

Fractionation and Characterization of Asphaltenic and Resinous Fractions of Natural Bitumen

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Abstract. In order to identify the finger prints of some fractions in bitumen and to study the changes that take place when heavy oil is upgraded, precipitation, fractionation, and characterization of asphaltenes and resins from natural bitumen were carried out using UV/vis and FTIR Spectroscopy. The sample was purified and the asphaltene fraction precipitated with n-hexane, fractionated into fractions A and B based on solubility and polarity with hexane/toluene mixture at a fixed ratio while resins recovered from maltenes was fractionated into subfractions X, Y, Z by liquid adsorption chromatography on a silica/alumina adsorption column with dichloromethane/methanol mixed solvent in the ratio of 4:1, 3:2 and 2:3, respectively. The results showed that crude asphaltene and its subfractions absorbed light of longer wavelength (465 – 640 nm), indicating that they are made up of polynuclear aromatic compounds. The results also revealed the presence of alkyl side chains and major oxygenated groups in both crude asphaltene and its subfractions (A and B). The spectra of crude resin and its subfractions showed that they absorbed radiation of longer wavelength (490-580 nm), which are characteristic of polynuclear aromatic compounds with the extended conjugated system. However, IR spectra revealed that all the fractions including the crude resin contained aromatic rings with alkyl side chains and oxygenated groups.

Keywords: Asphaltenes, resin bitumen, subfractions, fractions, characterization UV/vis, FTIR,

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1.0 Introduction

Asphaltene is a solubility class of compounds found in crude oils. They are black to dark brown solids defined by their insolubility in *n*-alkane solvents. The structure of asphaltene molecules is polynuclear aromatic rings with alkyl side chains and heteroatoms such as nitrogen, oxygen, and sulfur attached (Wilt *et al.* 1998). Current efforts towards the exploitation and production of heavy and extra-heavy oil have compelled the petroleum industry to introduce and develop new crude oil preparation techniques which are based on the degradation of high-molecular-mass petroleum compounds to high proportion of lighter fractions in the petroleum feedstock (Grinko and Golovko, 2011). The most common methods usually employed for increasing the yield of light fractions

involves the destruction of heavy crude oil feedstock through thermal, microbial and chemicals methods (Grinko and Golovko, 2011; Hashemi-Kiasari *et al.*, 2014; Muaraza and Galadima, 2015). Therefore, it is informative to know the interaction the macromolecular asphaltene and other heavy fractions undergoes when they are converted to lighter fraction (Bisiriyu *et al.*, 2017). Structural changes are always accompanied by vibration or functional group changes. Hence knowledge of functional groups before and after changes can provide information on the level of interaction that occurs during the changes. Most structural studies have been reported bulk asphaltenes and resins without deep considerations of their fractions (Grinko and Golovko, 2011). For example, Aemani and Rabbani (2015) used FTIR technique to characterize asphaltene samples from Iran the results they obtained were applied to the results to oil-oil correlation and structural characterization. Coelho *et al.* (2011) also used FTIR method to study asphaltene and reported the existence of a linear correlation in the infra-red intensities of the symmetric and asymmetric aromatic hydrogens in methyl substituted arene in the 2900 to 3100 cm^{-1} and the out of plane deformation in the 700 to 900 cm^{-1} regions. In their study, Wilt *et al.* (1998) used FTIR to determine asphaltene in petroleum crude oil. Poveda-Jaramillo *et al.* (2016) used FTIR, UV and other techniques to characterized asphaltene from Colombian Colorado light crude oil. According to Cruz *et al.* (2017), UV-vis spectroscopy is a simple and practical technique that allows the characterization of crude oil through dilution in a solvent. Consequently, they used UV-vis spectroscopy, dynamic light scattering and microscopy to characterize asphaltene fractions. Also, literature is relatively scanty on asphaltene and resin of Nigerian origin. Therefore, the present study is aimed at obtaining different fractions of asphaltenes and resins with varying polarity and solubility and to characterize them using FTIR and UV spectroscopy techniques. The proposed chemical structures of asphaltene and resin are shown in Figs. 1 and 2.

2.1. Sampling

Bitumen samples were collected into a plastic container from the bitumen deposit at Mile 2 in

Odigbo Local Government Area, Ondo State located in the Nigerian bitumen belt of southwestern Nigeria. 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 (Bakare *et al.*, 2015).

2.2. Purification of crude bitumen

In order to remove particulate matter, bitumen (ca. 40 g) was dissolved with 200 cm^3 of dichloromethane (DCM) in a beaker using ultrasonicator (DR-LQ20) for 30 minutes.

