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Characterisation of Agbabu Natural Bitumen and Its Fractions Using Fourier Transform Infrared Spectrometry

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Abstract
Physico-chemical characterization of bitumen is very germane to its applications. There have been many physico-chemical investigations on Agbabu natural bitumen (ANB), but there appears to be some discrepancies in the results of some of the findings. Thus, the need to re-examine some of the physico-chemical parameters of the ANB.
Raw sample of ANB was obtained from one of the observatory wells in Agbabu, Ondo State, Nigeria. The sample was dehydrated, purified and asphaltene component precipitated through addition of n-pentane to the sample. The maltene component was fractionated into saturate, aromatics and resin using column chromatographic method. The purified ANB sample and its fractions were each subjected to infrared analysis. In addition, the elemental composition and trace metals in the whole purified ANB were quantified using CHNS-O Analyzer (FlashEA® 1112) and Atomic Absorption Spectrometer (AAS) respectively.
Infrared spectral features obtained for the whole bitumen and its fractions bear a good degree of resemblance to the results of earlier workers on the subject with some minor differences. The values obtained for structural indexes from Infrared (IR) spectra showed that all the fractions contained branch and straight chain hydrocarbons. The structural indexes also showed that asphaltenes and resin fractions are strongly polar, both of which contain hetero–atomic compounds. Results of compositional analysis are: C (86.62%), H(10.98%), S (0.92%) N (0.48%), O (0.83%), Maltene (78.34%) aand Asphaltene (21.67%). The concentrations of the trace metals are: Mg (792.00 ppm), Mn (28.40 ppm), Fe (3633.10 ppm), Ca (1082.10 ppm), Zn (17.50 ppm), Cu (17.90 ppm), Cr (153.90 ppm), Pb (93.78 ppm), Ni (103.65 ppm), V (156.53 ppm) and Na (3740.00 ppm). Results of compositional and trace metals analyses of this study are at variance with the earlier results on characterization of ANB in the literatures. The differences in the results might be attributed to variation in the method of sample preparation especially the inclusion of dehydration of the raw ANB in the purification step prior to characterization as introduced in this study.
Keywords*:* Aromatics, Asphaltenes, Agbabu Natural Bitumen, IR, Resins, Saturates

Introduction

Bitumen is a thick, black and visco-elastic material consisting of a complex mixture of saturate, aromatic, resin and asphaltene with some trace metals such as iron, nickel, and vanadium. Bitumen is known to contain heterocyclic compounds having composed largely of about 80 percent by weight of carbon, 10 percent by weight of hydrogen, 6 percent by weight of sulphur, small amounts of oxygen and nitrogen. It is substantially soluble in some solvents such as carbon disulphide and trichloroethylene and become molten when heated (Zhang, 2009; ASTM, 2009).
Bitumen is obtained from the refinery during petroleum refining as a residual product of distillation process or as a natural deposit formed from accumulation of ancient microscopic organism and other living thing in mud on the bottom of the ocean or lake (Read and Witeoak, 2003). Bitumen, either in natural form or obtained from petroleum consists of four fractions, namely: saturate, aromatics, resin and asphaltene. Conventionally, bitumen is usually fractionated into components, using the method called 'SARA' fractionation/analysis. This involves de-asphaltination or separation into maltene and asphaltene via solvent precipitation method using n-pentane. Subsequently, the maltene is fractionated into saturate, aromatics and resin by chromatographic method. Another method involves the use of High Performance Liquid Chromatography which is similar in approach to SARA analysis. However, using the method requires extraction of asphaltene before performing the operation (Petersen, 1984; Orea *et al.,* 2002). The quality of these components plays a major role in the suitability or otherwise of bitumen for various applications. By inference, therefore, appropriate characterisation of these components is a very important pre-requisite for bitumen application.
Nigeria is endowed with a large deposit of natural bitumen which is found in Nigerian bitumen belt of southwest Nigeria (Adegoke *et al.,* 1991). The belt lies on the onshore areas of eastern Dahomey (Benin) Basin, with Longitude 3°45'E and 5°45'E and Latitude 6°00'N and 7°00'N. One of the notable towns located within the belt is Agbabu and it was in this town that the natural bitumen was first discovered in 1900 in Nigeria. Although, commercial exploitation of its materials is yet to commence, scientific investigation of this very useful

engineering material is on the rise on daily basis. Hence, there is avalanche of information on this material in literature. Some of the earlier works on ANB include that of Oderinde and Olanipekun, (1990) and that of Adebiyi and Omole, (2007). Both carried out studies on characterisation of components of ANB sample. It is however, observed that there are many discrepancies in the results of some earlier studies (Oderinde and Olanipekun, 1990 and Adebiyi and Omole, 2007). A plausible reason for this might be due to different point of sampling within the bitumen belt or the level of purification of the bitumen prior to its characterisation. One of the aspects of purification hitherto left undone is the removal of moisture in the bitumen prior to its characterisation. This work intended to remove the moisture inherited in Agbabu bitumen as pre-step to purification method reported in the literature. Thereafter, the purified ANB would be characterised and some of structural parameters of the whole bitumen and its fractions will be determined using FTIR.
Thus, this study aimed at extracting moisture from the raw sample of ANB, purify and fractionate it into components (SARA). Thereafter, the purified ANB and its fractionated components will be separately characterised using FTIR, CHNSO analyser and AAS.

