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Thermophysical Characterization of the Bulk Parameters Analysis of Plain Bitumen Seepages Deposit at Agbabu Area of Ondo State South Western Nigeria with their Corelation Matrix Properties

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ABSTRACT

Thermophysical characterization and physicochemical analysis is a necessary step in probing into the engineering properties of the heavy unconventional oil (Bitumen) in order to outline the best method of production, modification and refining of the heavy oil. Also to determine the economic viability of its production, processing, modifying, refining and it's upgrading as a synthetic oil as well as its other uses for engineering purposes. The data assays of this engineering properties of the bitumen samples were obtained through comprehensive experimental studies on four different samples of bitumen following a procedure outlined according to America society for testing and materials. The parameters studied are: softening point, kinematic viscosity, specific gravity, America petroleum institute gravity, (API gravity), water content, gum content, ductility point, penetration point, of the samples were also analysed.

Results show API gravity with the range of (8.88–10.78^0), specific gravity (1.01—1.04), kinematic viscosity (4.4x10^3–5.3x10^{3}cSt), water content (1.62– 3.48%), gum content (1438–6434mg/ml), softening point(46—47%), ductility point (74—76cm), penetration point (60—70cm),Ash content (20---23%) These results suggest that the bitumen samples have similar physicochemical characterization and shows strong positive correlation within samples, and this indicates that they are geologically and genetically related and they are viable economically to be processed, modified, as well as upgraded so as to enhance the production of synthetic oil which will serve as supplement so as to lasting the life span of the conventional oil and its other engineering purposes.

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 estimate the bulk parameter of the bitumen samples which serve as the thermo-physical parameters of seepages of the plain bitumen samples 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 thermo physical properties 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 contaminant

2. PROCEDURE

DETERMINATION OF SOFTENING POINT
ASTM D-3461

Procedure: the degree of its consistency of the bitumen sample is now as softening point. It is the temperature at which bitumen can readily flow, it is measure as the temperature at which a steel bass passes through the bitumen sample in a mole when heated on the water at specified condition [9]. Ring and ball apparatus is normally used in this analysis, The bitumen sample is heated above 75^0C and simultaneous a mixture glycerol and dextrin is prepared on a glass surface thoroughly mix together, this was done to avoid the bitumen sample being stick to the plate [10]. Then the bitumen sample was pour carefully into the rings, it was allowed to cool for thirty minutes in the air. Distilled water was then pour in a beaker, the distilled water was heated slightly, and the beaker is filled in such a way that its water level is 15mm above the specimen to be put in the beaker. The ring and the ball guide was assembled, and arranged on the metallic frame, the frame was then placed in water and it was left for 60 minutes, and after that a steel ball which was already cool for like 5 minute is then placed on the top of the ball guide. And the whole assembly is placed on the heating plate, the stirrer was fixed and the hot-plate was switch on while the thermometer was inserted, the heating was done at 5^0C per minute and this is controlled using energy regulator. As the heating continues the bitumen softens and the steel ball was seen falling down, along with the bitumen, and the temperature at which the steel ball touched the ground is noted for the two steel ball. The arithmetic mean of the two temperatures is recorded as the softening point.

2.13 Determination of penetration point
ASTM D-5

Procedure: Penetration of bitumen is necessary to determine the grading of bitumen by measuring its consistency [11]. Penetration point is defined as the distance travelled by a standard needle of specific size, weight and shape under specific condition of time and temperature in one-tenth of millimeter, the instrument needed to measure the penetration of bitumen sample is called pentrometer, the instrument used in this analysis is simple manual pentrometer. The bitumen is first heated above its softening point to a temperature of 90^0C. It was stirred to remove air bubbles and make it homogenous, it was then pour in container and allow to cool for one hour, then the water - bath is turned on and set to temperature of 25^0C which is allowed it to stay for one-half hour. The specimen is brought into the base of the pentrometer, and the needle was cleaned with benzene, and then dried. The needle assembly was set in such away to have a free movement using fine adjustment screw. Then the needle assembly is allowed to penetrate the sample for 5 seconds using a digital timer, in order to avoid any human error, and this is done for different spot of a given sample with a distance of 10 mm from each point and the average of the readings is recorded as the penetration value.

Determination of ductility point.
ASTM D-13 was employed during this analysis

Procedure: Ductility point of dead oil sample is the property by which bitumen sample can be pulled without breaking, the ductility point of bitumen was measured using a rectangular tank with a copper liner sheet called ductility apparatus. A bricket mold is used to prepare the sample as follows, the bitumen sample is heated to allow free flow and simultaneously a certain mixture of dextrin and glycerol is prepared on a glass surface in order to avoid sticking of bitumen sample to the surface and the interior. The bitumen samples were then pour into the bricket- mold and then placed in a water bath for cooling, after which it was then removed from the bath, and then placed into the rectangular tank, the adjustment screw gear were then released which allow the movable plate to move in opposite direction by stretching the bitumen specimen, then the stretching points of the sample was observed and recorded as the ductility point.