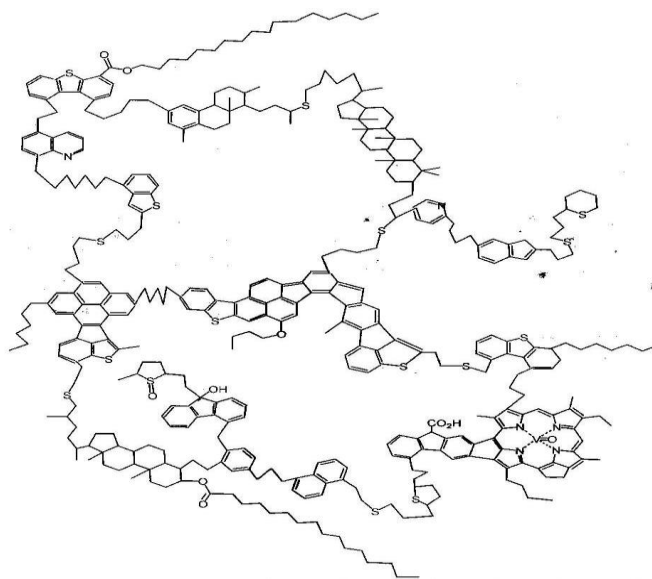


Fig 1: Hypothetical structure of asphaltene
(Source: Anigbogu, 2011).

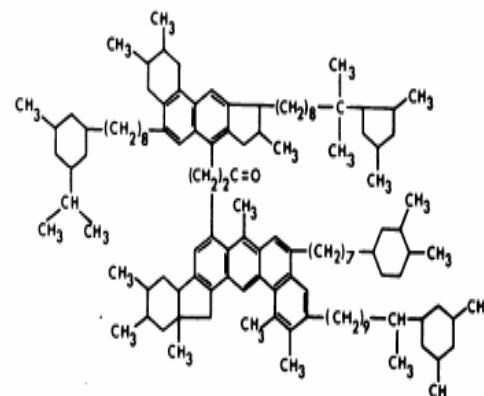


Fig. 2: Hypothetical structure of resin molecule
(Source: Gafonova, 2000).

2. Material and Methods

The solution obtained was filtered with a Whatman filter paper and the filtrate was left to dry completely (Muhammad, 2009).



2.3. Precipitation of asphaltenes

Bitumen (ca. 1.00 g) was treated with *n*-hexane (40 cm³) in a conical flask and was sonicated regularly. The bitumen was dissolved in dichloromethane before the asphaltenes were precipitated with *n*-hexane. The mixture was stirred for 30 minutes and was allowed to equilibrate for 24 hours. The asphaltenes were recovered from the mixture by centrifuging at 3500 rpm for 10 minutes. The recovered asphaltenes were re-dissolved with DCM (1.00 cm³) and re-precipitated with *n*-hexane (40.00 cm³). The mixture was sonicated for 10 minutes and the asphaltenes were recovered by centrifugation. This procedure was repeated and the asphaltenes recovered were transferred into a pre-weighed beaker with a little amount of DCM and allow to dry (Muhammad, 2009).

2.4 Fractionation of asphaltenes

Fractionation of asphaltenes was carried out by dissolving asphaltenes in toluene followed by the addition of *n*-hexane at a ratio of *n*-hexane: toluene (hextol) designed to precipitate only some asphaltenes (Barrera *et al.*, 2013; Yamchi, 2014). A clean beaker (100 cm³) was weighed and 3.00 g of asphaltenes was measured into it. Toluene was added and the mixture was left overnight and later placed in an ultrasonic bath (DR-LQ20) for 5 minutes.

The corresponding volume of *n*-hexane according to the desired hextol ratio was added and the mixture was sonicated for another 45 minutes. It was allowed to settle for 24 hours, the solution was centrifuged at 4000 rpm for 5 minutes to separate precipitated asphaltenes from the mixture. The supernatant was decanted and the solid left was transferred with DCM into a clean beaker and this was named as fraction "A". The supernatant was then placed in a fumed cupboard to evaporate the hextol and the residue was named as fraction "B". The two subfractions were allowed to dry until there was no difference in mass (Yamchi, 2014).

2.5 Fractionation of maltenes

Alumina (1.00 g) was measured and transferred into a 50.00 cm³ pre-cleaned beaker. 50 mg of the sample was measured and dropped at the center of the alumina, thoroughly to achieved uniform distribution in the alumina. A glass column was rinsed with *n*-hexane and a piece of cotton wool was inserted into it. Silica gel (10.00 g) was

measured and then wetted with *n*-hexane. It was then transferred and packed into the column to form a stationary phase. 1.00 cm layer was formed by adding alumina and the sample was loaded and covered with another 1.00 cm thick layer of the alumina. The saturated compound was eluted with 40 cm³ *n*-hexane; aromatics were eluted with 70 cm³ mixture of *n*-hexane and DCM (7:3), while resins were eluted using 70 cm³ mixture of DCM and methanol (7:3). They were later concentrated with a rotary evaporator (Muhammad, 2009).

2.6 Fractionation of resins

Resin recovered from fractionation of maltenes was fractionated into three subfractions named X, Y, and Z by liquid adsorption chromatography on a silica gel/alumina adsorption column with DCM/MeOH mixed solvents taken in the ratio of 4:1, 3:2 and 2:3, respectively. The ratio between the solvents was chosen in a way that approximately the same yields of the fractions in terms of the initial mass of the resins were obtained (Grinko and Golovko, 2011).

