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FATLIQUORING POTENTIALS OF SULPHONATED *Lophira lanceolata* SEED OIL AND ITS APPLICATION ON SHOE UPPER LEATHER

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ABSTRACT

Lophira lanceolata seeds were collected during the winter, dried and deshelled. The seeds were ground to smaller sizes to increase the surface area. N-hexane was used as the solvent for the extraction followed by the characterization and production of fatliquor. The following parameters were determined from the oil: solubility, acid value (AV), saponification value (SP), iodine value (IV), refractive index (RD) of the trial/control sulphonated oil and the results were observed to be 3.8 %, 204mgKOH/g, 74%, and 1.459 respectively. The functional groups were determined using Fourier Transform Infrared (FTIR). FT-IR analysis of the sulphated product confirmed the presence unsaturation (–C=C-). After the characterization, the oil was used for the production of sulphated fatliquor which was tested on three pieces of retanned goat skins divided along backbone line into two equal halves each. One half used as control while the other side used as a trial. The fatliquor was applied in the order of 3%, 5% and 7% and same percentages were used on the control samples. The leathers were dried, conditioned, staked, toggled and the following physical properties of the leather were examined for both trial and control samples: ball burst test, tensile strength, water absorption, percentage elongation and the results gave 3.48,3.27kg/mm,35.98,35.72 N/Mm^2,40.21,40.90% respectively. The sulphonated Lophira lanceolata oil had good characteristics as a leather fatliquor as shown by the physical and strength properties of the fatliquored leather. The results obtained revealed that Lophira lanceolata can effectively be used to manufacture fatliquor to be used to lubricate leather in fatliquoring process.

Keywords: Lophira lanceolata, oil, fatliquor and leathers.

INTRODUCTION

Fatliquors are oil-in-water emulsions required in leather processing for the purpose of leather lubrication (Nkwor *et al.,* 2019). Leather, at the time of completion of the tannage, does not contain sufficient lubricants to prevent it from drying into a hard mass. Almost all light leathers need a greater softness and flexibility than is imparted by tannage. To be precise, fatliquors are surface-active softening agents used as lubricants in leather. It is produced by the emulsification process of introducing sulphate or sulphite groups into the structure of oils and fat (Affiang, *et al.,* 2018).

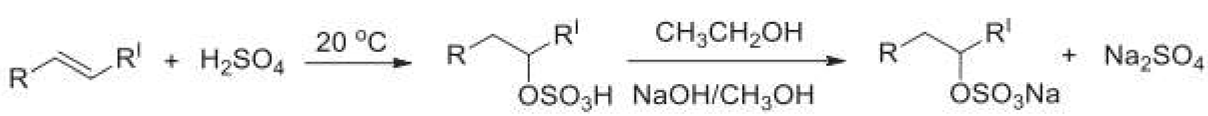

Figure 1: Sulphonated (Sulphated oil) (Nkwor *et al.,* 2019).

Fatliquoring is the last of the wet chemical operations to which the leather will be subjected to and it has the most pronounced effect on how soft leather will be and it contributes greatly to its tensile strength. The more fatliquors that are added, the softer the hides will be (Gupta & Ronak, 2007) and its importance cannot be overemphasized (Nkwor, *et al.,* 2019). This is attained in the fatliquoring process by introducing oil into the leather so that the individual fibres are uniformly coated. The percentage of oil on the weight of leather is quite small, from 3-10 %. The precise manner in which this small quantity of oil is distributed throughout the leather materially affects the subsequent finishing operations and the character of the leather. Proper lubrication or fatliquoring greatly affects the physical properties of break, stretch, stitch tear, tensile strength, and comfort of leather. Over lubrication will result in excessive softness and raggy leather in the bellies and flanks. Under lubrication or improper penetration, results in hard bony leather that may crack in use. (www. en. kimyasal. boun. edu. tr/webpage).

Figure 2: *Lophira lanceolata* tree

Characteristics of the Plant and the Oil from the Seed

So much work has been done on the characteristic of several seed oils by different researchers, this could be traced back to the fact that oils are in high demands for industrial applications and human consumption; consequently, there is an increased need to search for oils from non-conventional sources to augment the available ones and also to meet specific applications (Kyari, 2008). Dwarf red ironwood (*Lophira lanceolata*) is a small to medium-sized deciduous tree growing up to 16 metres tall with exceptional specimens to 24 metres. The tree has a narrow crown with ascending branches and a straight or twisted bole that can be branchless for up to 7.5 metres and up to 70cm in diameter. *Lophira lanceolata* is a multipurpose tree, valued especially for its oil, timber and many medicinal applications. The oil and other products of the tree are traded on a local scale (Abakaka *et al.,* 1989 as cited by Kyari, 2008) studied oils from rubber for their peroxide value and iodine value (IV). They also gave values for the saponification number and moisture content. They concluded that the values were comparable to those of palm oil and groundnut oil. The iodine values and the peroxide value were 65% and 27.5 ml/ kg, respectively. Nonviho *et al.* (2014) carried out research on *Lophira lanceolata*,and found out that it has saturated and monounsaturated fatty acids to be 31% and 58.08% respectively. From their work the yield of the oil was found to be 43.32%, acidity 0.18 %, iodine value 76.59g/100g, peroxide value 21.84ml/kg and the saponification value was found to be 201.57ml/g.