2.0 METHODOLOGY

2.1 Determination of Percentage Moisture Content

The moisture content determination was carried out using infrared moisture analyser (Sartorius AG Germany). About 2g of bitumen sample were placed in the analyser and the equipment set on for 5 minutes. The moisture content of the sample was read from the meter of the equipment after the stipulated time.

2.1.1 Extraction of Moisture from Bitumen Sample

A modified method of Vernon *et al.* (1999) as described below was employed for extracting moisture from ANB. 100g of raw natural bitumen sample were spread on a tray to a thickness of 1cm. 1g of calcium chloride granular salt was then spread over the sample at room temperature and the mixture stirred manually with stirring rod for three (3) minutes. The mixture of the salt and the sample was transferred to a hot oven at 65^0C to get rid of moisture. Meanwhile, the moisture content was monitored using infrared moisture analyser (Sartorius AG Germany), MA 35M-00023012 until it was approximately zero. This took about three weeks for complete extraction of moisture. The added salt was drained alongside the moisture as salt solution. The essence of calcium chloride in the sample is to ease moisture separation at lower temperature (65^0C).

2.2 Purification of Raw ANB Sample

The Bitumen sample was purified using the modified method of (Robinstein and strausz, 1979). About 100g of dehydrated raw ANB were dissolved in 1000mL chloroform and filtered. The bitumen in the filtrate was recovered by vacuum evaporation of the solvent.

2.3 Characterisation of Purified ANB

2.3.1 Elemental Analysis

Determination of percentage composition of carbon, hydrogen, sulfur, nitrogen and oxygen content of purified was carried out using the Elemental Analyzer (FlashEA® 1112) at Medac Ltd, Analytical and Chemical Consultancy services, United Kingdom. The FlashEA® 1112 Elemental Analyzer is configured as a CHNS-O analyser to determine the composition of carbon, hydrogen, nitrogen, sulphur and oxygen in an organic or inorganic substance. CHN&S in purified ANB were analysed by "dynamic flash combustion" method. The oxygen was determined differently by pyrolysis of the sample in helium gas inside a reactor furnace which was maintained at about 1060ºC.

2.3.2 Metals Analysis of ANB

Digestion of the purified ANB was as described by Amorin *et al*., (2007). Purified natural bitumen sample (0.5g) was weighed into a beaker and 12mL of digestion mixtures of HNO_3, H_2SO4, HCl, and H_2O_2 in the ratio of 6:2:2:2 (v/v) respectively was added. Thereafter, the mixture was brought to a slow boiling and evaporated on a hot plate until complete digestion was attained. To the cooled residue obtained, 5mL of 6NHCl was added, mixed together and filtered into a 50ml standard flask and content made up to the mark with double distilled water. The experiment was repeated trice for accuracy. The determination of the level of metals in ANB sample was carried out using the Atomic Absorption Spectrometer (Model P990)

2.4 Fractionation of ANB

2.4.1 Separation of purified of Agbabu natural bitumen into Asphaltene and Maltene

The purified ANB (1g) was separated into maltene and asphaltene fractions by gradually adding n- pentane (20mL) to the bitumen sample and stirred thoroughly for about five (5) minutes. The resulting mixture kept in the dark overnight and the precipitated asphaltene was removed by filtration. The asphaltene was purified by soxhlet extraction with n-pentane and further purified to get rid of remaining maltene by addition of dichloromethane (20mL) in a beaker. The maltene fraction was recovered from the n-pentane and

dichloromethane respectively by distillation. The determination of the level of metals in ANB sample was carried out using the Atomic Absorption Spectrometer (model P990).

2.4.2 Fractionation of Maltenes of Purified ANB by Column Chromatography

The method of Sonibare *et al.,* (2008) was used for the fractionation of maltene fraction. The maltene was fractionated using column chromatography on activated silica gel. 15g of silica gel was activated in a hot air oven at 120^{o}C for 6hours. 0.2g of glass wool was introduced into the column with the aid of a glass rod and then the silica gel was packed into the column.

The acidified sand was introduced into the column and 35ml of n-hexane was used to wash the column. The sample of the oil (maltene) was dissolved in 2ml of n-hexane and introduced on the surface of the sand in the column. The maltene was then fractionated into its components (saturate, aromatics and resin) using n-hexane (20ml), mixture of n-hexane (36ml) and dichloromethane (4ml) and mixture of dichloromethane (15ml) and methanol (15ml) respectively. All the fractions were collected in a separate flask and separately rid of solvent by vacuum evaporation in a rotary evaporator. The flasks after evaporation of the solvent in each of the fractions were removed and kept in a desiccator to cool to a constant weight. The experiment was carried out trice and mean value calculated to obtain the percentage composition of the saturate, aromatics and resin fractions.

The percentage compositions of the fraction of the ANB were calculated as follows:

% composition of asphaltene = Weight of the asphaltene X 100
Weight of the ANB sample

% composition of maltene = Weight of the maltene X 100
Weight of the ANB sample

The maltene after fractionated into saturate, aromatic and resin according to **2.4.2,** the percentage composition of each of the fractions was calculated.

