



WWJMRD 2019; 5(4): 81-85
www.wwjmr.com
International Journal
Peer Reviewed Journal
Refereed Journal
Indexed Journal
Impact Factor MJIF: 4.25
E-ISSN: 2454-6615

M. N. Yaro
Department of Chemistry,
Federal University Dutse,
P.M.B. 7156, Dutse, Nigeria

Hamza Badamasi
Department of Chemistry,
Federal University Dutse,
P.M.B. 7156, Dutse, Nigeria

Aminu Dauda
Department of Chemistry,
Federal University Dutse,
P.M.B. 7156, Dutse, Nigeria

Iiyasu A. Bashir
Department of Chemistry,
Federal University Dutse,
P.M.B. 7156, Dutse, Nigeria

Correspondence:
M. N. Yaro
Department of Chemistry,
Federal University Dutse,
P.M.B. 7156, Dutse, Nigeria

Analysis of Asphaltenes and Naphthenic Acids in Nigerian Crude Oil

M. N. Yaro, Hamza Badamasi, Aminu Dauda and Iiyasu A. Bashir

Abstract

The sample (Nigerian crude oil) was collected from Kaduna Refinery and petrochemicals Company (KRPC). The asphaltenes content of the sample was isolated by precipitation and washed using dichloromethene (CH_2Cl_2). The co-precipitated maltenes contained in the asphaltenes were removed by soxhlet extraction using n-hexene (as solvent). The amount of asphaltenes extracted was weighed and analysed using GC-mass. Quantitative analysis of naphthenic acids was carried out by extraction using ethylenediamine solution, followed by petroleum ether. The amount of naphthenic acids extracted was also weighed, characterized using MS coupled with ESI in negative ion mode and identified using MS/MS experiment. The work showed that the amount of asphaltenes (688 mg) in Nigerian crude oil was found to be greater than the amount of naphthenic acids (227 mg); the asphaltenes component of the sample (Nigerian crude oil) was composed of C_4 to C_{10} hydrocarbons and; the naphthenic acids were carboxylic acids.

Keywords: Nigerian crude oil; asphaltenes; naphthenic acids; GC-mass; MS/MS experiment

Introduction

Liquid petroleum is a complex mixture of organic compounds principally hydrocarbons. Of these hydrocarbons, straight chain alkanes predominate. Cycloalkanes (ring or cyclic alkanes), such as cyclopentane, cyclohexane, and their derivatives are present in lesser proportion, and there are even small amounts of aromatic hydrocarbons. Traces of S, N, and O compounds are also presents in petroleum as conterminants. The predominance of alkanes (saturated hydrocarbons) and the absence of alkenes (unsaturated hydrocarbons) in petroleum indicate that fat and proteins were the likely starting points for petroleum formation (Hill and Holman, 1982). The view that petroleum is of biological origin is supported by the presence of organic nitrogen and sulphur compounds, optically active compounds, and complex organic compounds known as porphyrins, which are produced only by plants and animal (Bajah and Godman, 1975). Basically, petroleum mixture comprises of four (4) main classes of compounds, i.e. asphaltenes, resins, aromatic hydrocarbons and saturated hydrocarbons (ARAS) making the acronym SARA, when calls in the reverse order as reported by Nasir, *et al* (2015).

Asphatenes are a component of crude oil which plays a major role on the physical and chemical properties of crude oil. Asphaltenes are the largest molecules found in crude oil with many conjugated aromatic rings usually connected or bonded to a linear or cyclic saturated hydrocarbons and polar functional groups (Mullins, 1990). The presence of hydrocarbons and high viscosity of crude oil is associated with the asphaltenes component in the oil (Nasir, *et al* (2015). Asphaltenes are defined and characterized by a carbon to hydrogen ratio (C/H) close to 1, specific gravity (spg) near to 1, extremely aromatic, friable and infugible solid component of crude oil (Mullins, 1990). The problems associated with presence of asphaltenes in crude oil include: high viscosity; presence of heteroatoms (as contaminant); catalyst deactivation due to coke formation and; formation of tar mats in petroleum reservoirs, which in turn hinders crude oil recovery (Wilhelms and Larter, 1994). A part from these problems asphaltenes are a useful component of crude oil from which asphalt (bitmen) and pitch are obtained, which are used in constructions of roads as

protective coatings for road surfaces and as binding agents for roofing materials (Bajah and Godman, 1975). Asphaltenes also serve as a source from which resins can be obtained and, used in waste water treatment (Nasir, *et al* 2015).

