# RESOURCE UTILIZATION: PREPARATION AND APPLICATION OF A SULFITED FAT-LIQUOR BASED ON WASTE BEEF TALLOW FROM TANNERY

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**Abstract.** Leather industry is one of many traditional and characteristic industries in China. During the process of Leather manufacture, the problem of a certain the waste of resources and environmental pollution has been yielded. The waste tallow is one of the problems should be solved quickly. Based on the problem of the waste of resources and environmental pollution form the waste tallow of the leather industry, act waste beef tallow from tannery as raw material, determination of its physical and chemical properties, de-colorization, deodorization, amidation, esterification and sulfitation were done successively. Results showed that the acid value and the saponification value of the waste beef tallow was 45mgKOH/g, 207mgKOH/g respectively. When 10% hydrogen peroxide and 6% activated clay were successively used to decolorization and deodorization, the best effect was obtained. When n(ethanolamine) : n(waste beef tallow) is 4:1, the reaction temperature was 130-140°C and time was 2hrs respectively by 1.5% sodium formate as a catalyst, the acid value and hydroxyl value of the treated beef tallow was 15-30mgKOH/g, about 280mgKOH/g respectively. When the optimum dosage of sodium pyrosulfite is 20%, the fat-liquor obtained light yellow and good stability. The sheepskin garment leather fat-liquored by this fat-liquor is very soft.

## 1 Introduction

Fat-liquoring process is one of the most important processes in leather manufacture, which can give the leather certain physical, mechanical properties and properties of use [1]. The common fat-liquoring materials are modifiers of natural animal fat/oil, vegetable oil modified by sulfated, sulfited, oxisulphited, sulphonated and synthetic polymer[1]. Based on their different sources and modified methods, there are differences in emulsion particles, emulsion stability and so on so as to give different properties for Leather.

Because the raw hide or skins contain a certain fat/oil, it is necessarily removed by de-fleshing and de-greasing process in order to promote the penetration and combination of water-soluble materials in hide or skins, which produces lots of hide/skin scrapings. However, bad smell and odor will be produced if these hide/skin scrapings and grease can't be reused in time so as to cause environment pollution. According to statistics, the annual output of waste fat/oil from Tannery is about 3.8Mt in China, which can produce 0.45Mt refined oil according to 15% extraction rate of waste oil [2]. If the fat/oil were reused, it can not only make up the shortage of natural oil resources and save the resources, but also reduce the environmental pollution.

Some studies were carried out on the resource utilization of waste oil, which were used as emulsifier of diesel, stearic acid, bio-diesel and fat-liquor etc. Acted the waste tallow from Tannery the as materials, Fatty acid methyl-ester was prepared and ethanol-diesel emulsifier of alcohol- diesel was further prepared. When n(fatty acid methyl-ester)/n(di-ethanolamine) was 1.0,the reaction temperature was 130°C, the dosage of catalyst KOH was 1.0% and the reaction time was 5h, the emulsifying performance of the emulsifier was very good. The ethanol-diesel mixture prepared by adding the emulsifier is stable in the range of zero and 70°C with uniform particle size distribution and stable morphology [3]. Acted waste cooking waste oil as the material, firstly it was de-colored by activated clay and was de-hydrated, then the de-colored oil was saponified by sodium hydroxide on the condition of boiling, then white particles was obtained by the method of salting out which reacted with $Pb(NO_3)_2$, filtered and acidified by hydrochloric acid and oleic acid and stearic acid were obtained[4]. Acted the hogwash oil as raw materials, it was treated by a two-step esterification process, that is, Firstly

the free fatty acids in the hogwash oil were converted into fatty acid methyl-ester by concentrated sulfuric acid, and its acid value was reduced below 4mg/g. Then, the triglycerides in the hogwash oil were converted into fatty acid methyl-ester by acid as a catalysis[5]. The flash point and cold filter point of bio-diesel obtained by this way are better than 0# diesel, which is beneficial for storage and transportation. The hogwash oil was oxidated and sulfited and was prepared to leather fat-liquor which can give good elongation at break, tensile strength and softness for the fat-liquored leather[6].