% composition = F x 100
Weight of the maltene

Were F may be saturate, aromatics, resin

2.5 FTIR Analysis of the Purified ANB

Fourier Transform Infrared (FTIR) Spectrometer FTIR-8400s, SHIMADZU, with Spectra range: 4,000-400cm^{-1} was used to generate IR spectra of the whole ANB and its fractions. Sample for IR analysis were prepared using KBr pellets. The functional and structural indexes were calculated from the band areas (Lamontagne *et al*., 2001). The indexes are calculated using the following equation:

$$Aromatic\ structures\ (aromaticity\ index) = \frac{A_{1600}}{\sum A}; \dots\dots\dots\dots\dots (1)$$

$$Aliphatic\ structures\ (Alipatic\ index) = \frac{A_{1460} + A_{1376}}{\sum A}; \dots\dots\dots\dots\dots 2)$$

$$Branch\ chains = \frac{A_{1376}}{A_{1460} + A_{1376}}; \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

$$Long\ chains = \frac{A_{724}}{A_{1460+1376}}; \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

$$Oxygenated\ functions\ (carbonyl\ index) = \frac{A_{1700}}{\sum A}; \dots\dots\dots\dots\dots\dots (5)$$

$$Sulphoxide = \frac{A_{1030}}{\sum A}; \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (6)$$

$The\ sum\ of\ the\ area\ represents\ (\sum A) = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953,2923,2862)}$.

3.0 Result and Discussion

3.1 Moisture content

The moisture content of the raw ANB was found to be 11.06%. This result showed a slight difference in comparison with that of Adebiyi and Omode (2007) who found the water content in the bitumen separated from Agbabu bituminous sand sample to be 15.14%. Moisture extraction from bitumen prior to modification is necessary as the presence of moisture tends to reduce the adhesiveness of bitumen to aggregate during compaction in pavement construction.

3.2 Elemental Analysis (C,H,S,N, O) and Metals Composition of Agbabu Natural Bitumen

The results of C,H,S,N and O contents of ANB are as presented in Table 1. The results show that sulphur is the

most abundant of the hetero-atom (0.92%) and that ANB consists essentially of hydrocarbon with high carbon content (86.62%) and hydrogen content (10.98%). The elemental composition of ANB obtained in this study (Table 1) compared favourably with the findings of (Guma *et al.,* 2014). Guma *et al.,* (2014) analysed elemental composition of two bitumen samples (Ondo S.A. and Ondo S.B.) from different location in Agbabu and reported the percentage elemental composition for Ondo S.A as C (87.78), H (9.35), N (0.13), O (1.25), and S (1.32), while for Ondo S.B as C (86.91), H (9.31), N (0.66), O (1.74), and S (1.23).

Table 1. Elemental Composition of Purified ANB

Elements	**Carbon**	**Hydrogen**	**Sulphur**	**Nitrogen**	**Oxygen**	**Ash**	**H/C ratio**
(%)	86.62	10.98	0.92	0.48	0.83	0.17	0.127

The results of metal analysis are as presented in Table 2. The concentration of metals detected in ANB in decreasing order is as follows: Na>Fe>V>Mg>Ca>Cr>Pb>Ni>Mn>Zn>Cu. The concentration of Na is the highest (3655ppm) while Cu has the lowest (6.40ppm). The presence of some heavy metals such as vanadium, in a relatively large concentration together with chromium, lead, manganese and nickel in small amount may constitute environmental hazard and catalytic poisons during refining of the bitumen.

The concentrations of most of the metals as contained in Table 2. differ from that obtained by Obiajunwa and Nwachukwu (2000), Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007). The difference may be due to the fact that earlier studies of Obiajunwa and Nwachukwu (2000), Ipinmoroti and Aiyesanmi (2001) and Adeabiyi and Omole (2007) were made on bituminous sand why the present study used flow bitumen obtained from one of the observatory wells. The process of extraction of bitumen from bituminous sand might leached out some metals from the bitumen, hence the relatively lower concentrations of some metals reported by earlier workers.

Table 2. Metal Composition of Nigerian Natural Bitumen

Metals	**Adebiyi and Omole (2007)**	**Ipinmoroti and Aiyesanmi (2001)**	**Obiajunwa and Nwachukwu (2000)**	**Present study**
Mg	NDT	NDT	NDT	792.00
Mn	12.41	NDT	216.00	28.40
Fe	204.93	243.00	48,300.00	3633.10
Ca	NDT	NDT	NDT	1082.8
Zn	100.94	7.00	119.00	17.50
Cu	ND	BDL	72.00	17.90
Cr	NDT	NDT	NDT	153.90
Pb	57.49	80.00	69.00	93.78
Ni	20.22	21.00	NDT	103.65
V	7.59	37.00	NDT	156.53
Na	NDT	NDT	NDT	3740.00
Co	ND	NDT	NDT	NDT

ND: not detected, NDT: not determined, BDL: below detection limits (0.02ppm for Cu)

3.3 FTIR Spectra of ANB and its Fractions

The spectra of purified ANB and its fractions are as shown in Figures 1(a-e) and were interpreted based on previous reports by Adebiyi and Omole, 2007 and Anderson and Speight, 2001. The IR spectrum of purified ANB Figure 3(a) showed strong absorbances at 2,924cm^{-1} and 2,854cm^{-1} which correspond to C-H stretch in CH_3, CH_2, CH and also strong absorbances at 1,458cm^{-1} and 1,375cm^{-1} which correspond to C- H stretch in alkyl group and C-H bend in methyl respectively. These absorbance bands were peculiar to all the fractions of purified ANB with or without minor shifting. The absorption band at 1608cm^{-1} showed the presence of C-C stretch (in-ring) aromatics, while the weak peak 1697cm^{-1} could be due to carbonyl stretch C=O (str) in ketones, amides, aldehydes and carboxylic. Furthermore, the presence of shoulders around 868cm,$^{-1}$ 815cm^{-1}, and 744cm^{-1} as observed in ANB may be due to aromatic bending C-H modes and these correspond to C-H bend in aromatics.