Naphthenic acids as used in petroleum industry, refers collectively to all the carboxylic acids present in crude oil. Naphthenic acids are classified as monocarboxylic acids of general formula, RCOOH, where R represents the naphthenic component consisting of cyclopentane and cyclohexane derivatives (Brient *et al*, 1995). Naphthenic acids are composed predominantly of alkyl substituted cycloaliphatic carboxylic acids, with small amount of cycloaliphatic acids. The cycloaliphatic acids include single and fused multiple cyclopentane and cyclohexane rings. The carboxyl group is usually attached to a side chain rather directly to the ring aromatics, olefinic hydroxyls and dibasic acids are also present as minor components in naphthenic acids (Ikeh *et al*, 2014). The presence of naphthenic acids in crude oil contributes greatly to the acidity of the oil, which is the major source of corrosion in oil pipelines and distillation units in oil refineries. (Speight *et al*, 1999). Consequently, crude oils with high naphthenic acids concentrations are considered to be of poor quality and marketed at a lower price (Ikeh *et al*, 2014). It is desirable to determine the ring-type distribution and carbon number distribution of each ring type because the corrosivity of naphthenic acids is dependent on their sizes and structures (Messer *et al*, 2004). Naphthenic acids are very soluble in water if during processes in petroleum industries water contamination occurs, the naphthenic acids content in the affected (adulterated) water are toxic to human and, the oxidized fractions of the acids are also known to be toxic to mussels and fishes as reported by Herman *et al* (1994). On the other hand, naphthenic acids are important in many applications such as formation of oil-soluble metal soap, for driers and other catalysts, wood preservatives, tire code adhesion promoters and amine derivatives for inhibitors (Groove, 1987).

In order to minimize the problem of corrosion in oil pipe lines and distillation units in oil refineries, high viscosity of petroleum products, catalyst deactivation and presence of heteroatoms, (as contaminants), as well, as to improve the recovery of crude oil from petroleum reservoirs, this work report studies on the qualitative determination of asphaltenes (a component of crude oil which hinders crude oil recovery from petroleum reservoirs) and naphthenic acids component of crude oil which causes corrosion in oil pipelines and distillation units in oil refineries. The work also reports studies on the characterization of asphaltenes and identification of naphthenic acids in Nigerian crude oil.

Materials and Methods

Collection of Experimental Sample

The sample (Nigerian crude oil) was collected from Kaduna Refinery and Petrochemicals Company (KRPC), Kaduna. The crude oil was supplied to KRPC from Oziengbe South field located in Niger Delta Sedimentary Province, Onshore, Warri, Delta State- Nigeria.

Isolation and Purification of Asphaltenes from the Sample

The isolation and purification of the asphaltenes in the sample was carried out in light of the procedure described

by Nasir *et al* (2015) with few modifications. In this procedure, the asphaltenes (insoluble component) was isolated in pure form from the associated maltenes (soluble component) in the sample through the following steps:

Step 1: Initial Precipitation of Asphaltenes

A volume (12.50 cm³) equivalent to 10.00 g of the sample was accurately measured and placed in 250 ml conical flask containing 200.00 cm³ n-hexane. The mixture was stirred for two hours and, allowed to equilibrate for 24 hours at room temperature. The mixture was centrifuged at 3,500 rpm using magnetic stirrer for 15 minutes. The n-hexane soluble component (maltenes) was filtered as filtrate while the insoluble component (asphaltenes) was collected as residue.

Step 2: Reprecipitation of Asphaltene

In order to boost the recovery of asphaltene from the sample, the residue collected in step 1 above was carefully transferred into a 250 ml conical flask containing excess n-hexane (400 cm³). The mixture was gently stirred for 2 hours and kept at room temperature for 24 hours to ensure equilibration of component and homogeneity of the mixture. The mixture was centrifuged at the rate of 3,500 rpm for 15 minutes after which the asphaltenes were recovered as from the mixture by filtration.

