# Recycling of Spent Unhairing-Limming Liquor

**F. E. Faki, A. E. Musa, G. A. Gasmelseed, I. H. Elamin**

*Abstract*— **Unhairing – limming process is the most polluting operation in leather industry. In hair burn unhairing -limming method, lime and sodium sulphide and a huge amount of water are used to destroy and remove hair from hides and skins generating a large amount of effluent. Sodium sulphide is harmful to human and environment. As an effective substitution to sulphide has not yet been developed, recycling of lime – sulphide liquor has become one of the better options for pollution control. In the present study, direct recycling of unhairing – limming liquors was carried out. The liquors were reused 7 times after had been replenished with reduced quantities of chemicals and water. An average savings of about 28% in sodium sulphide, 32% in lime and 75% in water were obtained. The quality of crust leathers produced by recycling of limming liquor has not been changed comparing to control leathers.**

*Index Terms*— **Clean technology, Recycling, Unhairing – limming, Sodium sulphide**

## I. INTRODUCTION

In leather industry, hides and skins are converted to leather through a subsequent mechanical and chemical operations using a huge amount of water. As a result large amounts of solid and liquid wastes are generated. The leather industry produces wastes comprising of COD, BOD, suspended solids, chromium, dyes and sulphur [1].

The purpose of unhairing- liming process is to remove the hair and epidermis. The hides are treated with 3% sodium sulfide containing 25% sulfide and 3% hydrated lime (calcium hydroxide) in a 200% float (a solution consisting of 2 L of water per kg of skins or hides processed). The sulfide pulps the hair and the epidermis, the lime is used as a buffer to keep the pH at about 13, which causes the hides to swell, the collagen fiber network to open, and which helps the removal of the nonstructural proteins [2].

Sodium sulfide, used in the process of unhairing-liming, is one of the most dangerous materials used in the tanning process. Upon acidification, solutions containing sulfides will release hydrogen sulfide gas into the atmosphere. Hydrogen sulfide is the reduced form of sulfur. It is formed from the reduction of sulfate (SO42-) ions under anoxic conditions according to the following equations.

$$SO_4^{2-} + \text{organic matter} = S^{2-} + H_2O + CO_2$$
$$S^{2-} + H^+ = HS^-$$
$$HS^- + H^+ = H_2S$$

There are many problems related to the use of sulfur compounds such as the toxicity of hydrogen sulfide and its corrosiveness on the concrete such as in sewers. The presence of sulfide in wastewater may result in a poorly settling sludge besides the odor of hydrogen sulfide [2].

Limming effluents consists of sulphide, lime, decomposed hair keratin, globular protein and other non -collagen protein, as well as saponified fractions of native fat. The amount of liming effluents, including washing, fluctuates between 9 and 15 m3/t raw hide. Advanced unhairing and liming methods are mainly aimed at reducing the pollution load of suspended solids, sulphides, COD, BOD and nitrogenous materials [3].

The negative environmental impact of tannery wastes can be reduced either by the application of cleaner technology methods or by the treatment of wastewater and eco-friendly handling and processing of solid waste. Cleaner technology methods aiming at decreasing the effluent pollution load, decreasing or eliminating the use of harmful chemicals and using the solid waste produced as by product [3].

A modification of the method for unhairing limming process was proposed, in which the spent liquors decanted from this process are reused after being replenished by reduced amounts of chemicals and water. The proposed method uses fresh water for the first batch of hides or skins but subsequently recycles this wastewater for subsequent batches of hides or skins up to four cycles without affecting the quality of the final leather. The modified method reduces both the economic and environmental cost [2].

The possibility of minimizing the water consumption was studied by applying the reuse of spent liquors from the 2nd bating washing in the 1st bating washing and of reusing the liquors from pre deliming washing in the pre-deliming operation. The tests shows that the process can be carried out successfully without affecting the quality of wet blue leathers[4].

Also the reduction and further minimization of water consumption in leather processing were studied through optimization, recycle and reuse strategies [5].

It was showed that, the lime –sulphide unhairing liquors can be recycled 20 times, perhaps indefinitely. The only treatments necessary before reuse are temperature adjustment and replenishment with lime, sulphide and water. They observed that hides unhaired in a recycled liquor are not free of scud as hides treated in fresh lime liquors. Fat accumulates in recycled lime liquor if solid are not removed before reuse or if hides are not green fleshed. This accumulated fats would give greasy leather or adhere to the drum and be difficult to remove. Salted hides can be unhaired in reused lime liquors if they first have an adequate overnight soak to reduce their salt

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content. They also found that satisfactory unhairing can be achieved when lime liquors are recycled without removal of either the soluble proteins or the solids; it is only necessary to replenish with lime, sodium sulphide and water [6].