In saturate fraction Figure 1(b), the IR spectrum showed strong absorbances observed at 2,924cm^{-1}, 2,856cm^{-1}, 1,456cm^{-1} and 1,377cm^{-1}. These peaks were also observed in the spectrum of purified ANB with minor shift. There was disappearance of peaks at 869 cm,$^{-1}$ and 813 cm^{-1} but a minor shift of peak at 746cm^{-1} to 740cm^{-1} which was not prominent. This is an indication of trace aromatic compounds in the fraction which might be due to imperfection in the chromatographic separation.

In aromatic fraction Figure 1(c), the strong peaks in the IR spectrum were observed at 2,966 cm^{-1}, 2,875 cm^{-1},

1,458 cm^{-1} and 1,379 cm^{-1}. There was shift in peaks from 2,924 $cm^{-1}$to 2,966 cm^{-1} and 2,854 cm^{-1} to 2,875 cm^{-1} in comparison with the spectrum of purified ANB. There was also disappearance of peaks at 869 cm,$^{-1}$ and 813cm^{-1}. The spectra showed a new and .weak peak at 727 cm^{-1} which corresponds to C-H, bend in alkyl group. The peaks at 1604 cm^{-1} corresponds to C-C stretch (in-ring) aromatics. The peak observed at 1037 cm^{-1} corresponds to sulphoxide which is an indication of presence of traces of sulphur compounds. The intensity of the peak is however far lower than sulphoxide peak in resin.

Figure 1(d) corresponds to infrared spectrum of asphaltene. The spectrum showed peak which appeared as shoulder at 3,051cm^{-1} and may be attributed to C-H stretch aromatic carbon. The absorbance bands observed at 2,924cm^{-1}, 2,852cm^{-1}, 1,456cm^{-1} and 1,375cm^{-1} were also observed in the spectrum of purified ANB as in Figure 1(a) with minor shift. The absorption band at 1602 cm^{-1} corresponds to C-C stretch (in-ring) aromatics. Weak peak which appeared at 1693cm^{-1} could be due to carbonyl C=O (str) in ketones, amides, aldehydes and carboxylic while that observed at 1033cm^{-1} corresponds to presence of S-O stretch in sulphoxide. The appearance of absorption bands at 1693cm^{-1} and 1033cm^{-1} could be as a result of oxidative aging (Xiaohu and U. Issacsson, 2002). The three peaks at 868cm^{-1}, 813cm^{-1} and 746cm^{-1} which appeared as shoulder in asphaltenes were also observed in the spectrum of purified ANB.

The IR spectrum of resin Figure 1(e) showed broad and very conspicuous peak at 3362cm^{-1} which corresponds to NH, OH stretch (H-bonded) and makes it distinct from other spectra. The absorbances observed at 2,964cm^{-1}, 2,872cm^{-1}, 1,460cm^{-1} and 1,379cm^{-1} were common to the spectrum of aromatics in Figure 3(c). The peaks observed at 1708cm^{-1} and 1031cm^{-1} were also found in asphaltenes in Figure 1(d) but more intense. This confirms the degree of polarity of resin. The less intense peaks at 1606cm^{-1} corresponds to C-C stretch (in-ring) aromatics. A strong peak which appears at 742cm^{-1}corresponds to C-H bend aromatics, while that at 1265cm^{-1} could be attributed to C-O stretch in acids, esters and anhydride.

The results of IR spectra in Figure 1(a-e) showed a great deal of similarities in terms of identified functional groups with that of Adebiyi and Omole (2007). The spectral features of oil (saturate and aromatic) component showed absence of nitrogenous compounds unlike asphaltenes and resin. Besides, presence of hydrocarbons is indicated in all the components. These spectral results agree with many other studies on Nigerian bitumen (Oderinde and Olanipekun, 1990; Ekweozor and Nwachukwu, 1989) and Athabasca bitumen (Moschopedis *et al.,* 1981). The only difference lies in the fact that the IR spectrum of resin in Adebiyi and Omole's result did not reflect the broad and very conspicuous peak at 3454 cm^{-1} justifying the higher degree of polarity in resin.

The Infra-red spectra of purified Agbabu natural bitumen and its fractions are as presented in figure 1(a)-1(e).

