FATLIQUORING POTENTIALS OF SULPHONATED *Hura crepitans* L. SEED OIL

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ABSTRACT. Fatliquors are oil-in-water emulsions required in leather processing for the purpose of leather lubrication. They ensure that the collagenic fibres do not stick together on drying and as a consequence make the leather flexible. In this work sulphonated oil with negligible inorganic salt content has been synthesised from *Hura crepitans* L. seed oil. Both the unsulphonated and sulphonated oils were characterized by DSC, FT-IR, ^{1}H NMR, ^{13}C NMR, and ^{13}C NMR DEPT. The sulphonated oil and its blend with 7.5 % raw castor oil were applied onto light leather and compared with commercial fatliquor in the processing of shoe upper leather. The characteristics of the processed trial leathers were comparable with similar leathers made with commercially available fatliquors. This work raises the possibility of increasing the range of commercially viable, sustainable fatliquors in the leather industry.

KEY WORDS: *Hura crepitans* L., fatliquor, leather, lubrication, sulphonated

POTENŢIALUL DE UNGERE AL ULEIULUI SULFONAT DIN SEMINŢE DE *Hura crepitans* L.

REZUMAT. Agenţii de ungere sunt emulsii de tip ulei-în-apă necesare la prelucrarea pieilor pentru ungerea acestora. Aceştia împiedică lipirea fibrelor colagenice la uscare şi, prin urmare, fac pielea flexibilă. În această lucrare s-au sintetizat uleiuri sulfonate cu conţinut neglijabil de săruri anorganice din uleiul de seminţe de *Hura crepitans* L. Atât uleiurile nesulfonate cât şi cele sulfonate au fost caracterizate prin DSC, FT-IR, RMN ^{1}H, RMN ^{13}C şi RMN DEPT ^{13}C. Uleiul sulfonat şi amestecul său cu 7,5% ulei de ricin brut au fost aplicate pe piele uşoară şi au fost comparate cu grăsimile comerciale utilizate la prelucrarea pielii pentru feţe de încălţăminte. Caracteristicile probelor de piele prelucrate au fost comparabile cu cele ale pieilor similare fabricate utilizând agenţi de ungere disponibili în comerţ. Această lucrare prezintă posibilitatea lărgirii gamei de agenţi de ungere sustenabili şi viabili din punct de vedere comercial pentru industria de pielărie.

CUVINTE CHEIE: *Hura crepitans* L., ungere, piele, lubrifiere, sulfonat

LE POTENTIEL DE L'HUILE SULFONÉE DE GRAINES DE *Hura crepitans* L. COMME LIQUEUR GRASSE

RÉSUMÉ. Les liqueurs grasses sont des émulsions huile dans eau nécessaires pour la nourriture du cuir. Elles empêchent les fibres de collagène de coller pendant le séchage et rendent donc le cuir souple. Dans cet article, des huiles sulfonées avec une teneur négligeable en sels inorganiques de l'huile de graines de *Hura crepitans* L. ont été synthétisées. Les huiles non sulfonées et sulfonées ont été caractérisées par DSC, FT-IR, RMN ^{1}H, RMN ^{13}C et RMN DEPT ^{13}C. L'huile sulfoné et son mélange avec 7,5% d'huile de ricin brute ont été appliquées sur un cuir léger et ont été comparées aux liqueurs grasses commerciales utilisées dans le traitement du cuir pour les chaussures. Les caractéristiques des échantillons de cuir traités étaient comparables à celles de peaux similaires fabriquées avec des liqueurs grasses disponibles dans le commerce. Cet article présente la possibilité d'élargir la gamme de liqueurs grasses durables et commercialement viables pour l'industrie du cuir.

MOTS CLÉS : *Hura crepitans* L., liqueur grasse, cuir, lubrification, sulfoné

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INTRODUCTION

Hura crepitans L., also known as the sandbox tree, possumwood, or jabillo, is an evergreen perennial tropical plant belonging to the family *Euphorbiaceae* [1]. In Africa, these trees are usually planted as shade trees for roadsides and are also widely used to provide shade in front of residential, public buildings and parks. The trees are about 9 metres tall on the average. The bark is covered with lots of short spines; the woody fruits bear a resemblance to small pumpkin pods in which the seeds are housed with about 10-13 seeds in a pod. The seeds of these trees, when mature and dried, usually explode mechanically, littering the environment - thereby constituting a waste. These brown seeds have average diameters of about 1-5 cm [2].

These seed kernels contain a very high percentage of non-edible, golden yellow coloured oil [3]. Although several attempts have been made by researchers to proffer uses of this oil, such as metal soap production [4], biodiesel [5], it presently has no known commercial use. Other means of turning these oils into wealth are being researched; this work on sulphonation and subsequent use as a fatliquor in the leather industry is one example.