2.7 UV-vis spectroscopic measurements

The sample was dissolved in DCM. The UV-vis spectroscopic measurement was made on the solution in the range of 400-800 nm using a UV-vis spectrophotometer (UV-1800). The spectra measured gave some ideas on the polyaromatics structures in the asphaltenes and resins and the degree of distribution of polyaromatics condensed ring (Li *et al.*, 2002). The same procedure was adopted for the characterization of their subfractions A and B for asphaltenes and X, Y, and Z for resin

2.8 Fourier transform infrared spectroscopic (FTIR) analysis

Infrared spectroscopic measurement was made on the FTIR spectrophotometer (MB3000), using a transmission technique. The sample was dissolved in DCM and gently dropped on KBr powder with the aid of a syringe. The mixture was ground into a fine powder and the pellet was made. The infrared spectrum was acquired at a resolution of 4 cm⁻¹ from 4000 to 750 cm⁻¹. The infrared spectrum was scanned on the pellet 30 times (Li *et al.*, 2002).

3.0 Results and Discussion

The UV/Visible spectra of asphaltene and its subfractions are presented in Figs. 1 to 3 while data deduced from the spectra are recorded in Table 1.



The spectra data of crude asphaltene and its subfraction (Table 1) shows that they absorbed light in the visible region of the electromagnetic spectrum indicating that asphaltenes are highly unsaturated as shown in the hypothetical structure of asphaltene in Fig. 1.

