The Pharmaceutical and Chemical Journal, 2019, 6(3):77-82

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Extraction and Analysis of Petroleum-Related Substances (Maltenes and Asphatenes) from Water Hyacinth (*Eichhonia crassipes*)

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Abstract Fresh waterhyacinth was collected and processed. The physical and chemical parameters of the sample (waterhyacinth) were determined. A slurry of 40.000g waterhyacinth in 1dm^3 distilled water was prepared and subjected to naerobic fungal degradation at 33^{o}C for eleven (11) consecutive days, where fermented supernatant liquid was formed. The bioliquid content of the supernatant liquid was extracted by soxhlet extraction using absolute methanol at 60^{o}C for 72hours. The maltenes and asphaltenes contents of the biological were separated by precipitation. The work showed that the percentages of moisture ash and volatile solids contents of the substrate were 8.400%, 23.400% and 68.200%, respectively; the percentages of organic carbon and nitrogen in the sample were 6.300% and 0.300%, respectively and; the carbon to nitrogen ratio (C/N) of the sample was 21:1. The work also showed that out of 40.000g of the processed sample used, only 5.810g was consumed in the process (anaerobic fungal degradation); the amount of bioliquid extracted from 5.810g was 3.100g and; the amounts of maltenes and asphaltenes isolated from 3.100g bioliquid were 2.750g and 0.350g, respectively.

Keywords Waterhyacinth, anaerobic fungal degradation, bioliquid, maltenes, asphaltenes

Introduction

Anaerobic microbial digestion of biomass is a process by which biomass (lignocellulosic component) is subjected to microbial degradation in the absence of air under the influence of pH, temperature and concentration. The process leads to formation of biogas and bioliquid from which maltenes and asphaltenes are extracted [1]. In bioliguid, the proportion of maltenes exceeds that of asphaltenes and both the maltenes and asphaltenes contained about half of the total nitrogen and sulpur in the biomass, most of which are in the form of heteromolecules, which are condensed into both aromatic and naphthenic rings.

Based on the fact that bioliquid is very closely related to petroleum in terms of source and composition, Ekwenchi and Yaro [2] classified bioliquid on the basis of petroleum classification as follows:

- Praffinic bioliquid, in which the side chains in the bioliquid are over 75%
- Naphthenic bioliquid, in which the naphthenic rings in the bioliquid exceeds 70%
- Asphaltic bioliquid, in which the asphaltenes content of the bioliquid exceeds 60%
- Paraffinic–naphthenic bioliquid, in which the side chains in the bioliquid are 60-70% and the naphthenic rings are over 20%
- Naphthenic–aromatic rings, in which the naphthenic and aromatic rings inbioliquid exceed 30%.

Maltenes are a component of bioliquid composed of large amount of saturates, few aromatics and very small quantities of resins and organic polars [3]. Maltenes are relatively more paraffinic than asphaltenes and contained

less N, S and O. The praffinicity of bioliquid is compared based on the simple way of comparing the praffinicity of any fossil fuel or its fraction by showing the ratio of C to H (C/H) in the bioliquid or its components (maltenes and asphaitenes). The higher the C/H in the bioliquid, the more the maltenes content [3].

On the other hand, asphaltenes are also a component of bioliquid, which are generally aromatic in nature andtheir molecules consist of 10-20 condensed aromatic and naphthenic rings with paraffinic and naphthenic side chains [4]. Asphaltenes are defined and classified 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 bioliquid, which plays a major role on the physical and chemical properties of bioliquid [4].

In bioconversion technology (biogas and bioliquid production process), the raw material needed as substrate is biomass of different sources. Waterhyacinth (*Eichhornia crassipes*), a monocotyledonous freshwater aquatic plant belonging to the family pontederiaceaceis native of Brazil equador region is one of such substrates for appreciable production of biogas and bioliquid. Waterhyacinth is a well-known ornamental plant found in water gardens and aquarium, which bears beautiful blue to lilac coloured flowers along with its round to oblong curved leaves and waxy coated petioles. Waterhyacinth grows few inches to about a metre in height. The stems and the leaves of the plant contain air filled sacks, which help it to stay afloat in water as an invasive species that invades fresh water habitats and, listed along with some worst weeds [5].

