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CATALYTIC DECOMPOSITION OF *CASSIA TORA* LEAVES AND ANALYSIS OF ESSENTIAL AROMATIC OILS

Yaro, M. N.

Department of Chemistry,
Federal University, P.M.B 71
Dutse, Jigawa – Nigeria

Abstract

Ground and sieved sample of cassia tora leaves was subjected to anaerobic catalytic decomposition at 33^{O}C for 20 consecutive days. The liquid degradation product (bioliquid) formed was extracted from the supernatant liquid (decomposed slurry) by solvent extraction. The deasphaltened oils content of the bioliquid was isolated from the asphaltenes by precipitation. The essential aromatic oils were separated from the deasphaltened oils by column chromatography using organic solvents of different compositions. The fractions (essential aromatic oils) collected were chemically treated and dried. The dried fractions were further subjected to fractional distillation, where the major constituents of the oils were obtained at different temperatures. The fractionally distilled constituents were finally subjected to gc-mass spectrophotometry analysis for molecular characterization and proper classification. The work showed that bioliquid can be generated and extracted from cassia tora leaves; the deasphaltened oils content of the bioliquid (78.28 g) was significantly greater than the asphaltenes (69.60g); the essential aromatic oils content of the deasphltened oils were in the order: light oil (0.345 g) > middle oil (0.251 g) < heavy oil + green oil (0.424 g). The work also showed that the major constituents of the: light oil (monoaromatics) were benzene, toluence and xylene; middle oil (diaromatics) were methylphenols and naphthalene; heavy oil (polyaromatics) were anthracene and naphthalene and; green oil (also polyaromatics) were anthracenes.

Keywords: Cassia tora leaves; anaerobic catalytic decomposition; bioliquid; deasphaltened oils; essential aromatic oils.

Introduction

Cassia tora known as "*Tafasa*" in Hausa is an under-shrub plant with short oval green leaves and yellow flowers, which produces long but thin pods containing many seeds. *Cassia tora* is a common weed of Northern Nigeria, which is mostly, disperses by man, animals, water and wind. The leaves of *cassia tora* are used in making soup and as mild laxative. Additionally, the leaves of *cassia tora* can be cooked and mix with ground nut cake and, consumed mostly by the rural populace of Northern Nigeria and Niger Republic (Especially, the poor ones). The leaves can also be used as supplement to *Moringa pterygosperma* leaves in making food known as "*Dambu*" in Hausa when mixed with grits (Yaro, 2009).

Anaerobic catalytic decomposition of the lignocellulosic component of biomass (*cassia tora* inclusive) leads to formation of biogas and bioliquid from which deasphaltened oils and asphaltenes are extracted (Ekwenchi and Yaro, 2012). The proportion of Deasphaltened oils in the bioliquid always exceeds that of asphaltenes (Oladapo, 1988). Deasphaltened oils are a component of bioliquid, which is composed of large amount saturates, few aromatics and very small quantities of resins and organic polars (Ekwenchi *et al,* 2013). The saturates contents of Deasphaltened oils always exceeds the aromatic oils. Both the maltenes (deasphaltened oils) and asphaltenes contained about half of the total nitrogen and sulphur in the saturates, most of which are in the form of heteromolecules, which are condensed into both aromatic and napthenic rings(Oladapo, 1988). Aromatics are a special class of cyclic compounds based on benzene (C_6H_6), 6 carbon ring compound from which all other aromatic compounds are derived (Ababio, 1985). Aromatic hydrocarbons contains delocalized π electrons around a ring of carbon atoms. As a group, they are also called arenes, the most famous arene is benzene consisting of only one ring and more complicated arenes are made when two or more rings are joined together such as in naphthalene and anthracene molecules (Mattewes, 1996). Based on number of ring per molecule, aromatic compounds can be monoaromatics, diaromatics or polyaromatic and, in any of these circumstances, the number of π electron must be equal to 4n+2, where n is the number of ring (Masa'udu, 1987). In general, aromatic compounds are those possessing the ring structure of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior (Murray,1979). Aromatic hydrocarbons were so named because many of them have strong aromas (Bajah and Godman, 1975).