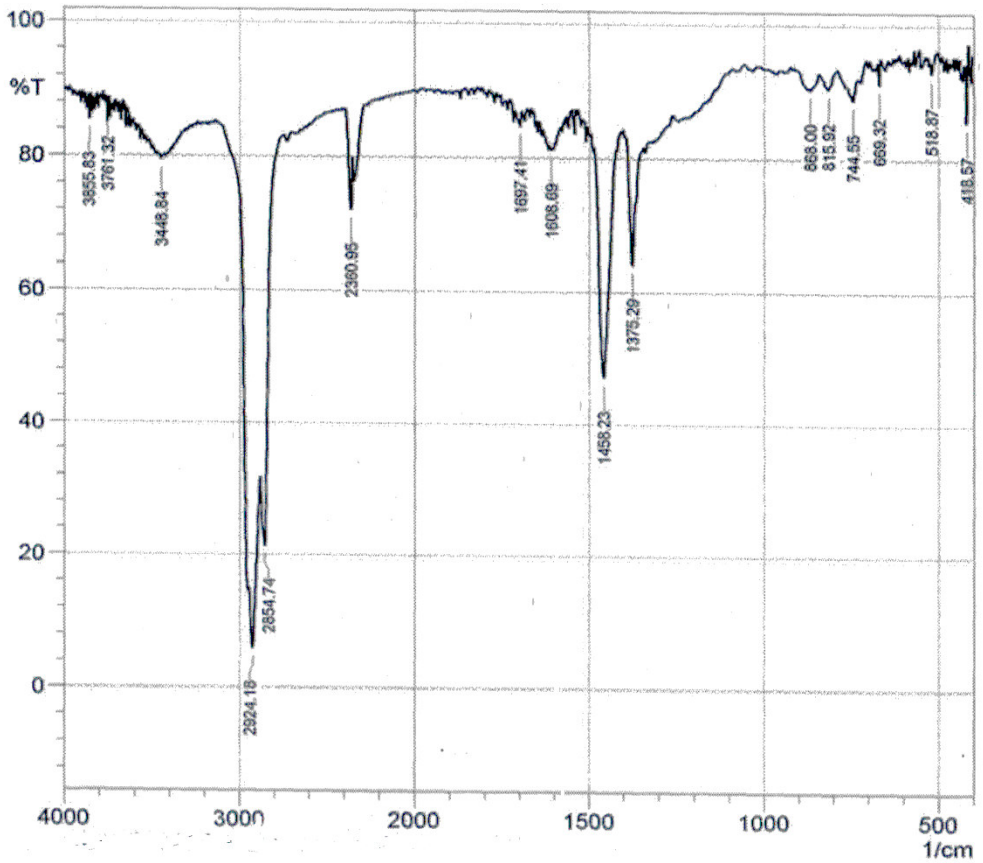

Figure 1(a). FTIR of purified ANB

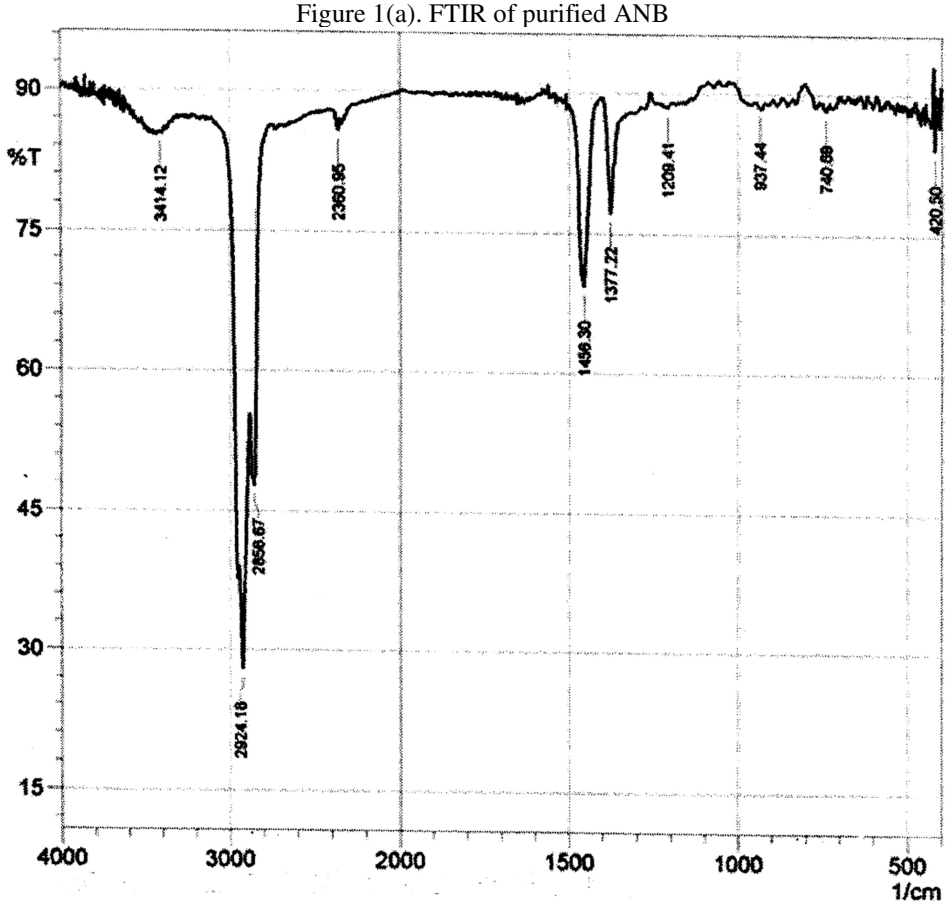

Figure 1(b). FTIR of saturated component of Purified ANB

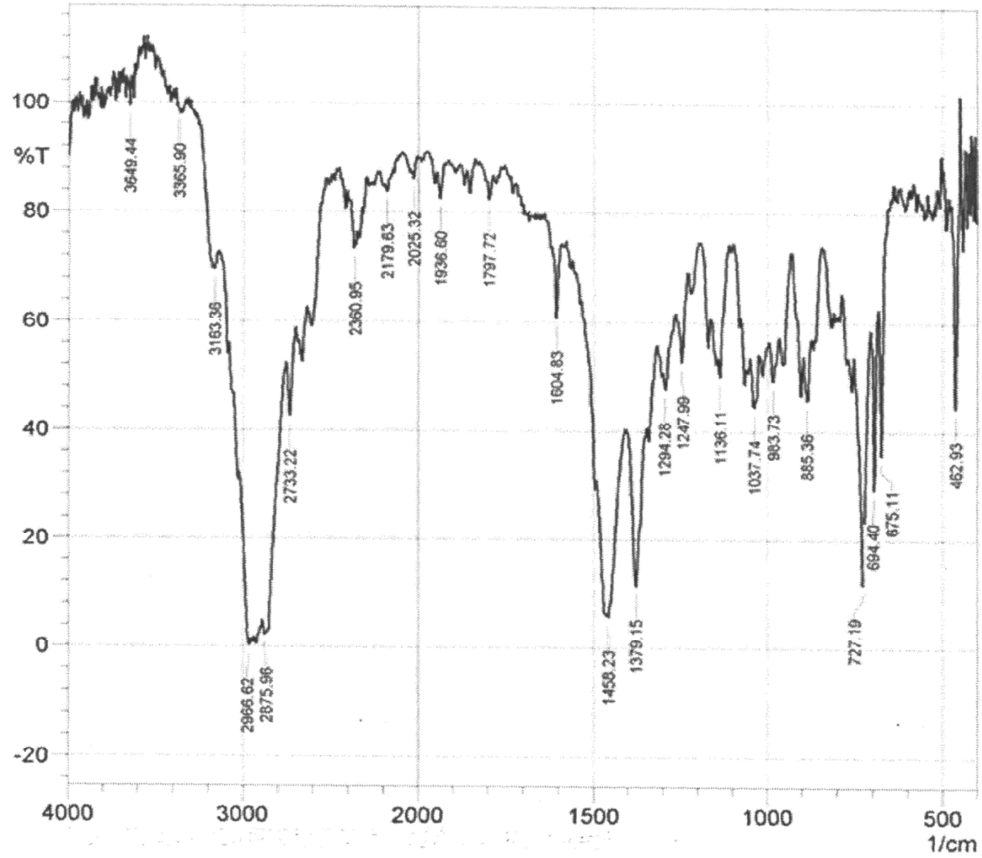

Figure 1(c). FTIR of naphthenic aromatic component of Purified ANB

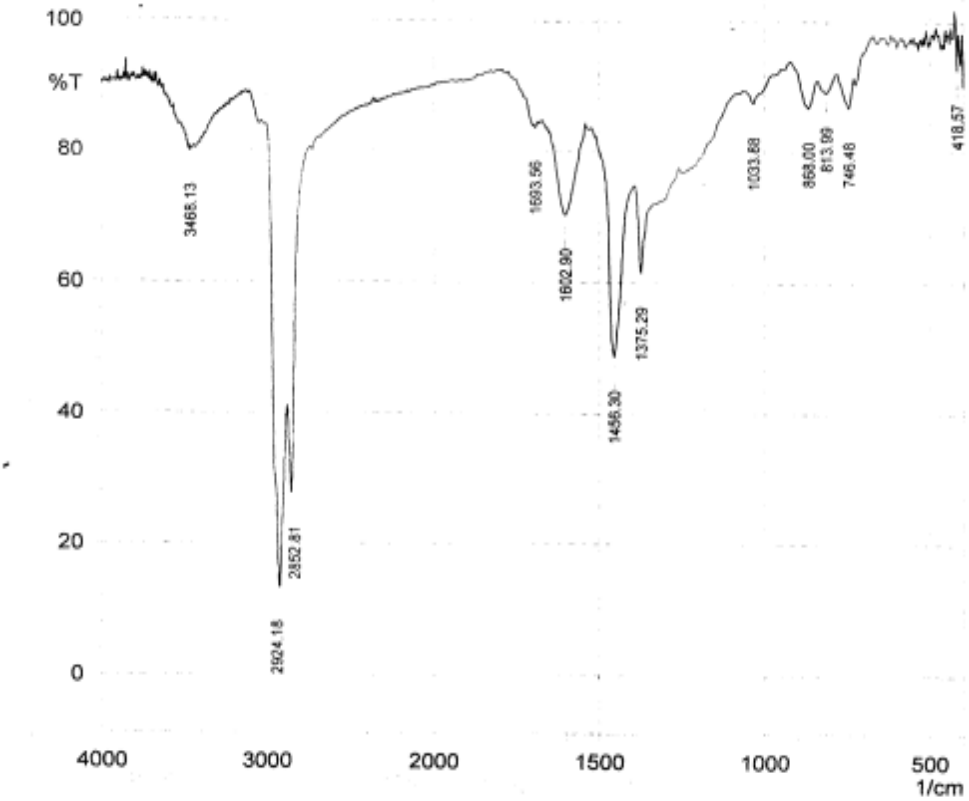

Figure 1(d). FTIR of asphaltene component of Purified ANB

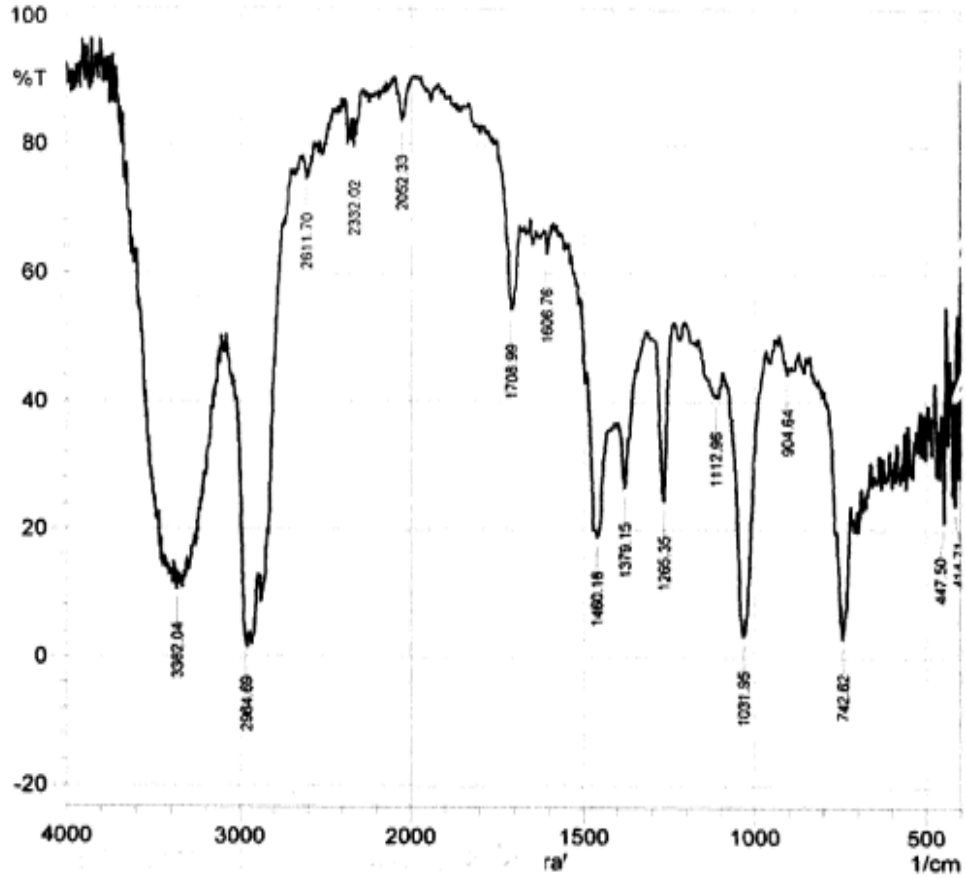

Figure 1(e). FTIR of resin component of Purified ANB

Assignment of Functional Groups in Bitumen Fractions from Figure 1 (b-e) is discussed in Table 3 based on previous results by (Adebiyi and Omole, 2007 and Anderson and Speight, 2001).

Table 3. Assignment of Functional Groups in ANB Fractions in Figure 1(b-e)

Identified functional Groups	**Wave number, cm^{-1} in ANB**
	(a) Saturate
C-H asymmetric stretch in CH_3	2966
C-H out of phase stretch in CH_2	2874
C-CH_3 and methylenic asymmetric	1467
C-CH_3 asymmetric	1379
Aromatic bending H-C modes	727