In order to justify the importance of waterhyacinth as substrate for bioliquid production, as well as to investigate its potential as primary source from which maltenes and asphaltenes can be extracted, various analyses were carried out in the present work. The work reports the procedure through which bioliquid was generated and collected from waterhyacinth through anaerobic microbial degradation under the operational conditions of concentrations, pH and temperature. The work also reports the results of the quantitative determination of the maltenes and asphaltenes contents of the bioliquid.

Materials and Methods

Collection and Identification of Experimental Plant

Fresh and mature waterhyacinth was collected from a pond situated in Tofa town, Tofa Local Government Area, Kano State – Nigeria. The plant was carefully examined and identified by a taxonomist in Botany laboratory of the University of Jos – Nigeria. The plant was dried under shade, after which it was ground and sieved to a mesh size of 250×10^{-6}m.

Determination of Physical Parameters of the Sample

The physical parameters of the sample (moisture, ash and organic matter) were determined as follows:

Determination of Moisture Content

The moisture content of the sample was determined by heating 5.000g of the processed sample at 105^{o}C for four (4) hours in an oven. The weight of the moisture in the sample was evaluated as the different between the weight of the sample before heating and the weight of the sample after heating. The process was carried out in triplicate and the average weight of the moisture was evaluated. The percentage of the moisture content of the sample was evaluated from the average weight of the moisture and the weight of the weight of the sample before heating using the following expression:

$$\text{Moisture (\%)} = \frac{\text{Average weight of the moisture}}{\text{weight of the sample before heat}} \text{ X } 100 \quad (1)$$

Determination of Ash Content

The ash (inorganic matter) content of the sample was determined by heating 5.000g of the sample in a muffle furnace for 8 hours. The temperature of the muffle furnace was allowed to gradually rise from 100^{o}C to 600^{o}C during the first hour of the process. (*i.e* the gradual increase in the temperature of the muffle furnace in the first hour was carried out at 100^{o}C per 10 minute), after which the temperature (600^{o}C) was maintained for the remaining seven (7) hours. The process was carried out in triplicate according to the method described by Musa [5] with few

modifications. The percentage of ash content was evaluated from the average weight of the ash obtained and the weight of the sample before ashing as follows:

$$\text{Ash (\%)} = \frac{\text{weight of the ash obtained}}{\text{weight of the sample before ashing}} \text{ X } 100 \quad (2)$$

Determination of Organic Matter Content

The percentage of the volatile solids (organic matter) content of the sample was evaluated from the percentages of the moisture and ash contents of the sample earlier obtained as follows:

Organic matter (%) = 100% - (% moisture + % ash) (3)

Determination of Some Chemical Parameters of the Sample

The chemical parameters of the sample (organic carbon and total nitrogen) were determined as follows:

Determination of Organic Carbon

The organic carbon content of the sample was determined by Walkley – Black method using 0.500g of the sample as described by Yaro [6] with few adjustments. The percentage by mass of the organic carbon in the sample was evaluated using the following expression as adopted by Yaro [7].

$$\text{\% organic carbon} = \frac{CVk_2Cr_2O_7 - C'\,(TFeSO_4 - TB)\,0.003xF\ x100}{\text{weight of the sample used}} \text{ X } 100 \quad (4)$$

where $CVk_2Cr_2O_7$ = molar concentration x volume of $K_2Cr_2O_7$

C' = molar concentration of hydrated $FeSO_4$

T_{FeSO4} = titre value of hydrated $FeSO_4$ with sample

T_B = titre value of hydrated $FeSO_4$ for blank titration

F = Correlation factor (i.e a recovery factor for what might be lost) = 1.33

0.003 = naturally existing percentage by volume of CO_2 in the air.

Determination of Total Nitrogen

The total nitrogen content of the sample was determined by micro – Kjeldahl method using 0.500g of the sample as described by Yaro (2014) with few adjustments. The reactions for the process are illustrated by the following equations as reported by Yaro (2011):

$$N_{2(g)} + 3H_2O_{(1)} + H_2SO_{4(conc.)} \longrightarrow (NH_4)_2SO_{4(aq)} + 3/2O_{2(g)} \quad (5)$$

$$(NH_4)_2\,SO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow 2NH_{3(g)} + Na_2SO_{4(aq)} + 2H_2O_{(1)} \quad (6)$$

$$NH_{3(g)} + H_3BO_{3(aq)} \longrightarrow NH_4^+{}_{(aq)} + H_2BO^-{}_{(aq)} \quad (7)$$

$$NH_4^+{}_{(g)} + H_2BO_{3(aq)} + HCl_{(g)} \longrightarrow H_2BO_{3(aq)} + NH_4Cl_{(aq)} \quad (8)$$

