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### EXTRACTION AND CHARACTERIZATION OF HEAVIER SATURATED HYDROCARBONS FROM BANANA LEAVES AS ALTERNATIVE FUELS FOR DOMESTIC AND INDUSTRIAL USES

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#### ARTICLE INFO

#### ABSTRACT

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*Digested slurry of banana leaves was generated by anaerobic microbial fermentation of banana leaves at 33°C for 10 days. The liquid degradation product (bioliquid) was extracted from the slurry by soxhlet extraction using absolute method at 60°C for 72 hours. The extract obtained (bioliquid) was recovered from the extracting solvent (absolute methanol) by evaporation using rotary evaporator and subsequently concentrated to a constant weight. 1.0g of the concentrated bioliquid was used for the separation of asphaltenes and deasphalted oils (maltenes) by precipitation. The deasphalted oils were separated into fractions by column chromatography. The saturate fractions of the deasphalted oils were further separated into n-alkanes, iso-alkanes and cyclo-alkanes by adduction. The n-alkanes were adducted using urea solution while the iso-alkanes and cyclo-alkanes were adducted using thiourea solution. The adducts (n-alkanes, iso-alkanes and cycloralkanes) were analysed by GC-mass spectrometry. The work showed that the amounts of bioliquid, maltenes, asphaltenes and saturate were 3970.00 mg, 2114.00 mg, 1856.00 mg and 38.00 mg, respectively and; the amounts of n-alkanes, iso-alkanes and cyclo-alkanes in the saturate fraction were 22.64 mg, 10.36 mg and 2.57 mg, respectively. The work also showed that the types of n-alkanes, iso-alkanes and cyclo-alkanes identified were C<sub>15</sub>-C<sub>35</sub>, C<sub>18</sub>-C<sub>27</sub> and C<sub>23</sub>-C<sub>28</sub>, respectively.*

#### Introduction

In nature there are many raw materials from which bioliquid can be extracted. For instance, any biodegradable material whose organic content is greater than 2% can be degraded by microorganisms to yield bioliquid and biogas (Ariane, 1985). The process is carried out in a certain ranges of temperature usually (22°C -38°C) and pH

(usually 6.2 -7.6) in the presence of moisture under airtight conditions (Khandelwal and Mahdi, 1986). It should be noted that the generation of bioliquid occurs concurrently with the generation of biogas (Yaro, 2011). Bioliquid can simply be described as the extract obtained from fermented slurry by soxhlet extraction using suitable solvent (Oladapo, 1988).

The choice of the solvent depends solely on the nature of the fermentation product. Biological is usually composed of maltenes (deasphalted oils) and asphaltene (Oladapo, 1988). Maltenes are component of bioliquid, which is insoluble in liquid propane but soluble in n-pentane, which are generally composed of saturates (n-alkanes, iso-alkanes and cyclo-alkanes), aromatics and small quantities of resin and polar compounds. In bioliquid the quantity of maltenes exceeds that of asphaltene (Ekwenchi *et al*, 2013). Asphaltene are a compound of bioliquid which are insoluble in paraffin naphthas but soluble in carbon disulphide (CS<sub>2</sub>). Asphaltene are chiefly composed of resins and polars (Oladapo, 1988). A simple way to compare the paraffinicity and aromaticity of any fossil fuels and its relations such as bioliquid or its fractions (maltene and asphaltene) is by determining the ratio of hydrogen to carbon atoms (H/C), which drops sharply from maltene to asphaltene because asphaltene are more compacted with many condensed aromatic rings (Oladapo, 1988). This work reports studies on the possibility of generating bioliquid from banana leaves through anaerobic fermentation. The work also reports studies on the possibilities of isolating maltene from bioliquid; fractionating the saturate content of maltene by column chromatography; adduction of the n-alkane, iso-alkane and cyclo-alkane from maltene using saturated urea solution and thiourea solution and; characterization of hydrocarbons using GC-mass spectrometric analysis.

## **Materials and Methods**

### **Sample Collection and Treatment**

The sample used (banana leaves) for the researches were collected from a group of banana plants planted by Kano Agricultural and Rural Development Agency (KNARD) in Bichi town, Kano State-Nigeria. The banana leaves were fresh and mature at the time of

collection. The sample was prepared according to the method described by Ekwenchi *et al* (2013).

