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ADDING VALUE TO LAMPANTE OIL: HIGH QUALITY LEATHER FATLIQUORING AGENT VIA THE LOW- GRADE OIL SULFONATION

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ABSTRACT: Waste recycling and adding value to the low-cost by-products via transferring them into of-value products have a double benefit (environment, economic). Saving efforts to getting rid of this polluted by-product is another noble target. The recent work is a trial to add value to low-grade Lampanate olive oil. This oil does not find the best utilization in the primitive stresses. The oil was chemically modified to formulate an effective and low-cost leather fatliquor. The oil was chemically treated through a critical sulfonation process based on the higher degree of unsaturation and the probability of formation of glyceride sulfonates. The sulfonated oil has been adjusted to the ideal pH value and extracted by the salting-out technique. The desirable milky, pale-yellow emulsion and avoiding oil discharge, are mainly controlled by the sulfonating agent to oil ratio, the goal achieved at optimal ratio (1/10 acid to oil), at ambient temperature, and one hour stirring time. The analytical and chemical evaluation of the treated oil shows that the oil doesn’t suffer major degradability and possesses the specific characters to be utilized as a lubricating agent. Therefore, the Saponification value and acid value were found in the acceptable range. The emulsion efficiency has been evaluated; the emulsions showed great resistance towards metallic ions, hard water, and pH variation. The SEM image of the lubricated leather well showed that the fatliquor was able to transfer the oil droplets into the leather fiber. The oil droplets were able to reach individual fibrils and coated them with a thin layer film of the lubricant promoting over sliding and reduce fibrils sticking which demonstrates the physio-mechanical properties enhancement.

Keywords: lampnate oil – leather – fatliquoring – saving resources – sulfonation

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1. INTRODUCTION

Nowadays, the rapid increase in industrial activates creates intensive competition for natural resources. Sustainability and saving resources have become an urgent need. Strict environmental rules create a great constant demand for environmentally friendly resources. Vegetable oils gained great importance as oleo-chemical resources. They are safe and environmentally friendly compared with non-degradable mineral resources, in addition to their competitive advantage over high-priced and nonrenewable mineral oils. They are characterized by low volatility. They mainly are triglycerides of high molecular weight. They resist the viscosity-temperature change and the presence of polar ester group gaining them great adhering power. Therefore, they are excellent lubricating or liquoring agents- base. Several vegetable oils have been utilized such as palm oil, rice bran, flax and soya oil(Żarłok, Śmiechowski et al. 2014), sunflower oil, castor oil(Pakkang, Uraki et al. 2018). Olive oil, in particular, is well - dispersing oil/water emulsion forming emulsion of micro size. Olive oil of low quality and higher acidity is traditionally named Lampante olive. The unacceptable smell and taste make this oil not meet consumers' requirements as human food. Sometimes it hasn't the same typical green or gold of the extra and virgin oils. From a technical point of view, Lampante olive oil has to refine and purified to improve the smell and taste. Therefore, it meets the requirements of consumers as human food and these processes may not be available in the primitive presses, so it is disposed of or used as fuel which represents a great loss. In line with the principle of sustainability and optimization of resources, this work intends to add value to this oil by using it as a basic material for softening leather after appropriate chemical treatment. oil /water emulsion is expected to be an excellent medium for leather or textile fiber liquoring or lubricating. The tanning process involves treating the hide or skin with a tanning agent (such as chromium sulfate) so the skin gains resistance to bacterial attack and putrefaction. As a result, the protein chains which are the true hide or skin structure are fixed by the action of the tanning agent, and the leather becomes harch, unflexible, and useless. Therefore, the Tanned hide or skin has to fat liquored, so it returns its flexibility. Therefore, the term leather fatliquoring attributed to the process of incorporating fatty matters into inter fibers species of hard tanned leather, the process involves treatment of hard tanned leather with warm aqueous fat or oil solution, so the oil droplets penetrate the interwoven structure and add fatty mass to the tanned leather(Nkwor and Ukoha 2020), consequently, the introduced fat promote sliding of the protein chains, and the mechanical properties of the tanned leather (durability, tensile strength, elongation at breaks) are enhanced so the leather can be used in different applications. The emulsion has to possess considerable stability. The oil droplets of micro-size are formed into the aqueous medium. Such stability enables the droplets to penetrate the fibers (Habib 2018). In the other words, oil droplets must possess a great affinity to the fiber and have a penetrating power. Moreover, penetrating is not sufficient for lubrication or liquoring. Therefore, the fatty matter may be exhausted in the opposite direction via the reversible process, and the fatty matter can’t be housed into the fiber, consequently, the desired liquoring effect will not be recognized and the fiber bundles will not be coated with fatty materials (Żarłok, Śmiechowski et al. 2014). On the other hand, the big droplet well causes fat spew and greasy surface leading to deceptive liquoring. The process is sensitive and requires careful study to reach the ideal conditions for emulsion formation that able to act as a mass carrier(Habib 2017). The oil has to subject to chemical modification to create hydrophilic heads. In general, the sulfonated oils are favorable modified oil as excellent fiber liquoring. Therefore, they have considerable penetrating power and a lubricating effect. pH value, particle size, the stability of the emulsion, and the ratio between the emulsifying portions to the neutral oil are the main factors affecting the efficiency of the process(Janardhanan, Vijayabaskar et al. 2012). The ratio between emulsifying and neutral oil in the emulsion is a significant parameter. The effective fatliquor formulations have to contain about 50% neutral oil, 25% emulsifying fraction and the complementary of the solution is water, this condition creates particles of about 25 - 30 nm. In other words, the ratio of the emulsifying part to neutral oil has to be 1: 2, so the particle size can do the desired liquoring effect. Higher emulsifying fractions produce micro-emulsions, where the oil is on the limit of suspension and solubilization when the particle size is about 5 -25 nm(Covington 2009). Therefore, the desired lubricating effect can be recognized when the lubricant droplets coat the fibril bundles. Anionic