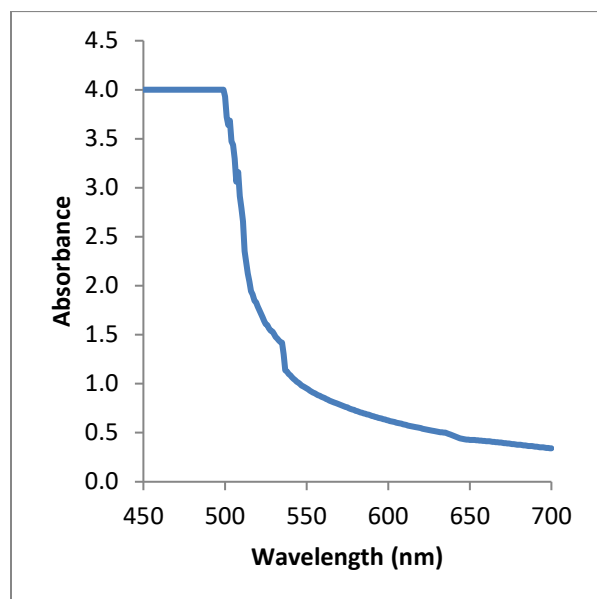


Fig. 1: UV- vis spectrum of crude asphaltene

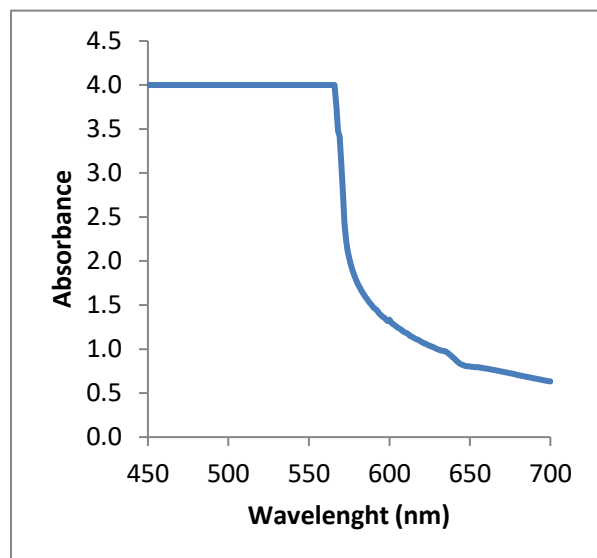


Fig. 2: UV-vis spectra of asphaltene fraction A

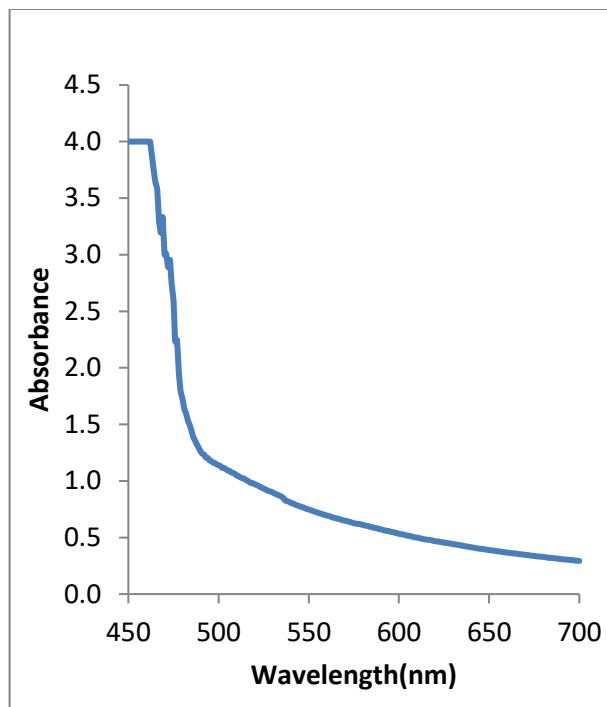


Fig.3: UV-vis spectrum of asphaltene fraction B

The UV/vis spectra of crude asphaltene and its subfraction show that they all contain polynuclear aromatic structures based on their absorbance at the following wavelengths: 465, 470, 475, 480, 510, 512, 520, 530, 570, 575, 600 and 640 nm, respectively. Since asphaltenes are polycyclic aromatic compounds, it's obvious that the wavelength of the individual aromatic constituents will vary considerably. Their ability to absorb light in the visible region of the spectrum suggests the presence of fused benzene rings or polynuclear aromatic systems in asphaltene and in the subfractions which are unsaturated and highly conjugated in nature. Their absorption is similar to those found in the literature (Anigbogu, 2011; Concawe, 2012).

The range of absorption bands for both crude asphaltenes and its subfraction is between 465 – 640 nm which correspond to the bands expected for highly conjugated polynuclear aromatics structures such as benzenoid (Anigbogu, 2011; Concawe, 2012).



Table 1: UV/Vis data of asphaltene and its subfraction

Crude		Fraction A		Fraction B	
Absorbance	λ (nm)	Absorbance	λ (nm)	Absorbance	λ (nm)
3.70	510	3.50	570	3.20	465
3.20	515	2.00	575	3.00	470
2.00	520	1.40	600	2.90	475
1.40	530	0.80	640	2.30	480
1.20	535	----	-----	1.50	485

The range observed for the absorption bands asphaltene and its fractions also indicates the presence of chromophore in the asphaltenes (Anigbogu, 2011). This explain why asphaltenes are coloured and the chromophore that maybe found in asphaltenes includes: conjugated double bonds involving aromatic hydrocarbon as indicated by the infrared spectra of the crude asphaltene and fraction B. According to molecular orbital theory, the likely electronic transitions are $\delta \rightarrow \delta^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \delta^*$. The observed range for the wavelengths of absorption is relatively small and agrees with the frontier molecular orbital theory that expect the energy gap (the difference between the energy of the lowest unoccupied molecular orbital and the energy of the highest molecular orbital) to be relatively small if successful transition must occur (Anigbogu, 2011).

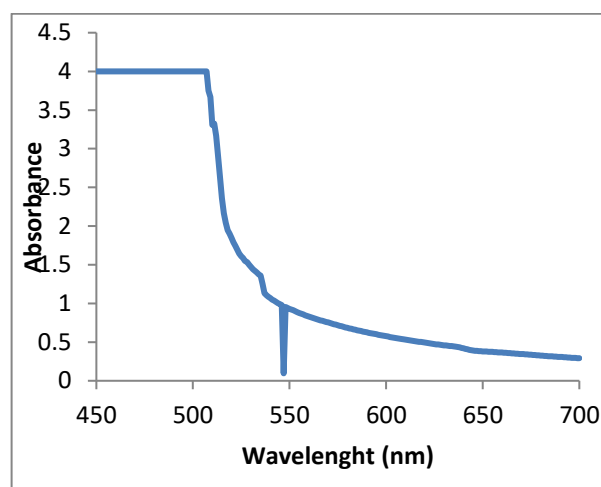
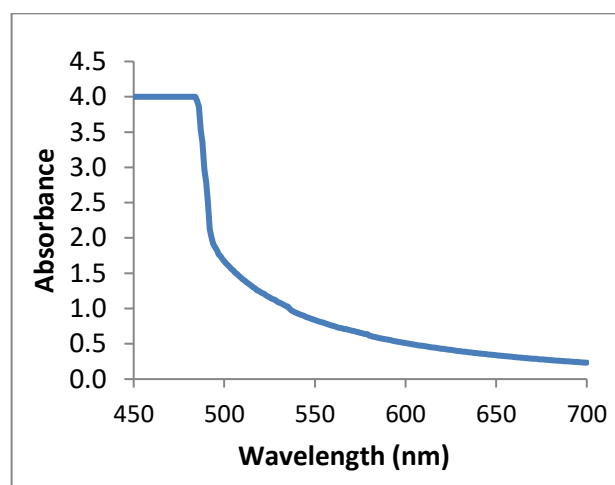
In Tables 4 to 7, the UV-vis spectra of resin and associated fractions are presented while absorption data obtained from the spectra are recorded in Table 2.

The UV/vis spectra of crude resin and associated fractions suggest that they are polynuclear aromatic hydrocarbons because they showed absorbances at 498, 510, 525, 530, 538, 540, 545, 548, and 580 nm. The weak absorbance observed at the visible region also suggests that they exhibit some degree of unsaturation.