### **Preparation of the Slurry**

The slurry was prepared by dissolving 40.00 g of the prepared sample in 250 cm<sup>3</sup> distilled water containing 1.8 g yeast and vigorously stirred for homogeneity. The slurry was immediately (after preparation) used for bioliquid generation.

### **Fermentation of Slurry and Extraction of Bioliquid**

The prepared slurry was placed in a reactor (500 cm<sup>3</sup> Buchkner flask). The reactor was made airtight and placed in water bath operated at 33°C. The fermentation process was allowed to continue for 10 consecutive days. The bioliquid was extracted from the fermented slurry by Soxhlet extraction using absolute methanol (as extracting solvent) at 60°C for 72 hours. The bioliquid was recovered from the extracting solvent by evaporation using rotary evaporator and, subsequently concentrated to a constant weight at 37°C in fume cupboard.

### **Isolation of Maltene by Precipitation of Asphaltene**

For the isolation of maltene from the bioliquid, 1.0g of the concentrated bioliquid was dissolved in a mixture of methanol and n-hexane in the ratio 1:40 (v/v) and kept in refrigerator for 24hrs. The maltene being the soluble component of the bioliquid was carefully removed from the asphaltene (insoluble component) by decantation.

### **Separation of Saturate from Maltene by Column Chromatography**

The saturates were collected from the maltene by column chromatographic separation using n-hexane as eluent. The column used was a glass column of 40cm length and 0.85cm internal diameter with a bed volume of 22.72cm<sup>3</sup> as evaluated. The column was

first packed with silica gel of particle size 0.63 – 074nm (activated at 100°C overnight in an oven) followed by alumina of particle size 3.74µm in the ratio 1:2 (silica gel to alumina). The sample (maltenes) to packing materials ration was 1:70 for silica gel and 1:140 for alumina, where 5.13g of silica gel and 10.13g alumina were used as packing materials. The packed column was first washed with 30cm<sup>3</sup> n-hexane before loading the sample after which 72.5 mg of the sample was loaded in the column as concentrated solution of n- hexane and eluted with 30cm<sup>3</sup> n- hexane. The fraction collected was dried in fumes cupboard as saturates (Yaro, 2011).

**Urea Adduction of n-alkanes from Saturates**

In order to adduct n-alkanes content of the saturate, 38.0 mg of the saturates

collected above was dissolved in n-hexane and a saturated solution of urea in acetone was subsequently added. White crystals were formed, which contained the suspected n-alkanes. When no more crystals were formed with addition of saturated urea solution, the addition of saturated urea solution was stopped and the crystals formed were filtered off, washed with n-hexane and dissolved in distilled water. The dissolved crystals were extracted several times with n-hexane using separating funnel. The extract obtained, which contained the suspected n-alkanes were air-dried in a beaker to a constant weight and weighted as n-alkanes (Ekwechi *et al*, 2013).The percentage of the n-alkanes adducted from the saturates was evaluated as follows:

$$\% \text{ n-alkanes} = \left[ \frac{\text{weight of n-alkanes adducted} \times 100}{\text{weight of the saturate used}} \right]$$

**Thiourea Adduction of Iso-alkanes and Cyclo-alkanes**

The urea non adducts (i.e, iso-alkanes and cycloalkanes) in the aqueous solution were adducted using thiourea solution in methanol in the ratio 1:1 (v/v). The aqueous solution containing the iso-alkanes and cyclo-alkanes was mixed with the thiourea in methanol and kept at room temperature for 4 days, where crystals were formed. The crystal formed were then filtered off and washed with benzene and subsequently dissolved in

distilled water. The dissolved crystals were extracted several times with benzene. The benzene- extract obtained was air-dried in a beaker to a constant weight and weighed as cyclo-alkanes. The filtrate on the other hand, was also air-dried in a clean and dry beaker and weighed as iso-alkanes (Ekwenchi *et al*, 2013). The percentages of both the cyclo-alkanes and iso-alkanes adducted from the saturates were each evaluated as follows:

$$\% X = \left[ \frac{\text{weight of adducted} \times 100}{\text{weight of the saturated used}} \right]$$

where x = cycloalkanes or iso-alkanes as the case may be

**GC –Mass Analyses of N–alkanes, Iso-alkanes and Cyclo-alkanes**

For the analysis of the saturated hydrocarbons content of the maltenes, the gc-mass spectrometre used was

6890N network GC- system coupled with the 5973 network mass selective system. The temperature range of the oven of the column used was 150°C -

300°C and the auxiliary temperature of the column (i.e. the maximum temperature 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 30cm and the maximum capacity of the column was 10 µL. the carrier gas used was helium. The mass spectra of the hydrocarbons (n-alkanes, iso-alkanes and cyclo-alkanes) analysed were shown as a plot of relative abundance versus m/e and printed out. The respective structures of n-alkanes, iso-alkanes, and cyclo-alkanes were elucidated from the labeled peaks of the mass spectra and the corresponding fragmentation patterns of the labeled peaks (Yaro, 2011).

