Determination of Total Acidic Number and High Temperature Simulated Distillation (HTSD) Modelling of Plain- Bitumen (Seepages) Deposit at Agbabu area of Ondo State South Western Nigeria with their Correlation Matrix Properties

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ABSTRACT

*Characterization and chemical analysis is a necessary step in identifying the chemical constituents of the heavy unconventional oil (Bitumen) which will definitely proffer a way forward for the production, modification and refining of the heavy oil. This study presents naphthenic acidic content of four different bitumen deposit location which is considered to be the initial step before the production with respect to design and operational condition and specification of the refinery. Acidity of crude causes wearing of equipment, deactivation of catalyst as a result of coke formation, hence it need to be determined in order to predict the cost of production, refining, modification and upgrading of the heavy oil couple with the pseudo-component of range of hydrocarbon mixture in the heavy component, a high temperature simulated distillation in accordance to the ASTM procedure was modelled in this study in order to simulate the true atmospheric boiling point of all the pseudo-components in the unconventional oil using gas chromatography flame ionization detector (GCFID) so as to ascertain the economic viability of processing the Ondo state bitumen deposit. The results of the total acidic number of the bitumen samples ranges from (**1.7---2.0 mg/g**) and this serves as an indication according to ASTM standard that the bitumen deposit has high naphthenic acid content which will entail high cost of processing, refining, modification and upgrading of the Nigeria bitumen deposit.*

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 total acidic content (TAN) of the bitumen samples not limited to this but with the inclusiveness of the simulation of true atmospheric distillation of the bitumen sample and this will serve as the thermo-physical parameters of plain bitumen seepages 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.

METHOD

TOTAL ACIDIC NUMBER (TAN)

Total acidic number determination is an indication of the fuel quality and this can be ascertained by following the procedure as stated in ASTM- D 664, and this can be referred to a *neutralization number[9]*. Crude oils with high total acidic number will increase the cost of refining and this can lead to increase in the purchase of crude oil globally [10]. When the TAN value of crude is >1.0 mg KOH/g, such crude is considering to have high TAN value and this will definitely affect the decision of the refiners as to make a concise decision regarding the cost of refining. In the United States certain crude have the TAN value that ranges from 2.1 to 3.1 mg, respectively [11]. Although, the TAN number does differ by given the real picture depending on the acidic content of the crude oil. Yet, naphthenic acids in the crude oil could appear in an advanced form and this can pose a serious form of difficulties in identifying the refinery unit that will be affected due to high TAN crude oil [12]. The implication of high TAN value shows the presence of naphthenic acid which in turn corrode the distillation unit in with the deposit of sludge and existing gum and these if not addressed, can lead to that can lead to the blockage of pipelines and pumps [13].

The research is on to finalize the analyses of the (TAN) value in a sample of oil which is the cause of corrosion of equipment. Installation of materials such as metal catalyst can hasten the decarboxylation process. In the analysis of TAN, toluene/isopropyl and alcohol/water is always used against potassium hydroxide in the volumetric analysis based on this, the results are usually given in mass express in terms of potassium hydroxide per gram of sample (mg KOH/g)[14]. Crude oils having high acid numbers have a high potential to cause corrosion problems in the refineries, especially in the atmospheric and vacuum distillation units where the hot crude oil first comes into contact with hot metal surfaces. Crude oil typically has a TAN value on the order of 0.05–6.0 mg KOH/g of sample [16].