The leather industry makes use of a process that converts animal hide (or skin) into a non-putrescible substrate. During this process natural fat from the animal hide is removed to aid penetration of water born chemicals. When tanned leather without fatliquor is dried it produces a hard, intractable material which is difficult to work with; this is due to the collagen fibres sticking together. The inclusion of fatliquor (oil-in-water emulsion) into leather is often the last of the wet processing stages of leather manufacture and lubricates the leather fibres preventing this sticking and producing softer leather. It also reduces the frictional forces between the leather fibres thereby making them slide over one another easily, improving the flexibility, tensile strength and other mechanical /physical properties of leather [6].

Most natural oils (from animal and plant sources) used in fatliquor production have major food uses and this unhealthy competition affects a nation's total available reserve [7-9].

This paper describes the use of *H. crepitans* seed oil for the preparation of a sulphonated leather fatliquor and its consequent use in the processing of a leather shoe upper. This research gives a possible commercial application for this abundant, underutilized, non-edible oil.

EXPERIMENTAL

Materials and Methods

Mature and dried *H. crepitans* pods were collected from Fatilami Park in Abakaliki, Ebonyi State, Nigeria. Wet blue goat skins were obtained from the tannery at the Institute for Creative Leather Technologies (ICLT), The University of Northampton (UoN), Northampton, United Kingdom. Reagents used in the laboratory for synthesis and analysis were of analytical grade while those used for leather processing were of commercial/industrial grade. The samples of pods, seeds and leaves were identified in the Biology unit of the department of Biology/ Microbiology and Biotechnology of the Alex Ekwueme Federal University Ndufu-Alike, Ebonyi State, Nigeria and voucher samples kept. The pods were cut open and the seeds removed. The seeds were manually decorticated and the endocarp gently removed to get the creamy white cotyledons. These creamy white cotyledons were sun dried for five days and the cotyledons were coarsely ground (approximately 2 mm) using the kitchen hand grinder before extraction [3]. The extraction of the oil from the seeds was carried out in a soxhlet apparatus using n-hexane as a solvent.

Characterisation of H. crepitans Oil

Physicochemical properties of *H. crepitans* oil (HCO) were determined according to the methods recommended by the Society of Leather Chemists and Technologists (SLTC, 1996). Fatty-acid composition of HCO was determined using its methyl ester prepared with the method described by Adewuyi *et al*. [5] on an Agilent 19091S-433HP-5MS gas chromatograph attached to a mass spectrometer. The injection and detection temperatures were 280 and 300°C respectively. Helium was used as the carrier gas at a flow rate of 20 ml/min. The area percentages were recorded with a standard Chemstation Data system. For the mass spectrometry, an ACQ

mode scanner (with scan range of 15-500 atomic mass unit and voltage of 2094) was used and the mass spectra were compared with the NIST11 mass spectral library.

Differential scanning calorimetry (DSC) of the oil was performed using a DSC 2 Star System (Mettler Toledo). The purge gas (nitrogen) had a flow rate ~60 ml/min. Samples of oil, of between 5-7 mg, were weighed into low pressure aluminium crucibles, and sealed hermetically. The sealed crucibles were pierced prior to analysis [10]. An empty, hermetically sealed aluminium crucible with a pinhole was used as a reference. A temperature profile of -80 to 180°C was run using the following temperature program: -80°C isotherm for 3 min; dynamic ramp at -80°C to 180°C (at 10°C min^{-1}), isotherm at 180°C for 3 min; isotherm at 30°C for 2 min. The resulting DSC data was analysed for peak temperature, onset temperature and melting temperature for comparison. All DSC experiments were carried out in triplicate and average values are reported. Melting temperature was considered to be the temperature at the end of the melting transition [11].

Sulphonation Process

Concentrated sulphuric acid (45 ml) was added dropwise into 150 g of *H. crepitans* seed oil (with constant stirring at 20°C for 2 h). The crude mass was dissolved in 450 ml of ethanol, and neutralised using 15% NaOH (solubilised in methanol). The salts were filtered off under vacuum. The solvent was removed and recovered using a rotary evaporator. The resulting sulphonated oil was ready for use.

Characterisation of the Sulphonated Oil

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} using a Shimadzu 8400S FT-IR instrument (Shimadzu, Milton Keynes, UK). ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR and distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR, spectra of both the unsulphonated and sulphonated oils were acquired on a Bruker Biospin® AV500 – 5mm BBO probe with Z axis gradient, TOPSPIN v 2.1, ^{1}H=500.13 MHz, ^{13}C=125.76 MHz (Brucker, Coventry, UK). The thermal behaviour of the unsulphonated and sulphonated oils was determined using the Mettler DSC 2 Star System in temperature range of -80 to 180°C.

Physicochemical Tests on the Sulphonated Oil

The specific gravity, pH, stability of the emulsion, total organic SO_3 and percentage ash were determined according to the standard methods recommended by the Society of Leather Chemists and Technologists [12].

Fatliquoring Process

Wet blue goat skin, shaved at 1.2-1.3 mm was divided into four quarters such that the sampling positions (BS EN ISO 2418:2002) [13] were uniformly represented in all the four quarters. Further treatments on each of the four quarters of the wet blue goat skins labelled NC, PC, A1 and A2 respectively were simultaneously carried out (with the aid of four separate tanning drums/ baths) using a conventional shoe upper manufacturing process (fatliquoring process) (ICLT SR 15/31) [14].

