Optimization of a novel enzyme treatment process for early-stage processing of sheepskins

Y. F. Lim, J. E. Bronlund, T. F. Allsop, A. N. Shilton and R. L. Edmonds

ABSTRACT

An enzyme treatment process for early-stage processing of sheepskins has been previously reported by the Leather and Shoe Research Association of New Zealand (LASRA) as an alternative to current industry operations. The newly developed process had marked benefits over conventional processing in terms of a lowered energy usage (73%), processing time (47%) as well as water use (49%), but had been developed as a “proof of principle”. The objective of this work was to develop the process further to a stage ready for adoption by industry. Mass balancing was used to investigate potential modifications for the process based on the understanding developed from a detailed analysis of preliminary design trials. Results showed that a configuration utilising a 2 stage counter-current system for the washing stages and segregation and recycling of enzyme float prior to dilution in the neutralization stage was a significant improvement. Benefits over conventional processing include a reduction of residual TDS by 50% at the washing stages and 70% savings on water use overall. Benefits over the un-optimized LASRA process are reduction of solids in product after enzyme treatment and neutralization stages by 30%, additional water savings of 21%, as well as 10% savings of enzyme usage.

Key words | enzyme, fellmongery, leather, optimisation

INTRODUCTION

The preliminary stages of ovine leather processing consist of processes designed to prepare the sheepskins for tanning operations. This is conventionally achieved by a prolonged strong alkali and sodium sulphide treatment to remove wool and unwanted protein components, followed by a series of washing stages with water, leaving behind important collagen and elastin proteins.

The effluent discharge of lime sludge and its sulphide content from pre-tanning operations is considered hazardous to the environment (Skrypski-Mäntele & Bridle 1995) and therefore research has been undertaken into other alternatives for use in place of these conventional chemicals (Sundar et al. 2006). Most of the work has been focused on either replacing or lowering use of lime to aid removal of hair from lamb slats, to potentially replace lime with sodium hydroxide, hydrogen peroxide to lower the quantity of lime used (Valeika et al. 1997; Marsal et al. 1999). Some research has also been directed at eliminating or reducing the dependence on sulphide and alkali use by developing enzyme treatments (Cassano et al. 2000; Thanikaivelan et al. 2003).

A novel enzyme treatment process was also developed recently by the Leather and Shoe Research Association of New Zealand (LASRA) as an alternative to current industry standard beamhouse operations. The main feature of the new process is the replacement of alkaline-sulphide processing of sheepskins by the application of a single step enzyme process to conventionally depilated skins which gives increased processing efficiency (Allsop 2007). A process flow chart of the new process is seen in Figure 1 below.
This new process reported a reduction in water use of up to 49% which will directly reduce the volume of effluent water generated. Moreover, the additional sulphide added during conventional processing was eliminated further reducing effluent treatment demands. A reduction of up to 73% of energy usage was achieved primarily by reducing process water heating and the processing time by 47% (Allsop 2006). A significant proportion of energy savings in the process was because of the reduction in contact time required in the rotating vessels. Energy was also saved by avoiding heating of the enzyme bating stage which is required in the conventional process. The new process utilizes existing capital equipment in tanneries more efficiently and consequently production rates could be increased almost two fold (with the saved time) with little need for new capital.

The benefits of the novel process have been demonstrated as a ‘proof of principle’ but required further optimisation to provide a design suitable for industrial application. To be suitable for rapid adoption by industry, the process must satisfy a number of requirements; the ability to generate good quality products, require minimal changes to plant or operation layout and reduced resource usage (e.g. water and chemicals). The objective of this work was to develop a new process design to best achieve these requirements. To achieve this, the LASRA process was optimized in two parts. Firstly the alternatives to the initial washing stages were investigated and secondly a reorganization of the enzyme/neutralization stage was undertaken.

**METHODS**

Up to 6 sheepskins weighing approximately 12.7 kg were used in four pilot scale trials. The data obtained was analyzed in detail to provide a basis for construction of mass balances including detailed characterization of raw skins entering the process and the compositional changes caused by the enzyme and washing stages. The mass balances were then used to investigate a range of potential modifications and assess their benefits in terms of resource use and product quality. The investigated modifications included recycling process streams, utilization of multi-stage processing, segregation of process streams and in-situ clean-up of process streams.