The oxygen content in bitumen is usually less than 1wt, but some higher concentration numbers can be seen, usually caused by the atmospheric oxidation of the asphaltenes during handling. Oxygen in the crude is mostly responsible for the acidity of the crude, because most of the oxygen is present as carboxylic group [12]. The acid functional group of crude oil is also known as *naphthenic acid*, although they are mostly present in aromatic (ring) or aliphatic (chain) structures. Acidity of any crude is measured in terms of TAN value (total acid number), also known as the *basicity number*, originating from the type and amount of base used for titration. (TAN is expressed in units of milligrams KOH per gram of the sample. The higher the TAN value is, the higher will be the sample's acidity [14]. Bitumen falls in the category of high-acid (TAN >1) crude because its TAN value is mostly above 2.0. The market value or demand of a crude oil decreases with the increase in TAN value because of its highly corrosive behavior. Other oxygenated compounds in the bitumen are present as phenolic functional groups. Note that, unlike sulphur and nitrogen, almost all of the oxygen in the bitumen is present in the VGO fraction and not in the heavier resid fraction. The TAN, is usually determined using the detailed principle of ASTM D- 664 [12].

ASTM D-664

Acidity of a crude oil is measured by a simple potentiometric or pH titration method by neutralizing the acid functional group by using a basic solution, such as sodium or potassium hydroxide (KOH). The TAN value is defined as the milligrams of KOH required to neutralize the acidic group of one gram of the oil sample; thus, the TAN value is expressed in units of mg KOH/g. The TAN value is also known as the *basicity number*. The basic apparatus used are conical flask, Burette, retort stand, pipette, and weighing balance and the reagent are phenolphthalein, ethyl alcohol, and potassium hydroxide of a known Normality. In the test method, the sample normally dissolved in toluene/isopropyl alcohol/water is titrated with potassium hydroxide and the results are expressed as milligrams of potassium hydroxide per gram of sample (mg KOH/g). Crude oils having high acid numbers have a high potential to cause corrosion problems in the refineries, especially in the atmospheric and vacuum distillation units where the hot crude oil first comes into contact with hot metal surfaces. Crude oil typically has a TAN value on the order of 0.05–6.0 mg KOH/g of sample

Procedure: 1g sample of the bitumen is dissolved in a conical flask with certain amount of ethanol then warmed in a water bath at 40^0C in order to ensure thorough mixing of the mixture, three drops of phenolphthalein are added to the mixture for uniform homogeneity, then the mixture is now titrated against potassium hydroxide in the burette, the colour change was noted and the value of the total acidic content is determined according to the given formulae

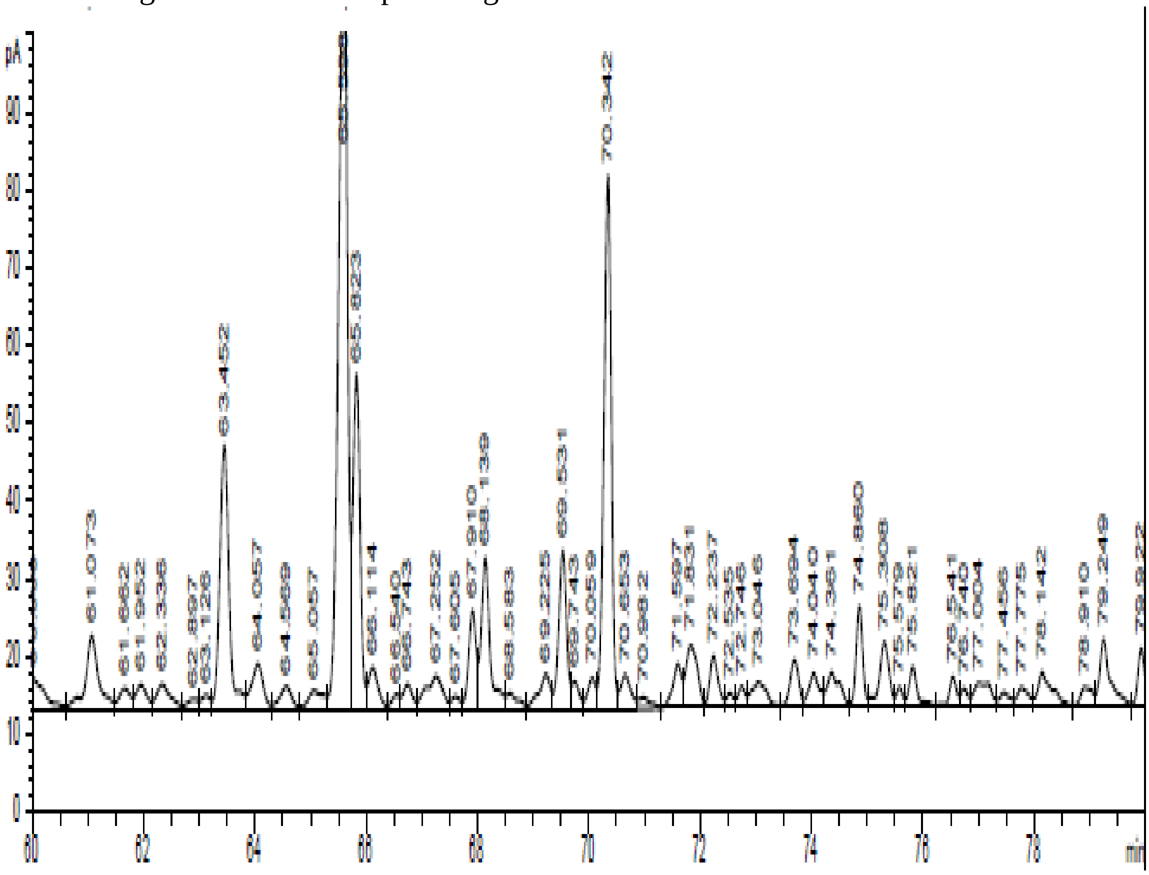
TAN = (titre vol x NX M)/ m. Where the N is the normality of the potassium hydroxide and M is the molar mass of potassium hydroxide and m is the amount of the bitumen sample.

