CHARACTERIZATION AND PRODUCTION OF FATLIQUOR FROM PUMPKIN (*CUCURBITA MAXIMA)* SEED OIL FOR LEATHER AND ALLIED INDUSTRIES

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ABSTRACT

The leather industry is ranked first in foreign exchange earnings from non-oil export products in Nigeria. Unfortunately, 5-10% of fatliquor applied to the resultant leather articles are imported with attendant negative effects on value addition and job creation. It is imperative to look inward into plants that can give good yield of oil that can be converted into fatliquor. Based on this, oil from Cucurbita maxima (kabewa) seed was extracted and characterised and results presented as follows: Saponification value 198.18mgKOH/g, iodine value 68.56, acid value 6.95mgKOH/g, pH 5.5 and 50% oil yield. Heavy metal contents were analysed using AAS indicated Fe^{2+}0.4357ppm, Ni^{2+} 0.0424ppm and Pb^{2+} 0.0021ppm. FT-IR analysis revealed –OH, -CH≡CH-, and –C=O as the functional groups present in the oil. GC-MS determination showed that the dominant fatty acids present in the oil include: palmitic acid ($C_{16}H_{32}O_2$), oleic acid ($C_{18}H_{32}O_2$), stearic acid ($C_{18}H_{36}O_2$), palmitoleic acid ($C_{16}H_{30}O_2$) and myristic acid ($C_{14}H_{28}O_2$). The yield of the oil was good and can be used alone or in combination with other fatliquors after subjecting it to sulphation.

Keywords: *Leather, Fatliquor, Cucurbita maxima, Functional groups, oleic acid, Sulphation,*

Introduction

Oils are triglycerides extract which are liquid at ambient temperature. This could be vegetable oils from plant or animal sources. They are either hydrophobic or lipophilic in character. Vegetable oils are essential in meeting global nutritional demand and are utilized for food and other industrial purposes (Idouraine *et al.,* 1996). Vegetable oils are used industrially in the making of soap, candles, perfumes and cosmetic products. Despite the broad range of sources for vegetable oils, the world consumption is dominated by soybean, palm, rapeseed, and sunflower oils with 31.6, 30.5, and 8.6 million tons consumed per year respectively (Stevenson *et al.,* 2007). These oils from plant seed are produced either by mechanical extraction using oil mills which is termed as crushing or pressing which yield less oil or by chemical extraction using solvents which produce higher yield, is quicker and cost effective. These known and established sources no longer meet the increasing demand on vegetable oils for both industrial and domestic purposes (Idouraine *et al.,* 1996).Oils in the leather industries are used in the production of fat liquor and oil tannage. Some of the oils used are; Sperm whale oil which is obtained from head cavities and blubber of the whale and is an ester of fatty alcohol with iodine value of 71 -93. It's very good oil for leather lubrication but became very scarce due to worldwide whale conservation program (Sarkar, 2005). Jojoba oil is a vegetable oil from a desert plant called Jojoba which is having 50 per cent oil yield by weight and is reported to have the same quality as whale (sperm) oil in fatliqour. Cod oil are commonly used for chamoising (Leathers that are extremely soft mostly used for cleaning of glasses) and also in the production of fatliquor. Other oils that can be used in the leather industry are Linseed, cotton seed, neat foot, tung and olive oils etc.

The oils are classified into drying oil (cod oil, linseed oil, sunflower oil), Semi drying oil (cotton seed oil, corn oil) and non-drying oil (castor oil, sperm oil, olive). Despite increase in technology and research over the years, lubrication of leather still remain very essential in the manufacturing process as it increases the flexibility, pliability, softness and gives comfort to the user in whatever form of finished goods the leather eventually end up. Fatliquoring is concerned with imparting softness, mellowness, fullness and roundness; preserving grain break; regulating elasticity of the fibre and imparting a pleasing handle to leather so as to improve its aesthetic value. These properties also face some challenges during application such as: the electronic charges of the leathers, stability of the emulsions, uptake, types, colours and quantity of dyestuff, the method of drying (Tuck, 1981, Covington and Alexander, 1993). With over loaded demand for fatliquor, shortage in industrial demand became imminent. Therefore other sources need to be established with scientific proofs of their characteristic to meet the present challenge. Fatliquor may be ionic, cationic or non-ionic. Anionic fatliquors are commonly employed for fat binding with chrome tanned leathers which are cationically charged. Anionic fatliquors are commonly prepared by sulphation, sulphonation or bi-sulphitation of oils and fats (Sivakumar *et al.,* 2008; Cheng *et al.,* 2012). Sulphation process was considered for this work.