In this paper, waste beef tallow was taken as raw materials, its physical and chemical indexes were measured. Then, it was modified by de-odorization, de-colorization, amidization, esterification and sulfite successively and the fat-liquor was obtained so as to achieve the purpose of resource utilization.

## 2 Experimental procedures

### 2.1 Materials

Waste tallow was used as raw materials which origins from a tannery located in Zhangpu city, Fujian province, China. Sodium pyrosulfite, p-toluene sulfonic acid, maleic anhydride, hydrogen peroxide solution, sodium methoxide were obtained from Shanghai lianshi chemical re-agent co., Ltd. Activated clay was obtained from Zanyu S&T co., Ltd, Zhejiang province,China. PASTOSOL BCN60, TRUPON SWS, TRUPON DB were obtained from TRUMPLER Chemicals s.p.a, Germany. All chemicals used for leather processing were of commercial grade, others are analyzed grade.

### 2.2 Plan of modification of waste tallow from Tannery and its application

Waste beef tallow is shown in Fig.1. Based on its color and smell, modified scheme of waste beef tallow is also shown in Fig.2. The main content of modification and application includes testing of some indexes of waste beef tallow from Tannery, de-coloring and de-odorization of waste tallow from Tannery, aminification reaction, esterification & Sulfite reaction of waste tallow from Tannery, etc, which can make Waste tallow into fat-liquor. Then emulsion stability, application properties of the fat-liquor will be tested.

**Fig. 1.** Waste tallow from Tannery.

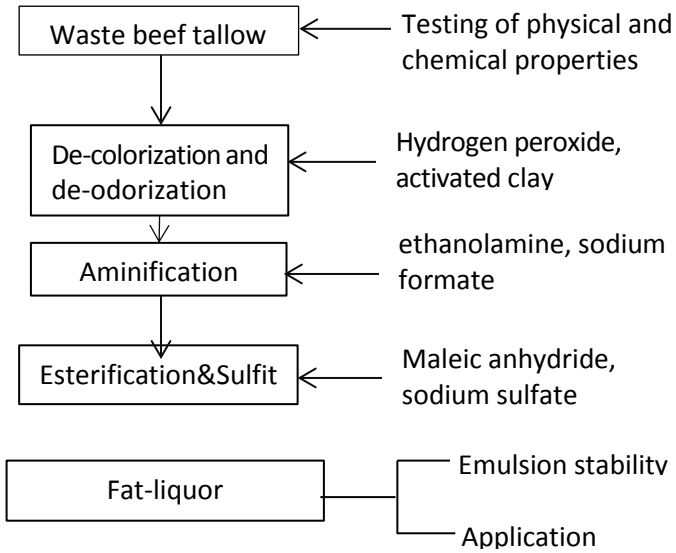


**Fig. 2.** Modification and application technology of waste tallow for Tannery.

### 2.3 Testing of some indexes of waste tallow from Tannery

The saponification value, acid value and hydroxyl value of Waste beef tallow were tested according to GB/T5534--200,GB/T5530--2005/ISO660:1996 and SN/T0801.20-1999 standards respectively, which can become references of modification methods based on the appearance, smell and structural characteristics of Waste tallow.

### 2.4 De-coloring and de-odorization of waste tallow from Tannery

The methods of de-coloration and de-odorization of oil include oxidation, reduction and physical adsorption, etc. According to the appearance and smell of the waste beef tallow, physical adsorption method and oxidation method were combined to achieve better de-colorization and de-odorization. Therefore, hydrogen peroxide solution and activated clay were used as de-coloring and de-odorizating materials. The experimental scheme is shown in Table 1.

**Table 1.** Experimental scheme for decolorization and deodorization of Waste tallow from Tannery.

| Hydrogen peroxide/% | Amount of activated clay/% | Clay first and then hydrogen peroxide | Hydrogen peroxide before clay |
|---|---|---|---|
| 5 | 4 | A certain amount of clay +5% $H_2O_2$ | A certain amount of $H_2O_2$+4% clay |
| 10 | 6 | A certain amount of $H_2O_2$+4% clay | A certain amount of $H_2O_2$+6% clay |
| 15 | 8 | A certain amount of clay +15% $H_2O_2$ | A certain amount of $H_2O_2$+8% clay |

#### *2.4.1 De-coloration and deodorization of Activated clay*

a. 100g Waste beef tallow was put in a 250mL three-mouth flask and was heated to 110°C on the condition of stiring.
b. 4%-8% active clay was added and continue stirring for 30min. Then it was filtered on the condition of vacuum.
c. The filtered oil was placed in the divide funnel and stayed overnight. Then the water was separated the next day.