The parameters selected to characterize the various flow streams of the mass balances were; insoluble solids (IS), total dissolved solids (TDS), total solids (TS), moisture content and total Kjeldahl nitrogen (TKN). The washing...
stages of the process involved removing sulphide and other soluble and removable solids from the skin.

Assessment of the effectiveness of 1 to 4 washing configurations arranged either co-currently or in a counter-current operation were investigated. Each scenario was compared in terms of minimization of water usage and minimizing the amount of residual solids remaining in the de-wooled, washed sheepskins (slats). This was done as individual fellmongeries in different areas have varying concerns. By optimization to both targets, the results could be applied to a number of individual fellmongery operations.

Pilot scale trials of 2 half skins of approximately 2 kg in total in mini-rotary pilot scale drums were conducted to validate the findings of the mass balance study.

The enzyme treatment stage, involved a 6 h alkaline proteolytic enzyme treatment process followed by the neutralization of highly alkaline sheepskins. The effectiveness of adding a coarse or micro filtration treatment prior to recycling of the wash liquors or restructuring the process flows (e.g. recycling the enzyme process float directly and not after the neutralization process) were evaluated on the basis of minimising the amount of soluble and washable insoluble solids present in the treated skins. 13–16 kg pilot scale sheepskin treatment trials were conducted to validate the mass balance findings.

### RESULTS AND DISCUSSION

#### Optimization of the washing stages

The results of the mass balance study show that for the washing stages, a 2 stage counter-current washing stage configuration was optimal for the following reasons:

1. Practicality (e.g. this system requires no additional equipment to that already available in conventional processing plants and no increase in processing time was needed).
2. Compliance to main operational constraints (e.g. minimum and maximum float volumes in the processing drums)
3. Had the best results of both forms of optimization over other modification options which were also both practical and compliant.

Tables 1 and 2 show the optimization results for the washing stages for both water usage and slat quality respectively for each potential process modification.

For both optimization targets, there were marked improvements with the counter-current configurations. There were small improvements delivered by adding a third washing step for both co-current and counter-current arrangements but the additional processing time and equipment required would offset the existing benefits of the LASRA process. By minimizing the water used (to achieve the requisite skin composition), a fresh water reduction of almost 40% was possible compared to the initial LASRA process. Overall this resulted in 70% less water used for the washing operations compared to conventional fellmongering operations. By using a fixed quantity of water, the TDS remaining in the washed skins were 50% lower using the 2 stage counter current configuration. This increased washing effectiveness provided downstream benefits in terms of product quality.

#### Table 2 | Optimization of processes to a set level of water usage

<table>
<thead>
<tr>
<th>Process</th>
<th>Total water used (% initial skin input)</th>
<th>TDS content in slats (kg/kg initial skin weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Stage cross current</td>
<td>200%</td>
<td>0.022</td>
</tr>
<tr>
<td>LASRA process (2 stage)</td>
<td>200%</td>
<td>0.017</td>
</tr>
<tr>
<td>3 Stage cross current</td>
<td>200%</td>
<td>0.013</td>
</tr>
<tr>
<td>4 Stage cross current</td>
<td>200%</td>
<td>Na</td>
</tr>
<tr>
<td>2 Stage counter-current</td>
<td>200%</td>
<td>0.009</td>
</tr>
<tr>
<td>3 Stage counter-current</td>
<td>200%</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*Lower values indicate cleaner skins and therefore better quality.

#### Table 3 | Results of duplicate validation trials showing the second wash stage of both the LASRA process and the 2 stage counter-current washing configuration

