samples with low sulphur content have low specific gravity and vice versa. Studies such as [1,15,18] had already shown that, API gravity varies inversely with specific gravity and also the % sulphur contents. Other studies such as [11,12,26] had also reported a direct variation between sulphur content and specific gravity of crude oil samples. Therefore, the negative correlation observed API gravity and specific gravity; API gravity and % sulphur contents as well as the positive correlation observed between specific gravity and % sulphur contents of the oil blends in this study is as expected.

API gravity determines the grade or quality of crude oils. Generally, crude oil samples with API gravity greater than 31 are classified as light crude oils, those with API gravity of between 22-31 are classified as medium crude while those with API gravity of 20 and less are referred to as heavy crude oil (API, 2011). A comparison of the values of API gravity obtained for the crude oil blends in this study with that of API Standard (2011)(fig 1) shows that, most of the crude oil blends obtained from Nigeria are light crude oils. Exceptions are samples C and G which falls under the medium crude oil category (fig 1). Light crude oil samples are in high demand and are of high market value because Heavy crude is harder to handle (it is too thick to pump easily through pipelines unless diluted with light crude) and is more expensive to refine to produce the most valuable petroleum products such as petrol, diesel and aviation fuel. In the process of refining crude oil into useful products, it is generally observed that, the heavier the oil, the more difficult its refining process [3].

% sulphur content determines whether a particular crude is sweet or sour. Crude oil samples are classified as sweet if its sulphur content is less than 0.5%. Anything greater than 0.5% is termed sour. With respect to their sulphur contents, all the crude oil blends used in this study were found to be of low sulphur with reference to compared to API standard (fig 2). These crude oil samples can thus be classified as sweet crude. Sweet crude samples are generally preferred to sour because it has less corrosion/pollution potential which leads to increase cost of production and is therefore more suited for the production of the most valuable refined products [28]. The above observations for the API gravity and Sulphur contents of Nigeria's crude oil samples are in agreement with results earlier reported by [22]. The result of this study therefore confirms that, most of the crude oil blends obtained from Nigeria are generally of low sulphur content and are also predominantly of light crude oil category. This implies good quality which enhances their preferences in the oil market and refinery operations.

4.2. Viscosity, Water Content, Pour Point, Salt Content , % Nitrogen and Acid Number.

Viscosity is a measure of internal friction of a liquid which is the reluctance of a liquid to flow. It therefore indicates the flowing ability of Crude oil from one point to another [13]. The result of this study shows that crude oil blends from this region are relatively of low viscosity. This implies that, they have the ability to flow rapidly during spillage (table 1). Viscosity of petroleum is of importance in studying the energy losses during production. Any engineering activities including piping and pipeline construction require the knowledge of the viscosity of the crude oil to enhance transportation. Viscosity also plays an important role in reservoir simulations as well as in determining the structure of liquids [1]. Therefore, the low viscosity

obtained for the crude oil blends indicates that the blends can easily flow when transported through pipes thus making for easy transportation. The implication however is that, the crude oil samples from Nigeria have the ability to readily flow into the environment in events of oil spillage to cause pollution. The negative correlation observed between viscosity and temperature (0.067) also agrees with those observed by [11]. The result shows that higher temperature favours viscous flow of the oils.

For water and % nitrogen contents the values were also appreciably low in the samples. A knowledge of water and % nitrogen contents content of any crude oil is important in the refining, purchase and sales of crude oil because corrosion problems associated with these parameters [13,25]. The low water and % nitrogen contents of the crude oil blends also show that they are of high value. Pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications [4]. The pour point values of the blends (table 1) are low and indicate that the oils can easily be utilized under low temperature conditions.

Salt content and acid number are important index for refining operations. High values of any of these parameters indicate high corrosion tendency of crude oil [10]. The values of these parameters obtained for crude oil blends in the area show that these blends possess very low corrosion potentials.

4.3. Heavy metals

Heavy metals are often found to be part of crude oil samples [9]. Possible sources of trace metals in crude oil are: through incorporation and diagenesis of metal complexes of the original biological materials; through incorporation into the organic matrix during diagenesis of the biological materials in the source rocks either from clay minerals or interstitial aqueous solution; through an aqueous phase during primary and secondary migration and from formation waters or reservoirs' rock minerals [9]. The levels of most of the trace elements obtained in this study were generally low. This agrees with reports that light crude oil samples usually contain relatively low trace metal contents compared to the heavy crudes [6,21].

