Characterization of Sulfited Fat From Limed Hides Fleshing as a Leather Fatliquor

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Abstract. The limed fleshing is generated in the beam house process, is the largest amount of waste, rots easily and causes a pungent smell that pollutes the environment. The use of limed fleshing in fatliquor is an effort to suppress the occurrence of pollution. The purpose of this study is to determine the physico-chemical properties of fatliquor from limed fleshing. Delimed fleshing with ammonium sulfate and water on a rotating drum. Fat was extracted from delimed fleshing using the wet rendering method and purified using n-hexane. The fat from delimed fleshing was characterized and then processed into a fatliquor. The fatliquors is prepared by reacting fat with aqueous sodium bisulfite (0.5, 1.0, 1.5, 2.0, and 2.5 mol/kg based on fatty matters) at a temperature of 85 °C for 2 hours. The results showed that fat from limed fleshing can be used to produce fatliquors substances. Based on the physico-chemical properties, the best fatliquors agent is prepared by treating sodium bisulfite with 2.0 mol/kg based on fatty matters.

1. Introduction
The processing of one metric ton of wet raw hide produced ± 200 kg of leather and more than 600 kg in the form of waste [1], [2], [3]. The generated waste is in the form of hair, trimming, fleshing, chrome shaving, chrome split, and buffing dust. Fleshing generated in the beam house process, it is the from green hide and or from a limed hide. In the tanning industry it is usually obtained in the form of limed fleshing. Fleshing is a type of waste which has the largest amount, that is, 56 - 60% of the total weight of waste[4].

Fleshing contains large amounts of fat, protein, minerals and water [5]. Sutyasmi [6] reported that fleshing contain 50-80% protein and 20-40% fat. Therefore fleshing is a good medium for the growth of microorganisms. Proteins and fats in fleshing are degraded by microorganisms into simple compounds and cause foul odours. Therefore it needs to be addressed immediately so as not to cause environmental problems. According to The International Union Environment Commission (IUE-2, 2008) [7] that green and limed fleshing can be used for tallow (fatty material) and gelatin. In addition to this, fleshing can also be used for animal feed, biogas, biodiesel, bioenergy recovery, and compost [8]. Extraction of fat from the fleshing using the wet rendering method gave a higher yield than organic solvents [9]. Fleshing fat can be used as cosmetics, fuel, fatliquor, and soap [6].

Fatliquor is a chemical that can be emulsified in water. It acts as a lubricant for the leather and has the ability to soften the texture of the leather. There are several types of consumer fatliquors, such as
an-ionic, cationic, non-ionic, multi-charged, amphoteric, solvent and complexing fatliquors[10]. An ionic fatliquor which is processed from fatty substances by sulfating and sulfitation can be dispersed well on the skin, has a low sensitivity to acids, and is most widely used in tanning leather processes. Besides that fatliquors from vegetable oils can inhibit ageing and Cr IV formation in leather [11]. Some researchers have processed fleshing fat into a fatliquor [12, 13] and [8] process fleshing fat into sulphating fatliquors, while [14] processes olein from fleshing fat separations into sulphitic fatliquors. This study aims to determine the physico-chemical properties of fatliquors which are processed by sulfitation of fat extracted from limed fleshing as an effort to use waste and reduce the risk of pollution in the environment. In addition, it is also to tread waste into products that have added value and reducing pollution in the environment.

2. Material and Method

2.1. Material and apparatus

The material used is in the form of limed hide fleshing, ammonium sulfate, n-hexane, sodium bisulfite, sodium chloride, sodium bicarbonate. The limed fleshing used comes from a small leather tanning industry in Yogyakarta. The chemical sodium bisulfite is from Sigma-aldrich, while ammonium sulphate, n-hexane, sodium chloride and sodium bicarbonate are from Brata-chem Yogyakarta.

The apparatus used includes balance, rotary drums tanning, water baths, glassware, vacuum filters, electric stirrers, pH meters, thermometers, and a number of equipment to test the physico-chemical properties.