**Results**

The results of all the analyses carried out are shown in Tables 1 to 5 and on Figs. 1 to 3 below. Table 1 gives the amount of bioliquid extracted from 40.00 g fermented slurry of banana leaves, the amounts of maltenes and asphaltenes obtained from 3970.00 mg bioliquid and the amount of saturates fractionated from 78.00 mg of the maltenes component of the bioliquid used. Table 2 gives the amounts of n-alkanes, iso-alkanes and cyclo-alkanes adducted from 38.00 mg of saturates. Tables 3, 4 and 5 show the molecular ions and molecular formulae of the elucidated n-alkanes, iso-alkanes and cyclo-alkanes, respectively. Figs 1, 2, and 3 show the mass spectra of n-alkanes, iso-alkanes and cyclo-alkanes, respectively.

**Table 1: Amounts of Bioliquid, Maltenes, Asphaltenes and Saturate Extracted from 40.00g: Banana Leaves.**

Component	Quantity (mg)
Bioliquid	3970.00
Maltenes	2114.00
Asphaltenes	1856.00
Saturates	38.00

**Table 2: Amounts and Percentages of the N-alkanes, Iso-alkanes and Cyclo-alkanes Adducted from 38.00 mg Saturates Fraction of Maltenes**

Component adducted	Amount (mg)	Percentage (%)	Molecular sieve
n-alkanes	22.64	59.58	urea solution
iso-alkanes	10.36	27.26	thiourea solution
cyclo-alkanes	2.57	6.76	thiourea solution
<b>Total</b>	<b>35.57</b>	<b>93.60</b>	urea and thiourea solutions

**Table 3: GC- Mass Spectrometric Analyses of N- alkanes in the Bioliquid**

S/N	Molecular ions	Retention time (min)	No. of C-atom	Elucidated molecular formula
1	261	19.987	19	C <sub>19</sub> H <sub>40</sub>
2	282	20.989	20	C <sub>20</sub> H <sub>42</sub>
3	296	21.921	21	C <sub>21</sub> H <sub>44</sub>
4	310	22.847	22	C <sub>22</sub> H <sub>46</sub>
5	324	23.696	23	C <sub>23</sub> H <sub>48</sub>
6	338	24.539	24	C <sub>24</sub> H <sub>50</sub>
7	352	25.346	25	C <sub>25</sub> H <sub>52</sub>
8	366	26.117	26	C <sub>26</sub> H <sub>54</sub>
9	380	26.841	27	C <sub>27</sub> H <sub>56</sub>
10	394	27.607	28	C <sub>28</sub> H <sub>58</sub>
11	408	28.373	29	C <sub>29</sub> H <sub>60</sub>
12	422	29.346	30	C <sub>30</sub> H <sub>62</sub>
13	436	30.391	31	C <sub>31</sub> H <sub>64</sub>
14	450	31.643	32	C <sub>32</sub> H <sub>66</sub>
15	464	33.139	33	C <sub>33</sub> H <sub>68</sub>
16	478	34.913	34	C <sub>34</sub> H <sub>70</sub>
17	492	37.092	35	C <sub>35</sub> H <sub>72</sub>

**Table 4: GC- Mass Spectrometric Analyses of Iso-alkanes in the Bioliquid**

S/N	Molecular ions	Retention time (min)	No. of C-atom	Elucidated molecular formula
1	254	18.987	18	C <sub>18</sub> H <sub>38</sub>
2	268	20.038	19	C <sub>19</sub> H <sub>40</sub>
3	282	20.893	20	C <sub>20</sub> H <sub>42</sub>
4	296	21.973	21	C <sub>21</sub> H <sub>44</sub>
5	310	22.952	22	C <sub>22</sub> H <sub>46</sub>
6	324	24.074	23	C <sub>23</sub> H <sub>48</sub>
7	338	25.433	24	C <sub>24</sub> H <sub>50</sub>
8	352	27.089	25	C <sub>25</sub> H <sub>52</sub>
9	366	29.226	26	C <sub>26</sub> H <sub>54</sub>
10	380	31.944	27	C <sub>27</sub> H <sub>56</sub>