	Aromatics
C-H asymmetric stretch in CH_3	2956
C- H out of phase stretch in CH_2	2874
C=C (str), aromatic compound	1604
C-CH_3 and methylenic asymmetric	1464
C-CH_3 asymmetric	1379
Aromatic bending H-C modes	727
	Asphaltene
C-H in-phase stretch in CH_2	2924
C-H out -of -phase stretch in CH_2	2852
C=O (str) in carbonyl/carboxylic	1693
C=C (str), aromatic compound	1602
C-CH_3 and methylenic asymmetric	1456
C-CH_3 asymmetric	1375
Sulphoxide	1033
One H on ring	868
Two adjacent H on ring	813

Four adjacent Hydrogen on ring	746
	(d) Resin
NH, OH stretch (H-bonded)	3362
CH (str), alkanes	2964
C=O (str) in carbonyl/carboxylic	1708
C=C (str), aromatic compound	1460
C-CH_3 asymmetric	1379
Sulphoxide	1031
Four adjacent Hydrogen on ring	742

3.4 Structural indexes of Purified ANB

The calculations of infrared indexes were based on equation by (Lamontagne *et. al.,* 2001) as shown in the Table 4.

Table 4. FTIR Structural indexes of fractions of purified ANB

	value Index					
Fractions Of ANB	**Sulphoxide**	**Carbonyl**	**Aromaticity**	**Aliphatic**	**Branch Chain**	**Long Chain**
Saturate	0	0	0	0.212	0.383	0
Aromatic	0.025	0	0.022	0.380	0.471	0.029
Resin	0.319	0.048	0.020	0.156	0.400	0
Asphaltene	0.020	0.008	0.091	0.216	0.333	0

The values of sulphoxide, carbonyl, aromatic, aliphatic, branch chain and long chain indexes in the saturate fraction are 0, 0, 0, 0.212, 0.383 and 0 respectively. The zero values of sulphoxides and carbonyl indexes in the saturate fraction imply that there is no oxygenated function in the saturate fraction. Thus, there is no absorption band for carbonyl and sulphoxide at 1700cm^{-1} and 1030cm^{-1} respectively in the IR spectrum. The zero value of aromaticity means absence of naphthenic aromatic compound in the saturate. The values of aliphatic, branch chain and long chain indexes are 0.212, 0.383 and 0 respectively, and are indicative of aliphatic hydrocarbons in the saturate fraction.