A negative control (designated NC) was processed without any fatliquor; a positive control (designated PC) was processed using a commercial fatliquor, Trupon DXV (Trumpler Gmbh, Worms, Germany, an imported fatliquor commonly used in the Nigerian leather industry). Sample A1 was processed using pure sulphonated *H. crepitans* oil; Sample A2 was processed using a blend of pure sulphonated *H. crepitans* oil and 7.5% raw castor oil. Leather dyeing was omitted to enable the Sudan IV staining (for fatty substances) to be carried out effectively after the leather manufacture.

The chrome tanned leather was wet back by the addition of water (300%) and wetting agent-Bermanol WAU (0.2%) in the drums at a temperature of 30°C. After 20 minutes run, the water was drained. It was then neutralised by addition of water (100%), sodium formate (1%) for 5 minutes and sodium bicarbonate (0.25%) for 30 minutes at 35°C, drained, washed with water (200%) and drained. On addition of water (100 %) and replacement syntan (Trupotan GDL) (6%) in the drum, it was run for 15 minutes and vegetable tannin added at 30°C and allowed to run for 30 minutes. Water (200%) and Acrylic resin (3%) were added and allowed to run for

another 30 minutes at 35°C before drainage. It was further washed with water (200%) for 5 minutes at 50°C and drained. Sulphonated *Hura crepitans* oil, labelled A2 mixed with water (1:3) (8%) was added and allowed to run for 50 minutes at 50°C. Formic acid (1%) was added and allowed to run for 20 minutes, washed for 10 minutes twice and horse dried.

Mechanical / Physical Properties of Leather

All leather samples: NC, PC, A1 and A2 were conditioned according to BS EN ISO 2419:2002 [15] prior to staking twice using a Cartigliano PAL 160 leather staking machine (Cartigliano) and subsequent mechanical testing.

The mechanical properties of leather samples were all determined using standards; softness (BS EN ISO 17235:2015) [16], tensile strength (BS EN ISO 3376:2011) [17], elongation at break and tear strength of leather (BS EN ISO 3377-2:2011) [18] and grain strength (BS EN ISO 3379:2015) [19]. Thin cross sections (50 µm) of the leather samples were cut with a Leica 1850 cryostat microtome (Leica, Wetzler, Germany) (set at -20°C) and used in the Sudan (IV) stain test for the determination of extent of penetration of the fatliquors between the leather fibrils.

RESULTS AND DISCUSSIONS

Characterisations

Fatty Acid Composition

The fatty acid composition of unsulphonated *H. crepitans* oil (HCO) is shown in Table 1.

Table 1: Fatty acid profile of the extracted oil

Fatty acid	Percentage composition
Palmitic acid	27.54
Oleic acid	27.24
Linoleic	33.06
Linolenic	7.45
∑ Saturated fatty acids	27.54
∑ Unsaturated fatty acids	67.75
Others	4.71

It was observed that linoleic acid (33.06%) which is an unsaturated fatty acid is the main fatty acid present in *H. crepitans* oil. Other major fatty acids present are oleic acid (27.24%) and palmitic acid (27.54%). The iodine value of the unsulphonated oil (Table 2) is consistent with the total unsaturated fatty acids (67.75%). The double bonds present in the unsaturated fatty acid were targets in the sulphonation process.

Physico-chemical Properties

The physico-chemical properties of unsulphonated *H. crepitans* oil (HCO) and sulphonated *H. crepitans* oil (SHCO) are shown in Table 2. A high percentage of oil clearly indicates that *H. crepitans* seed contains a sufficiently large quantity of oil which can be chemically modified for the synthesis of fatliquor via sulphonation. The oil yield value of 52.76% is in close agreement with what is obtained for the seed (53.61%) as reported by Okolie *et al*. [20], (53.81%) by Abdulkadir *et al*. [2] but higher than what was reported by Adewuyi *et al*. [5] (37.75%). Variations in properties of oil maybe due to the differences in variety of plant, cultivation, climate, ripening stage, the harvesting time of the seeds and the extraction methods used [21].

The golden colour possessed by *H. crepitans* oil is the colour of most vegetable oils and would not be detrimental to the final colour of the article produced. Its smell which is inoffensive conveys the likelihood of the oil not influencing the odour of the finished leather product. The specific gravity of the oil is in line with the density of most vegetable oils [22]. The oil has an iodine value of 117, which signifies a high quantity of unsaturated fatty acids [22]. The decreased iodine value observed in the sulphonated product signifies a low level of unsaturation as most of the C=C bonds in the unsulphonated oils have been used up in the sulphonation reaction. The sulphonated oil produced from the oil has a high percentage of SO_3 (5.87%). High percentage of SO_3 in a fatliquor is an indication of a deeper penetration prospect of sulphonated *H. crepitans* oil when used in leather fatliquoring [6]. The very pale brown colour of the 10% solution did not affect the colour of the finished leather product and suggests that the finished leather product could be dyed to any choice of colour by the tanner.