2.2. Extraction of fat from limed hide fleshings

Lime separated from waste using 2% w/w ammonium sulfate and 200% w/w water on a rotating drum for one hour. Then the treatment is drained, after that the fat is extracted with water (fleshings and water ratio is 1:2 w/v), heated at 90° C for 2 hours. The fatty phase (at the top) is separated, then purified with n-hexane (the fat and hexane ratio is 1:5 w/v) at ambient temperature and stirred for 15 minutes. The insoluble part of organic solvent is separated by filtration. Finally, organic solvent (hexane) was removed from fat by distillation.

2.3. Preparation of sulfited fat based fatliquors

Sulfited fat from limed fleshing based fatliquors were synthesized by the following procedure. Briefly, 200 g fat was taken in glass beaker, heated to a temperature of 85 °C, than the fat treated with sodium bisulfite (0.5, 1.0, 1.5, 2.0, 2.5 mol / kg base on fatty matter) in the form an 40% aqueous solution, which was added drop by drop under continuous stirring for 2 hours, It was then cooled to room temperature, and then washed with 10% sodium chloride solution and neutralized with 20% sodium bicarbonate solution to pH 7 ± 0.2. After neutralization, the mass is left for overnight and then separated using the salting-out technique.

Analysis of fatty matter and sulfited from limed fleshing

The extracted fats from limed fleshings were subjected to fatty analysis as acid value, ash, colour, iodine number, moisture, peroxide value, saponification value. Analysis of the fats according to the standard analysis method. Beside that, it was also tested for fatty acid composition using gas chromatography mass spectrometry.

The sulfited fatliquor investigated by measuring the ash, moisture, oil content, SO₃ bound, total alkalinity, iod number, ph, and emulsion stability. In addition, to investigate the reaction between fat and sodium bisulfite, functional group tests were performed with Fourier-transform infrared spectroscopy (FT-IR).
3. Results and Discussions

3.1. Extracted fats properties

The yield and chemical properties of extracted fats from limed hide fleshings presented in table 1. The results showed that good enough extraction yield (11,10%), low moisture (0,30%) and ash (0,26 %) content. This situation indicates that fats is not easily damaged due to hydrolysis, and the mineral content of fats is very low. The minerals that are included in a wet rendering process are insoluble in hexane and are easily separated by filtration.

| No | Item                        | unit     | Value  |
|----|-----------------------------|----------|--------|
| 1  | Yield                       | %        | 11,10  |
| 2  | Moisture                    | %        | 0,30   |
| 3  | Ash                         | %        | 0,26   |
| 4  | Free fatty acid             | %        | 6,33   |
| 5  | iodine value                | g I₂ /100 g | 85,61 |
| 6  | Saponification number       | mg KOH/g | 12,75  |
| 7  | Peroxide value              | ml. eq/kg | 4,61   |
| 8  | Fatty matter                | %        | 85,76  |
| 9  | Colour                      | -        | yellowish |

Table 1. Chemical properties of extracted fats from limed hide fleshings

Fatty acids are straight-chain carboxylic acids (either saturated or unsaturated). They are derived from the hydrolysis of fats. Free fatty acids are saturated fatty acids resulting from hydrolysis and fat/oil oxidation reactions and contain cholesterol [15]. Hydrolysis and oxidation reactions are the main causes of oil damage. At low water levels, oil damage is possible due to oxidation or enzymatic reactions.

The iodine value is usually used to determine the degree of saturation of oil. The higher the iodine number indicated the higher the double bond and the faster dries of fats. Iodine value of limed hide fleshings fats (85,61) is classified into the non-drying oils. According to Priebe & Gutterres [5] that the iodine number of fat from cow skin is 56,99 - 61,35. Therefore it’s insusceptible to polymerization and autooxidation [8]. Fat extracted has a low iodine value, that indicates a low quantity of unsaturated fatty acid.

The saponification number indicates the number of milligrams of sodium hidroxide (KOH) used to soap one gram of fats. The saponification value depends on the molecular weight of fats. Short chain fatty acids have a low molecular weight. Fat composed of short-chain fatty acid will have a high saponification value, whereas the high molecular weight of fats has low saponification value [16]. The results of saponification value is 12,75, this indicates that fats is arranged in a long chain fatty acid.