Resin has a complex structure that is made up of different aromatic compounds and because they are polyaromatics in nature it is expected that each aromatic structure should absorbs light of the different wavelengths. The absorption bands which are in the range of 490-580 nm for both crude resin and its fractions corresponds to the bonds in polynuclear aromatic systems like benzenoid. These are in agreement with those reported by Anigbogu (2011) and Concawe (2012).

The absorption bands of the resin and its fractions

which are within the range, 490-580 nm also indicate the presence of chromophore in resin and its fractions (Anigbogu, 2011). Consequently, the resin is coloured and may have conjugated double bonds in their aromatic systems (as chromophore that is often common in resin) which are indicative in the resin and in the X and Y fractions.

**Fig. 4: UV-vis spectrum of crude resin****Fig. 5: UV-vis spectrum of fraction X**

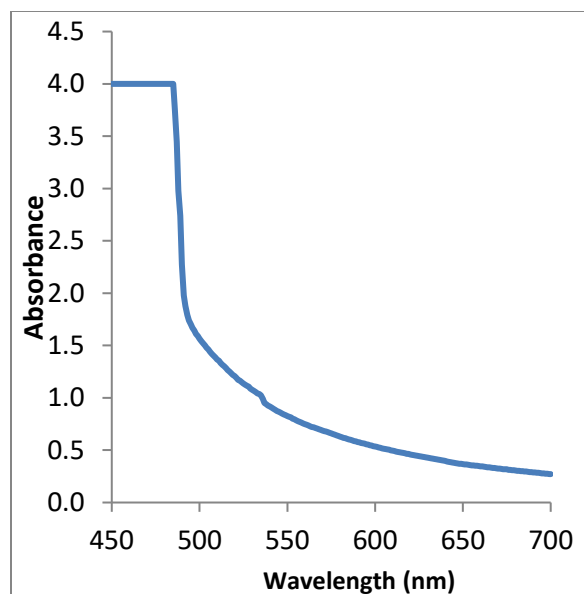


Fig.6: UV-vis spectrum, of fraction Y

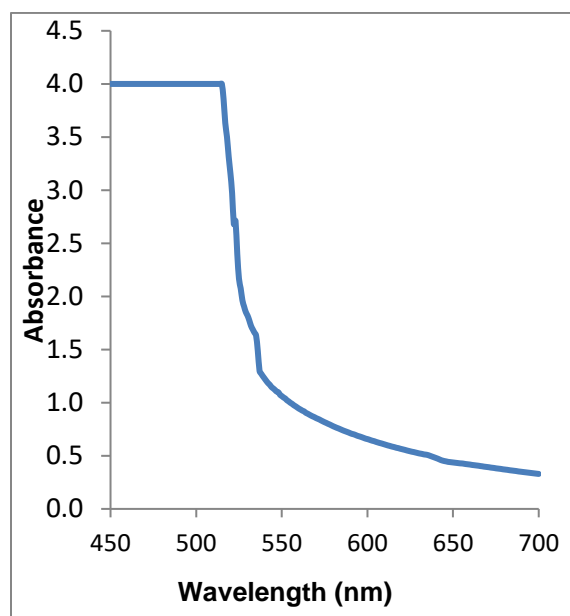


Fig. 7: UV-vis spectrum of fraction Z

Peaks and frequencies of IR absorption deduced from the infrared spectra (spectra shown in Figs. 8 to 14) of crude asphaltene and associated fractions as well as functional group assignments are presented in Table 3.

FTIR spectra of crude asphaltene and associated fractions (Table 3) indicated strong and broadband absorption at 3450 cm^{-1} typical of O-H stretch (H-bonded). The two strong absorptions at 2925 cm^{-1} and 2850 cm^{-1} to assigned to C-H stretch in (CH_2) and (CH) attributed to alkyl groups. The band at 1650 cm^{-1} is attributed to C=O stretch in carboxylic acids, ketone, and amide.

A weak band absorption band at 1500 cm^{-1} which is ascribed to C=C stretch in aromatic compounds was crude asphaltene and fraction B but absent in fraction A while a band at 1425 cm^{-1} which is characteristics of CH_2 (deformation) in ketone was absent in crude asphaltenes but present in fraction A and B, respectively. Also, the spectra revealed a band at 1350 cm^{-1} which might be due to the availability of C-N (stretch) in aromatic amine was absent in crude asphaltene and fraction B but present in fraction A. The band observed in the range $1275 - 1200\text{ cm}^{-1}$ is often assigned to C-O stretch in ester or ether was present in crude asphaltene and fraction A but absent in fraction B. Also a strong band at 1050 cm^{-1} due to S=O stretch in sulfoxides or sulfonic acids was absent in crude asphaltene and in fraction B present in fraction. The absorption band at 750 cm^{-1} is a characteristic of C-H (deformation) in benzene ring with three adjacent hydrogen atoms and was present in both crude asphaltene and fraction A but absent in fraction B. The observed IR bands are in agreement with those reported by Muhammad (2015) and Bakare *et al.* (2015) for asphaltene. The IR spectra characteristics of crude asphaltene showed the absence of some functional groups such as S=O and C-N which were present in one of its fractions. This suggests—the heterogeneity of asphaltene.