#### *2.4.2 De-coloration and deodorization of hydrogen peroxide*

a. 100g Waste beef tallow was put in a 250mL three-mouth flask and was heated to 65-75°C on the condition of stiring.
b. Hydrogen peroxide was slowly added dropwise and the time was 30-40min. then it has been reacted for 3h at 75-80°C.
c. The de-colored oil was placed in the divide funnel and stayed overnight. Then the water was separated the next day.

#### *2.4.3 De-coloration and deodorization of hydrogen peroxide & Activated clay*

a. Firstly the optimal amount of active clay was used to decolorization and deodorization. Then different amount of hydrogen peroxide was used. The operation procedure is the same as 2.4.1 and 2.4.2.
b. Firstly the optimal amount of hydrogen peroxide was used to decolorization and deodorization. Then different amount of active clay was used. The operation procedure is the same as 2.4.1 and 2.4.2.

#### *2.4.4 Test methods of effect of De-coloration and deodorization*

Color and smell of de-colored and de-odored were tested by the manual scoring method. The score is in the range of 1 and 5. The higher is the score, the lighter is the color and the lighter is the smell.

### 2.5 Amideation reaction of waste beef tallow from Tannery

In order to increase the number of hydroxyl groups of Waste beef tallow from Tannery, ethanolamine was used to react with Waste beef tallow. According to the influence of reaction time, molar ratio of reactants and dosage of catalyst on ester exchange reaction, the orthogonal experiment was carried out. Scheme design and experiment are shown in Table 2, Table 3 and Table 4 [7].

**Table 2.** Levels of different factors

| level | A/n（Waste beef tallow）：n（ethanolamine） | B/time/h | C/ Dosage of Catalyst /% |
|---|---|---|---|
| 1 | 1:2 | 4 | 0.5 |
| 2 | 1:3 | 3 | 1 |
| 3 | 1:4 | 2 | 1.5 |

**Table 3.** Experimental scheme of Aminification reaction

| No. | A/n（Waste beef tallow）：n（ethanolamine） | B/time /h | C/ Dosage of Catalyst /% |
|---|---|---|---|
| 1 | 1:2 | 4 | 0.5 |
| 2 | 1:3 | 4 | 1 |
| 3 | 1:4 | 4 | 1.5 |
| 4 | 1:2 | 3 | 1 |
| 5 | 1:3 | 3 | 1.5 |
| 6 | 1:4 | 3 | 0.5 |
| 7 | 1:2 | 2 | 1.5 |
| 8 | 1:3 | 2 | 0.5 |
| 9 | 1:4 | 2 | 1 |

A certain amount of de-colorized and de-odorized waste beef tallow was placed in a three-necked flask, and a certain amount of ethanolamine and sodium methylate was added. The temperature was raised to 130-140°C, and the condensation reflux had been conducted for 2-4hrs.The test method for the acid value and hydroxyl value of the aminated waste tallow is the same as 2.3.

**2.6 Esterified & Sulfite reaction of aminated waste beef tallow**

The aminated waste beef tallow was esterified with maleic anhydride and then modified with sodium pyrosulfite. A certain amount of aminated waste tallow was placed in a three-neck flask. When the water bath temperature reached 65-70°C, p-toluene sulfonic acid, maleic anhydride were added, and then heated to 80-90 °C for 2h. Then drop the temperature to 65-70°C, add a certain amount of 30% sodium hydroxide solution, and adjust its pH to 4-5. Then a certain amount of sodium pyrosulfite was slowly added to a three-necked flask whose dosage of sodium pyrosulfite was 10%, 15%, 20%, 25% and 30% respectively. Then the pH was adjusted to 6.5-7.0 with 30wt% sodium hydroxide solution, and the oil content of the fat-liquor was adjusted to 60%. At last, the degree of sulfite of the aminated waste beef tallow and the emulsion stability of the fat-liquor were determined[8].