Determination of Specific gravity and API gravity.

ASTM D-1298

Procedure: A clean and dry specific glass bottle was weighed with the stopper and this was recorded as the weight of the pycnometer denoted as (**A**). after this, the weight of the specific gravity bottle was noted with boiled water inside, and this was allow in bath for 30 minute at a constant temperature of 27^0C and it was recorded as mass of the pycnometer with water which was denoted as **B.** The sample was then heated slightly above its softening point, at a temperature that is slightly above 60^0C and then the bitumen sample was then poured into the pycnometer and partly filled and this was denoted as **C**. Finally, freshly boiled water was added to the bitumen sample in the pycnometer, and the weight was noted as the mass of the bitumen with the water and that of the pycnometer as **D.** *The calculation is calculated as follows*

$$\text{relative density} = (C - A)/[(B - A) - (D - C)]$$

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$$\text{Density} = \text{specific gravity} \times W_T$$

$$°\text{API} = \frac{141.5}{\text{specific gravity @ } 60/60°\text{F}} - 131.5$$

3.8 Determination of Kinematic Viscosity @ 40^0C and 100^0C,

ASTM D 445 was employed in the determination of kinematic viscosity @ 40^0C and **ASTM 446** @ 100^0C Procedure: The redwood viscometer was cleaned with methanol and dried with air till the last trace of the solvent was removed. The bitumen sample was already heated up to 55^0C such as to allow the bitumen to flow, hence The viscometer was then filled with 50ml of sample and the electrical heater appliance was turned on, the water bath was stirring continuously to ensure uniform distribution of heat, this was continued till the thermometer measured 40^0C. Hence, the stop watch was used to check the time taken for the bitumen sample to flow through the orifice immediately after the stop bulb was removed, the measuring cylinder of 50ml capacity under the orifice was used to receive the bitumen sample, and the time was recorded. The water bath was further reheated to the temperature of 100^0C and the sample was added to the viscometer, the stop watch was used to note the time taken for the measuring cylinder to be filled and the time taken was also recorded, and these values were used to calculate the kinematic viscosity, absolute viscosity and the viscosity index using the calculation is illustrated bellow; Kinematic viscosity (v) = c x t

Where c= calibrated viscometer constant cSt/s

t = flow time (efflux time) in seconds.

Dynamic viscosity is calculated as (μ) = p x v

Where p is the density of oil and v is kinematic viscosity.

III. RESULTS AND DISCUSSION

The range of values for the thermos-physical parameters obtained for the bitumen samples are: density **(1.005---1.016), specific gravity (1.021–1.058);** API gravity **(8.46–9.98);** viscosity **(4.6 x10^3 – 5.5x10^3cP)** softening point **(46—47^{0}C),** ductility point **(74---76),** penetration point **(60--70) and gum content ((1438 – 6434 mg/100ml),**

TABLE 1. SHOWING THE KINEMATIC VISCOSITY OF THE BITUMEN SAMPLE.

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

Table 2: Result of the bulk properties of the bitumen samples.

Parameter	Unit	AB	OI1	OI2	IL1	IL2	LD
Density @ 15^{0}C	**g/cm**	**1.005**	**0.983**	**0.989**	**1.011**	**1.008**	**1.016**
Specific gravity @ 60F		**1.021**	**0.985**	**1.011**	**1.012**	**1.018**	**1.058**
^{0}API Gravity		**8.46**	**9.98**	**9.93**	**9.72**	**8.88**	**8.88**
Gum content	**mg/100ml**	**1357**	**2636**	**3093**	**2574**	**1459**	**6535**
Softening Point	**^{0}C**	**45**	**46**	**45**	**46**	**45**	**47**
Ductility point	**cm**	**74**	**75**	**75**	**74**	**75**	**76**
Penetration Point	**Cm**	**60**	**62**	**69**	**66**	**65**	**70**
ASH CONTENT	**%**	**20**	**21**	**22**	**20**	**21**	**23**

VISCOSITY	**cSt**	**$4.6x10^3$**	**$5.5x10^3$**	**$4.7x10^3$**	**$4.8x10^3$**	**$5.5x10^3$**	**$4.7x10^3$**

Table 2. Pearson's correlation matrix of SARA--PONA and API gravity

	S	DU	P	V	G	SP	AS	D	API
S	1.01	1.01							
DU	1.02								
P	1.01	1.01	1.01						
V	0.12	-0.27	0.06	1.01					
G	0.58	0.86	0.66	-0.72	1.01				
SP	-0.84	-0.75	-0.84	-0.04	-0.42	1.01			
A	0.25	-0.08	0.22	0.76	-0.58	-0.56	1.01		
D	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