Although basic hydrocarbons functional groups were identified in all the compounds, the presence of O-H and C=O groups in all the spectra indicate that asphaltene maybe polar. (Li *et al.*, 2002; Bakare *et al.*, 2015). The IR spectra of crude resin and associated fractions are presented in Fig. 11 to 14 while Table 4 is recorded absorption data deduced from the spectra



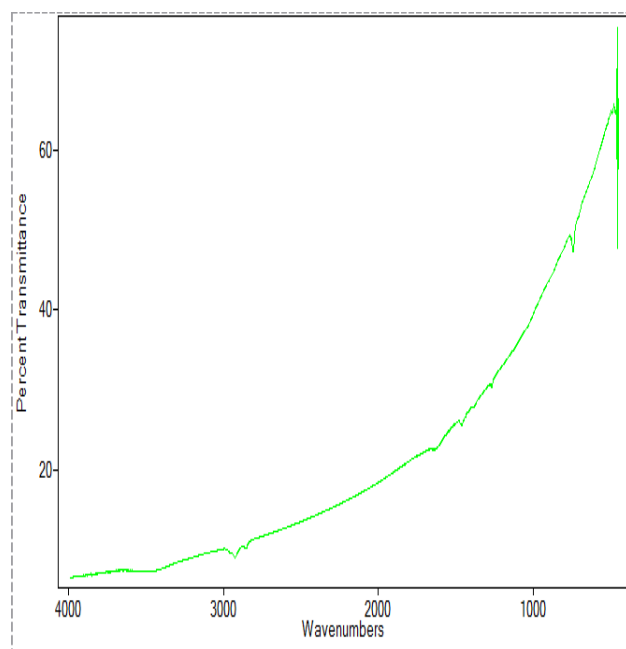
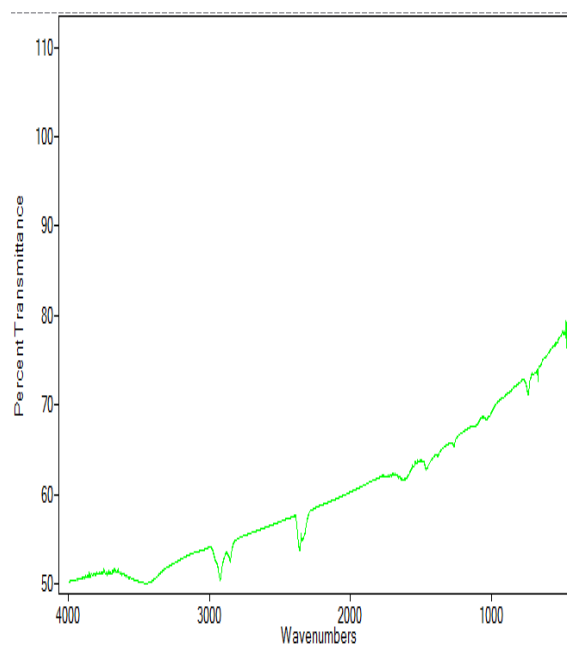
Table 2: UV/Vis spectra of resin and its subfractions

Resin							
Crude Resin		Resin X		Resin Y		Resin Z	
A	λ (nm)	A	λ (nm)	A	λ (nm)	A	λ (nm)
3.40	510	2.00	490	1.80	490	2.70	525
2.00	525	1.00	530	1.10	530	1.60	536
1.30	538	0.70	580	–	–	1.30	542
1.10	540	–	–	–	–	1.20	548
1.00	545	–	–	–	–	–	–

Table 3: Assignment of functional groups to FTIR bands in crude asphaltene and its fractions

Wavenumber (cm ⁻¹)	Crude	Fraction A	Fraction B	Interpretation
3450	+	+	+	O-H stretch (H- bonded)
2925	+	+	+	C-H stretch in alkyl (CH ₂)
2850	+	+	+	C-H stretch in alkyl (CH)
1650	+	+	+	C=O (str.), in carboxylic acids
1500	+	-	+	C=C asymmetric str. in aromatics
1425	-	+	+	CH ₂ (def.), in ketone
1350	-	+	-	C-N (str.), in aromatic amine
1275 – 1200	+	+	-	C-O (str.), in ester/ ether
1050	-	+	-	S=O (str.), in sulfoxides
750	+	+	-	C-H (def.), in ring with three adj. H-atoms