The percentage by mass of the total nitrogen in the sample was evaluated using the following expression:

$$\%N = \frac{(T_{HCl} - T_B)(M_{HCl}\,X\,0.014)V_1}{\text{weight of the sample used X } V_2} \text{ X } 100 \quad (9)$$

where T_{HCl} = titre value of 0.01M HCl with sample

T_B = titre value for blank titration

M_{HCl} = molar concentration of HCl = 0.01M

0.014 = weight by volume of nitrogen gas per dm^3= 14g/1000cm^3

V_1 = Volume of distilled water added to the digest = 60cm^3

V_2 = Volume of digested sample (aligout) pipetted = 10cm^3

Estimation of Carbon to Nitrogen Ration of the Sample

The carbon to nitrogen ration (C/N) of the sample was evaluated from the percentages of organic carbon and total nitrogen of the sample earlier obtained as follows:

$$\text{C/N} = \frac{\text{\% organic carbon}}{\text{\% total nitrogen}} \text{ X } 100 \quad (10)$$

Materials and Methods

Preparation and Anaerobic Digestion of Slury

A slurry was prepared by dissolving 40.000 g of the prepared (processed) sample of waterhyacinth in $1dm^3$ distilled water 40g $1dm^3$ containing 1.800g yeast. The slurry formed was subjected to anaerobic degradation process for 11 consecutive days at 33^oC in an air-tight reactor. The digested fermented slurry generated was decanted and the supernatant liquid of the fermented slurry was collected by decantation.

Extraction of Bioliquid from Supernatant Liquid

The supernatant liquid collected was subjected to soxhlet extraction using absolute methanol (as extracting solvent) at 60^oC for 72 hours. The extracted bioliquid was recovered from the extracting solvent by rotary evaporation and, concentrated to a constant weight at 37^oC in fume cupboard according to the method described by Ekwenchi *et al* [3] with few modifications.

Precipitation of Asphaltenes

In order to precipitate asphaltenes and isolate maltenes from the bioliquid, 1.000g of the concentrated bioliquidwas dissolved in a mixture of $1cm^3$ methanol and $40cm^3$ n-hexane and kept in refrigerator for 24 hours. The separation and collection of the asphaltenes and maltenes were carried out according to the method described by Ekwenchi*et.al* [3] with few modifications.

Results and Discussion

Results

The results of all the analyses and estimations carried out in this work are presented in Tables 1 to 4 below.

Table 1: Percentage Composing of the Physical Parameters of Waterhyacinth

Parameter	Percentage by mass (%)
Moisture	8.400
Ash (inorganic matter)	23.400
Volatile solids (organic matter)	68.200

Table 2: Percentages of Organic Carbon and Total Nitrogen Contents with Corresponding C/N of Waterhyacinth

Parameter	Composition
Organic carbon (C)	6.300 %
Total nitrogen (N)	0.300 %
Carbon to nitrogen ratio (C/N)	21.11

Table 3: Analysis of Bioliquid Production Potential of 40.000 g

Parameter	Quantity (g)
Weight of substrate before extraction	40.000
Weight of substrate after extraction	34.190
Amount of substrate consumed	5.810
Amount of bioliquid generated	3.100

Table 4: Amounts of Maltenes and Asphaltenes Extracted from 3.100g Bioliquid

Component	Quantity (g)
Maltenes	2.750
Asphaltenes	0.350

Discussion

The physical parameters of water hyacinth analyzed before digestion are shown in Table1. From the results (Table 1), it could be seen that the percentage of volatile solids (organic matter) was 68.200%, which was higher than the percentage of ash(23.400%) and moisture (8.400%) This is not surprising because the major components of biomass are lignin, cellulose, hemicelluloses and lignocelluloses, which are all organic in nature as reported by Maduagwa (2000). The high organic matter and relative low ash (inorganic matter), as well as the low moisture contents observed in the sample are clear indications of biogas and bioliquid (maltenes and arphaltenes) production potential of the substrate (waterhyacinth). This is based on the statement of Yarima and Abubakar (2005), which says in biogas production, only the carbonaceous compounds (mainly carbohydrates) are converted into degradation products (biogas and bioliquid).