DISCUSSION

Specific Gravity and API Gravity

The thermo-physical properties with a specific reference to specific gravity and API gravity are two main distinct classifications that are used to make an accurate definition of heavy oil in an oil and gas industry. The specific gravity actually indicates how light a particular oil is. The lower the specific gravity, the higher the API gravity, and this implies a great yield of light fractions that can be obtained by distillation process. The relative density of the dead oil ranges from (0.97- 1.00), and it can be seen that when these values are compared with the one obtained (0.91 – 1.013) by Adebayo, (2004) at another bitumen location in Ondo state, it really shows a good indication that the bitumen is of good quality. Low API gravity is a good parameter that shows perhaps the bitumen sample is biodegraded or it is associated with sulphur -rich oils [12]. While bitumen samples, that exhibit high oil API gravity implies the association of the samples with clay-rich source rocks [13].

Generally, API gravity of bitumen increases as the specific gravity decreases, high API gravity determines the amount of asphaltene content in a given sample of bitumen oil, asphaltene is very sensitive to air oxidation, and this can bring about the change in characteristics of the sample as well as colour change. The API gravity of the bitumen samples is in a close proximity, the values are in a very close range of (8.88 – 9.88), and this is in accordance within the specifications of the high way authority of Nigeria (NGS2005).

The value outlined by Adebayo, (2004) which is 1.013 for the asphalt standard is also a good indication that the ranges of the value are within the acceptable range.
A comparative analysis was made for the result obtained in this analysis with that of bitumen samples from Alberta Canada, the bitumen sample in Nigeria is of a good parameter compared to the bitumen sample from Alberta Canada which shows range of values for specific gravity and API gravity to be (0.9917 - 1.0085) and (9.8 – 13.2),[14]. Synthetic oil is produced in the Canada from the deposit of bituminous sand, from this we can proffer sound reliable information that the heavy oil deposit in Nigeria could be explored for the production of synthetic oil both for local consumption and for the purpose of exportation.

Kinematic Viscosity
Viscosity is briefly discussed as the opposition to free flow and this can as well be described as the measure of internal friction of a liquid, which is the resistance of a liquid to flow. This serves as an indicator that the easy flowing ability of dead oil absolutely depends on viscosity. Viscosity is generally discussed in two ways, first, the general opposition to the flow of fluid that is known as absolute viscosity and the restriction to flow against the gravity, which is known as kinematic viscosity. Moreover, this is usually employed in production of bitumen. During steam injection, viscosity serves as key index that affects the injection system functionally. The lower the viscosity, the more wearing of some functional part of the pumping system[15]. This can create a destructive effect that is the hysteresis losses of power due to pump leakages and injection. Likewise, a high viscosity fluid brings about excessive pump resistance and filter damage at higher line pressures. The effect of a very reduced viscosity value is that the oil has a great amount of light component, the obtainable results show that that the bitumen samples have a high range of viscosity which varies from (4.4×10^3 – 5.5×10^3cSt) andthis is never a surprise, since dead oil is not a conventional oil, and it is higher than that obtained by (Kogbe, 1996) which range from 3.05×10^3 – 4.00×10^6cSt, and this is in a good conformity with the value obtained by Ekweozor and Nwachukwu, (1989) [16]. And from this a good judgement can be drawn that the bitumen deposit in Nigeria has a high value of viscosity. The high viscosity obtained for the bitumen samples is an indicator that oils cannot easily flow when transported through pipes, except if the viscosity is reduced to a given specification otherwise it thus makes transportation difficult, the implication however is that, the oil samples have the ability to remain in situ which cannot be produced conventionally and this prevents flow into the environment in events of spillage that might cause pollution.

Existent Gum
The level of unsaturated hydrocarbons in petroleum oils, in the presence of oxygen which eventually produced gum is known as existent gum. The gum content as given in the standard specification of bitumen grading system ranges from 1257.00 to 6435.00 mg/100ml [12]. This implies that the samples under investigation have considerable amount of unsaturated hydrocarbons.

Softening point
The degree of consistency of any given sample is known as softening point. It is the temperature at which bitumen can readily flow, it is the measure of temperature at which a steel bass passes through the bitumen sample in a mole when heated on the water at specified condition. Ring and ball apparatus is normally used in this analysis, the bitumen sample is heated above 750^0Cand simultaneously a mixture of glycerol and dextrin is prepared on a glass surface which are thoroughly mixed together, this was done to avoid the bitumen

sample being stuck to the plate. Then the bitumen sample was poured carefully into the rings, it was allowed to cool for thirty minutes in the air. Distilled water was then poured in a beaker, the distilled water was heated slightly, and the beaker was filled in such a way that its water level was 15mm above the specimen to be put in the beaker. The ring and the ball guide was assembled, and arranged on the metallic frame, the frame was then placed in water and it was left for 60 minutes, and after that a steel ball which was already cool for like 5 minute was then placed on the top of the ball guide. And the whole assembly was placed on the heating plate, the stirrer was fixed and the hot-plate was switched on while the thermometer was inserted, the heating was done at 50^0C per minute and this was controlled using energy regulator.