Cucurbita Maxima Plant Description

This fruit (*C.maxima*) is of different varieties as it differs in shape, colour and size which may be due to climate differences, weather and the type of soil it is grown on (Wessel *et al.*, 2003). The plant has a size of 0 – 1.5ft in height and 0 – 30ft in width. Most of the colours found are green, yellow, yellow with white strips, and green with white strips. The characteristics, physically observed of the plant are that they are decorative berries or fruits, edible flowers prostate seed start and tolerances to heat and humidity.

Plate 1:*Cucurbita maxima* Fruit (Source: Field work)

Plate 2: *Cucurbita maxima* Seeds (Source: Field work)

The seed of *C. Maxima* has a high level of unsaturated fatty acid which includes triglycerides with palmitic acid, stearic acid, oleic acid and linoleic acid as the dominant fatty acids (Applequist *et al.,* 2006).It is reported that the oil extracted from a *C. maxima* seed contains the following: Iodine value 105.12, Saponification value187.93, Acid value 4.07, (Nakic-Naderal *et al.,* 2006). This present work x-rayed the opportunities for the leather industry by comfirming the functional groups present and the degree of saturation and unsaturation of the oil prior to sulphation (fatliquor) and if properly harnessed could increase our foreign exchange earnings through value addition and job creation.

Methodology /Sample Collection: The *C.maxima* (kabewa) fruit was collected from Kagarko Local Government Area of Kaduna State. It was opened and the seed collected and air dried for 15days. The seed was ground to a fine powder using the grinder (Laboratory Mills, Model 4) with 2mm mesh size and oven dried for 3hr at 60°C then stored in a polyethylene bag.

Determination of Moisture Content of the Seed: The method employed by Dauda (2014) was used to determine the moisture content.

Soxhlet Extraction: A soxhlet extraction was carried out using n-hexane as solvent reported by Adebayo *et al.,*(2012) and percentage yield calculated.

Chemical Analysis of the Extracted Oil: The following parameters were considered in analysing the quality of the extracted oil as follows: saponification, (SLC 303-SLO 1/4) iodine (SLC 305-SLO 1/6), acid values (SLC 304-SLO 1/5) and ester value (Leafe, 1999).

Determination of Heavy Metals in the Extracted Oil by Digestion: Quantitatively, 2g of C. maxima seed oil was weighed and transferred into a beaker followed by 1g of copper sulphate (catalyst), 25cm^3 of concentrated H_2SO_4 was added and carefully transferred into Kjeldahl flask and digested for 4hr, cooled and followed with 50cm^3 of distilled water and heated for 15min cooled, filtered and finally made up to 100cm^3. This solution was analysed for iron, nickel and lead residual heavy metals present using atomic absorption spectrophotometer (Onwuka, 2005).

Fourier Transform Infrared (FT-IR) Analysis of *C. maxima* oil: In order to determine the presence of functional groups in the raw oil FTIR-8400S, SHIMADZU was employed (Ariful *et al.,* 2015).

Gas Chromatography-Mass Spectroscopy (GC-MS) of C. maxima Seed Oil: This was carried out using GC-MS-QP2010 Plus SHIMADZU, Japan under the following conditions: Column Oven Temperature (80°C), Injection temperature and mode (250°C and split),flow control mode (linear velocity), pressure (108.0 KPa), column flow (1.58ml/min), linear velocity (46.3cm/sec), ion source temperature (230°C) interface temperature (250°C), solvent cut time (2.50min) detector gain mode (relative), detector gain (0.00KV), threshold (1000) and n-hexane as the methylating solvent (Emmanuel *et al.,* 2014).

Production of Fatliquor from C. maxima Seed Oil: About 500ml of the oil extracted was placed into an acid resistant vessel surrounded with ice-blocks. Then 50ml of 0.02M H_2SO_4 was slowly added under continuous stirring. The contents were stirred for 30min to prevent loss of combined SO_3, 100ml of 0.01M NH_3 was added to the solution and kept in a separating funnel overnight to convert the acid sulphate to its alkali salts. Sodium sulphate was removed by washing with brine, intermittently to pH 6.5 and the resultant fatliquor ready for leather processing (Nyamunda *et al.,* 2013; Ariful et al., 2015).