More attention is usually given to the edible oil containing seeds as opposed to the non-edible ones, without realizing that some non-edible oils in some seeds possess invaluable industrial applications that can make them more economically valuable than their edible counterparts(Kyari, 2008).

Currently, the need to preserve resources allocated for the importation of oils for indigenous utilization and industrial applications proffers reinvigorated incentives in the quest for innovative sources to complement the conventional ones. More attention has hence been directed to under-utilized local plant seeds for viable advancement and utilization. The aim of this research investigation was to search for oils from non conventional sources, because of increasing needs for oil for industrial applications (Ifijen *et al.,* 2020).

MATERIALS AND METHODS

Collection of sample and Preparation

Mature seed samples of *Lophira lanceolata* were obtained from Zuturung Mago of Zangon Kataf Local Government area of Kaduna State, Nigeria. The samples were identified in the Herbarium Unit, Department of Biological Sciences, Ahmadu Bello University, Zaria, Kaduna State, Nigeria. The seeds were dried, and deshelled. These samples were dried to decrease the moisture content before crushing. The vegetable oils were extracted using n-hexane as a solvent with the aid of the Soxhlet- apparatus. Wet blue goat skins were obtained from the tannery at the Nigerian Institute of Leather and Science Technology Zaria.

Determination of Acid Value

Oil (10g) was weighed accurately and place in a 250ml conical flask, then 50ml of the ethanol-ether solution was added and shake properly. The mixture was reflux gently until the substance is completely dissolved. It was then titrated with a solution of 0.1M sodium hydroxide until a pink colouration was observed which persists for 30s. The volume of sodium hydroxide titrant used was measured and the acid value was calculated according to equation 1:

$$\text{Acid value} = V_{NaOH} \times \frac{5.61}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where V NaOH = Volume of sodium hydroxide titrant used (ml), W =Weight of the fatty oil being examined (g) When the acid value is lessthan 10, it is suggested that a 10-ml semi-micro burette may be used for the titration.

Determination of Saponification Value

The saponification value (SV) is the number of mg of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the substance. 2g of the test oil was accurately weighed into a flask of 200 ml, 25 ml of alcoholic potassium hydroxide was added, a reflux condenser was attached and heated in a boiling water-bath for 30 minutes with a frequent rotation of the contents of the flask. It was allowed to cool and immediately 2 drops of phenolphthalein indicator was added. The content of the flask (the excess of alkali) was titrated with 0.5M hydrochloric acid to the endpoint. A blank test was conducted also and the volume of HCl consumed was recorded. The SV calculated using equation 2.

$$\text{Saponification value} = \frac{(a-b)\times 0.02805\times 11000}{Weight\ of\ sample} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where a= volume of HCl consumed by blank, b= volume of HCl consumed by the sample

Determination of Iodine Value (IV)

The method specified by ISO 3961 (1989). 0.4 g of the sample was weighed into a conical flask and 20 ml of carbon tetrachloride was added to dissolve the oil. Then 25ml of Dam reagent was added to the flask using a safety pipette influenced chamber. A stopper was inserted and the content of the flask vigorously swirled. The flask was then placed in the dark for 2hr 30min. At the end of this period, 20 ml of 10% aqueous potassium iodide and 125 ml of water added using a measuring cylinder. The content was then titrated with 0.1M sodium-thiosulphate solution until the yellow colour almost disappeared. A few drops of 1% starch indicator were added and the titration continued by adding thiosulphate drop-wise until blue coloration disappeared after vigorous shaking. The same procedure was used for the blank test and for other samples. The IV is calculated using equation 3 (Kyari, 2008).

$$IV = 12.69c\,\frac{(V1-V2)}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where: c – concentration of sodium thiosulphate used, V1 – the volume of sodium thiosulphate used for the blank, V2 – the volume of sodium thiosoulphate used for determination, m – the mass of the sample.