**2.7 Application of the fat-liquor origined from Waste beef tallow of Tannery**

The fat-liquor was applied in the fat-liquoring process of shaved sheepskin wet blue. The process is shown in Table 4. The softness, fullness and other characteristics of the fat-liquored leather were tested.

**Table 4.** Fat-liquoring process of the fat-liquor in shaved sheepskin wet blue.

| Process | T/°C | Material | Dosage /% | Time/min | Note |
|---|---|---|---|---|---|
| washing | 35 | water | 200 | | |
| retanning | normal temperature | PASTOSOL BCN-60 | 0.3 | | |
| | | formate acid | 0.3 | 60min | pH3.7-3.8，washing |
| | | water | 200 | | |
| | | chrome tanning agent | 4 | | |
| | | chrome tannins | 3 | 120min | |
| | | sodium formate | 0.5 | | |
| | | baking soda | 0.5 | 30min | pH4.0，stop/overnight |
| neutralization | 30 | water | 200 | | |
| | | Sodium formate | 1.0 | 30min | |
| | | Baking soda | 2.0 | 3×20min | pH6.0，washing |
| fatliquoring | 50 | water | 200 | | |
| | | fatliquor | 18 | 90min | |
| | | formate acid | 1.2 | 3×20min | pH3.5,washing hang dry |

## 3 Results and Discussion

### 3.1 Some indexes of Waste tallow from Tannery

Testing results of relevant indexes of waste beef tallow from Tannery is shown in Table 5. As can be seen from Table 5, the acid value of the oil is 45mgKOH/g which is higher than normal natural oil and show that it has high content of free fatty acids. The saponification value of Waste tallow is 207mgKOH/g and the relative molecular weight is 813g/mol, which is in the range of 650 to 970g/mol. In addition, Waste beef tallow (18-22°C) appearance of dark-brown solid at room temperature and odor.

**Table 5.** Related indexes of Waste beef tallow from Tannery.

| Test project | Test results |
|---|---|
| Outside view | Dark-brown solid |
| Acid value / mgKOH/g | 45 |
| Saponification value / mgKOH/g | 207 |
| Relative molecular mass | 813g/mol |

### 3.2 Results of deodorization and decolorization of Waste beef tallow from Tannery

Results of active clay, hydrogen peroxide and their combination are shown in Table 6, Table 7, Table 8 and Table 9. As can be seen from Table 6, the color of Waste beef tallow is significantly changed with the amount of activated clay. When the amount of activated clay is 6%, the color is the lighter than others .However, the smell of Waste beef tallow is still large. So the de-odorization effect of activated clay is not good. In addition, the acid value of Waste beef tallow treated with clay decreased slightly, which show that it had little influence on the acid value of Waste tallow. As can be seen from Table 7, the color of the oil becomes obviously lighter with the increase in the amount of hydrogen peroxide, which is lighter than that of activated clay. The deodorization effect of hydrogen peroxide is better than that of activated clay. Therefore the optimal amount of hydrogen peroxide is 10%.

**Table 6.** De-colorization and de-odorization effect of activated clay for Waste beef tallow.

| Amount of activated clay/% | Color | Smell | Acid value（mgKOH/g） | Stability（24） |
|---|---|---|---|---|
| 4 | 3 | 1 | 42.0 | good |
| 6 | 4 | 1 | 40.5 | good |
| 8 | 2 | 1 | 41.8 | good |

**Table 7.** De-colorization and de-odorization effect of Hydrogen peroxide for Waste beef tallow.

| Hydrogen peroxide/% | Color | Smell | Acid value（mgKOH/g） | Stability（24h） |
|---|---|---|---|---|
| 5 | 3 | 3 | 43.2 | general |
| 10 | 4 | 3 | 42.3 | good |
| 15 | 4 | 3 | 41.1 | good |

**Table 8.** De-colorization and de-odorization effect of activated clay and hydrogen peroxide for Waste beef tallow.

| Amount of decolorizing material | Color | Smell | Acid value ( mgKOH/g ) | Stability ( 24h ) |
|---|---|---|---|---|
| 10%$H_2O_2$+4% clay | 4 | 3 | 44.3 | good |
| 10% $H_2O_2$+6% clay | 5 | 3 | 41.0 | good |
| 10% $H_2O_2$+8% clay | 5 | 3 | 41.2 | good |

As can be seen from Table 8 and Table 9, the color, when hydrogen peroxide and activated clay are along used for de-coloration and de-odorization, the color and smell of Waste beef tallow is lighter than one of hydrogen peroxide and activated clay. Among them, the use of hydrogen peroxide, then the use of clay, de-colorization & deodorization effect is good. Considering the effect and cost of de-colorization and de-odorization, 10% hydrogen peroxide and 6% activated clay was used.