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fatliquors are the most favorable emulsion used, sulfated and sulfited oils offering the highest performance rates in this regard. Therefore, they show great stability against some chemicals. Moreover, they have a great affinity for fibers. The sulfited oils can be distinguished by the direct connection of sulfit group to the alkyl chain. R-$OSO3^-$ Na^+ = alkyl sulfates portion in sulfated fatty oil (ester of sulfuric acid). R-SO3 - Na+ = salts of true sulfonic acid (alkyl aryl sulfonates). R: represents a long simple or modified hydrocarbon chain ranging between 12-18 carbon atoms (hydrophobic part). First, sulfonated oils were produced in 1850 from inedible grades of olive oil. It was used as emulsifying, wetting agents, and dying assistance in textile processing. Sulfonated tallow is favored as a textile finishing agent. Many types of oils; namely, neat foot, cotton-seed, rapeseed, corn, and rice oil are also used as raw materials for sulfonated products (Mohamed, Habib et al. 2009) · From a technological point of view, sulfonated oils are characterized by a group of typical effects. The most important of which are wetting, penetrating and spreading, foaming, dispersing, emulsification and detergency. Generally, they are classified according to their principal use as detergents, wetting agents, emulsifying agents, and dispersing agents. Sulfo-group – SO_2-OH is “hydrophilic", has an affinity for water. The dual nature of the molecule is an essential condition for surface activity. Sulfonated oil products are employed in numerous individual cosmetic preparations; creams/ lotions/ makeup, toilet soap, shaving preparations, hand cleaning compositions. Surface active agents have been utilized in medicinal and health care applications such as pharmaceuticals, germicidal, and disinfectants. Sodium alkyl sulfates are effective in the treatment of gastric and duodenal ulcers. The alkyl sulfates are said to exert beneficial action by inhibiting the action of pepsin rather than by decreasing the corrosive effect of HCl. Regarding the processing and the lubricant preparation of Sulfated oils (R – OSO_3H), the oil should have a considerable degree of unsaturation. The value of the bounded SO_3 has to be at a considerable level of 3 – 4 % or 6-8% for the lubricants of high sulfated oils. From the chemical point of view, the sulfonation process involves reaction with SO_3, SO_3 is a vigorous electrophile, forming a black char (380 kJ/kg). TO overcome this problem the gas should be diluted, therefore, it is introduced into the bulk of the reaction as a dilute electrophile. The oils are mainly a triglyceride with a considerable degree of unsaturation, some triglycerides may be split under the effect of acid result in the libration of fatty acids and mono and diglycerides formation. Therefore, the reaction involves the addition onto unsaturated double bond or ester formation through –OH group into mono and diglycerides, the overall product is ester sulfonate. The degree of sulfation is a sensitive parameter, it governs the surface-active behavior of the lubricant(Sharphouse 1983). Moreover, it represents a significant parameter in both the particle size and the stability of the emulsion. The lubricant emulsion of the oils of low-level of sulfation suffers low stability and breaks down in the presence of acids or mineral salts. Therefore, these lubricants can be used only to lubricate the outer surface (the thin layer). The medium sulfated oils are more stable to coagulation and possess great penetrating power. The high-level sulfating oils have great stability against coagulation and are used to lubricate the heavy fibers(Attenburrow 1993). Olive oils are classified and priced according to acidity. According to the International Olive Oil Council, ‘virgin olive oil is the oil obtained from the fruit of the olive tree by solely mechanical without the harsh condition of temperature or chemical solvents, therefore the process does not lead to any chemical change(Council 2003). Virgin olive oil that has acidities lower than 3.3 degrees (% (w/w) free fatty acid content calculated as oleic acid) is suitable for consumption without any treatment. From a chemical point of view, olive oil is mainly a triglyceride of mixed fatty acids. The low-grade olive oil of acidity higher than 3.3 degrees is well known as lampante, the word lampante referrers to the Greek word, meaning "oil of light", where this oil is burned for light and heating. Lampante olive oil has to subject to harsh chemical treatment to decrease acidity to become edible oil. In the recent work, we aimed to add value to the low-grade lampante oil by transferring them into a value-added lubricant agent.