It is reported that excessive amounts of salt in lime/sulphide unhairing system reduces unhairing rates, contracts grain surface, reduces solubility of lime, reduces alkaline swelling and reduces hydroxyl ion fixation. Also a buildup of pigment matter in limming liquor could lead to discoloration and a fat build-up could lead to unwanted fat deposits on the hides [7].

The recycling of unhairing –limming liquor was studied up to 7 cycles. The researchers observed that the unhairing power of an old lime liquor was greater than that of a fresh one. As lime has a limited solubility (0.125%), undisolved lime is always present. This undisolved lime dissolve when its equilibrium solubility is distributed by recycling [8].

This is because under very alkaline conditions, some of the young keratin decomposes to produce sulfur compounds in the liquor. These in conjunction with lime, accelerate the breakdown of further keratin. Thus, the lime causes unhairing and the more keratin breakdown impurities it contains, the more rapidly it unhairs [9].

The recycling of spent unhairing-limming solution was carried out from soaking through retannage up to 7 cycles with a considerable saving in chemicals and water and without changing the quality of the leathers as compared with the leathers obtained without recycling [10].

In this paper, recycle/reuse of unhairing – limming liquor has been studied. Unhairing – limming liquor from the control batch has been successfully recycled for subsequent batches with appropriate replenishments. The objective of this study is to protect the environment from unhairing- limming process waste and to save chemicals and water through recycling of unhairing – limming effluent

## II. MATERIALS AND METHODS

### A. Materials

Wet salted sheep skins were purchased from the local market. Chemicals used for beamhouse, tanning and post-tanning processes were of commercial grade and that used for the analysis of leathers and spent liquors were of analytical grade. Sodium sulphide (60% flake) and lime (62% ($Ca(OH)_2$) were used for unhairing –limming process. All processes were carried out using a well-controlled experimental stainless steel drum 600mm × 1200mm.

### B. Unhairing – Limming and Recycling Methods

The skins were divided into 10 batches. The first batch was used as a control and the other batches were used as experiments. After washing, the skins of control batch were soaked in a plastic container for 24hrs. The next day they were drummed with 250 % water and 2.5% sodium sulphide based on the soaked weight for 30 minutes. After that 2.5% lime was added and drummed continuously for one hour. Then 5 min every hour for the following 4 hours and stand overnight. The drum was running at 6 rpm and the total running time was 21hrs.

The next day, spent liming liquor from control batch was collected, filtered through a mesh screen to remove hair, sampled, analyzed for sulphide and calcium contents and reused for the next cycle after being replenished with calculated amount of sodium sulphide, lime and topping with the required amount of water. This recycling process was repeated 7 times. Delimming, bating, pickling, tanning and post- tanning processes were carried out common to all experimental and control batches using the normal recipe.

### C. Analysis of Unhairing Limming Liquor

The sulphide content of used lime liquor was determined after each use by titration with sodium thiosulphate in the presence of iodine solution and starch as indicator). Calcium hydroxide was determined by titration with 0.1N hydrochloric acid using thymolviolet as indicator.[8]. The pH was determined using a pH meter suitable for use at pH values above 9.0 [11].

### D. Determination of Pollution Load of Spent Liquors

The spent unhairing -limming liquors from control and the last experiment (cycle7) were also analyzed for biological oxygen demand (BOD5), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS) according to standard procedures [11].

### E. Physical Testing of Crust Leathers

The physical properties of the crust leathers from control and experimental leather (cycle 7) such as tensile strength, percentage elongation at break, grain crack strength and tear strength were measured as per standard procedures [11].

The specimens were cut from official position using a clicking machine and conditioned at 20°C ±2°C and 65% ±2% RH over a period of 48hrs.

Specimens for tensile and tear strength were cut parallel and perpendicular to the backbone and the thickness of each specimen was measured using a standard thickness gauge at three positions on the grain side and three positions on the flesh side, and then the mean of the six measurements was calculated. The area of cross section of each specimen was calculated by multiplying its width by its thickness. Each value for tensile and tear strength represents the average of four samples (2values along the backbone and 2 values across the backbone). Each value for grain crack strength is the average of three samples.