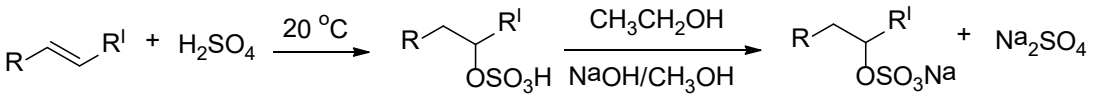
Similarly, the sulphonated oil which is odourless, has no influence on the final odour of the produced leather unlike most leather products with a unique fishy smell.

Contrary to previous published works [23-25], the fatliquor detailed in this work is virtually free from inorganic salts; a disparity likely caused by differences in the method of production.

Table 2: Physicochemical properties of both unsulphonated and sulphonated *H. crepitans* oils

Parameter	Unsulphonated oil (HCO)	Sulphonated oil (SHCO)
Percentage Yield (w/w%)	52.76	74.86
Colour	Golden yellow	Brown red
Odour	Inoffensive	Odourless
Appearance of 10% Solution	-	Translucent
Colour of 10% solution	-	Very pale brown liquid
pH of 10% Solution	-	7.36
Stability of 10% solution	-	Stability > 24hrs
% Ash Content	-	Trace
% SO_3	-	5.87
Specific gravity (at 20°C)	0.920	0.942
Acid Value (mg KOH g^{-1})	6.17	5.93
Free fatty acid (% oleic acid)	3.09	2.97
Iodine value (g/100)	117	27
Saponification value (mg KOH g^{-1})	210	196

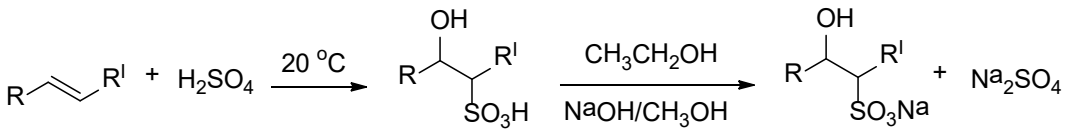
Sulphonation Process



Sulphonated (Sulphated) oil

Scheme 1. Sulphonation of *H. crepitans* oil to produce sulphonated (Sulphated) oil

The side reaction can be found below:



Sulphonated oil (true sulphonates)

Scheme 2. Side by side reaction of the sulphonation of *H. crepitans* oil

Apart from the sulphated and true sulphonates, the reactions (as shown in schemes 1 and 2) also yielded a large quantity of Na_2SO_4 (a drying agent), which was vacuum filtered, thus making the sulphonated *H. crepitans* free from water.

Fourier Transform Infra-Red (FT-IR) Results

The FT-IR spectra of unsulphonated HCO and the corresponding sulphonated SHCO are shown in Figure 1a and 1b. In Figure 1b, the absence of the peak at 3009 cm^{-1} (C-H stretching frequency of non-conjugated unsaturation) as

found in Figure 1a depicts the attack of H_2SO_4 on the –C=C- to form the sulphonated product. In Figure 1b the peak at ~1198 cm^{-1} (S=O stretching) is absent in Figure 1a. This confirms the formation of sulphonation reaction. Other prominent peaks found in both samples are at (2853 cm^{-1}) C-H stretching frequency of alkene, (1744 cm^{-1} (C=O stretching frequency of ester), 1464 cm^{-1} (bending frequency of unsaturated alkene), 721 cm^{-1} (bending frequency of saturated carbon atom). The wide peak in the range at 3200-3600 cm^{-1} is the OH stretching of alcohols and could be attributed to traces of alcohol left in the sulphonated product.