2. EXPERIMENTAL

2.1 Olive oil sulfonation

Low-grade Lampnate olive oil was delivered from a local olive oil press. The oil was charged into a three-necked round flask fitted with a thermometer, stirring rode, an inlet to add the chemicals. The oil was then individually treated with the acid at different oil / acid ratios (1.25, 2.5, 5, -10 %). The acid was slowly added drop-wise at a long-time duration to avoid mass discharge. The temperature of the reaction was set at room temperature or below 30°C (avoiding temperature increase) where the reaction is exothermic. After one hour the sulfonated product was then isolated through salting out and the pH of goods was adjusted to the neutral point (6.5 -7) by using 20% sodium bicarbonate solution. The emulsion of the sulfonated fatty material was then slowly formulated by adding the desirable weight in warm water (at 50 °C) at continuous stirring and the dispersing of the substance was observed.

2.2 Sulfonated oil evaluation

The progress of sulfonation has been tested through measuring the combined SO_3%, different factors affecting on the ability of micro size droplet formationa such as cid value total desulfated fatty matter and the progress in the change iodine value, the stability against electrolytes, stability against pH variation have been tested according to the standard test methods. The presence of sulfate group into treated oil was identified by FT-IR spectroscopic analysis; it was performed by using FT-IR (Mattson500, USA spectrophotometer).

2.3. Leather fatliquoring process

The wet blue leather samples were cut into small parts of 2 x 1 Cm^2 areas. The samples were soaked in distilled water for a half-hour duration time. the water was siphoned out and the samples were washed with distilled water. The pH of the leather samples was adjusted to 6.5 -7 using 1.5 % sodium acetate (based on the weight of the goods) followed by 0.75% NaHCO3 in situ until greenish-blue with Bromo-cresol green. The fatliquoring process was achieved under continuous stirring at a fixed temperature of 55°C and an agitation time of one hour. Therefore, the sulfonated oil has been added to the goods to form a worm aqueous solution. The fatliquor emulsion concentration was varied over range (2-10 %). The process has been carried out individually at different emulsion concentrations (2, 4, 6, 8, and 10 %, based on the weight of the goods), and 2 % commercial surfactant has been added, and the goods were agitated at further 40 minutes. After complete liquoring the emulsion was siphoned out and the fibers were washed with running water for 15 min. The clean samples were dried into the open air at room temperature to complete drying and engaged to further evaluation.