Determination of Refractive Index

A refractometer was used in this determination. The sample was transferred into the glass slide of the refractometer by opening the prism box and a drop of the oil placed on the ground surface of the lower prism. It was then closed and the box flattened again, making sure that the oil did not flow away. The cross wires of the telescope are then focused by rotating the eyepiece and adjusting the mirror to get good illumination. By means of the lower knob, the prism box turned slowly backward and forwards until the field of view became coloured fringe. By means of the upper knob, the compensator rotated until the coloured fringe disappeared and the lighted image showed a sharp edge. The prism boxes rotated until the sharp edge coincide with the intersection of the cross-wires in the telescope. The index of refraction was read off on the scale through the eyepiece (Kyari, 2008).

Fourier Transforms Infrared (FT-IR)

To investigate the presence of H-C-S and H-C-O-S group in the sulphonated fatliquor, the oils were characterised by FT-IR measurement (600-4000 cm-1), normal resolution of 4 cm-1 usinga Shimadzu 8400S FT-IR instrument (Shimadzu, Milton Keynes, UK) according to the method reported by Nkwor *et al.*(2019).

Production of Fatliquor (Sulphonation of the Oil)

The oil was weighed, placed in a beaker. The beaker was placed in a larger basin containing an ice block. Concentrated sulphuric was added drop wise in ratio 1:3 to the oil with constant stirring at 18-20°C temperature and below. Reaction carried out slowly (3 hours were given to complete the reaction after adding the sulphuric acid). The sulphated oil was shaken with 10% sodium chloride solution and then kept in a separatory funnel overnight in which the mixture separated into two layers. The pH of the separated upper layer sulphated liquor was adjusted to pH 5.5 by adding sodium bicarbonate solution and the resulting fatliquor then applied on leather.

Application of Fatliquor

All other tanning processes (soaking, unhairing, liming, deliming, bating, pickling, chrome tanning, and neutralization, retanning) were kept constant for the production of shoe upper leather, at fatliquoring the leather samples were divided into two halves each along the backbone line one side serving as a control and other as the trial sample. The fat liquors (control and trial) were applied in the order of 3%, 5% and 7% using three chrome retanned crust.

Tensile Strength and Percentage Elongation at Break (SLTC/IUP6)

This is a load per unit area of the cross-section required to pull apart or break a strip of leather. The leather sample was cut in a dumb-bell shaped 1cm × 15cm. The specimens were prepared from the leather. Tensile strength (kg/cm^2) and elongation at break (%) were conducted according to SLTC/IUP6 using the tensile strength machine and the reading was evaluated base on the equations 4 and 5.

Tensile strength (kg/cm^2)

$$= \frac{breaking\ load\ (kg)}{thickness\ (cm) \times width\ (cm)} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Elongation at break %

$$= \frac{length\ at\ break\ (cm) - initial\ length\ (cm)}{initial\ length\ (cm)} \ldots\ldots (5)$$

Water Absorption Test (SLTC/IUP7)

In preparing the specimen for this test the leather sample was cut in a circular disc of 4.4mm diameter and then conditioned according to SLTCSLTC/IUP3. The thickness of the disc was measured according to SLTC/IUP4. The weight of the disc was taken and the disc was placed in the Kubelka apparatus, the apparatus was filled with distilled water to the $0.00cm^3$ level. The leather sample was immersed in the water for 30 minutes after the 30minutes the apparatus was turned at a right angle to allow the water to drain to the bulb and complete draining achieved in 1 minute after which the reading was taken. The procedure was repeated for intervals of 1hr, 2hrs, 3hrs and 24hrs. The temperature of water maintained between 0-20 ^{0}C. The water absorption (Q) was calculated (volume of water absorbed per weight of the sample) using equation 6.

$$Q = \frac{Volume\ of\ water\ absorbed \times 100}{Mass\ of\ sample} \ldots\ldots\ldots\ldots (6)$$

Ball Burst Test

The sample was cut just as in the water absorption test. The sample was conditioned according to SLTC/IUP3 clamped on the machine according to SLTC/IUP9 and the machine put on, distension washed until the occurrence of a crack on the grain surface then the red button was pressed so the instrument recorded the load and distension. The loading continues until the disk bursted and the instrument was stopped and the results were printed out.

RESULTS AND DISCUSSION

Table 1 which indicated the yield as 42% means the seed of this plant contained an appreciable amount of oil which can be produced in a commercial quantity if the plant is grown on a large scale for fatliquor production and other medicinal applications.