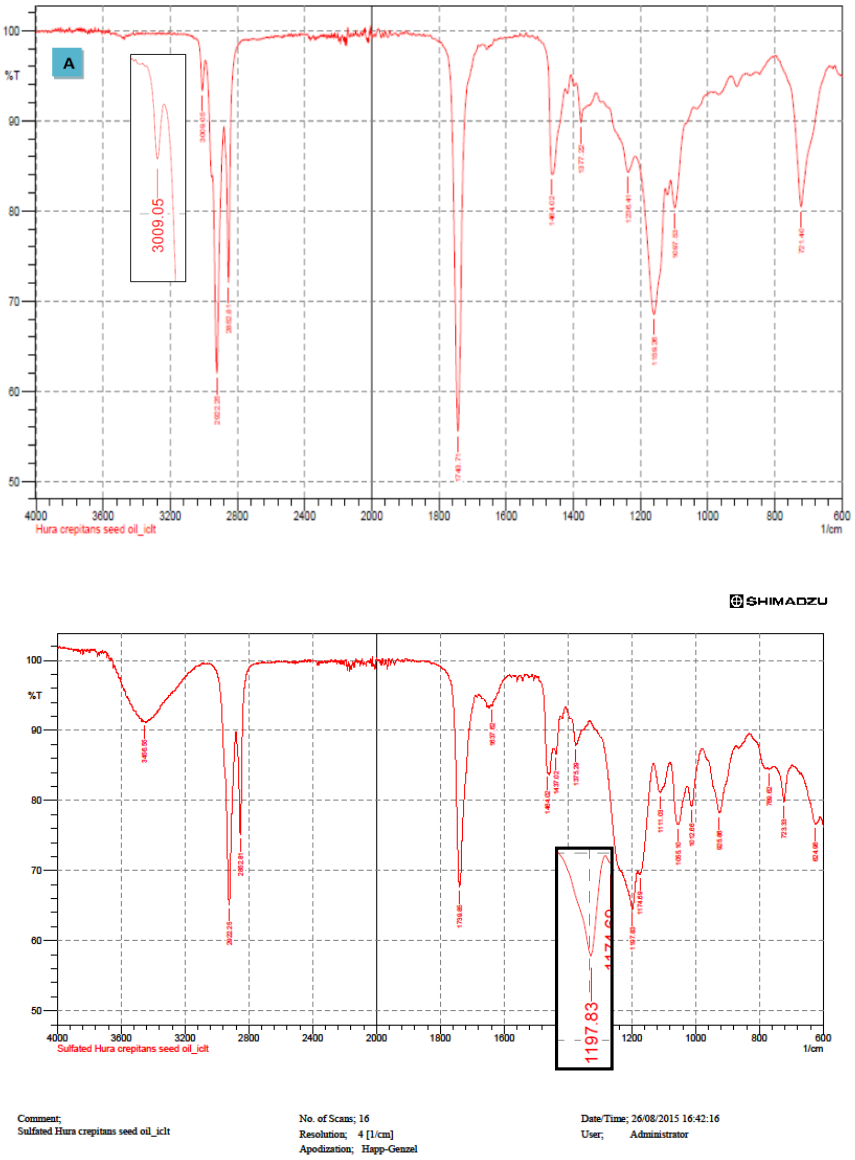
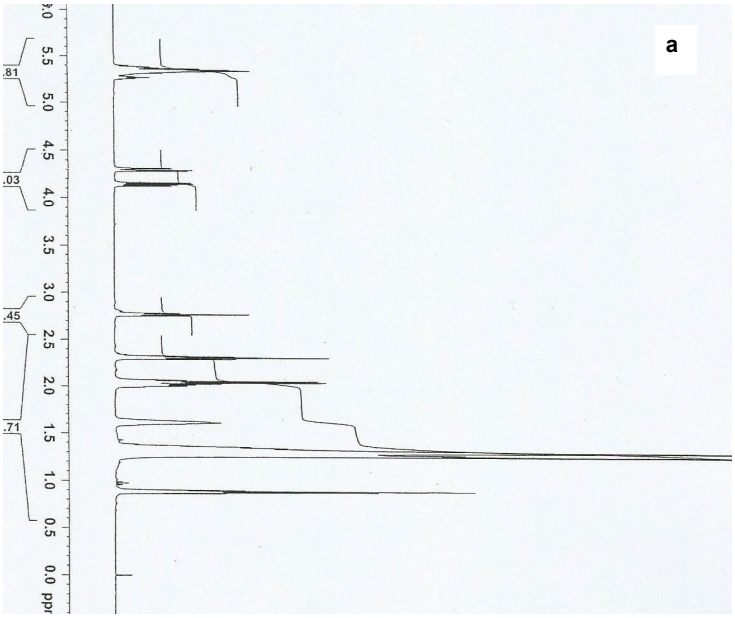


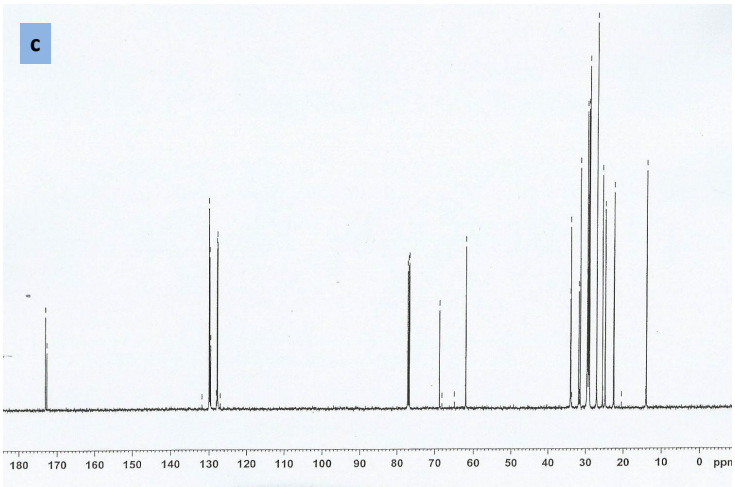
Figure 1. FT-IR spectra of unsulphonated *Hura crepitans* seed oil (A) (insert: expanded section of signal showing 3009.06 cm^{-1}) and sulphonated *Hura crepitans* seed oil (B) (insert: expanded section of signal showing 1197.83 cm^{-1})