The oils fractionated from the aromatics components of deasphaltened oils are regarded as the essential aromatic oils, which are classified into light oil (benzole), middle oil (carbolic), heavy oil (creosote) and green oil (anthracene) based on the number of rings and the types of functional groups they possessed. This classification is in accordance with the classification of fractionally distilled oils obtained from coal tar made by Murry (1979).

The applications of the essential aromatic oils include the following: aromatic nitro compounds are of considerable importance in the manufacture of arylamines, the most important of which is phenylamine known as aniline ($C_6H_5NH_3$); formation of explosives such as methyl 2,4,6,-trinitrobenzene known as 2,4,6-trinitrotoluene which is represented as TNT; production of diazonium salts, which themselves have numerous synthetic applications, example, in the manufacture of azo-dyes and phenols and; phenylamine is used in the manufacture of anti oxidants, which is used as vulcanizing accelerator in the rubber industry, in the synthesis of drugs and in the preparation of diazonium salts (Murry, 1979). The action of chemicals such as H_2SO_4, HNO_3, halogens and oxidizing agents on the distilled oils obtained from coal tar (which are mainly aromatics of different kinds) produces large number of derivatives, which are used in the manufacture of dyes, drugs, insecticides, plastics and other organic chemicals (Atkinson,1979).

In order to minimize the cost of production of the aforementioned products, which are synthesize from fractionally distilled oils obtained from coal tar and, many other products from other different sources, which are relatively very expensive and hard to get when compared with the ones generated

from the available local resources in our immediate environment (*Cassia tora*, inclusive), this work reports studies on: the use of the leaves of *cassia tora* as alterative substrate from which deasphaltened oils can be obtained; the separation of essential aromatic oils (monoaromatics referred to as light oil, diarommatic referred to as middle oil and polyaromatics referred to as heavy oil and green oil) from the aromatic component of the deasphaltened oils obtained from *cassia tora* and, the fractional distillation of the essential aromatic oils. The work also, report studies on the molecular characterization of the fractionally distilled oils collected from *cassia tora* for proper classification and applications.

Experimental

The materials used for the research were *cassia tora* leaves, distilled water and yeast. The *cassia tora* leaves were fresh and mature at the time of collection. The leaves were dried under shade (indoor) for 14 days after which they were ground and sieved to a particle size of less than 250 μm.

Catalytic Decomposition of *Cassia tora* Leaves.

For the decomposition of *cassia tora* leaves, 150.0 g of the processed sample of the leaves was dissolved in 1dm^3 of distilled water containing 6.75 g yeast. The mixture was subjected to anaerobic catalytic decomposition for 20 consecutive days at 33^0 C in a reactor. The supernatant liquid generated was decanted from the sludge (digested *cassia tora leaves*) according to the method described by Ekwenchi and Yarfo (2012).

Extraction of Liquid Degradation Product (Bioliquid) and Isolation of Deasphaltened Oils.

The supernatant liquid obtained was subjected to soxhlet extraction using absolute methanol at 60^{o}C for 72 hours, where the liquid degradation product was extracted. The recovery of the extract (bioliquid) from the extracting solvent (absolute methanol) was carried out by rotary evaporation. The bioliquid was concentrated to a constant weight on hot plate at 37^o C in a fume cupboard. The deasphaltened oils were isolated from the bioliquid by precipitation from 5.0 g of the concentrated extract in a solution mixture of 5 cm^3 methanol and 200 cm^3 hexane which was kept in a refrigerator for 24 hours, where the deasphaltened oils being the soluble component of the bioliquid retained in the matrix of the solution mixture while the asphaltenes being the insoluble component settled down and removed from the solution mixture. The deasphaltened oils was finally isolated from the solution mixture by air-drying in fume cupboard (Ekwenchi *et al*, 2013).