Step 3: Washing of Recovered Asphaltenes

The Asphaltenes recovered in step 2 above were carefully transferred into pre-weighted vial containing small amount of dichloromethane (CH₂Cl₂), but greater in quantity than the amount of asphaltenes recovered. The mixture of the recovered asphaltenes and CH₂Cl₂ was left for 30 minutes after which the excess solvent (excess CH₂Cl₂) was removed using stream of nitrogen gas (N₂) from nitrogen cylinder. The drained asphaltenes (washed asphaltenes) was kept in a fume cupboard at an ambient temperature for complete dryness to a constant weight.

Step 4: Removal of Co-precipitated Maltenes by Soxhlet Extraction

The asphaltenes collected in step 3 was subjected to soxhlet extraction using n-hexane as extraction solvent at 80°C for 72 hours. The asphaltenes (n-hexane insoluble) were recovered from the extracting solvent by rotary evaporation. The recovered asphaltenes were concentrated to a constant weight at 37°C in fume cupboard and weighed.

GC-Mass Analysis of Asphaltenes

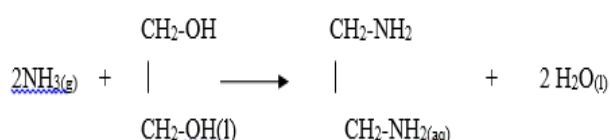
In order to characterize the asphaltenes recovered, GC-Mass spectrophotometer (6890 N network GC-system) coupled with the 5973 network mass selective system was used, the temperature range of the column was 150-500°C; the auxiliary temperature of the column (i.e. the maximum temperature of the column set for the analysis) was 320°C. The column was capillary in shape with an internal diameter of 0.25 mm; the length of the column was 30 cm; the maximum load capacity of the column was 10 µl; the pressure of the column was 10⁻⁷ mm Hg; the carrier gas was helium and; the concentration of the sample solution was 1.00 mg of asphaltenes in 5.00 cm³ of the n-hexane. The analysis was carried out according to the procedure described by Yaro (2015) with few adjustments.

Quantitative Analysis of Naphthenic Acids

In order to quantitatively determine the naphthenic acids in the sample, ethylenediamine solution and petroleum ether were used as extracting solvents.

Preparation of ethylenediamine solution

The ethylenediamine solution (also known as ammoniated ethyleneglycol) used for the determination was prepared by bubbling excess ammonia gas (NH_3) through ethyleneglycol in a 3 necked round bottomed flask at constant flow rate. The round bottomed flask was maintained at 0°C in an ice bath for 2 hours for the solution to be saturated (Ikeh *et al.*, 2014). The equation below illustrates the reaction for the formation of ethylenediamine.



Determination of Naphthenic Acids

The determination of naphthenic acids in the sample was carried out in light of the procedures described by Ikeh *et al.* (2014) with few modifications. The process was achieved through the following steps:

Step 1: Extraction of Naphthenic Acids Using Ethylenediamine

A volume (20.00 cm^3) of ethylenediamine was added into a 100 ml beaker containing 12.50 cm^3 (equivalent to 10.00 g) of crude oil. The beaker was maintained at 0°C in an ice bath for 1 hour. The solution was gently stirred and subsequently transferred into a round bottomed flask and heated at 65°C for 1 hr. The heated solution mixture was accurately transferred into a separating funnel and kept for 30 minutes for cooling and equilibration. On cooling, 2 liquid phases (layers) were formed: the top phase (oil layer) and the bottom phase (ethylenediamine layer, which contained the extracted naphthenic acids). The layers were quickly separated because if the layers are left for long period of time in the separating funnel, they may recombine. The top layer was discarded and the bottom layer (also known as ammoniated naphthenic acids salt layer) was subsequently transferred into a clean round bottomed flask and heated at 135°C using an oil bath for 2 hrs in order to remove all the NH_3 , which relatively has low boiling point compared to naphthenic acids. On complete removal of NH_3 , the solution turned yellow and the heating was stopped. The yellow solution (ethylenediamine containing undecomposed naphthenic acids) was then transferred into a separating funnel while hot and, left for 30 minutes at an ambient temperature for cooling.

Step: 2 Isolation of Naphthenic Acids from Ethylenediamine Using Petroleum Ether

To the cooled yellow solution obtained in step 1 above, 20.00 cm^3 of petroleum ether was added and, the naphthenic acids content of the solution were extracted. The suspension formed was left for 30 minutes, where 2 layers were formed. The bottom layer (ethylenediamine layer) was discarded, leaving behind the top layer (petroleum ether containing naphthenic acids) in the funnel.