Nuclear Magnetic Resonance (NMR) Spectroscopy Results

The ^1H NMR of HCO and SHCO are shown in Figures 2a and 2b respectively while the ^{13}C NMR and ^{13}C NMR DEPT spectral diagrams are found in Figures 2c, 2d, 2e and 2f, respectively.


a
.81
.03
.45
.71
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


b
99.18
0.82
5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 pp


c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

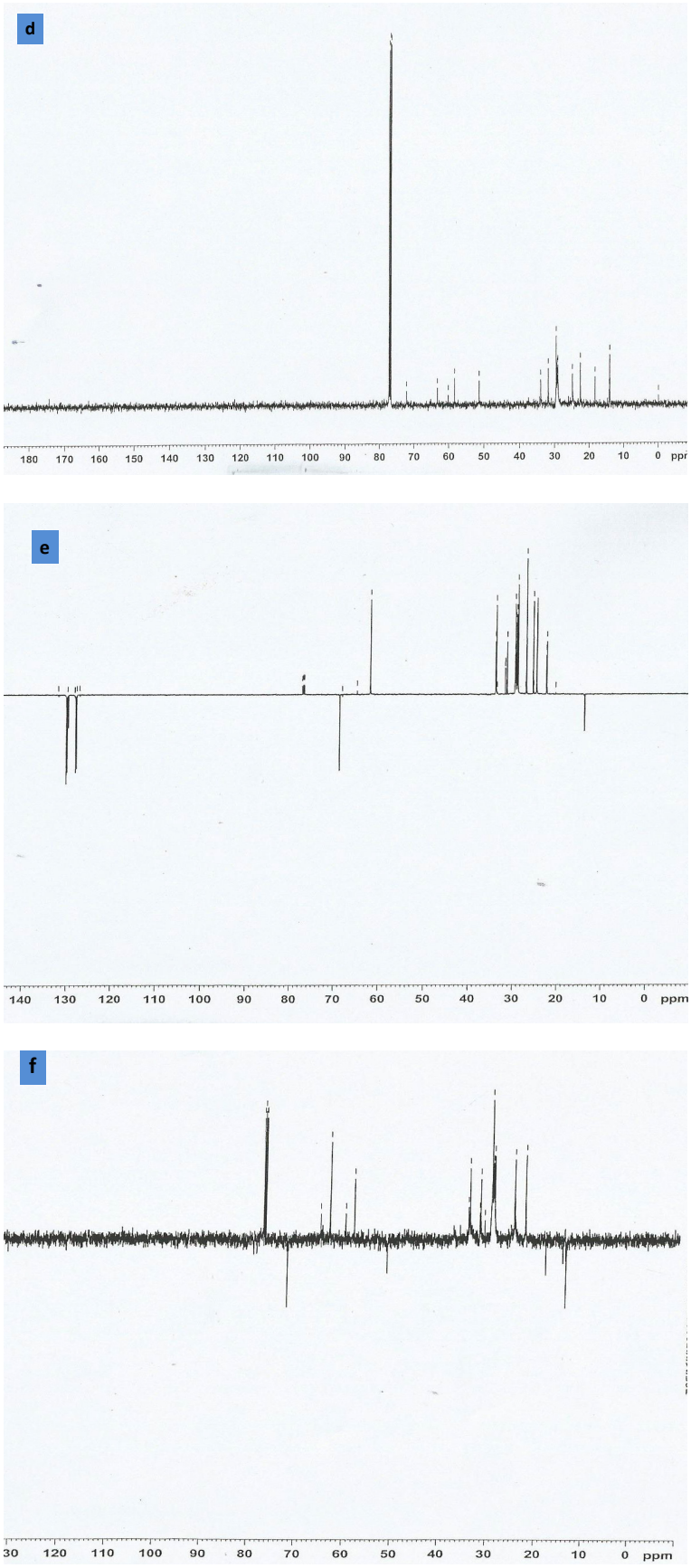


Figure 2. NMR spectroscopy results: (a) ^{1}H NMR of HCO (b) ^{1}H NMR of SHCO (c) ^{13}C NMR of HCO (d) ^{13}C NMR of SHCO (e) ^{13}C NMR DEPT of HCO (f) ^{13}C NMR DEPT of SHCO in deuterated chloroform

In the ^{1}H NMR, the multiplet observed at δ 5.29 (Figure 2a), in the unsulphonated oil are due to the olefinic protons attached to the C=C double bond. These protons are sp^2 hybridized and as such their NMR signals are deshielded by the influence of the diamagnetic anisotropy of the π system. Sulphonation / sulphation and sulphitation usually lead to the saturation of the double bond. The sp^3 hybridized protons formed are thus expected to be shielded relative to the sp^2 olefinic protons. The newly formed protons (H-C-S or H-C-O) in the two reactions formed (scheme 1 and scheme 2) showed signals at δ 3.6 and 3.73 ppm (Figure 2b). It is important to note that the slight deshielding observed for these protons relative to the rest of the protons in the sulphonated oil (Figure 2b) is due to the inductive effect of the electronegative sulphur and oxygen atoms. The inductive effect, however, causes less deshielding than diamagnetic anisotropy.