+ = present, - = absent, str. =stretch, def. = deformation, adj. = adjacent


Fig. 8: FTIR spectrum of crude asphaltene

Fig. 9: FTIR spectrum asphaltene fraction A

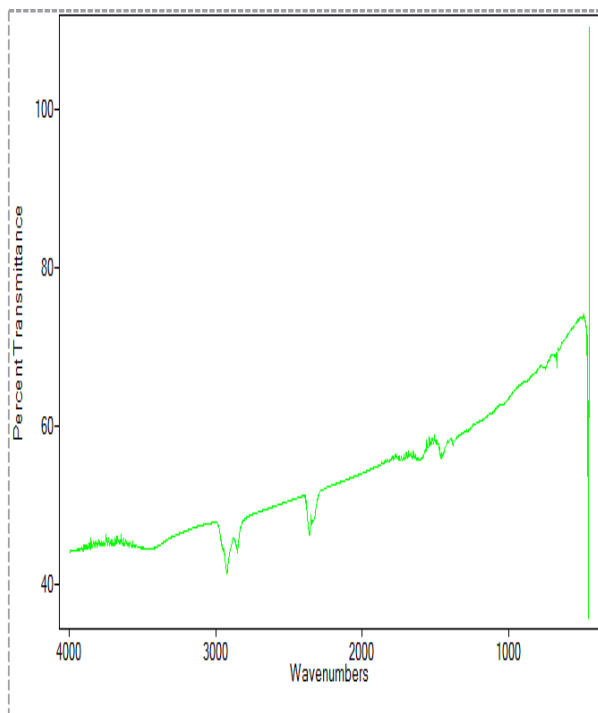



Fig. 10: FTIR spectrum fraction B

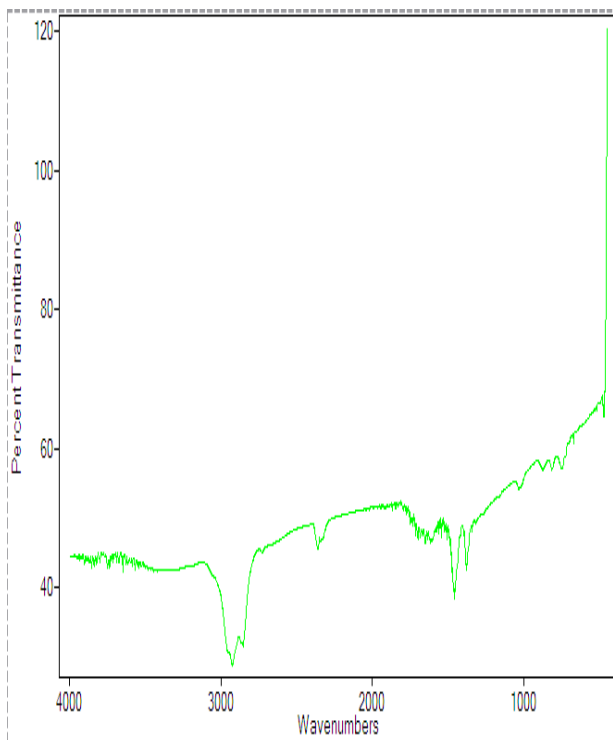


Fig. 12: FTIR spectrum of fraction X

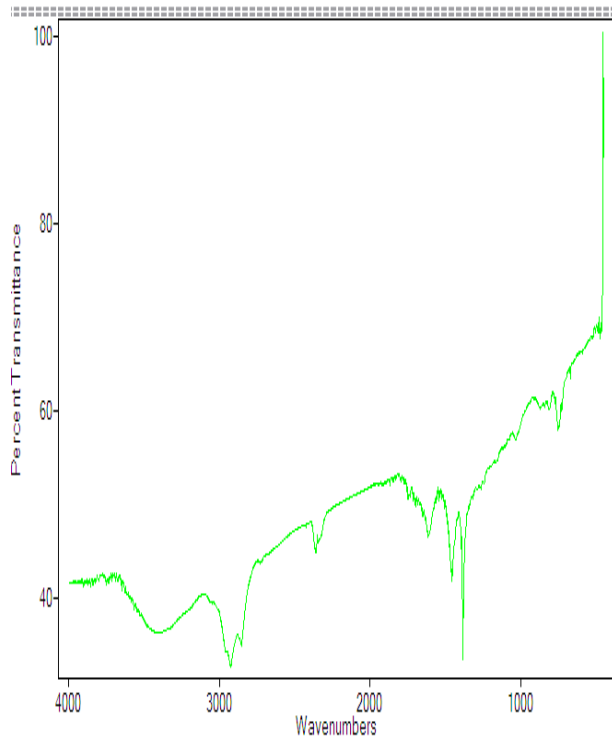


Fig. 11: FTIR spectrum of crude resin

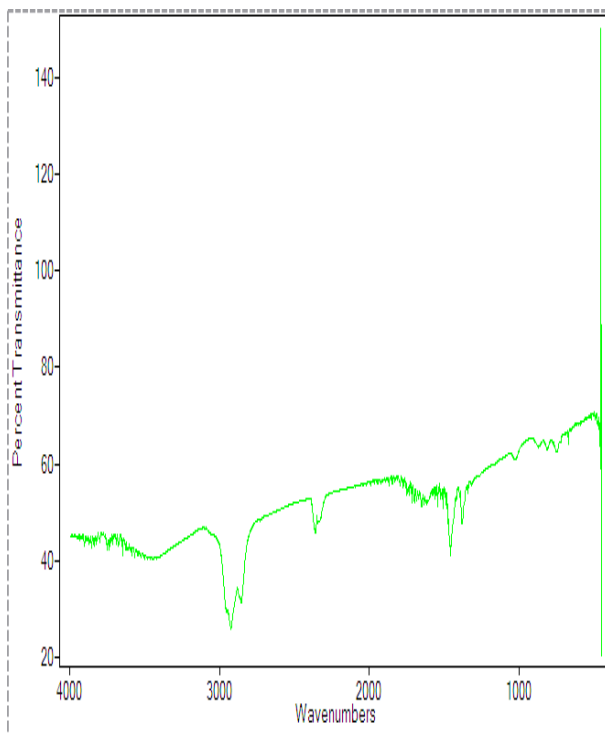


Fig. 13: FTIR spectrum of fraction Y



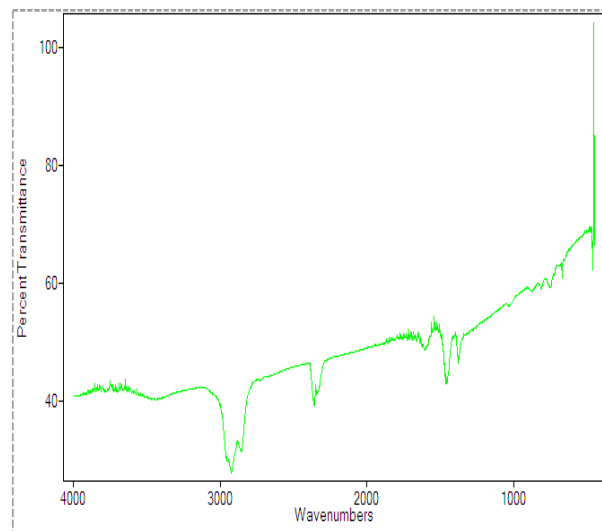


Fig. 14: FTIR Spectrum of fraction Z

From the results recorded in Table 4, it is evident that there is a strong OH stretch vibration on the spectra of the crude resin and its fractions.

The absorption bands at 2925 and 2850 cm^{-1} signify the presence of alkyl C-H stretch in CH_2 and CH_3 respectively. The absorption band at 1650 cm^{-1} may be due to C=O stretch in carboxylic

acids, aldehyde, ketone or amide while a weak band at 1500 cm^{-1} is attributed to C=C asymmetric stretch in aromatic compounds, which are absent in resin fraction Y.

The band at 1425 cm^{-1} corresponds to CH_2 deformation in ketone and is only present in fraction Y. The spectra also showed a strong absorption band at 1350 cm^{-1} attributed to C-N stretch in aromatic amine. The presence of S=O stretch was indicative by the observed absorption band at 1050 cm^{-1} in the crude resin and in fraction Z. However, the absorption band at 750 cm^{-1} signifies C-H deformation in aromatic ring.

According to Mat *et al.* (2006), resin molecules are composed of a highly polar end group, which may include sulphur, oxygen, or nitrogen, and a long non-polar end group. Nitrogen is present in resin in the form of pyrrole and indole group, and sulfur is found in the form of cyclic sulfides (Gafanova, 2000; Mat *et al.*, 2006). There are molecular considerations that lead to emulsion stability, which are the presence of carbonyl groups in the interfacial active components, and the presence of -OH and carbonyl groups. This may help resins molecule to form a mechanical barrier through