2.4 Evaluation of the fatliquored wet- blue leather

The amount of oil added to the fatliquored leather was measured according to the method reported by stamps(Stamp and DH 1974). To test adding fatty material in the leather fiber, the surface study of the liquored and unliquored wet-blue leather has been studied by scanning electron microscope SEM. The samples were subjected to Sputter Coater – Edwards - Model S - 150 A, Eng). Moreover, the visual properties of fat-liquored leather were observed.

3. RESULTS AND DISCUSSION

Olive oil is mainly composed of triglycerides that are composed of glycerol with fatty acids of general formula Me –(-CH_2) n- COOH., n is always even number of 18 -22. The fatty acids may be saturated, unsaturated, or polyunsaturated. Table 1 shows the major fatty acids into olive oil.

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Table 1. Fatty acid composition of olive oil 20

Fatty acid	No. of carbon	Ratio	Type
Oleic	18	55-83	Mono-unsaturated
linoleic	18	3.5-21.5	Di-saturated
Palmitic	16	7-20	saturated
Stearic	16	0.5-5	saturated
Linoleic	18	0-1.5	polyunsaturated

Unsaturated fatty acids represent the major constituents of the oil. Therefore, the oil has a high iodine value and a higher degree of unsaturation, providing high ratios of unsaturated double bonds -(C=C)-. Moreover, triglycerides may be split under the effect of acidic conditions or stirring at elevated temperature causing the release of free fatty acids and mixing of mono and diglycerides providing – OH function groups. Consequently, two active centers are available, the unsaturated double bond and hydroxyl group, that are represent the function groups that interact with acid, and the resulted product is ester sulfate according to the following schem:

$$-CH{=}CH- + HO\text{-}SO_3H \rightarrow -CH\text{-}CH\text{-}OSO_3H$$

$$-CH(OH)\text{-}CH_2\text{-} CH{=}CH- + HO\text{-}SO_3H \rightarrow -CH(OSO_3H)\text{-} CH_2\text{-} CH{=}CH-$$

Schem 1: sulfation reactions on oil

However, tri or di-glycerides may split into lower glycerides (mono or di) in the presence of sulfuric acid leading to form glycerides sulfonate. Therefore, the sulfo group acts as a hydrophilic portion, that causes self emulsification for the oil. Generally, the treated fatty matter gains surface-active properties and can form an emulsion in an aqueous system. However, the emulsion should have specific properties to act as a lubricant and transfer the fatty mass into the leather fiber. These properties are governed by particle size. The stability of the emulsion against harsh parameters such as electrolytes, acidity, and alkalinity providing a good predictor of the ability of the emulsion to do the desired lubricating effect and the ability of the microdroplets to penetrate the surface and adding mass. The sulfonation process has been carried out through careful conditions to avoid the discharge of matter, so the sulfonating agent was added drop-wise at a slow rate at intervals of time.

3.1 Evaluation of the sulfonated oil

The decrease of the oil saturation provides an excellent indication for the double bond breaking and the progress of oil sulfonation. Other parameters such as SO_3 % and the ratio of desulfated fatty matter provide an important indication in this regard. The data in table 2 show a remarkable decrease in iodine value with an increase of the ratio of sulfonating agent (sulfuric acid)

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indicating the progress in double bond conversion and oil sulfonation, the significant increase of SO_3 ratio confirm the addition of sulfate ion and forming ester sulfonate. In addition, the required SO_3 ratio for fatliquor formation (≥ 5) has been recognized at a higher ratio of sulfuric acid (10%). An increase in the acid value may be attributed to the splitting of the glycerides under acidic conditions and introducing sulfate ions. The data in the table revealed that the ratio between the sulfated and un-sulfated (neutral oil) is 1:2 at a higher sulfuric acid ratio means the sulfated oil can be emulsified into an aqueous medium without losing its liquoring effect (Covington 2009).