Results and Discussion

Results for physical and chemical parameters analysed are shown in **Table 1**. Moisture content of the extract (*C. maxima* oil) was found to be 05.50% which was above 04.70% as reported by Shobha (2012) but within the range for storage of agricultural seeds of 5-10% (Prochazkova and Bezdeckova, 2008). The implication is that it can be kept for a long period of time without spoilage or decay because it is not highly susceptible to microorganisms attack as supported by Ajayi*et al.,* 2006).

C. maxima oil was extracted using the soxhlet extraction method with n-hexane (at 69^{0}C) as the solvent which produced a yield of 50% at pH 5.5 this is lower than that reported for European varieties with 54.9% (Murkovic *et al.,* 1996) and does not agree with Shobha (2012) 42.71% Indian specie and Younis *et al.,* (2000) of African species with 21.9 – 35%. But tally with El-Adawy and Tara, 2001 on the Egyptian varieties with 51%. Though it has been claimed such differences in oil yield (content) can be attributed to genetic diversity and climatic condition (Stevenson *et al.,* 2007).Therefore it can be considered a potential source of vegetable oil for industrial use. Saponification value is an indicator of the average molecular weight of fatty acid and hence the chain length. It is inversely proportional to the molecular weight of Lipid. *C. maxima* seed oil was found to be 198.18mgKOH/g slightly higher than 195mgKOH/g reported by Shobha (2012). Saponification value around 290 gives an appreciable amount of the fatty acid with low proportion of lower fatty acids. Iodine value indicates the degree of unsaturated fatty acid (triglyceride molecule of the oil) present in the oil by measuring the amount of iodine that can be absorbed by unsaturated acid. The sample (*C. maxima* seed oil) gives an iodine value of 68.56 which is in total disagreement with the report of Markovic and Bastic (1975) with 116.0 – 133.4 for cucurbita species. Neither does it correspond with Alfawaz (2004) 105.1Acid Value: This measure oil acidity and normally reflects the amount of fatty acid hydrolysed from triacylglycerols. Acid value simply means mg of KOH required to neutralize free acid present in 1g oil. *C. maxima* has high acid value of 6.95 above 1.15% edible limit (Ahsan et al., 2015) which measures the degree of rancidity of the oil and serves as an index for oil freshness.

The result for heavy metals analysis is presented in **Table 2**. Heavy metal of the oil has the concentrations measured in ppm. The analysed oil contained lead (Pb), Iron (Fe) and Nickel (Ni) with concentration of 0.002, 0.4357 and 0.0424ppm respectively. This indicates that the content of these metals are very negligible which make the oil safe for human consumption without detrimental effect to human health. The result for functional group analysis is presented in **Figure 1**. Fourier Transform Infrared (FT-IR) analysis revealed the following functional groups: OH, C ≡ C, C=C with frequencies at 3464.27, 2161.31 and 1733.10 respectively, which in turn determines the chemical property of the oil.
The result for the GC-MS is presented in **Figure 2; Table 3**. This analytical method was used to determine the fatty acids present in *C. maxima* seed oil. Saturated and unsaturated fatty acids were predominantly present in the oil. The result revealed the presence of palmitic acid, oleic acid myristic acid, stearic acid and linoleic acids in the oil.

The fatliqour produced by the sulphation process was carefully controlled to avoid charring the oil; this was achieved through the use of ice blocks and gentle flow (drop wise) of the sulphuric acid into the reacting chamber during the production. The fatliqour produced at this stage was opaque in nature (emulsion) indicative of high degree of sulphation. This physical evaluation gives an insight into the presence of SO_3incorporated into the organic matrix. In a situation where a milky emulsion is formed, it denotes low degree of sulphation. The function of SO_3 is to drive the anionic material (emulsifier) to the positively charge leather surface.

Conclusion

C. maxima seed has high oil yield when extracted with n-hexane and has good fatty acids profile such as: palmitic, oleic, linoleic and stearic acids present which is similar to that of other vegetable oil like rape seed oil used for the production of fatliqour. Based on the result of this work, *C. maxima* seed oil can be considered a potential raw material for fatliqour production in the leather industry if proper emulsification is achieved by the introduction of any of these groups; phosphate, sulphonate and sulphite groups into the structure of the oil by the addition of surfactants (Cheng *et al.,* 2012).