**Table 5: GC- Mass Spectrometric Analyses of Cyclo-Hydrocarbons in the Bioliquid**

S/N	Molecular ions	Retention time (min)	No. of C-atom	Elucidated molecular formula
1	324	20.074	23	C <sub>23</sub> H <sub>46</sub>
2	338	25.439	24	C <sub>24</sub> H <sub>48</sub>
3	352	27.137	25	C <sub>25</sub> H <sub>50</sub>
4	366	29.226	26	C <sub>26</sub> H <sub>52</sub>
5	380	31.944	27	C <sub>27</sub> H <sub>54</sub>
6	394	35.440	28	C <sub>28</sub> H <sub>56</sub>

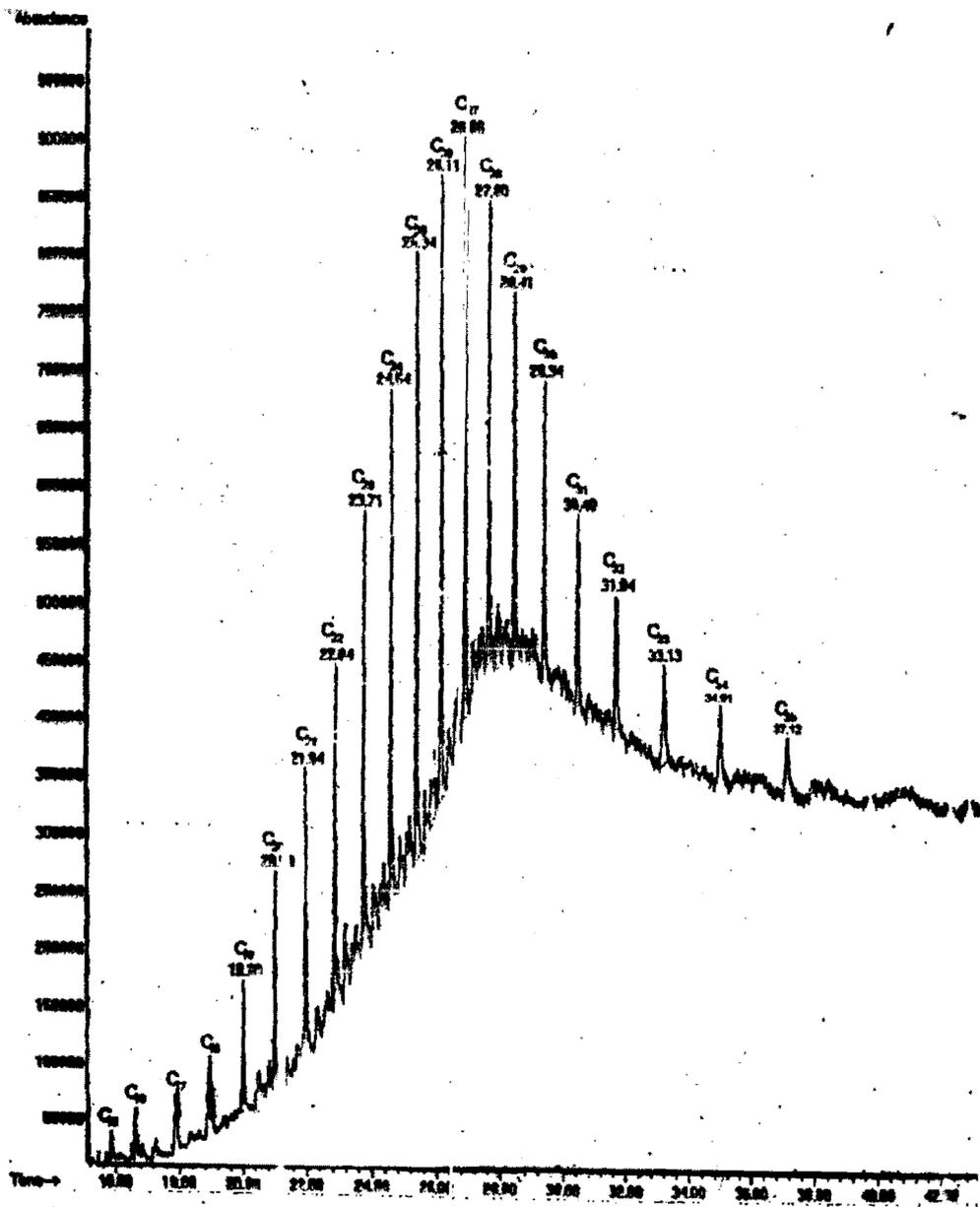


Fig.1: Mass Spectra of N-alkanes in the Bioliquid Analyzed.