The values of sulphoxide, carbonyl, aromatic, aliphatic, branch chain and long chain indexes in the aromatic fraction are: 0.025, 0, 0.022, 0.380, 0.471 and 0.029 respectively. The sulphoxides index value of 0.025 in aromatic fraction is an indication of the presence of certain amount of sulphur compounds. This is in agreement with the submission of Yousefi, (2008) that the oil fraction of bitumen contains variable quantities of sulphur compounds such as thionaphtenes, cyclic sulphurs and mono and dibenzo-thiophene derivatives. The value of aromaticity index (0.008) in the aromatic fraction indicates the presence of naphthenic aromatic compounds in the aromatic fraction. Also, the value of aliphatic, branch chain and long chain indexes which are 0.380, 0.471 and 0.029 respectively, showed the presence of aliphatic hydrocarbons in the aromatic fraction. This may be due to the presence of compounds like alkylated benzenes.

In resin fraction, the values of sulphoxide, carbonyl, aromatic, aliphatic, branch chain and long chain indexes are: 0.319, 0.048, 0.020, 0.156, 0.40 and 0 respectively.

The index values of 0.319 and 0.048 for sulphoxide and carbonyl in the resin showed the presence of oxygenated sulphur and carbon accounting for the presence of heterocyclic compounds in the resin fraction. Hence, absorption bands of sulphoxide and carbonyl at 1031cm^{-1} and 1708 cm^{-1} in the IR spectrum. The aromaticity index value of 0.020 indicated the presence of aromatic structure in the fraction while the index values of 0.156, 0.40 for aliphatic and branch chain hydrocarbon respectively, showed the presence of aliphatic compounds with branch chain.

The values of sulphoxide, carbonyl, aromatic, aliphatic, branch chain and long chain indexes in the asphaltene fraction are 0.020, 0.008, 0.091, 0.216, 0.333 and 0 respectively.

The index values of 0.020 and 0.008 for sulphoxide and carbonyl in the asphaltene showed the presence of heterocyclic compounds in the asphaltene fraction. Hence, the absorption bands of sulphoxide and carbonyl at 1033cm^{-1} and 1693cm^{-1} respectively in the IR spectrum. The aromaticity index value of 0.091 indicated the presence of highly condensed aromatic structure in the fraction. The 0.216, 0.333 index values for aliphatic, branch chain hydrocarbon compound respectively, showed the presence of aliphatic compounds with branch chain.

The values of aromaticity indexes of the fractions are in the decreasing order as shown in Table 4: asphaltene (0.088) > resin (0.021)> aromatics (0.008)> saturate (0) implying that asphaltene is highly aromatic compared to other fractions. The aliphatic index value for all the fractions is an indication of the presence of aliphatic hydrocarbons. The sulphoxide and carbonyl index values for aromatics, resin and asphaltene are 0.365 and 0.056, 0.020 and 0.007 and 0.025 and 0 respectively with zero values for saturate fraction. Therefore, the values

of index calculated from FTIR spectra of ANB fractions revealed the presence of heterocyclic compounds in resin and asphaltene. In addition, the presence of variable quantities of sulphur compounds such as thionaphtenes, cyclic sulfurs and mono and dibenzo-thiophene derivatives in aromatics was establised. The value of aliphatic index for the aromatic fraction suggests the presence of alkylated rings in the fraction, while the aliphaticity value of the saturate fraction also suggests that the fraction contains branch and long chain hydrocarbons and naphthenic cycles with low polarity.

3.5 Maltene and Asphaltene Components in Purified ANB

The results of separation of ANB into its major components (asphaltene and maltene) are presented in Table 5. The results showed insignificant difference compared to what was obtained by Fabiyi and Omole (2007) and Oderinde and Olanipekun (1990) with average values of 78.34% and 21.67% and 74.73% and 25.27% for maltene and asphaltene, respectively. The minor difference might be due to the fact that the bitumen used by Fabiyi and Omole (2007) and Oderinde and Olanipekun (1990) were extracted from bituminous sands.

Table 5. Comparison of Maltene and Asphaltene in ANB as reported by some Authors

Component	**Adebiyi and Omole (2007)**	**Oderinde and olanipekun (1990)**	**Present Study**
Maltene (%)	78.34	74.73	73.05
Asphaltene (%)	21.67	25.27	26.80

The maltene component was further fractionated into saturate, aromatics and resin components, the percentage compositions of which were found to be 19.45, 24.27 and 27.90%, respectively. The results compared reasonably with that of Rojo *et al.* 2004 who submitted that bitumen composed of saturate (17.4-20%), aromatics (19-22.5%), polar aromatics (21.9-26.6%) and asphaltenes (25-33%). Thus, Agbabu natural bitumen can be categorised as sol-type bitumen which implies that the saturate and aromatic composition have enough solvating power to disperse the asphaltene. This attribute makes Agbabu natural bitumen suitable for road construction.

4.0 Conclusions

The IR analysis of the ANB and its fractions showed that Agbabu natural bitumen, like bitumen from other parts of the world contains a mixture of paraffinic, aldehydric, anhydic, aromatic, and hetero-atomic-containing compounds. Most of the infrared spectral features are in agreement with earlier findings reported for the ANB. There were some qualitative and quantitative differences in metals found in ANB in this study compared to the earlier studies. Method of purification and bitumen form might account for this. Infrared structural indexes of the ANB found in this study also differed from the earlier ones reported. It can therefore be inferred that the method of sample preparation for the characterization of ANB needs to be standardised in order to solve the problems of discrepancies in physicochemical parameters of ANB as given by different authors.

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