<table>
<thead>
<tr>
<th>Process run name</th>
<th>IS (mg/l)</th>
<th>Average IS</th>
<th>% TS (dry solids basis)</th>
<th>Average % TS</th>
<th>% TKN (w/w total protein)</th>
<th>Average % TKN</th>
</tr>
</thead>
<tbody>
<tr>
<td>LASRA process (2 stage)</td>
<td>3,960</td>
<td>4,140</td>
<td>3.03</td>
<td>3.20</td>
<td>1.32</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>4,520</td>
<td>4,920</td>
<td>3.37</td>
<td>2.87</td>
<td>1.28</td>
<td>1.28</td>
</tr>
<tr>
<td>2 Stage counter-current</td>
<td>1,640</td>
<td>1,630</td>
<td>1.37</td>
<td>1.58</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td>Washing configuration</td>
<td>1,620</td>
<td>1,630</td>
<td>1.38</td>
<td>1.58</td>
<td>0.57</td>
<td>0.57</td>
</tr>
</tbody>
</table>
Table 3 shows the results of validation trials (done by optimizing for product quality) comparing the LASRA process with the 2 stage counter current washing configuration identified in the mass balance study. A lower value for all parameters for the 2 stage counter-current washing configuration is indicative of a cleaner product thus confirming the results of the mass balance study.

Optimization of enzyme treatment stages

A further enhancement of the novel enzyme treatment process was to drain the enzyme float prior to neutralization thereby allowing recycling of the undiluted enzyme and neutralization floats in subsequent treatments. This modification allowed a potential reduction in raw materials usage (e.g. enzyme or acid). Accumulation of dissolved solids (TDS) in processed sheepskins was the key process design characteristic for optimization of the enzyme treatment stage by mass balances. This was because recycling options have potential to retain dissolved solids within the processed skins and thereby raising the potential for compromising finished skin quality.

The results of the mass balance study are shown in Figure 2 for 10 sequential runs. With the assumption that the process floats had reached equilibrium between dissolved solids in the skins and surrounding liquor prior to drainage, it was then possible to estimate the amount of residual TDS in sheepskins produced by the enzyme treatment and neutralization processes. The separation of float for recycling before the neutralization process was best as it had the lowest TDS accumulation in sheepskin products of up 30% less TDS as compared with the LASRA process. The mass balance studies showed that significant enzyme losses were present in the modified process. This was predominantly due to enzyme being present in the liquor retained in the skin after drainage of the enzyme float. The amount of enzyme lost in this way in the unmodified LASRA process were less than for the proposed modification of separating the float before the neutralization process, due to the enzyme being at lower concentration. Practically however, the combined neutralisation float is twice the volume (at approx 50% enzyme strength) required to be recycled in subsequent batches. As a consequence of this the proposed modification saves 10% more enzyme over the un-optimized process.

Figure 2 | TDS accumulation comparison between the LASRA process with potential modification measures that may be applied to it.

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The results of the pilot scale validation runs comparing the TS as well as IS accumulation of the LASRA process with the proposed modification can be seen in Figures 3 and 4 below.

Figures 3 and 4 show that the pilot scale validation trials confirm that the separation of the float before the enzyme treatment process improves the LASRA process. This is especially evident with the final product characteristics showing an improved quality of float. The concentration of dissolved solids in the neutralisation liquor can be used as a measure of processed skin quality because the water remaining in the skin has TDS levels in equilibrium with this stream. The modified process achieves better performance because the neutralization process is now acting as an extra washing stage to offset any detrimental qualities attributed to the use of recycled float in the enzyme treatment processes.

Overall evaluations of the optimized new process

Figure 5 shows the optimized process design resulting from the investigation.

In comparison with Figure 1, it can be seen that both configurations are similar with the same processing time.
and capital equipment used although the flow regimes are arranged differently. In both scenarios drum and energy utilization are equivalent.

**CONCLUSIONS**

Through application of engineering analysis, a refined process meeting the industry needs has been developed. The process maximizes the initial benefits of the LASRA proof of principle process. Benefits over conventional fellmongering operations include reduction of residual TDS in the skins by 50% at the washing stages and 70% savings on water use overall. As compared with the un-optimized LASRA process, there is now a 30% reduction of solids contained in the processed skins (pickled pelts) by the modified configuration of the enzyme treatment and neutralization processes with a recycling system. Savings of enzyme usage was 10% with a recycling system of floats.

The optimised process offers significant benefits for industry, in terms of product quality and resource use. It is recommended that the process be trialled on a commercial scale to demonstrate these benefits first hand in industry. Adoption of the process can be very rapid due to the utilisation of existing equipment used in conventional processing.

**REFERENCES**