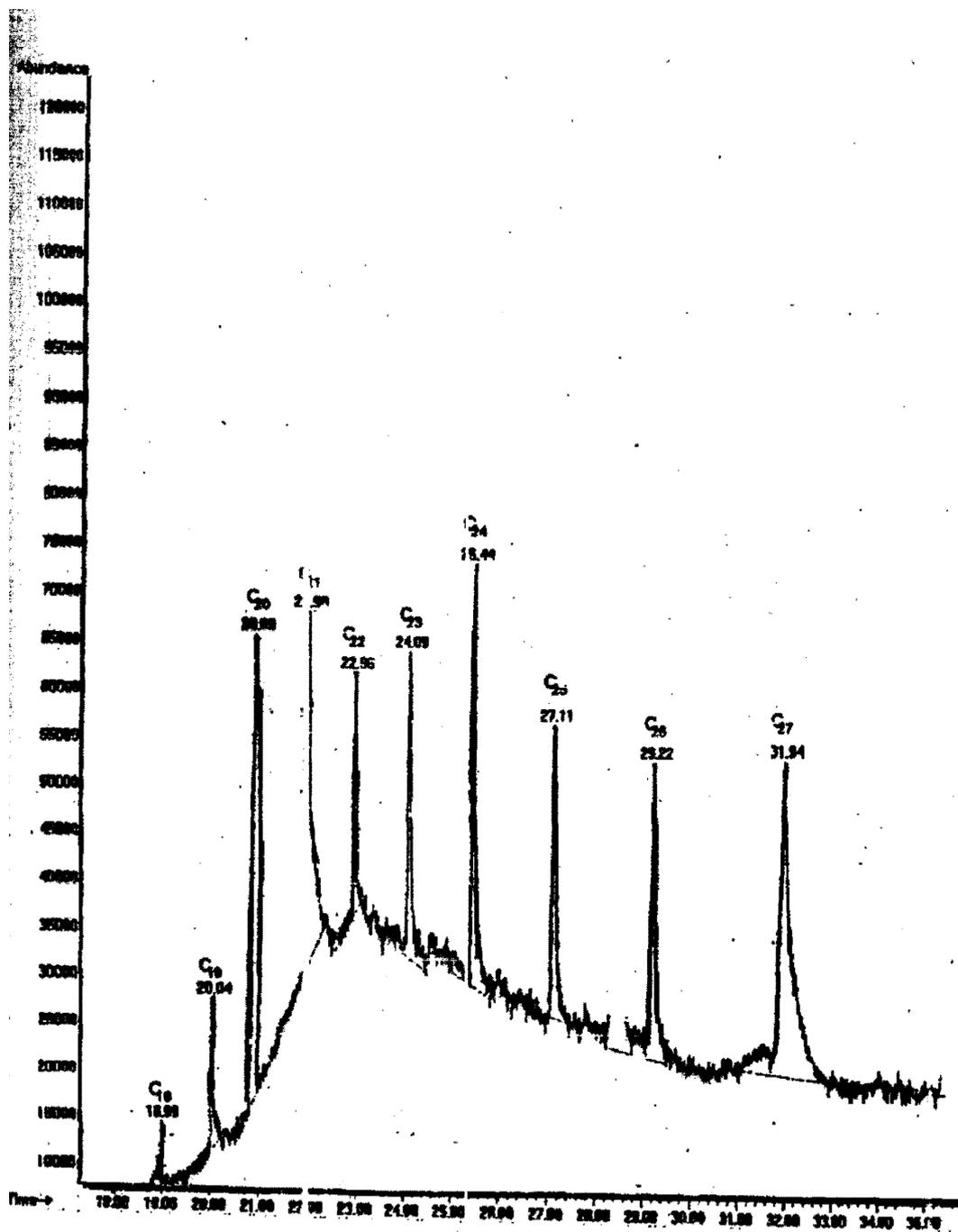


Fig.2: Mass Spectra of Iso-alkanes in the Bioliquid Analyzed.