Peroxide numbers are used to assess the degree of damage to the oil. Unsaturated fatty acids can bind oxygen to their double bonds to form peroxide. The smaller the peroxide number means the better the oil quality. The fatty matters content extracted is quite high (85,76%), which indicates that can be chemically modified for fatliquor [13].

The fatty acid analysis composition of extracted fats from fleshing ismethyl butyrate (C₈H₁₆O₂) 23,84 %, methyl tetradecanoate (C₁₄H₂₉O₂) 2,87%, myristoleic acid methyl ester (C₁₃H₂₇O₂) 1,13%, cis-10-pentadecenoid acid methyl ester (C₁₆H₃₁O₂)17,18%, methyl palmitoleat (C₁₀H₂₁O₂) 2,97%, methyl octadecanoate (C₁₉H₃₉O₂) 9,48%, trans-9-elaidic acid methyl ester (C₁₉H₃₈O₂) 34,52%, methyl linoleate (C₁₉H₃₂O₃) 1,48%, methyl cis-11-eicosenoate (C₂₀H₄₁O₂) 1,39%.

3.2. Sulfited fatliquors properties

Table 2 shows the physico-chemical sulfited fatliquor properties of fleshings fats, ash (0,50 - 0,77%) and moisture (1,84 – 3,84), saponification number (18,8-26,38 mg KOH/g), content fatliquor are higher than untreated fats, but neutral fat (80,12-83,14%) and iodine value (48,96-69,99%) lower than
untreated fats. SO₃ 1.84-2.48%, total alkalinity 0.21-0.83%, pH 6.0-9.1, emulsion stability 74-290 minutes, and yellow colour.

Table 2. The physico-chemical properties fatliquor of fleshings fats

| Item                  | Unit        | Untreated fats | Treated fats (mol sodium bisulfit/kg fats) |
|-----------------------|-------------|----------------|-------------------------------------------|
|                       |             |                | A₁ (0.5) | A₂ (1.0) | A₃ (1.5) | A₄ (2.0) | A₅ (2.5) |
| Ash                   | %           | 0.26           | 0.65     | 0.50     | 0.73     | 0.77     | 0.70     |
| Moisture              | %           | 0.30           | 2.50     | 1.84     | 2.50     | 3.84     | 2.52     |
| Fatty matter          | %           | 85.76          | 83.14    | 80.23    | 80.12    | 81.52    | 82.43    |
| SO₃                   | %           | -              | 1.84     | 1.90     | 1.98     | 2.46     | 2.48     |
| Total alkalinity      | %           | -              | 0.39     | 0.27     | 0.21     | 0.83     | 0.62     |
| Iodine value          | mg KOH     | 12.75          | 19.24    | 26.38    | 18.8     | 19.94    | 26.01    |
| Emulsion stability    | minute      | -              | 74       | 74       | 290      | 114      | 104      |
| Colour                |             | yellow         | yellow   | yellow   | Yello    | yellow   |

Note: A₁ = 0.5; A₂ = 1.0; A₃ = 1.5; A₄ = 2.0; A₅ = 2.5.

The duration of the fat liquoring process in the leather tanning is usually 50 – 90 minutes depending on the leather types [14]. Baseline on emulsion stability table 2, only treated fats with 1.5; 2.0; and 2.5 mol sodium bisulfit/kg fats which meets the demands of the tanning process.

The Indian Standard requirements for the sulphited fatliquor (IS 14488-1998) [17] are ash < 3.5%, total alkalinity < 5%, fat content ≥ 60%, total SO₃ ≥ 1.8%, this means that all treatments meet these standards. The Indian Standard 14488-1998 requires that the pH of fatliquor is 6.5 to 7.5, thus only treatment A₄ (2.0 mol sodium bisulfit/kg fats) approaches the standard.

The processing of fatliquors from fat fleshing by sulfitation using sodium bisulfit 2.0 mol/kg of fat results in a fatliquors that has the best physico-chemical properties. However, a full evaluation must be applied to the skin/hide lubrication process. Results of application to the skin/hide can be used to assess the quality of fatliquors.