Hewlett Packard model

Determination of boiling points distribution based on high temperature simulation distillation (HTSD) using gas chromatography flame ionization detection (GCFID). Hewlett Packard model 5890.

ASTM D-5307: Procedure: 0.1µL of a crude sample of bitumen which was diluted in a solvent, was injected into the GC column Hewlett Packard model 5890, equipped with flame ionization detector, using a fused silica capillary column, where the main separation is actually taking place, with the incorporation of a hypodermal stringe, nitrogen was 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 60^0C held isothermally for 2min, and then increased to 250^0C 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. 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 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, it is plotted as a weight percentage of the sample eluted against the corresponding boiling point equivalent of *n*-paraffins. A simulation distillation module is the core of the software where parameters dealings with simulated distillation calculation are 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 of 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 as a default,

The reports module offers a number of ways to customize the reporting of SimDis and this is integrated in the drop down report list which presents available report format and data treatment option for output, such as calibration report, engineering report, complete percentage yield, standard cut point, and custom cut point. The result in this analysis was presented using the standard cut points against retention eluted time



Chromatogram of bitumen sample showing the range of simulated distillation mixture of the bitumen sample using GCFID.

III, RESULTS AND DISCUSSION

BITUMEN SAMPLE	TAN VLAUE (mg/g)
AB	1.7
OI1	1.8
OI2	1.9
IL1	2.0
IL2	1.8
LD	1.9

Key: AB- AGBABU. OI- ODE IIRELE, IL-ILUBINRIN, LD-LODA.