Separation of Essential Aromatic Oils from Deasphaltened Oils by column Chromatography

In order to separate the essential aromatic oils from the deasphaltened oils, a glass column of 60 cm length and 0.85 cm internal diameter with bed volume of 34.08 cm^3 was used. The column was carefully packed with a silica gel of particles size 0.063-0.074 nm (activated at 100^{O}C overnight in an oven) followed by alumina of particle size 3.74 μm in the ration 1:2 (silica gel to alumina). Silica gel was first put in the column because it is relatively denser than alumina in order to allow for uniform

sample size densities and prevent void volumes. The sample to packing material (sorbent) ratio was 1:70 as adopted by Mailabari (1983).The maximum load capacity of the column was72.5 mg. Before the separation commences, the packed column was first washed with 40 cm^3 hexane. This was done in order to eliminate air from the column (Yaro,2011). 2.00 g of the concentrated bioliquid was dissolved in 10.00 cm^3 n-hezene and subsequently poured in the packed column. The monoaromatic component known as light oil was eluted using 40 cm^3 of 5% benzene in hexane; the diaromatic component known as middle oil was eluted using 40 cm^3 of 15% of benzene in hexane and the polyaromatics component consisting of heavy oil and green oil was eluted using 40 cm^3 of a solution mixture of 20 cm^3 benzene, 20 cm^3 diethylether and 60 cm^3 methanol as adopted by Mailabari (1983).

Treatment of the Fractionated Oils

For the treatment of light oil, the fraction was placed in separating funnel and treated in stages according to the method described by Murry (1979) with few adjustments. The method is as follows:

Step 1: The fraction was shaken with cold dilute H_2SO_4, where basic compounds such as pyridine and phenylamine were removed.

Step 2: Water was added to the treated fraction in the funnel, where excess could dilute acid used in step 1 was washed (removed) from the fraction.

Step 3: After washing the treated fraction with water, dilute NaOH was added in order to remove the acid compounds formed in the fraction due to addition of cold dilute H_2SO_4 in the first step (step 1).

Step 4: Water was finally added to the treated fraction, where excess alkali (dilute NaOH) added in step 3 was washed out of the fraction and, leaving behind other important monoaromatics compounds (Oils) such as benzene, toluene and xylene in the fraction. The components (Oils) obtained were dried and fractionally distilled at 90^o C-170^o C.

In order to obtain the crystalline components of the middle oil (naphthalene), the fraction was first cooled and then separated by centrifuging. The phenols were then separated from the centrifuged fraction by treating with warm aqueous NaOH, which were further separated by fractional distillation at 170^oC – 230^oC according to the method described by Murry (1979), with few adjustments in the quality of the sample, volume of aqueous NaOH used and fractioning temperature used.

The green oil, which mainly consists of anthracene was separated from the heavy oil, consisting mainly a mixture of phenol and methylphanols (cresols) and naphthalene by shaking the fraction (Polyaromatics Oils) with naptha. The separated components (green oil and heavy oil) were each dried and subsequently fractionated by fractional distillation. The heavy oil was fractionally distilled at 230^o C-270^o C while the green oil was distilled at a temperature range of 270^o C -400^o C according to the method described by Murry (1979) with few adjustments in the quality of this sample and the respective fractionating temperatures used.

Characterization of Aromatics Oils by GC-Mass Spectrophotometry Analysis

The fractionally distilled components of the aromatic oils (light oil, middle oil, heavy oil and green oil) were characterized by gc-mass spectrophotometry analysis. A gc-mass spectrometer (6890N network gc-system coupled with 5973 network mass selective system was used. The column of the gas- chromatograph used was capillary in shape, 30 cm long and 0.25 mm internal diameter with maximum capacity of 10µL. The carrier gas used was helium. The sample was first dissolved in n-hexane and, 6µL was injected into the gas- chromatograph at an injection temperature of 200^{o}C for components separation by volatilization. The volatilized components were after separation of the carrier gas, passed into the ionization chamber of the mass spectrometer, where they were bombarded with high energy electrons and transformed into ions. The ions formed were then accelerated in an electric field, where they were separated according to their mass to charge ratio (m/e) by a magnetic field. The relative abundance of the ions was counted by a detector. The output of the detector was amplified and recorded by a chart recorder. The mass profile of the compound detected was shown as a plot of relative abundance versus m/e and printed out (Harrison and de Mora, 1996).