The relatively higher levels of Ni, Fe and V observed in the result should be expected because these are metals commonly associated with crude oil samples [15]. Furthermore, most soils associated with the areas where crude oil is found in Nigeria are also associated with appreciable deposits of metal ores such as iron [24]. Vanadium and nickel are commonly associated with iron ores. Studies such as [2,18,19] had already identified these elements in crude oil samples obtained from Nigeria. Other possible sources of iron in crude oil samples could also stem from drilling equipments and machineries which are predominantly made of iron. A relatively high levels of Ni and V has been reported to be associated with most crude oil samples obtained from marine environment. This is expected for marine source rocks where there is an abundant input of porphyrin – precursor chlorophylls to the organic matter derived from algae and bacteria [5]. Most of the crude oil samples used for this study were obtained from offshore platforms and oil wells which are associated with marine environment. This therefore justifies the relatively high levels of Ni and V in the crude oil blends compared to other metallic parameters investigated.

A comparison of trace metals in the oil samples with those of studies such as [2,18,19] shows that the result obtained in the present study is also within the range of the reported studies.

A further comparison of the levels of these heavy metals with recommended limits of these parameters in soil and water environment by the World Health Organization (WHO, 2011) shows that, levels of heavy metals such as Ni and V in the crude oil samples investigated are well above the levels recommended for these parameters in the environments. This implies that, crude oil samples from Nigeria are potential sources of heavy metals particularly Ni and V in the environmental. Vanadium – nickel ratio in the soil and water environment is indicative of presence of crude oil contamination.

4.4. Statistical analysis of the results

Statistical analysis of the results show that, the light crude oil samples obtained from Nigeria are similar in terms of API gravity (CV= 3.0 %) and sulphur contents (CV= 17.50 %). This is also the case of the medium crude blends in terms of API gravity (CV = 13.4 %) and sulphur contents (CV = 19.87 %). A plausible explanation for this observation is that, the crude oil

samples obtained from Nigeria are found predominantly in the Niger Delta region which is similarly drained by the Atlantic Ocean. Also, most of the crude oil blends in Nigeria are obtained offshore; therefore the observed similarity in terms of API gravity and % sulphur for each specification is also as expected. Positive correlations observed for most of the metallic parameters such as: Ni and V (1.00); Zn and Cu (0.84); Pb and Fe (0.17); Cd and Cr (0.15); Pb and Cr (0.16); Zn and Co (0.94); Zn and Cr (0.38); Zn and Ni (0.43); Zn and V (0.44); Cu and Fe (0.21); Cu and Co (0.91); Cu and Cr (0.49); Cu and Ni (0.39); Cu and V (0.37); Mn and Ni (0.28); Mn and V (0.26); Fe and Cd (0.29); Fe and Cr (0.17); Fe and Ni (0.11); Fe and V (0.094); Co and Cr (0.30); Co and Ni (0.54) and Co and V (0.54) also confirms the fact that these blends have similar physicochemical characteristics and may also have a common geological and formative history.

5. Conclusion

The result of this study has shown that crude oil blends obtained from Nigeria contain low level of sulphur. The blends are also predominantly of light crude oil category with a few samples belonging to medium crude oil grade. Therefore, most crude oil blends obtained from Nigeria can thus be classified as light-sweet crude oil blends. The result also shows that while API gravity of crude oil blends have negative correlations with specific gravity and % sulphur content; % sulphur content and specific gravity have a positive correlation. Further statistical analysis of the result shows that, each of specified crude oil blends (light and medium) are similar in terms of API gravity and sulphur contents. The low values of viscosity obtained for the blends indicate that, these oil samples can flow easily. This makes it easy for transportation through pipelines without the necessary addition of diluents at regular intervals often associated with heavy crude oil samples. However, the low viscosity associated with these oil blends implies that crude oil samples from Nigeria can easily flow and spread out rapidly into the environment in event of oil spillage. On the whole, the low levels % of water, salt contents and pour point observed for the oil samples coupled with other physiochemical parameters show that, Nigeria's crude oil blends have characteristics which enhance their preferences in the oil market and refinery operations.

Although the levels of some trace metals such as Pb, Cd, Cr, Mn, Zn, Cu, and Co were observed to be low when compared to recommended levels of these parameters by WHO (2011) in the environment, high values of Ni, V and Fe were observed in the crude oil blends. The results therefore show that, crude oil samples from Nigeria could be a source of heavy metals particular Ni and V in the environment. From the study result, it is concluded that crude oil obtained from Nigeria have a common geological and formative history.

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