The softening point of the sample under investigation ranges from 45^0C--- 47^0C and this shows an indication that the bitumen can be used for any engineering properties, its fluidity is very necessary. However, there is a need to determine which kind of materials is necessary to be used as joint and crack fillers

Ductility Point

Ductility of a material is discussed as the degree of consistency of a material without breaking. The distance between the gauge marks on the bitumen sample can be measured before and after the test, the percent elongation describes the extent to which the specimen stretches before fracture. Ductility is the ability of certain solids to undergo permanent changes in shape without breaking. For instance, the sample under study has ductility point ranging from 74cm---76cm, this measurement is highly important so as to note the degree of consistency, also before the application of the bitumen as binder. It is necessary to choose a sample that has high level of ductility so as to withstand applied stress. The ductility of a bitumen sample depends on its grade and this is compared to the standard given by the bureau of standard according to ASTM standard, the minimum of ductility regardless of the grade is given to be 50cm and the maximum is given to be 75cm. The sample under investigation shows a ductility point that has a considerable value for its various uses of application.

Penetration Point

Penetration of bitumen is necessary to determine the grading of bitumen by measuring its consistency. Penetration point is defined as the distance travelled by a standard needle of specific size, weight and shape under specific condition of time and temperature in one-tenth of millimeter, the instrument needed to measure the penetration of bitumen sample is called pentrometer, the instrument used in this analysis is simple manual pentrometer. The bitumen was first heated above its softening point to a temperature of 90^0C. It was stirred to remove air bubbles and make it homogenous, it was then poured in a container and allowed to cool for one hour, then the water - bath was turned on and set to temperature of 25^0C which was allowed to stay for one-half hour. The specimen was brought into the base of the pentrometer, and the needle was cleaned with benzene, and then dried which was then used to penetrate the sample. The value of 80/100 is discussed to be the range of its grade 80---100. Bitumen grading is essential in determining its durability and various specifications that needs to be selected when in use. Various ranges such as 30/40, 60/70, 80/100 had been outlined by the bureau of standard in India and according to the America society for testing and materials. A low penetration value ensures rigidity, while a great value like 180/200 prevents unnecessary brittleness. The penetration value of the bitumen under investigation is given to be 60/70, this serves as an indicator that the bitumen sample could find its application in a warmer region.

ASH Content

The ash content in bitumen sample is another good parameter that is used to decide the good thermo-physical properties of the sample, burning of bitumen sample on a large scale require the knowledge of their ash content. It is usually determining by heating and burning of bitumen sample in the presence of air and determine the mass loss. Its significant is necessary because it reduces the calorie value of fuel, so prior to the upgrading and modification of the bitumen sample, there is a need to determine the ash content in order to know the extent of the mineral content in the sample and this will give an insight to the degree of modification and processing which the sample needs to undergo. Ash content is also necessary to indicate and characterize loss on ignition (LOI) which is referred to as the mass loss of a combustion residue whenever it is heated in an air or oxygen atmosphere to high temperature. Usually the term LOI normally refers to as mass loss in a sample heated to 950^{0}C. The sample under study gives a considerable amount of ash content which ranges from 20----23% and this according to the ASTM standard, will serve as a good indicator that the sample will need a series of modification and upgrading prior to its use as fuel.

IV CONCLUSION

We have successfully used the thermophysical properties and correlation matrix properties parameters to carry out the analysis of the heavy oil samples that is obtained in Ondo state. The information that was discussed is basic and is a concise contribution towards effective analyses in utilizing the natural (bituminous sand) resources. With this analyses so far, it is hereby concluded that, the bitumen samples from the Agbabu, Ode Irele, Loda and Ilubirin villages in Ondo state have similar thermophysical properties, and of similar qualities with bituminous sand of good and acceptable qualities according to the ASTM standard and Bureau of standard in Indian. This by implication to a large extent is to say that the bituminous sand in Nigeria is of huge reservoir of liquid (crude- oil) of which, with the availability a precise technology, it could be upgraded, processed, modified, and as well refined to produce a synthesis Oil, which could serve as a plus to the lasting duration of conventional crude oil, and for other various application in the petrochemical industry which can be vital for chemical industry development. This analyses have given us the overview of the bulk analyses of the bituminous sand in the said various location which can be used to access and predict the method of production, modification, transportation, and refining, prior to upgrading.

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