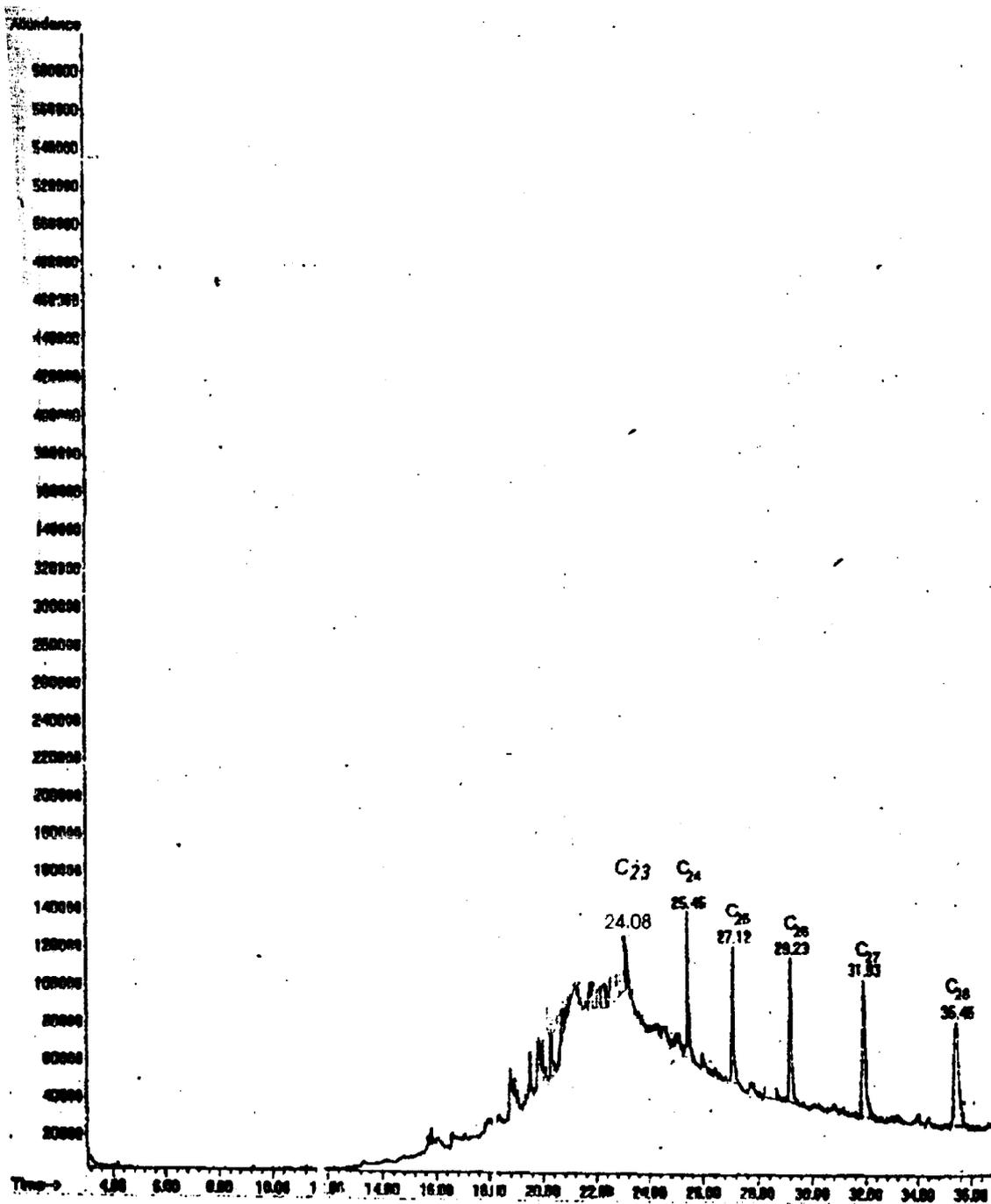


Fig.3: Mass Spectra of Cyclo-alkanes in the Bioliquid Analyzed.