Similar explanation can be used to explain the differences in carbon chemical shifts observed in the ^{13}C NMR for the unsulphonated and sulphonated oils. In the ^{13}C NMR spectra of the unsulphonated oil, (Figure 2c), the methyl group at the end of the acyl chains in glyceride moiety give one signal at around 14.1 ppm. It is well separated from other signals and hence easily recognized. The same values have been reported in literature [22, 26, 27]. In the ^{13}C spectrum the signals associated with the olefinic carbons appear highly deshielded at δ 127.09 to 131.85 ppm due to the diamagnetic anisotropic effect of the π system. Upon sulphonation, (Figure 2d), these signals disappeared completely due to loss of the double bonds. The new signals which appeared at 52 and 72 ppm belong to the sp^3 hybridized carbons (C-S and C-O) formed after the sulphonation reactions. The slightly deshielded position of these signals is also due to the influence of the inductive effect of the electronegative sulphur and oxygen atoms.

From the ^{13}C NMR DEPT spectra diagrams (Figure 2 (e) and (f), the two samples (unsulphonated and sulphonated oils) studied had similar results except for some slight differences observed as a result of the reactions underwent by the sulphonated oils. The terminal CH_3 could be seen phased down in both results at δ 14 ppm. The C-H-O of the glycerol backbone could be seen phased down at δ 68 ppm. In like manner the two CH_2O of the glycerol backbone phased up and were seen at δ 64 ppm and 62 ppm. The $-(CH_2)_2$ of the fatty acid chains phased up an were seen at various positions δ 20-30 ppm. The evidence of the formation of C-O-S and C-S bonds by the reaction with H_2SO_4 was shown by the absence of the HC=CH previously found phased down in unsulphonated oils δ 127 ppm and 131.87 ppm in the sulphonated oils. The C-O-S was observed phased up δ 65.27 ppm in the sulphonated oils and C-S bonds were equally observed phased up at various positions δ 60.16 ppm and 58.38 ppm. These C-O-S and C-S bonds were completely absent in the unsulphonated oils. Also, the additional signals at 51.44 ppm, 58.38 ppm which represent the –C-S peaks and the signal at 72.17 ppm which represent the –C-O-S peak are completely absent in the starting HCO.

Characterisation of the Sulphonated Oil

The stability test results (Table 3) show that 10% fatliquor emulsions of sulphonated *H. crepitans* oil is generally stable in various salt solutions used in leather manufacturing processes like deliming and pickling solutions. As soon as a stable emulsion particle hits the fibre structure, the sulpho fraction interacts electrostatically with it, causing the emulsion to lose its emulsifier and the neutral oil will be deposited (Fixation) [6].

The sulphonated oil had good emulsion stability towards pickle liquor and hard water but unstable when in contact with formic acid. Anionic fixation takes place only in acid medium. This is because collagen at a pH < IEP becomes cationic and therefore anionic fatliquors are

fixed. Addition of 10% emulsion of sulphonated oil (pH of 7.36) brings about an increase in the pH of 5% Chromium sulphate (pH of about 3) to a higher pH of about 3.8 to 4.2. This leads to the destabilisation of the emulsion and phase separation occurs thereby making it stable after about an hour. The table also shows that the prepared fatliquor can be used in the retanning and fatliquoring steps.

Table 3: Stability of 10% fatliquor emulsion towards pickle liquor, tan liquor and hard water

Solution added	Stability Status
5% Basic chromium sulphate (tan liquor)	Stable (1 hour)
5% $MgSO_4$ (hard water)	Stable
5% NaCl (found in pickle liquor)	Stable
5% Formic acid	Unstable

Differential Scanning Calorimetry (DSC)

Table 4: The thermal behaviour of HCO and SHCO

Oil Sample	Onset Temperature (°C)	Peak Temperature (°C)	Endset Temperature (Melting Point) (°C)
Unsulphonated	-30.85 + 0.40	-23.88 + 0.08	-15.21 + 0.53
Sulphonated	-10.17+ 1.05	3.48 + 0.25	11.91 + 0.12

A higher melting point found in the sulphonated oil signifies a phase transition and could be an indication that most of the unsaturated fatty acids have been used up in the sulphonation reaction; leaving behind saturated fatty acids (which have a higher melting point) than unsaturated fatty acid [28]. The DSC results also show that the oils are very stable within the temperature range studied.

Mechanical Properties of the Leather Samples

Mechanical properties of the leather samples were shown in Table 5.