Results and Discussion

Results

The results of all the analyses carried out in this work are shown in Tables 1-3 and depicted on figures 1,2 and 3. Table 1 shows the amount of bioliquid extracted from 150g/dm^3 slurry of *cassia tora* leaves and its components. Table 2 shows the fractions of essential aromatic oils fractionated from deasphaltened oils content of the bioliquid collected. Table 3 gives the major constituents of the essential aromatic oils and the respective temperatures ranges within which the constituents were fractionally distilled. Figure 1, 2, and 3 depicted the mars spectra of monoaromatics (light oil), diaromatics (middle oil) and polyaromatics (heavy oil + green oil), respectively.

Table 1: Bioliquid Content of 150g/dm^3 Slurry of ***Cassia tora*** Leaves and its Components.

Component	Quantity (g)
Bioliquid content of the slurry	148.88
Deasphaltened oils content of the bioliquid	79.28
Asphaltenes content of the bioliquid	69.60

Table 2: Analysis of Essential Oils (Aromaric Oils) Contents of Deasphaltened Oils by Column Chromatography

Fraction (Essential aromatic oils)	Quantity (g)
Light oil (monoaromatics)	
Middle oil (diaromatics)	0.345
Heavy oil + green oil (polyaromatics)	0.251
	0.424

Table 3: Analysis of the Constituents of Fractionated Essential Oils by fractional Distillation.

Components	**Temperature Range (°C)**	**Major Constituents**
Llight oil (monoaromatics)	70-170	Benzene, Pyridine, Toluene and Xylene.
Middle oil (monoaromatics)	170-230	Methylphenols and Naphthalene
Heavy oil polyaromatics)	230-270	Anthracene and Naphthalene.
Green oil polyaromatics)	270-400	Anthracene.