To determine the success of the fatliquor synthesis, an analysis of the resulting fatliquor function was performed. The analysis was performed by comparing the Fourier Transform Infra Red (FT-IR) spectrum of the fat before and after synthesis in a fatliquor. FT-IR absorption bands cm⁻¹ of fat and fatliquors extracted fat can be seen in the table 3.

Table 3. Identification of fat FT-IR absorption peaks and fatliquors.

| Atom bond | Wave range (cm⁻¹) | Fat | Treated fats (mol sodium bisulfit/kg fats) |
|-----------|-------------------|-----|-------------------------------------------|
|           |                   |     | A₁ (0.5) | A₂ (1.0) | A₃ (1.5) | A₄ (2.0) | A₅ (2.5) |
| C - O     | 1050-1150         | 1097,62; 1097,72; 1097,71; 1097,88; 1097,77; 1097,84; 1115,93 | 1115,97 | 1115,88 | 1115,73 | 1115,79 | 1115,81 |
| alkohol   | 1180-1300         | 1235,21 | 1235,04 | 1235,25 | 1235,17 | 1234,97 | 1234,68 |
| ester     |                   | - | - | 1641,81; 1654,16 | 1654,82 | 1654,81 |
| C = C     | 1620-1680         | - | - | 1641,81; 1654,16 | 1654,82 | 1654,81 |
|           |                   | - | 1657,95 |
The FTIR test showed that the absorption peaks on fatliquors was more than the absorption peaks in fleshing fat, except treatment A1. Treatment A1 shows that peaks are similar to the control treatment, only a slight shift in its peaks value. In the A2 treatment, three new peaks were added, two in the wavelength range of 1,620 to 1,680 and one in the wavelength range of 3,200 to 3,600. In the A3 treatment, two new peaks were added, in the wavelength range of 1,620 to 1,680 and in the wavelength range of 3,200 to 3,600. In the A4 treatment, two new peaks were added, in the wavelength range of 1620 to 1680 and the wavelength range of 3,200 to 3,600. In the A5 treatment, two new peaks were added, one in the wavelength range of 1,620 to 1,680 and three in the wavelength range of 3,200 to 3,600. The appearance of the new peak indicates that the synthesis of the fatliquoring agent was successful.

Functional groups located in the range of wavelengths between 4,000 and 2,500 at the absorption peak are NH, CH, and simple OH bonds. Functional groups located in the range of wavelengths between 2,000 - 1,500 at the absorption peak have a double bond of C = O; C = N and C = C. Functional groups that located in the range of 1,500 smaller wavelengths at the absorption peak mean that they are consist of different types of single bonds. If all peaks in the fourth region are identical to other spectral peaks, it can be stated that the two compounds are identical [18].

According to Covington [10], the reaction between bisulfite and fat will be produced by a functional group that binds to -SO₃H, OH and SO₃H, and OH and SO₃Na. The functional group is produced from the reaction of bisulfite with double bonds in fat, oxidation of double bonds in fat then reaction with bisulfite and reaction of carbonyl group and bisulfite.

Based on absorption peaks at FTIR it can be stated that there has been a reaction between fleshing fat with sodium bisulfite as indicated by the appearance of new peaks on FTIR. Addition of sodium bisulfite from 1 – 2.5 mole/kg of fat produces a new functional group in the wavelength region 2,000 - 1,500 and above 3,000.

4. Conclusion

By the sulfiting method using sodium bisulfite, fat extracted from fleshing using a combination of wet-rendering and n-hexane can be used as a fatliquoring agent of good quality for lubrican the skin. Sodium bisulfite can react with fat fleshing as evidenced by the appearance of new absorption peaks in FTIR assays. The ash content, total alkalinity, fat content and total SO₃ fatliquor from all treatments were in accordance with Indian Standards 14488-1998 as sulfited fatliquors. However, only A4 (2 moles sodium bisulfite / kg fat) is treated, which can meet the pH requirements of Indian Standards, although there is still a need for trials of fatliquors for the tanning process.

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