Table 1: Oil characterization

Yield (%)	Color	Solubility @ 25^0c	pH	Acid value (ml/g)	Saponification Value (ml KOH/g)	Iodine Value (%)	Refractive Index	Density (g/cm^3)
42	yellow	insoluble	4.8	3.8	204	74	1.459	0.95

The oil obtained was yellowish which is the colour as described by previous researchers with pH 4.8 showing that it is acidic as other oils due to the presence of carboxylic. Oxidative deterioration of oils can be stimulated by their free fatty acid contents via chemical oxidation and/or enzymatic and other physical factors like heat and light to form off-flavour components (Ajayi 2010 as cited by Ifijen *et al.*, 2020). The acid value was found to be 3.8% which is higher than what was obtained by Kyari, (2008). This shows that the oil obtained here is not good for consumption. This is because, previous studies have shown that for an oil to be considered for cooking, the free fatty acid content of the oils should not exceed the limits of 0.0–3.0 % (Ajayi 2010, Onyeike and Acheru 2002 as city by Ifijen *et al.*, 2020). The refractive index was the same as what was obtained by Kyari (2008). The saponification value of 204 mlKOH/g is in line with the accepted range of values that can be utilized in the production of fatliquor. This is because it has been established that oil with a higher value of saponification will produce a better fatliquor and the saponification value has a direct relationship with the molar mass of the fatty acid content of the oil as reported by Ajani *et al.* (2019) (Ifijen *et al.,* 2020). The iodine value is one of the important factors to be considered when producing fatliquors. The oil from this plant was found to contained iodine value of 74% which is a good value for the production of fatliquor. This assertion is in agreement with 70% minimum recommended standard of iodine value reported by Covington, 2009.

The FTIR results in Table 2 illustrate the Summary of the Functional groups present in FT-IR spectrum of the oil which shows the presence of unsaturated groups (–C=C-) and confirmed the possibility of forming the sulphonated product which is a justification of the iodine value. The FTIR result also indicates the presence of alkenes, carboxylic acids, aromatic rings, ethers, esters, nitro groups all these sum up to the constituents of fats and oils.

Table 2: Summary of the Functional groups present in FT-IR spectrum

S/No	Functional group	
1	C═C—H	asymmetric stretch aromatic ring/alkenes
2	H—C—H	asymmetric and symmetric alkanes
3	C=O	stretch carboxylic acids/ketones
4	N—H	bend amines-secondary
5	N=O	bend nitro group
6	C—O	stretch ethers, diethyl ether/stretch esters, methyl formate

Table 3 shows the test conducted on the leather samples. The trial sample and control have a similar property of water absorption with only fraction differences but this result shows that the fatliquor produced can substitute the imported ones. Table 4 shows the Lastometer test, also known as distension and strength of grains by the ball-burst test an important factor during the molding of a shoe (lasting). This test revealed the positive response of the leathers tanned in toe lasting conditions. Comparing the results obtained in the leathers, no significant difference was observed; indicating that a local resource can be relied upon.

Table 3: Water absorption (cm^3/g)

%	3%		5%		7%	
Time (min)	T	C	T	C	T	C
30	2.82	3.24	2.70	2.66	3.48	3.35
60	3.05	3.35	2.94	3.04	3.50	3.50
120	3.05	3.35	3.07	3.05	3.54	3.64
180	3.19	3.37	3.07	3.28	3.79	3.80
1440	3.29	3.45	3.43	3.79	5.00	4.08

T=trial, C=control.

Table 4: Comprising of % elongation, tensile strength and ball burst test results.

	3%		5%		7%	
	T	C	T	C	T	C
% elongation	34.33	33.98	30.36	33.55	40.21	40.9
Tensile strength(N/Mm^2)	30.24	30.45	32.12	32.10	35.98	35.72
Ball burst test (kg/mm)	3.48	3.27	2.50	2.31	2.98	2.89

T=trial, C=control.

The tensile strength and % elongation in Table 4 are two in one test using the same machine that determine strength of the leather and its ability to be stretch, the trial sample shows characteristics that are similar to the sample. All the tensile strength values of leather samples fat liquored were above the recommended standard for shoe upper leather. A higher value of tensile strength is a desirable property for all tanned leathers and is an indicator regarding the quality of leather. Tensile strength is one of the most important physical quantities of characterizing the mechanical properties of materials. It is a routine quality control test in the leather industry where maximum stress and breaking elongation of leathers are determined.These results on a general note conclude that trial fatliquor can be used in place of the imported ones. This would reduce the importation rate and encourage the use of the local content.

CONCLUSION

This research evaluates the leather fatliquoring potential of sulphonated *Lophira lanceolata* oil. The performance characteristics of the synthesized sulphonated oil and the physical characteristics of leather compared favourably with commercial leather fatliquor. The results showed that *Lophira lanceolata* oil of no commercial value can be a source of fatliquor for the leather industry. From the tests conducted on the final leather in which both the trial sample and control show similar characteristics, it is good to make use of local resources to boost our economy and create employment for the country rather than over dependence on foreign goods. On this note, it has been concluded that the locally made fatliquor should be put into use by cultivating plants that have a large quantity of oil with high iodine value.

Recommendations

Oil from *Lophira lanceolata* is highly recommended for the production of fatliquor as such there should be a plantation of this plant so that it can be produced in commercial quantity.

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