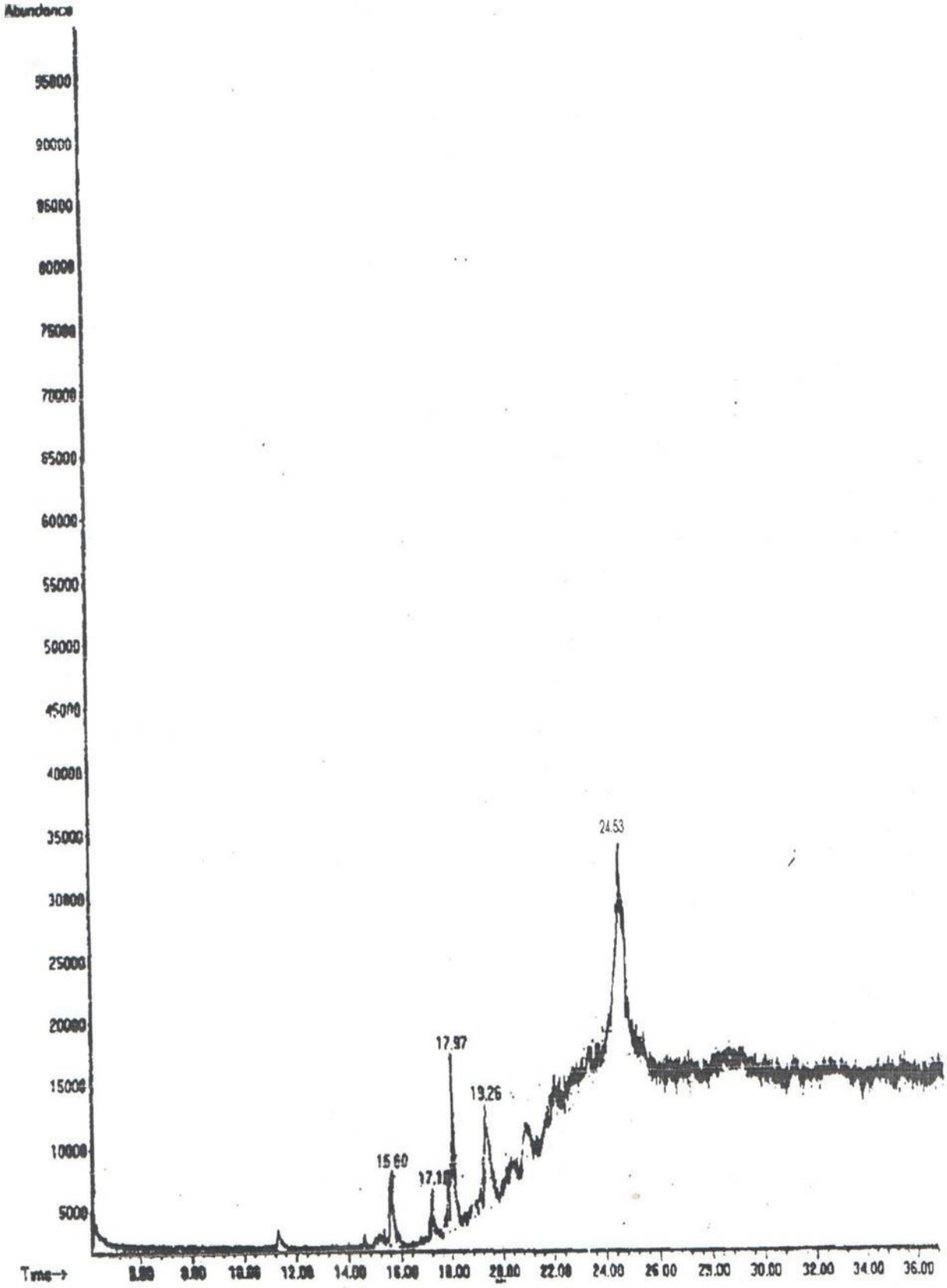

Fig. 1: GC -Mass Profile of Essential Monoaromatic Oils in the Deasphaltened Oils