Table 2 gives the percentages of carbon and nitrogen contents, as well as the carbon to nitrogen ratio of the substrate. The results (Table 2) indicated that the percentage of carbon (6.300%) exceeded the percentage of nitrogen (0.300%). The high percentage of carbon observed is connected to the fact that the proportion of carbon in biomass exceeded the proportion of any other constituent element (nitrogen inclusive) because carbon is the major constituent of plant materials (biomass) as pointed out by Maduagwu [8]. The high carbon and relative low nitrogen resulted in C/N of 21:1, which indicated that waterhyacinth is a good substrate for maltenes and asphaltenes production. This is based on the fact that, for a substrate to generate biogas and bioliquid, (maltenes and asphaltenes), its C/N should be maintained between 20:1 to 25:1 as reported [9].

Table 3 shows the amount of waterhyacinth consumed in the process (5.810g) and the quality of bioliquid extraction from the substrate (3.100g). From the amount of substrate consumed, it could be seen that only 5.810 g out of 40.000g of waterhyacinth used in the process was used by the micro-organism responsible for the production of maltenes and arphaltenes [9]. The amount of bioliquid extracted from the substrate indicated that only 3.100g out of 5.810 g were consumed in the process as the useful nutrients (component) of the waterhyacinth that were converted into maltenes and arphaltenes [6].

The amounts of maltenes and arphaltenes extracted from 3.100g bioliquid obtained are presented in Table 4. The results (Table 4) showed that the amount of maltenes extracted was relatively higher than the amount of asphaltenes. This may be associated with the conversion of some of the arphaltenes(aromatic ones) into maltenes by the microbes during the process of degradation (digestion). This is based on the fact that some microbes have the ability to synthesize alkanes (maltenes component) from aromatics content of asphaltenes by dearomalization of the aromatics in the biomass as reported [2].

Conclusion

Production of maltenes and asphaltenes was established. The work showed that through anaerobic microbial digestion of waterhyacinth, petroleum-related substances (maltenes and asphaltenes) that could be used as domestic and industrial fuels, as well as raw materials for the production of other useful organic substances can be generated and extracted using low skill technology.

References

[1]. Ekwenchi, M. M., Akunwanne, B. U., Okeke, N. R. and Ekpenyong, K. I. (1990): Gaseous fuel production by fungal degradation of elephant grass Fuel, 2 (69): 1569-1572.

[2]. Ekwenchi, M. M. and Yaro, M. N. (2012): Extraction of bioliquid and quantitative determination of saturates aromatics and organic polars from fermented banana leaves (*Musa Sapintum*) leaves. *Bayero Journal of Pure and Applied Sciences*, 5(2): 97-100.

[3]. Ekwenchi, M. M., Gumel, S. M. and Yaro, M. N. (2013): Production of biogas by microbial digestion of banana leave and adduction of paraffins from saturates using urea and uhiourea solutions. *Techno Science Africans Journal* (TSAJ), 8(1): 85-90.

[4]. Oladapo, A.O. (1988): Estimation of Maturation of Petroleum Asphaltenses and Maltenes. Unpublished B.Sc Project. University of Jos. Pp. 1

[5]. Musa, B. (2017): Extraction of bioliquid and quantitative analysis of maltenes and asphaltenes from water hyacinth (*Eichonia crassipes*): unpublished B.Sc. Project in the Depatment of Chemistry. Federal University Dutse. Pp.

[6]. Yaro, M. N. (2011): Studies on biogas and bioliquid production by fungal degradation of banana *(Musa sapintum)* leaves. Published Ph.D Thesis in the Department of Pure and Industrial Chemistry, University of Jos–Nigeria, Pp 101-121

[7]. Yaro, M. N. (2014): A Comparative study of biogas production potentials of banana leaves, elephant grass, maize stalk and water hyacinth as alternative fuels. *Biological and Environmental Sciences Journal for the Tropics (BEST), 11(3): 282-287*

[8]. Maduagwu, F. I. (2002): Effect of pH on anaerobic biodegradation of the lignocellulose from maize cob and maize stalk. Unpublished B.Sc. project submitted to the School of Science A.T.B.U Pp 22-28.

[9]. Ariance, V. B. (1985): A Chinese biogas manual: popularizing technology in Countryside, Intermediate Technology Publication London. Pp 22-44.