The top layer was washed with the distilled water, where the residual ethylenediamine was removed. The washed top layer of petroleum ether containing naphthenic acids was poured into a beaker and heated at 40°C , where the petroleum ether was removed, leaving behind the naphthenic acids in the beaker as dried extract (Wing *et al.*, 2006). The weight of the dried naphthenic acids obtained was measured and recorded.

Mass Spectroplometry (MS) Anaysis of Nephthenic Acids.

In order to characterized and confirm the types of naphthenic acids isolated from the sample (Nigerian Crude Oil), MS and MS/MS experiments were respectively conducted using thermo Finnigan Mass. In these experiments, a spectrometer controlled by Tuneplus software (excalibur) coupled with the electrospray ionization (ESI) source in negative ion mode was used. The concentration of the sample solution was 2.00 mg of the extracted naphthenic acids in 4.00 cm^3 of acetonitrile.

Characterization of Naphthenic Acids Using MS Couple with ESI Source in Negative ion Mode

For the characterization of the extracted naphthenic acids, MS coupled with ESI source negative ion mode was used. The mass scan ranges used were 50-125 m/z for standard compound (benzoic acid) and 250-500 m/z for the extracted naphthenic acids; the quantity of sample solution injected was 6 μl ; the sheath gas was maintained at 60psi, the volatilization temperature was 220°C ; the capillary voltage was 7 v; the spray voltage was 3.15 kv and the mass spectra were based on 3 microscan. The experiment was first performed on the precursor (benzoic acid), which was used as a standard and then on naphthenic acids. The analysis of benzoic acids was done in order to understand the characteristics fragmentation patterns of the naphthenic acids reference to those of the precursor. The experiment was carried out according to the procedure described by Ikeh *et al.* (2014) with few adjustments.

Confirmation of Naphthenic Type Using MS/MS Experiment

In this experiment, the determination of the molecular distribution, as well as the confirmation of the naphthenic acids extracted were carried out. For all the ions detected, the collision activated dissociation (CAD) energy was set in such a way that the MS/MS scan of the precursor and fragment ions could be detected. CAD energy was between 20-40%. The optimum peak isolation width was 1 Dalton (i.e. 1 Da), whereas a wider width more than 1 Da resulted in ions. The activation, Q was 0.25 and the activation time (Qt) was 30 μsec . The experiment was performed on both the standard compound (benzoic acid) and the extracted naphthenic acids, so as to understand the characteristics fragmentation patterns of the extracted naphthenic acids reference to the fragmentation patterns of the precursor (benzoic acid). The experiment was carried out according to the procedure described by Ikeh *et al.* (2014) with few adjustments.

Results and Discussion

Results

The amount of asphaltenes and naphthenic acids extracted from the sample are shown in Table 1. Table 2 shows the mass losses detected due to fragmentation of extracted

naphthenic acids in the sample. Fig 1 shows the chromatograph for the analysis of asphaltenes using GC-mass spectrophotometry. Fig 2 and 3 show the respective fragmentation patterns of the precursor (benzoic acid) and extracted naphthenic acids using MS/MS analysis.

Table 1: Amount of Asphaltenes and Naphthenic Acids Extracted from 10.00g of Nigerian Crude Oil.