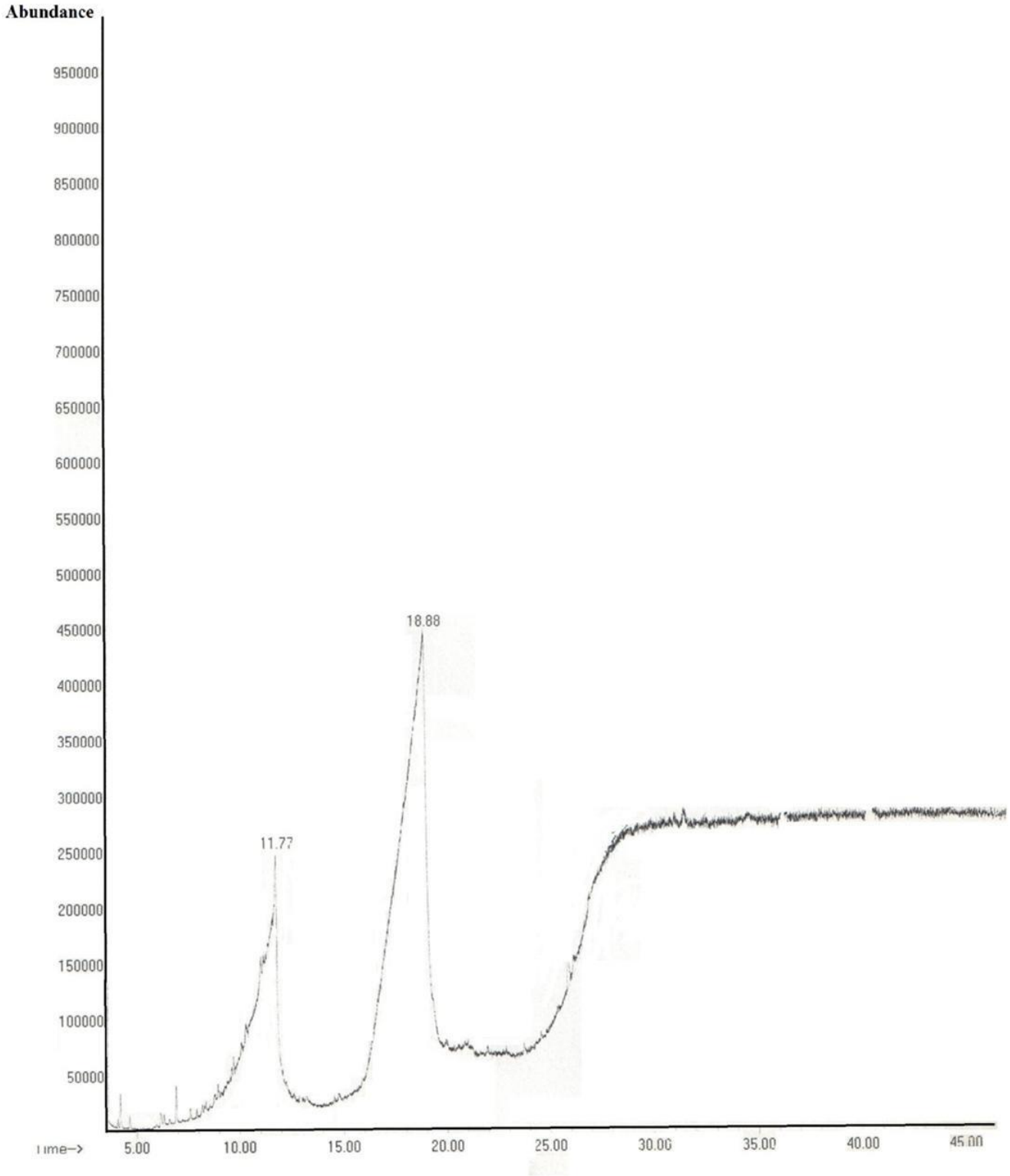

Fig.2: GC -Mass profile of Essential Diaromatic Oils in the Deasphaltened Oils

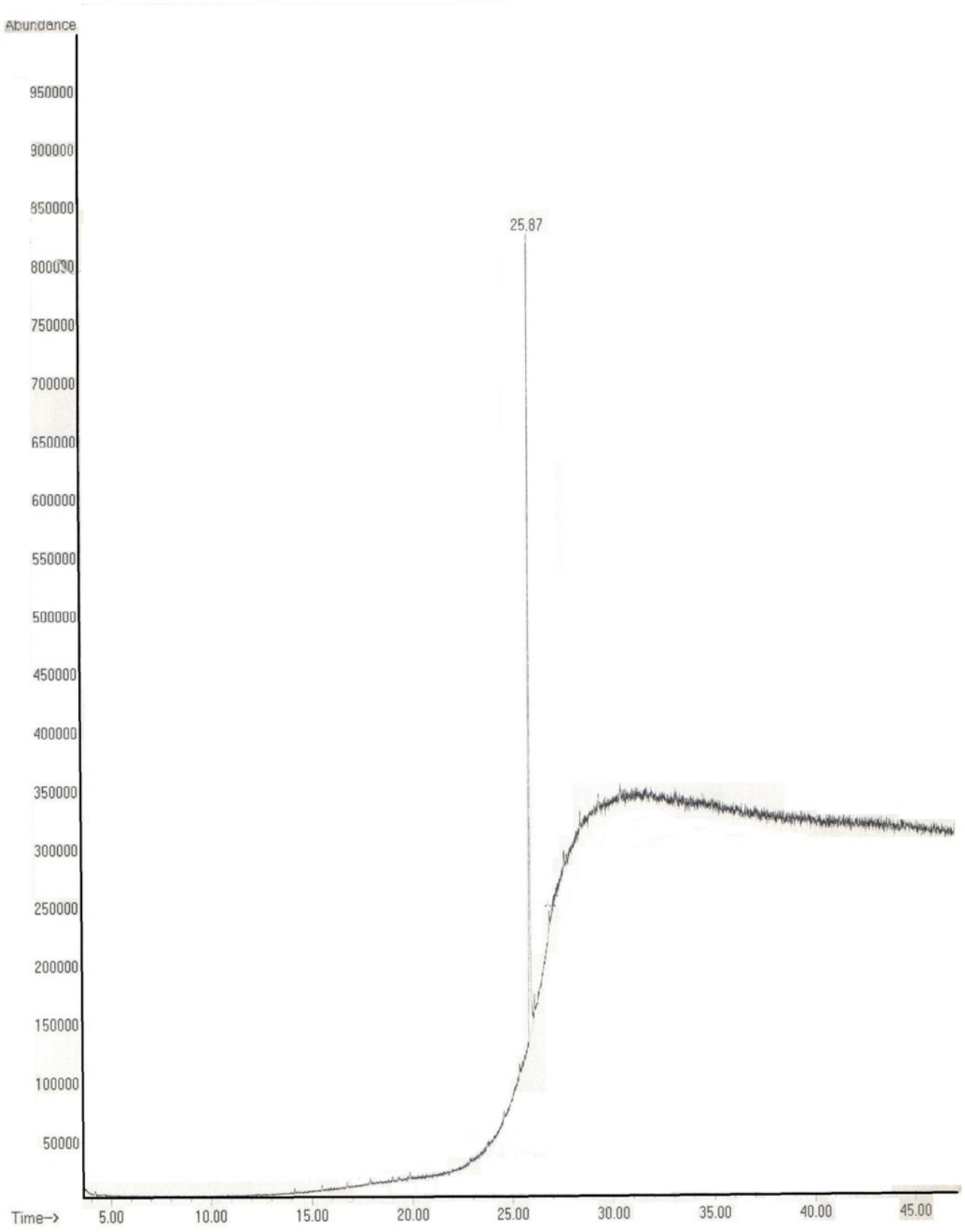

Fig. 3: GC - Mass Profile of Essential Polyaromatic Oils in the Deasphaltened Oils

Discussion

The quantity of deasphaltened oils and asphaltenes isolated from 148.88g of the bioliquid extracted from 150g/dm^3 slurry of *cassia tora* is shown in Table 1. From the result (Table 1), it could be seen that the quantity of deasphatened oils in the bioliuid was significantly higher than the quantity of asphatenes. This may be attributed to the consumption of some asphaltenes by the decomposers (microbes) during the decomposition of substrate in the slurry because during fermentation, microbes use polymeric compounds (usually asphaltenes) in the substrate as source of carbon for energy and nitrogen for growth (Garba, 1998).

Table 2: shows the quantities of the essential aromatic oils fractionated from the deasphaltened oils, which are depicted on Figs. 1, 2, and 3. The finger prints of these figures showed some other peaks, which are broad and, appeared at non integral values of m/e. These broad peaks observed may be attributed to the formation of metastable ions with lifetime of the order of 10^{-6} second, which disintegrated into fragments of considerable low energy (Dangoggo,2000). From the results (Table 2), it could be seen that the quantities of the fractions were in the order: heavy oil+ green oil> Light oil > middle oil

The relative high quantity of light oil when compared with the middle oil may be connected to the number of the major constituents in the fractions as shown in Table 3 and, depicted on Fig. 1, where five (5) sharp peaks are shown. These peaks served as index of the major constituents in the fractions (light oil). This is in accordance with the findings of Yaro (2011). The least quantity of middle oil observed in the deasphaltened oils when compared with individual quantities of other fractions (light oil and heavy oil + green oil) shown in Table 2, may also be connected to the number of the major constituents in the fraction (middle oil), where only two (2) major constituents were fractionated as shown in Table 3 and, presented on Fig. 2. This is also in accordance with the findings of Yaro (2011).