**Table 9.** De-colorization and de-odorization effect of hydrogen peroxide and activated clay for Waste beef tallow.

| Amount of decolorizing material | Color | Smell | Acid value ( mgKOH/g ) | Stability ( 24h ) |
|---|---|---|---|---|
| 6% clay +5% $H_2O_2$ | 3 | 2 | 45.3 | good |
| 6% clay +10% $H_2O_2$ | 4 | 2 | 42.3 | good |
| 6% clay +15% $H_2O_2$ | 4 | 2 | 41.7 | good |

### 3.3 Results of Amidation reaction of of de-colored & de-odored waste beef tallow from Tannery

Results of amidation reaction of the de-colored& de-odored waste beef tallow are shown in Table 10. As can be seen from the Table, the order of affecting factor is mole ratio of the reagent, the reaction time and the dosage of catalyst. The acid value of Waste beef tallow decreased from 45mgKOH/g to 15-30mgKOH/g after it is amidated. At the same time, the hydroxyl value of Waste beef tallow changed little with the change of reaction time, which shows that the reaction time had little effect on amidation reaction. From the results of the orthogonal experiment, the most appropriate reaction time is 2h. As the molar ratio of ethanolamine and Waste tallow increased, the hydroxyl value of it rise. Therefore, the optimal molar ratio of ethanolamine and Waste beef tallow was 1:4. In addition, with the increase of the amount of catalyst, the hydroxyl value of Waste tallow changes less. From the orthogonal experiment, the acid value of modified Waste beef tallow is smaller than others when the amount of catalyst is 1.5%.

**Table 10.** Results of orthogonal experiment of amidation reaction of de-colored waste beef tallow.

| No. | A/n(Waste tallow):n (Ethanol-amine) | B/reaction time/h | C/Dosage of Catalyst/% | Acid value/ (mgKOH/g) | Hydroxyl value/ (mgKOH/g) |
|---|---|---|---|---|---|
| 1 | 1:2 | 4 | 0.5 | 31.1 | 206.8 |
| 2 | 1:3 | 4 | 1 | 26.6 | 222.6 |
| 3 | 1:4 | 4 | 1.5 | 27.3 | 213.2 |
| 4 | 1:2 | 3 | 1 | 38.0 | 202.3 |
| 5 | 1:3 | 3 | 1.5 | 25.5 | 216.7 |
| 6 | 1:4 | 3 | 0.5 | 29.9 | 217.6 |
| 7 | 1:2 | 2 | 1.5 | 15.5 | 204.6 |
| 8 | 1:3 | 2 | 0.5 | 21.5 | 246.0 |
| 9 | 1:4 | 2 | 1 | 26.4 | 288.3 |
| K1 | 84.6 (613.7) | 85 (642.6) | 82.5 (670.4) | | |
| K2 | 73.6 (685.3) | 93.4 (636.6) | 91 (713.2) | | |
| K3 | 83.6 (719.1) | 63.4 (738.9) | 68.3 (634.5) | | |
| k1 | 28.2 (204.6) | 28.3 (214.2) | 27.5 (223.5) | | |
| k2 | 24.5 (228.4) | 31.3 (212.2) | 30.3 (237.7) | | |
| k3 | 27.9 (239.7) | 21.3 (246.3) | 22.7 (211.5) | | |
| R | 3.7 (35.1) | 10 (34.1) | 7.6 (26.2) | | |