Component	Quantity (mg)
Asphaltenes	688
Naphthenic Acids	227

Table 2: Mass loss Detected from Naphthenic Acids using ms/ms

Mass Loss (Da)	Corrospoding Fragment Components
18	M- H ₂ O
28	M- CO
44	M- CO ₂

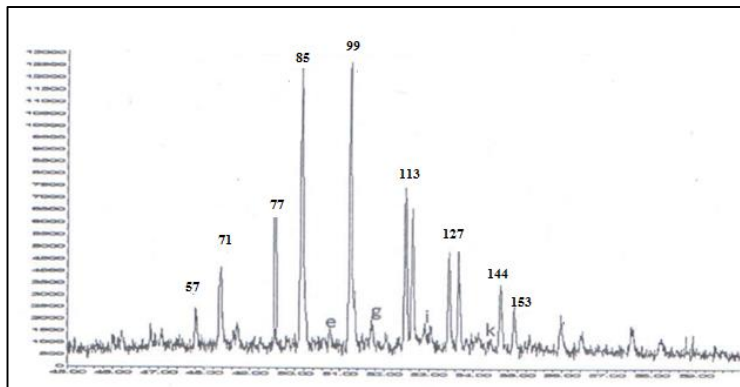


Fig.1: GC-Mass of Extracted Asphaltenes

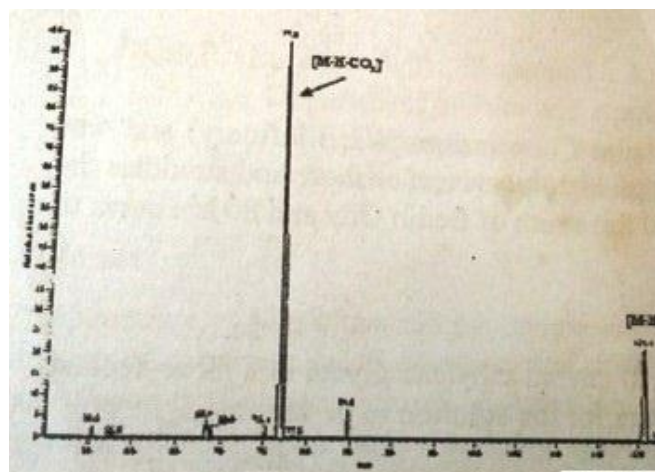


Fig.2: MS/MS Analysis of precursor in ESI Negative Ion Mode with the Mass range 50-125

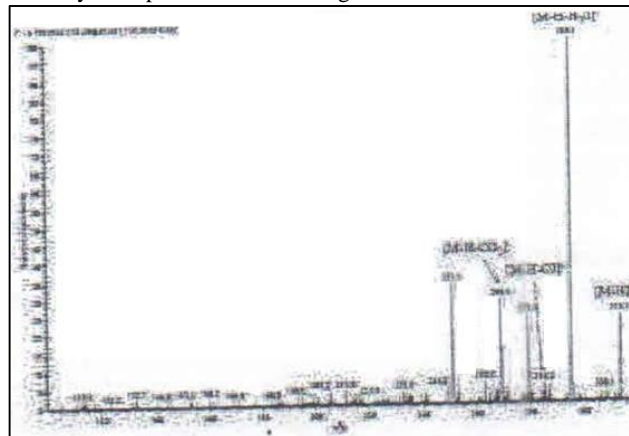


Fig.3: MS/MS Analysis of Extracted Naphthenic Acids in ESI Negative Ion Mode with Mass Range 100-305

Discussion

The results of the quantitative analysis of asphaltenes and naphthenic acids are shown in Table 1. The results (Table 1) showed that the amount of asphaltenes is more than 3 times the amount of naphthenic acids in Nigerian Crude Oil. This is not surprising because the majority of naphthenic acids found in crude oils are components of asphaltenes (Hunt, 1979). The result of GC-Mass analysis of asphaltenes is depicted on Fig 1. The chromatograph (Fig. 1) showed fragmentation ion peaks at 57, 71, 85, 99, 113, 127 and 144. These peaks corresponded to the molecular weight C_4H_9 , C_5H_{11} , $C_{12}H_{13}$, $C_{13}H_{17}$, C_9H_{19} and $C_{10}H_{22}$, respectively. This clearly indicated the presence of a homologous series of paraffinic side chains in the sample. The Figure (Fig. 1) also showed fragmentation ion peaks at 77, 127, and 153, which corresponded to the molecular weights of substituted benzene, naphthalene and anthracene, respectively. These peaks are clear indications of the presence of aromatic rings in the extract. This findings is in accordance with the findings of Ikeh *et al* (2014).

Fig. 2 depicted the fragmentation pattern of the precursor (benzoic acid) analysed using mass spectrophotometry coupled with the ESI source in negative mode. The peaks showed that there was mass loss each at 18, 28, and 44, which corresponded to the masses of H_2O , CO and CO_2 respectively. (Rudzinski *et al*, 2002). The figure (Fig 2) also showed a sharp and strong peak at 77, which corresponds to the mass of C_6H_5 . This also indicated the presence of benzene (Ikeh *et al*, 2014).