Table 2: the properties of sulfonated oil

Property	Result			
	1.25% acid	1.25% acid	5% acid	10% acid
Moisture%	6.2	7.3	8	8.4
Ash%	4.3	4.5	4.5	4.6
Acid value mg KOH/g oil	7.1	8	8.4	9.3
Iodine value mg I_2 /g oil	63	60	59	57
SO3%	2.3	2.6	3.6	5.2
Total de-sulfated fatty matters%	88	84	75	67.4

Table 3 illustrates the results of emulsion resistance against electrolytes. The data in the table revealed that the 10 % sulfonated oil shows higher resistance against all three electrolyte solutions. The milky desired aspect of the solution compared with the yellow color of other treated oil (treated with a low concentration of sulfating agents). The results are in accordance with the results cited in reference (Nkwor et al, 2020; habib, 2017). The different aspects developed at the stress of electrolytes as oil separation, duple phase separation, and stability are illustreated in the table. It is clearly appear that the optimal ratio of the acid for treatment of the oil at which the desired oil properties can be recognized 10% acid to oil ratio.

Table 3. Stability of 10 % sulfuric acid treated oil against electrolytes

Electrolyte	**Stability**			
	L1	L_2	L_3	L_4
5% Cr2(SO4)3	OS	OS	S	HS
5% Mg (SO4)	DP	DP	S	S
5% NaCl with 1.5% H2SO4	OS	DP	DP	S

L1-4 (sulfating agent ratio 1.25%. 2.5%, 5%,10 %) & Os oil separation, DP douple phase, S stable, HS high stable

Table 4 show the stability of the 10% treated oil against pH variation, the data in the table revealed to the fact that higher sulfonating acid ratio, the higher lubricant stability. Therefore, the L 4 show highest resistance against pH variation.

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Table 4 : the stability of the 10% treated oil against pH variation

Lubricant	pH		
	neutral	Acidic	Alkaline
L_1	S	OS	OS
L_2	S	DP	OS
L_3	S	S	DP
L_4	S	S	S

L1-4 (sulfating agent 1.25%. 2.5%, 5%,10 %) & Os oil separation, DP douple phase, S stable, HS high stable

FTIR spectra of olive oil before and after sulfonation are presented in figure 1. The spectrum showed characteristic absorption peaks of triglyceride. Band around 3007cm−1 is attributed to =C–H stretching vibration. Strong band absorptions were observed in the region of 3000– 2800 cm−1 refers to C–H stretching vibrations. The stretching bands at 2922 and 2853 cm−1vibrations are attributed to methylene–CH2– and methyl–CH3 – respectively which also observed at 1465 cm−1 & 1377 cm−1 bending vibrations. The large peak around 1720 cm−1 characterized to C=O double bond stretching. Stretching vibration of C–O appears at 1500–650 cm−1 25. The beaks appear in treated oil in at 1350cm-1 refers to sulfate group (Lerma-García, Ramis-Ramos et al. 2010) .