### F. Organoleptic Analysis of Crust Leathers

Softness, fullness, smoothness grain tightness (break), and general appearance were evaluated visually and by hand for control and experimental leathers. Three professional tanners graded the leathers on a scale of 0 – 5 points for each functional property, where 5 indicate (very good) and 1 indicate (poor) property. Values for organoleptic properties are the average of the three assessments.

### G. Chemical Analysis of Crust Leathers

The chemical constituents of crust leathers from control and experimental leathers (cycle 7) such as moisture content, chromic oxide content, oil and fats content, total ash content, water soluble matter, insoluble ash, hide substance and degree of tannage were determined according to standard procedures[11].

## III. RESULTS AND DISCUSSION

### A. Analysis of Spent Unhairing – Limming Liquors

Table 1 represents the analysis results of spent solution after each cycle rounded to the nearest milligram. Table 2 shows the percentage of chemicals based on soaked weight that added for each cycle and Table 3 gives a comparison between the consumption of chemicals and water with and without recycling.

Although there was a reduction in unhairing- liming liquor due to losses on recovery, screening and uptake by the skins, an average of about 75% recovery of unhairing- liming liquor was obtained. The chemical savings amounted to about 28% in sodium sulphide, 32% in lime and 75% in water. The average consumptions based on the soaked weight were 1.8% Na2S, 1.7% lime and 62% water. The removal of hair, scud and plumpness of the pelts were satisfactory in all cycles.

### B. Pollution Load of Spent Liquor

Figure 1 shows that the pollution load of $BOD_5$, COD, TDS, and TSS was reduced by 50%, 54%, 50%, and 42% respectively.

### C. Physical Properties of Crust Liquors

The values for physical tests for experimental and control leathers were presented in Table 4. From the table it is obvious that, the strength properties of experimental leathers are comparable to that of control leathers. The strength properties of both control and experimental leathers were found to be confirmative to Bureau of Indian Standard (BIS).

### D. Organoleptic Properties of Crust Leathers

The hand assessment of control and experimental crust leathers are presented in figure 2. It is observed that, the experimental leathers shows good softness, smoothness and general appearance compared to control leathers. This means that, the quality of crust leathers has not been affected by recycling of unhairing – limming liquors.

### E. Chemical Analysis of Crust Leathers

The chemical characteristics of the experimental and control leathers were presented in Table 3.4. The table reveals that the chemical characteristics of the experimental and control leathers were found to be approximately the same.

**Table 1.** Analysis results of spent unhairing- liming liquor used for each cycle

| Experiment | pH | $Na_2S$ (g/l) | $Ca(OH)_2$ (g/l) |
|---|---|---|---|
| Control (conventional) | 12.5 | 6 | 6.2 |
| Cycle 1 | 12.4 | 1.5 | 2.1 |
| Cycle 2 | 12.4 | 2.0 | 2.1 |
| Cycle 3 | 12.4 | 1.7 | 1.9 |
| Cycle4 | 12.4 | 1.5 | 1.9 |
| Cycle5 | 12.4 | 1.7 | 2.0 |
| Cycle6 | 12.4 | 1.7 | 2.0 |
| Cycle7 | 12.4 | 1.7 | 2.0 |

**Table 2.** Percentage chemicals added for each cycle

| Cycle No. | Water % | Na2S (%) | Lime (%) |
|---|---|---|---|
| Control (conventional) | 250 | 2.5 | 2.5 |
| Cycle 1 | 56 | 1.9 | 1.7 |
| Cycle 2 | 68 | 1.7 | 1.7 |
| Cycle 3 | 61 | 1.8 | 1.8 |
| Cycle4 | 62 | 1.9 | 1.8 |
| Cycle5 | 65 | 1.8 | 1.7 |
| Cycle6 | 63 | 1.8 | 1.7 |
| Cycle7 | 60 | 1.8 | 1.7 |

**Table 3**. Percentage chemicals added for each cycle

| Chemicals | Average consumption without recycling (%) | Average consumption with recycling (%) | savings (%) |
|---|---|---|---|
| Water | 250 | 62 | 75 |
| Na2S (%) | 2.5 | 1.8 | 28 |
| Lime (%) | 2.5 | 1.7 | 32 |

**Table 4.** Physical properties of crust leathers

| Test | Cycle No. | | |
|---|---|---|---|
| | Control | Cycle7 | BIS |
| Thickness (mm) | 1.5 | 1.5 | - |
| Tensile strength (kg/cm2) | 313.2 | 312.7 | 200 |
| Elongation % | 73 | 76 | 40-75 |
| Tear strength (kg/cm) | 33.3 | 36 | 25 |
| load at Grain crack (kg) | 14 | 13 | - |

Note: Values for tensile strength, elongation and tear strength are the average values of two determinations; one is parallel and one is perpendicular to the backbone. Values for load at grain crack are the average of three separate determinations.