Fig. 3 showed the fragmentation pattern of the extracted naphthenic acids at between 100-305 m/z for the ESI (negative ion mode) experiment conducted. At around 300m/z, a group of 3 strong peaks were observed at 18, 28 and 44, which showed that there were mass losses of 18Da, 28Da, and 44 Da due to the mass losses of H_2O (M-18), CO (M-28) and CO_2 (M-44), respectively. This clearly indicated the presence of carboxylic acids functional group in the sample. This findings is in accordance with the frontings of Rudzinski *et al* (2002); Ikeh *et al* (2014).

Conclusion

From the quantities and chemical natures of the asphaltenes and naphthenic acids determined, the presence work could serve as momental legacy for taking appropriate experimental measures towards minimizing the problems associated with the presence of asphaltenes and naphthenic acids in crude oils, as well, as improving the quality of the oils in terms of fuel value and environmental protection.

References

- Bajah, S. T. and Godman, A. (1975): Chemistry: A new Certificate Approach, (New edition), Longman Publishers, Ibadan-Nigeria. Pp 217-218.
- Brient, J. Wessner, P., Doyle, M., Krosetwitz, J. and Seidel, A. (1995): Encyclopedia of Chemical Technology, John Wiley and Sons Publishing Company, New York. Pp 1017-1029.
- Grove, S. (1987): Copper Naphthenate: An alternative wood preservative. Presented at the 41st Annual Meeting of the Forest Product Research Society. Louisville, Kentucky.
- Herman, D. C., Fedorak, P. M., Mackinno, M. D. and Costerton, J. W. (1994): Biodegradation of Naphthenic Acids by Microbial Populations Indigenous to Oil Sands Tailings. *Canadian Journal of Microbiology*; 40: 467-477.
- Hill, G.C. and Holman, J. S. (1982): Chemistry in Context (Second edition), the English Language Books Society (ESBS) and Nelson Publishing. Pp 290-302)
- Hunt, J. M. (1979): Petroleum Geochemistry and Geology, Freedman, W. tt. Company, San Francisco, USA. Pp 28-65.
- Ikeh, P. O., Zuru, A. A; Rahman, U. A., Muhammad, S. and Abubakar, L. (2014): Determination of Naphthenic Acids from Nigerian Crude Oil Using MS/MS Spectroscopy. Proceedings of the 37th International Conference, Workshops and Exhibition of Chemical Society of Nigeria (CSN), Held between 7th -12th September at Ibom Hall, IBB Way Uyo, Akwa Ibom State - Nigeria. Volume 2: 542- 546
- Messer, B., Terlenton, B. Beaton, M. and Philips, T. (2004): New theory for Naphthenic Acids Corrosivity of Ethabasca Oil Sands Crudes: Corrosion. No.04634.
 - Mullins, O. C. (1990): Asphaltenes in Crude Oil; absorbers or Scatters in the near infrared region, *Analytical Chemistry*; 62: 508-514.
- Nasir, S. Mansir, N., Sani, A. A. and Augie, N. M. (2015): Investigating Asphaltenes Composition in Crude Oil Samples Using Iatroscan TLC-FID Method. *Chemsearch Journal*; 6(2): 62-69.
- Rudzinski, W. E; Oehlers, L., Zhag, Y. and Najera, B. (2002): Spectroscopic Characterization of Naphthenic Acids. *Journal of Energy and Fuels*; 807(6): 241-251
- Speight, J. G. (1999): The Chemistry and Technology of Petroleum. New York, Merce, Dekker Publishers. Pp 215-216.
- Wang, Y., Chu, Z., Qiu, B., Liu, C. and Zheng, Y. (2006): Extraction of Naphthenic Acids Using Ethylene Glycol, *Fuel and Energy*; 85 (17-18): jhgfdsa cbn2489-2493.
- Wilhelms, A. and Larter, S. R. (1994): Origin of Tar Mats in Petroleum Reservoirs. Part I: Introduction and Case Studies. *Marine Petroleum Geology*; 11: 418-441
- Yaro, M. N. (2015): Extraction and Characterization of Heavier Saturated Hydrocarbons from lanana leaves as alternative fuels for domestic and industrial uses. *Techno science Africana journal (TSAJ)*; 11(2):158-168.