Table 4: Assignment of functional groups in crude resin and its fractions

Wave number (cm^{-1})	Crude Resin	Fraction X Resin	Fraction Y Resin	Fraction Z Resin	Interpretation
3450	+	+	+	+	O-H stretch (H-bonded)
2925	+	+	+	+	C-H stretch in alkyl (- CH_2 -)
2850	+	+	+	+	C-H stretch in alkyl (CH_3)
1650	+	+	-	+	C=O stretch in carboxylic acids
1500	+	+	-	+	C=C stretch in aromatic compounds
1425	-	-	+	-	CH_2 (def.) in ketone
1350	+	+	+	+	C-N stretch in aromatic amine
1050	-	+	+	-	S=O stretch in sulfoxide
750	+	+	+	+	C-H (def.) in benzene ring with three adj. hydrogen atoms

hydrogen bonding around the water droplets and prevent coalescence. The open chain carbonyl group promotes emulsion stability through H-bonding (Li *et al.*, 2002).

The observed presence of oxygenated sulphur and carbon accounts for the heterocyclic nature of the resin and in some of its fractions (Bakare *et al.*, 2015).

Our results for the functional groups and assignments for resin and its fractions does not contradict the findings of Bakare *et al.* (2015), Li *et al.* (2002), Gafanova (2000) and Mat *et al.* (2006). However, the IR spectra obtained by Bakare *et al.* (2015) did not show the presence of nitrogenous compound.



4.0 Conclusions

The results showed that crude asphaltene and its fractions absorbed light (in the frequency range of 465 – 640 nm indicating that they are made up of polynuclear aromatic compounds. The results also revealed the presence of alkyl side chains and major oxygenated groups in both crude asphaltenes and its fractions (A and B). It is also deduced from the findings of the study that resins are chemical entity containing aromatic structures with alkyl side chains as well as polar groups.

5.0 References

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