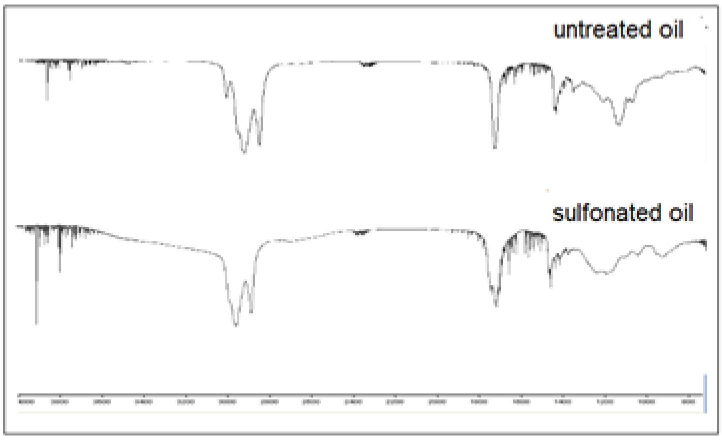

Fig 1. FTIR of sulfonated and untreated lampnate olive oil

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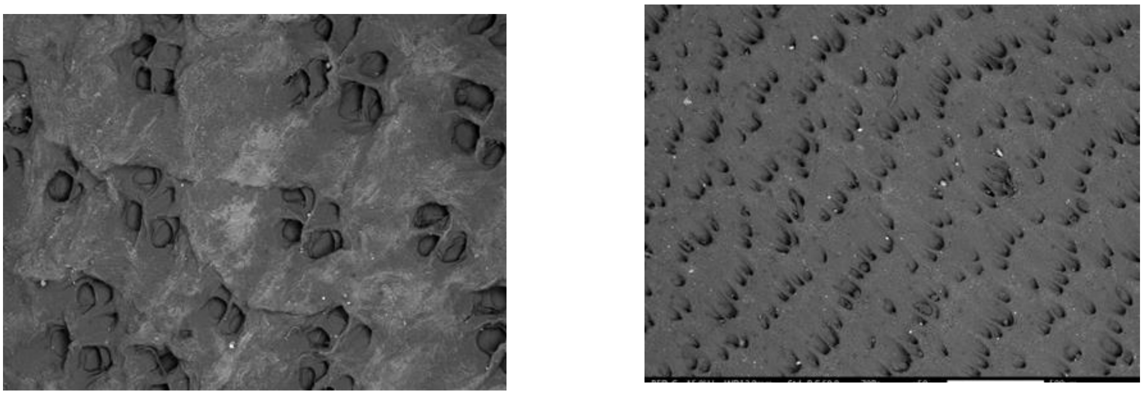
3.2 Evaluation of liquored wet-blue leather

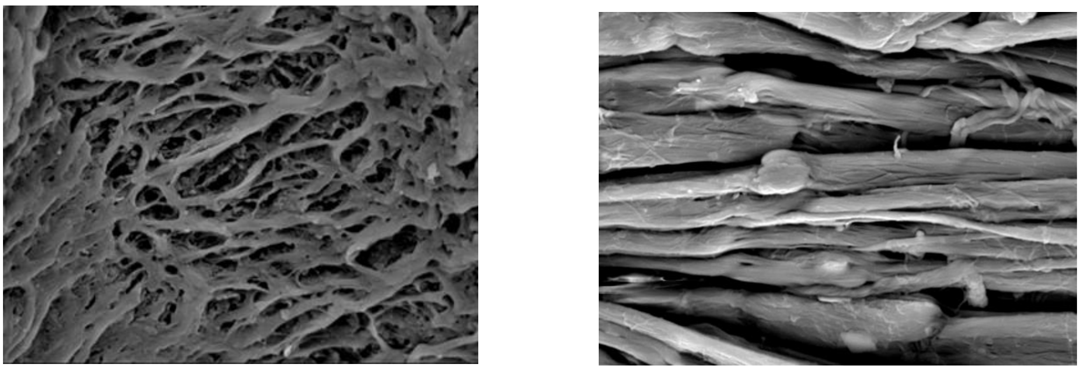
Table 5 shows the total fatty matter added relating to the concentration of the liquoring emulsion (sulfonated oil). In general, more concentrated liquors add more oil. The data in the table also revealed that the higher the emulsion concentration, the higher added fatty matter is, and the higher ratio of the added fatty matter was recognized at 10% fatliquor emulsion. Figure 2 shows the morphology of the wet-blue leather before and after liquoring with 10 % sulfated oil. Comparing the SEM images of Figure2 (a and b), the figures provide great evidence of enhancement of surface morphology of the lubricated leather. Figure 3(a and b) shows SEM image of the leather bundles before and after lubrication, the lubricated bundles show coating with the oil. Therefore, the lubricant was able to transfer the fatty matter into the fiber bundles promoting sliding which indicates successful lubrication and an improvement in physio-mechanical properties.



a-Surface of unliquored wet-blue leather

b- Surface of liquored wet - blue leather

Fig. 2 The morphology study of the surface of the fiber before and after lubrication



a-Unlubricant fiber

b-lubricant fiber

Fig. 3 SEM of lubricated and unlubricated fibers

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4. CONCLUSION

A low-cost leather fatliquor with an acceptable liquoring effect has been formulated from low–grade lampante olive oil. The oil was chemically modified through the sulfonation process to increase the affinity of oil to the water. The lubricant emulsion prepared at a higher ratio of sulfating agent 10 % exerts good emulsion stability and high resistance towards metallic ions and pH variation. The lubricant was able to obtain the desired filling effect and transfer fatty matter into the lubricated material. Studying fiber bundles and surface morphology of the lubricated fibers show significant coating of the bundles in addition to better surface outlook, confirming the success of the liquoring process. Therefore, the study was able to transfer a low-grade product into value-added material.

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