**Table 5.** Chemical analysis of leather

| Measurement | Cycle No. | |
|---|---|---|
| | Control | Cycle 7 |
| Moisture (%) | 6.2 | 5.9 |
| Fat content (%) | 8.1 | 9.8 |
| .5Ash content (%) | 4.9 | 5.1 |
| Insoluble ash (%) | 2.1 | 2.0 |
| Water soluble (%) | 1.1 | 1.2 |
| Cr2O3 content (%) | 5.51 | 4.8 |

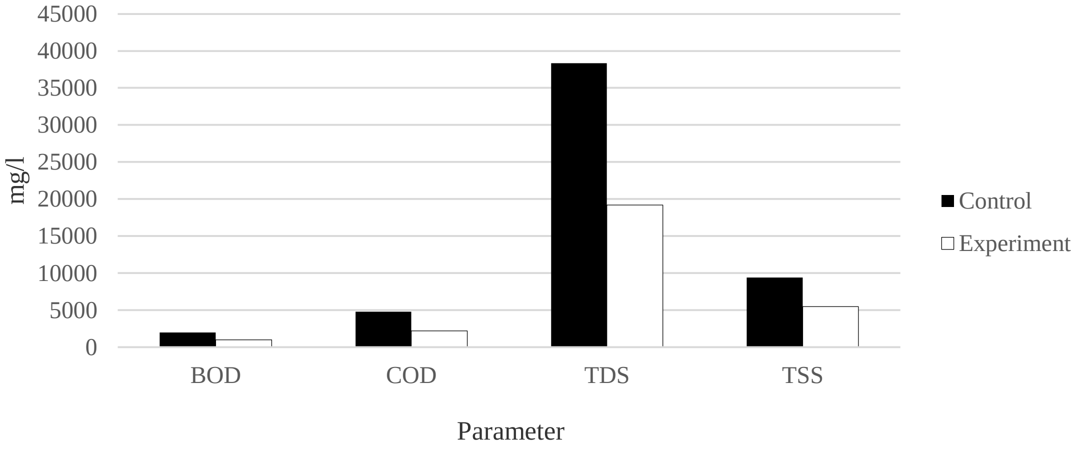


**Fig. 1.** Pollution load of spent liquors

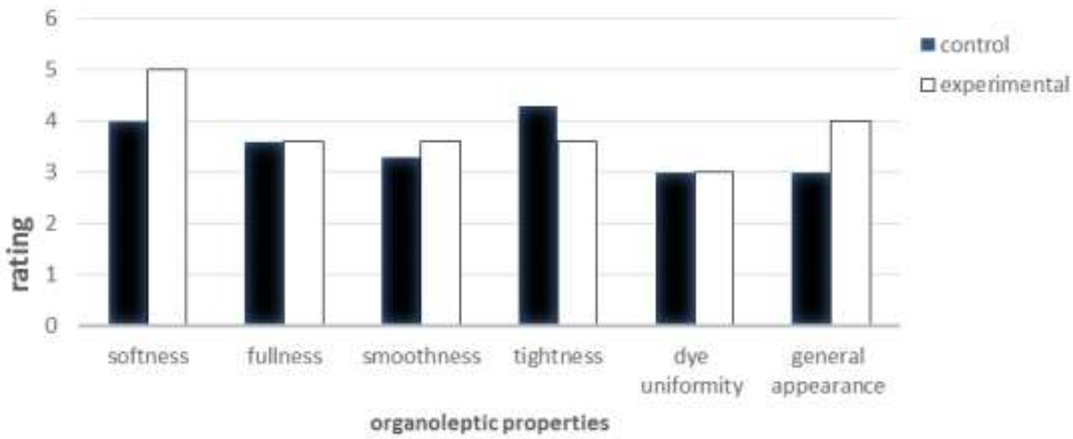


**Fig. 2.** Organoleptic analysis of crust

## IV. CONCLUSION

From the above discussion it can be shown that, recycling of the spent unhairing – limming liquor can safely be applied in tanneries without affecting the quality of produced leathers as shown by the chemical analysis, physical tests and organoleptic assessment. By applying recycling of unhairing-limming liquors we can also protect the environment and save chemicals and water.

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