## **Discussion**

The amounts of bioliquid extracted from fermented slurry of 40.00g of banana leaves and the corresponding maltenes and asphaltenes isolated are presented in Table 1. The results show that the amount of maltenes in the bioliquid outweighed the amount of asphaltenes obtained. The relative high maltenes observed may be attributed to the conversion of some asphaltenes (usually aromatics) into maltenes by the micro-organisms during fermentation of the substrate (Yaro, 2011). The high maltenes may also be connected to the dissolution of some gaseous degradation products (mostly C<sub>1</sub> – C<sub>4</sub> Saturated hydrocarbons) in the fermentation pit, which produced concurrently with the bioliquid during degradation (Yaro, 2011). The low asphaltenes detected in the bioliquid when compared with maltenes may be associated with the consumption of the polymeric hydrocarbons in the substrate as carbon source for growth and energy generation (Obinwanne, 1999).

The quantities and the percentages of the adducted components and the corresponding molecular sieves used for the adduction of n-alkanes, iso-alkanes and cyclo-alkanes are shown in Table 2. The results clearly shows that urea and thiourea solutions are good molecular sieves for separating paraffins of different molecular structures, because 93.60% of the paraffins in the saturates analyzed were adducted. This is in accordance with the findings of Mailabari (1983).

Structural elucidations of the n-alkanes, iso-alkanes and cyclo-alkanes were carried out using their respective fragmentation patterns and corresponding molecular ions were obtained and, shown in Tables 3, 4 and 5, respectively. The results show the distribution of components in the bioliquid, which indicated that most of the other components (i.e. monoaromatics, diaromatics, polyaromatics and polar/resins) were

converted into saturates, which were identified and presented in Table 3 (as n-alkanes). Some iso-alkanes and few cyclo-alkanes (when compared with the n-alkanes in the bioliquid) were also identified and presented in Tables 4 and 5, respectively. The conversion of some of the monoaromatics, diaromatics, polyaromatics and polars/resins components of the bioliquid into mostly n-alkanes can best be based on the assumption that the micro-organisms must have grown by using the aromatics and polars/resins compounds in the lignocellulose as carbon source (Khandelwal and Mahdi, 1986). It could also be associated with the fact that some micro-organisms have the ability to synthesize alkanes from aromatics in the substrate-feedstock into straight chain n-alkanes (Yaro, 2011).

From Fig.1, It could be seen that the n-alkanes in the bioliquid were from C<sub>15</sub>-C<sub>35</sub>. Even though, C<sub>15</sub>-C<sub>18</sub> were not labeled (i.e. the times at which they appeared were not indicated). From the general feature of the mass spectra (Fig. 1), it could be clearly seen that the finger prints of the spectra (i.e. the peaks of the n-alkanes) were serially arranged and, the approximate times at which appeared were very close to the respective number of the carbon atoms in their molecules. From this, it could be assumed that the n-alkanes were of similar properties and uses because the difference between any two (2) successive members identified was CH<sub>2</sub>. This is in accordance with the statement of Ababio, (1985). From the mass spectra of the iso-alkanes identified in the bioliquid (Fig.2), it could be seen that the iso-alkanes in the bioliquid were comparatively less in number compared with the n-alkanes. This may probably be connected to the conversion of most of the iso-alkanes into n-alkanes (Ariane, 1985). The figure (Fig. 2), also shows that only C<sub>18</sub>-C<sub>27</sub> iso-alkanes were identified in the bioliquid as presented in Table 4

Fig. 3 gives the mass spectra of the cyclo-alkanes in the bioliquid. From the peaks of the mass spectra, it could be seen that only 6 different cyclo-alkanes were identified in the bioliquid (Table 5). The low number of cyclo-alkanes identified in the bioliquid may be attributed to the decyclization of the cyclics into aliphatics as a result of microbial activities during the degradation of the substrate (Yaro, 2011).

### Conclusion

From the amounts of bioliquid extracted and saturates isolated coupled with the appreciable quantities of n-alkanes, iso-alkanes and cyclo-alkanes adducted, it can be concluded that banana leaves have the potential of generating petroleum related products (maltenes and asphaltenes) from which important

organic compounds that could be used as biofuels for domestic and industrial uses, with qualities similar to those of kerosene ( $C_{12}$ -  $C_{18}$ ), diesel oil and gas oil ( $C_{12}$  -  $C_{25}$ ) and as lubricants and waxes with more than 25 carbon atoms per molecule can be obtained.

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