Table 1: Physicochemical Characterization of *C. Maxima* Seed Oil

S/N	Analysis	Units	Result
1	Saponification value	(mgKOH/g)	198.18
2	Iodine value	(g/100g)	68.56
3	Acid value	(mgKOH/g)	6.95
4	pH		5.5
5	Ester Value	(mgKOH/g)	191.23
6	Oil yield		50%
7	Moisture content	(%)	05.50
8	Free fatty acid		3.492

Table 2: Atomic Absorption Spectroscopy (AAS) Analysis of the oil for Heavy Metals

S/N	Metal Name	Concentration (ppm)
1	Lead (Pb)	0.0021
2	Iron (Fe)	0.4357
3	Nickel (Ni)	0.0424

Table 3: GC-MS Result for C. maxima Seed Oil

S/N	Fatty Acid	Structure	This Work %	Ahsan et al., 2015
1	Palmitic acid	$C_{16}H_{32}O_2$	16.50	17.39
2	Myristic acid	$C_{14}H_{28}O_2$	7.00	
3	Oleic acid	$C_{18}H_{34}O_2$	48.57	40.58
4	Palmitoleic acid	$C_{16}H_{30}O_2$	3.34	
5	Stearic Acid	$C_{16}H_{32}O_2$	3.89	27.39
6	Linoleic Chloride acid	$C_{18}H_{31}ClO$	9.61	

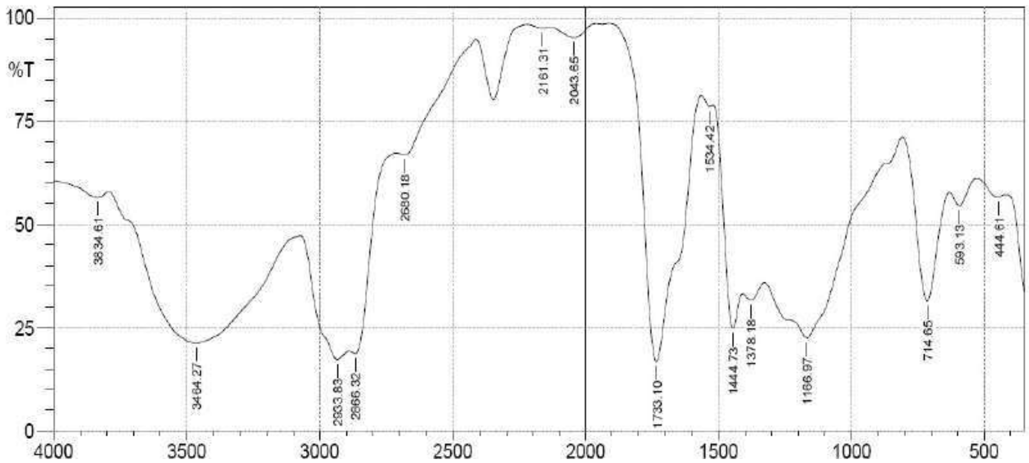

Figure 1: FTIR Result for *C. Maxima*

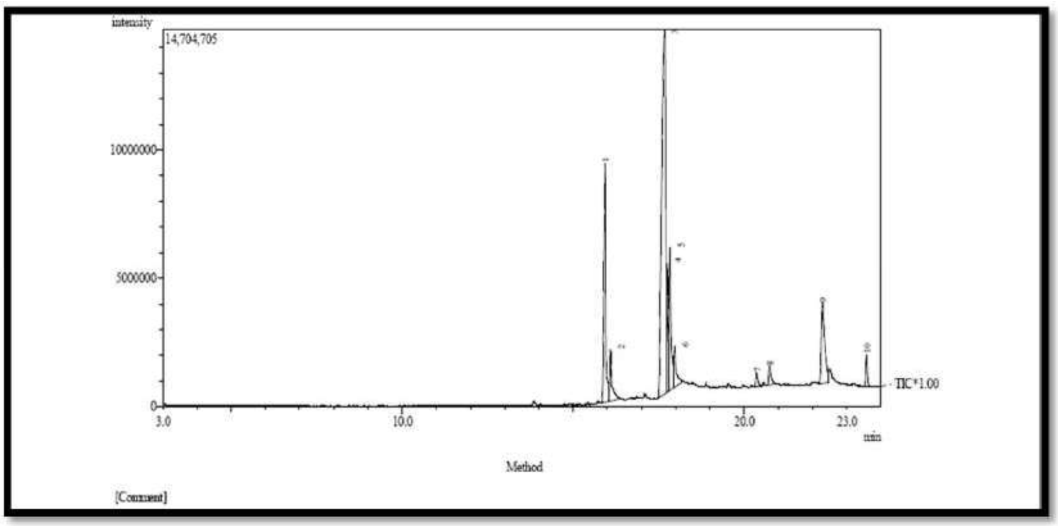

Figure 2:GC-MS Result for *C.Maxima*

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