Table 5: Mechanical properties of the leather samples

Properties	NC	PC	Pure	Blend
Average Softness	25.8	32.6	32.2	33.4
Average tear load (N)	352.5	409.2	505.5	613.3
Average Tensile strength (N/mm^2)	15.66	20.62	23.51	26.13
Average elongation at break (%)	34.79	41.86	36.40	45.02
Average grain crack strength (N)	200	330	410	370
Average Ball burst strength (N)	380	435	500	480

Note: NC = Negative control (without fatliquor), PC = Positive control (with commercial fatliquor), Pure = with pure sulphonated *H. crepitans* oil, Blend = a blend of pure sulphonated *H. crepitans* oil and 7.5% raw castor oil

It is evident from the strength or mechanical properties results that the leather fatliquored using sulphonated *H. crepitans* seed oil has better properties than the commercial fatliquor. The value of the mean tensile strength of the negative control (leather processed without fatliquor) was very low (15.66 N/mm^2) when compared with that of the fatliquored leather samples - PC (20.62 N/mm^2), A1 (23.51 N/mm^2). This can even be improved by the addition of 7.5% castor seed oil A2 (26.13 N/mm^2). (Castor oil is normally used in the tanning industry as a source of lubrication because of its humectant property). These enhancements in the strength properties of the leather from prepared fatliquors result from good lubrication of the leather fibres [29].

Stain Test Results

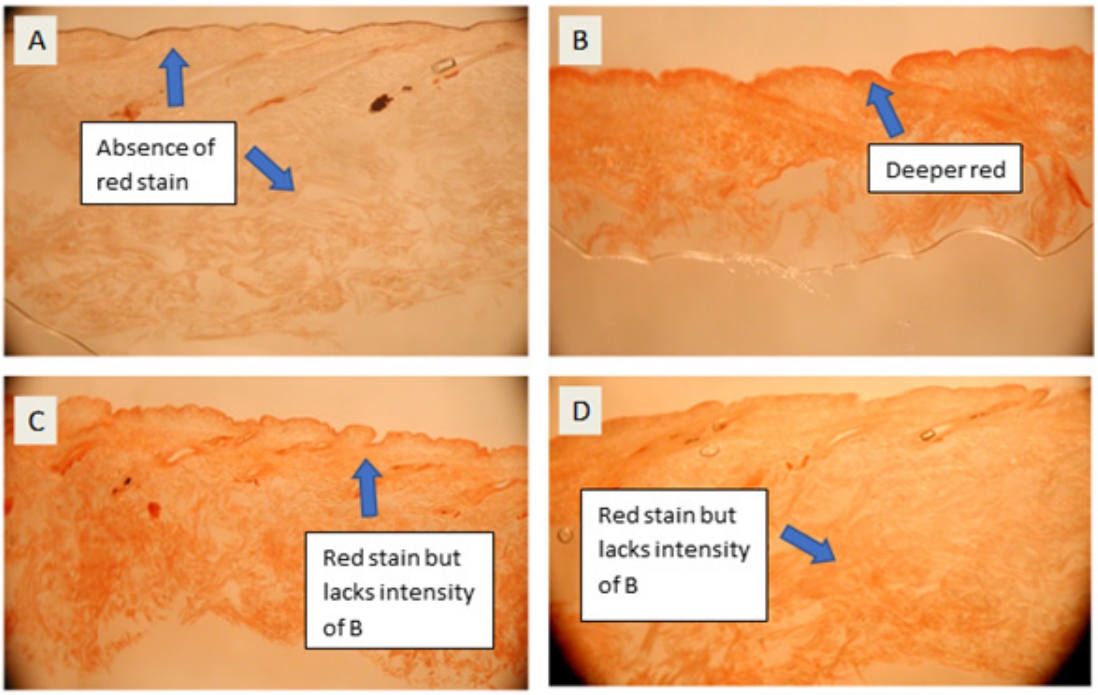


Figure 3. Staining test results showing cross section of goatskins fatliquored with: A) without fatliquor; B) with pure sulphonated *H. crepitans* fatliquor; C) with a blend of pure sulphonated *H. crepitans* fatliquor and 7.5% raw castor oil; D) with commercial fatliquor

The development of a deepening red colour in the stain as the figures move from Figure 3a to 3b signifies that the Sudan stain confirms the penetration of the sulphonated oils into the leather fibre structure [30].

Figure 3b, 3c, and 3d all show a deep penetration of fatliquor. The intensity of the red colour seen in Figure 3b-d indicates that the Sudan stain is detecting the presence of fats. Figure 3a indicates that no fat is present in the material. Figure 3c and 3d indicate that fatliquor is present, but the grain layer is not as deep in red colour as can be seen in Figure 3b. Surface lubrication is vital for grain strength when a leather is placed on the shoe last.

CONCLUSIONS

The sulphonation of *H. crepitans* seed oil (oil from underutilized seeds of no known market value), has been confirmed by the structural characterizations performed by FT-IR, ^{1}H NMR and ^{13}C NMR analysis. The sulphonated oil has no odour which will affect the smell of the finished leather product and is quite stable in pickle liquor and hard water. The leather processed by the sulphonated *H. crepitans* fatliquor had better tensile strength, double edge tear, and grain strength than that processed with commercial/imported fatliquor. This provides evidence that the sulphonated *H. crepitans* fatliquor is comparable and could even outperform commercial products for the production of leather shoe upper. It highlights the suitability of sulphonated fatliquor made from *H. crepitans* – a quite sustainable source.

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