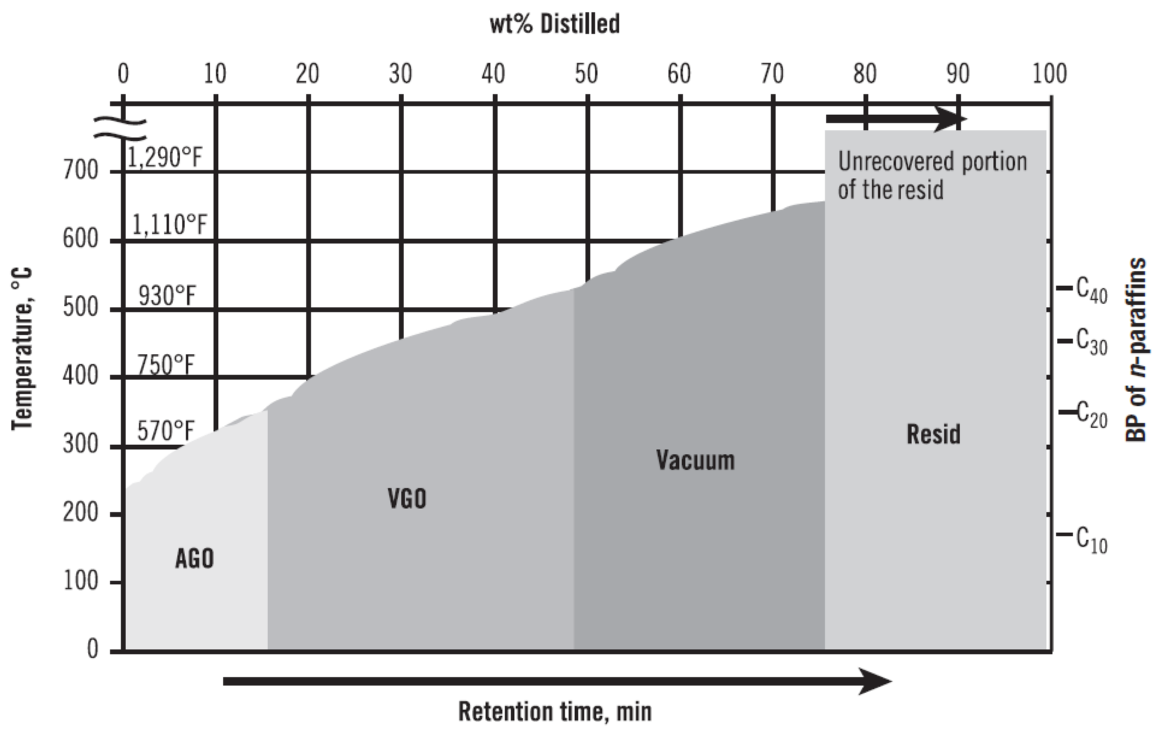


Figure 2; Distribution pattern of high temperature simulated distillation

DISCUSSION

Acidity of a crude oil is measured using a pH titration method by neutralizing the acid functional group with a basic solution, such as sodium or potassium hydroxide (KOH). The TAN value is defined as the milligrams of KOH required to neutralize the acidic group of one gram of the oil sample; thus, the TAN value is expressed in units of mg KOH/g. The TAN value is also known as the *basicity number*.

It has a good significant as a measure of the naphthenic acid corrosion of a given fuel. Lubricating oil formulation can be checked fundamentally using the total acidic number of the sample. In this study, the TAN value of the bitumen sample gives a range of (1.7--- 2.0) Mg/g and this is relative low in acidic contents when compare to the TAN value that is reported and discussed by (Adewole, 2006), which gives the value of TAN to be 2.5Mg/g of the sample. Likewise, also the pseudo component of the residual curve analysis in the simulated distribution show effective series of wide range of hydrocarbon in the bitumen sample and this gives us an insight towards a visible atmospheric true boiling point temperature.

IV. CONCLUSSION

The accuracy in characterization of bitumen sample is necessary prior to it's a decision making regarding its exploitation, and this is paramount and essential to its engineering properties for proper decision on bitumen upgrading, refining and modification. In this research, a concise and inexpensive method is employed based on the theoretical information regarding the bulk properties of the bitumen sample in Nigeria, and the results obtained shows that the bitumen sample has a considerable amount of acidic content while compare the value given by the ASTM and the residual curve analysis was used to predict the distribution pattern of the simulated distillation as displace in the chromatogram and its boiling point distribution of the pseudo component with a perfect correlation deduction. This by implication to a large extent is to say the bituminous sand in Nigeria is of huge reservoir of liquid (crude- oil) of which, in the contest of 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 the 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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