### 3.4 Results of Esterified & Sulfite reaction of aminated waste beef tallow

Effects of different amounts of sodium pyrosulfite on the stability, sulphiting degree and state of Fat-liquor emulsion are shown in Fig.3 and Table 11. As can be seen from Fig.3, the 1:9 sulfite emulsions have good stability. As can be seen from Table 11, the color of the fat-liquor gradually lightens with the increase of the amount of sodium sulfite, which maybe that more -$SO_3Na$ groups in the butter increases improves the hydrophilic and emulsifying properties of the sulfite fat-liquor. The sulphiting degree of the fat-liquor rise with the dosage of sodium pyrosulfite increases.when

the dosage of is sodium pyrosulfite 20%~30%, the degree of sulfite reaches more than 18% and the sulphiting degree of the fat-liquor is high.


**Fig. 3.** Stability of 1:9 sulfited fat-liquor emulsion.

**Table 11.** Emulsion stability, sulphiting degree and state of the sulfited fat-liquor.

| Heavy sodium sulfite dosage | 10% | 15% | 20% | 25% | 30% |
|---|---|---|---|---|---|
| 1:9 emulsion stability | Not layered | Not layered | Not layered | Not layered | Not layered |
| Sulphiting degree | 2.9% | 6.5% | 18.3% | 20.9% | 25.6% |
| State | Yellow paste | Yellow paste | Light yellow paste | Light yellow paste | Light yellow paste |

### 3.5 Results of application of the sulfited fat-liquor

The sheepskin garment leather fat-liquored by the sulfited fat-liquor is soft and full, which shows that it has good fat-liquoring properties.

## 4. Conclusion

During the process of Leather manufacture, cleaner production and resource utilization of solid waste are the requirements for the sustainable development of leather industry. Waste beef tallow is one of the solid wastes whose refined oil is dark brown solid and bad smell. The acid value, saponification value of the refined oil of Waste beef tallow is 45mgKOH/g and 207mgKOH/g. The fat-liquor was prepared from Waste tallow by de-colorization with hydrogen peroxide and active clay, amidation, esterification and sulfited, which has light color and good fat-liquoring performance.

When Waste beef tallow was de-colorized and de-odorized with 10% hydrogen peroxide and 6% activated clay, the color and smell of the de-colored ,de-ordorized waste tallow are light.

Ethanolamine was used for the amidation reaction of the decolorized and deodorized waste beef tallow. The optimal conditions were that 1.5% catalyst (sodium methanol), n(ethanolamine):n(oil) at 4:1, 2h, and 130~140°C. The acid value, hydroxyl value of the amidated oil was 15-30mgKOH/g and 280mgKOH/g respectively.

By esterified reaction with equal molar maleic anhydride & Sulfited reaction with 20% sodium pyrosulfite successively, the modified fat-liquor has high sulphiting degree, yellow paste appearance and good emulsion stability which can give good softness for leather.

## References


1. *Shan, Z. H. Chen, H. Luo, J. X. et al.: 'Tanning Chemistry and Technology', Beijing: Science press, 2017*
2. *Yu, C. Z. Chen, Y. F. Ma, X. Y. et al.: 'Countermeasures of Environmental Pollution of Leather Industry ', The environmental condition of world leather industry, 2 004,33(17):31-36*
3. *Ma, J. Z. Ma, D. Lv, B. et al. 'Preparation of Ethanol-diesel Emulsifier from Leather Waste Oil'. Petroleum refining and chemical industry, 2011, 42(10):73-77.*
4. *Guo, T. Du, L. L. Wan, H. et al. 'Study on Preparation of Stearic Acid and Oleic Acid from Waste Food Oil' . Food science and technology, 2009, 34(8):109-112*
5. *Zhang, Y. 'Preparation of Biodiesel from Gutter Oil'. China oils and fats, 2008,33(11):48-50*
6. *Duan, B. R. Tan, S. Z. Wang, Q. J. et al. 'Preparation of Fatliquor from Waste Oil by Sulfite Oxidation and Its Application in Leather Making'. China leather, 2012,41(1):43-47*
7. *Li, Y. Y. Hu, C. R. 'Experimental Design and Data Processing'. Beijing: chemical industry press,2015.*
8. *Luo, X. M. Ding, S. L. Zhou, Q. F. 'Physical and Chemical Analysis of Leather'. Beijing: China light industry press,2013*