This high quantity of heavy oil+green oil observed in the deasphaltened oil when compared with the individual quantities of the other fractions may be associated with the combination of the oils (heavy oil+green oil), which were separated together (as polyaromatics) as shown in Table 2 and, depicted on Fig. 3. The strength (sharpness) of the peak of the mass spectra of the figure (i.e. Fig. 3) in which only one (1) strong peak appeared, indicated that there are large quantities of different constituents of essential polyaromatic oils in the fractions. This is in line with the statement of Morgan and Robinson (1975), which says strength of peak indicates the presence of substance in the sample.

Conclusion

From the outcome of the various analyses carried out in this work, it can be concluded that important organic compounds such as benzene, toluene xylene, pyridine, naphthalene, anthracene, etc that can be used for various industrial applications could be generated and isolated from *cassia tora* leaves.

References

Ababio, O. Y. (1985): New School Chemistry Certificate Science Series, (Revised Edition), Africana FEP Publishers Limited, in association with FEP International Private Limited, Hamzet Building, 22/26 Park Road,Sabongari, Zaria. Pp 466.

Atkinson, A. (1979): Modern Certificate Chemistry, (First Edition), Oxford University Press, London. Pp 118.

Bajah, S. T. and Godman, A. (1975): Chemistry: A new Certificate Approach,(New Edition), Longman Publishers, Ibadan –Nigeria. Pp 228.

Ekwenchi, M. M and Yaro, M. N. (2012): Extraction of Bioliquid and Qualitative Determination of saturated, aromatics and organic Polars from fermented Banana (*Musa sapintum*) leaves. *Bayero Journal of Pure and Applied Sciences (BAJOPAS)*: 5(2):97-100.

Ekwenchi, M. M., Gumel, S. M. and Yaro, M. N. (2013): Production of Biogasby Microbial digestion of Banana leaves and adduction of paraffins from saturates using urea and thiorea solutions. *Techno Science Africana Journal (TSAJ);* 8(1):85-90.

Garba, B. (1998): Studies on the chemical composition of biogas and kinetic of its production at varying temperatures. Unpublished Ph.D Thesis in the Department of pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto-Nigeria. Pp 112.

Mailabari, B. K. (1983): Chemical composition of total hydrocarbons and quantitative determination of n-alkanes in Nigeria butmen, Unpublished B.Sc. unpublished project in the Department of Pure and Industtrial Chemistry, University of Jos Nigeria. Pp. 2-10.

Masa'udu, A. K. (1987): CHE 202 (Organic Chemistry) Aromatics and their Derivatives, a lecture delivered to NCE II Students in the Department Chemistry, Advanced Teachers' College, Gumel.

Morgan, E. D. and Robinson, R. (1975): An introduction to Organic Chemistry. (Aliphatic and Alicyclic Compounds), Hutchison & Co. Publishers Limited, London. Pp 252-262.

Murray, P. R. S. (1979): A Modern Comprehensive Text for Schools and Colleges, (Second Edition). Heinemann Educational Books PublishersLimited, 48 Charles Street, London. Pp.130-131.

Yaro, M. N. (2009): Important of green plants to man. A lecture delivered during Science week organised by Dawakin Tofa Students Association (DASA).

Yaro, M. N. (2011): Studies on biogas and bioliquid production by fungal degradation of banana (*Musa sapintum*) leaves. Unpublished Ph.D Thesis in the Department of Pure and Industrial Chemistry, University of Jos- Nigeria. Pp 191-230

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