

Environmental Assessment of Dehydration Processes for Bovine Leather

by

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Abstract

The purpose of this work is to compare the environmental impact of two systems for processing bovine leather: (i) a new continuous system that consists in dehydration and tanning and post-tanning by immersion versus (ii) the traditional system using drums.

In order to better assess the environmental impact of this new tanning system, the life cycle assessment methodology has been chosen to perform calculations on various impact categories, including the global warming potential (CO₂ equivalent emissions), and the energy consumption for both the traditional and the new tanning processes.

When assessing the environmental impact of the new system, it is clear that a reduction in the use of acetone during the process will positively affect the environmental outcomes. In this regard, results show reductions on the impacts in eight out of the eleven impact categories analyzed as well as reductions on energy consumption. However, the acetone loss considered (5%) led to higher impacts compared to the traditional system in three specific impact categories, which can be improved by reducing the acetone emission to 2.5%.

Introduction

The leather industry can be a source of environmental pollution that has some negative effects on the ecosystem. Among the several phases of leather production, the tannage and post-tannage are the most polluting processes due to the fact that these processes are performed in drums. Processing in drums is usually associated with high pollution loads.¹ A great variety of studies have been carried out in order to minimize this impact: Recycling of pickle-tanning floats, recovery and treatment of chrome floats, high exhaustion of such floats,²⁻⁴ management of solid waste containing chrome, and the use of other tanning agents to substitute chrome.⁵⁻⁹

The present work is based on the knowledge acquired in four previous papers.¹⁰⁻¹² These studies explored the development of an industrial-scale prototype to obtain a new collagenic material by dehydration as a by-product of dehydrated bovine hides (the main purpose of the research project). Once the optimum process was established, a dehydration system for bovine hides was studied in order to obtain a dry and very porous substrate at an industrial stage. This system facilitates the application of tanning agents, dyes and fats by immersion in aqueous solutions and enables reductions in process time, chemicals and water consumption when compared to the conventional process.

In a previous study,¹³ Life Cycle Assessment was used to detect the environmental “hot spots” in the chrome-tanned bovine leather industry. The objective of the present work is to evaluate these reductions using the new process in relation with the traditional one by means of a life cycle assessment. The life Cycle Assessment (LCA) methodology has been chosen to perform a more reliable and quantifiable environmental comparison between the traditional and the new tanning processes. To this end, calculations on various impact categories; including the global warming potential (GWP) and the energy consumption comparing both production systems are presented in this work.

LCA is a recognized tool to make decisions for a great variety of applications,¹⁴⁻¹⁶ since it enables the evaluation of the environmental impact of a particular process as well as the comparison of this impact with that of the alternative process. LCA methodology is regulated by the ISO 14040 and 14044^{17,18} international standards. Unlike the basic material and energy balances, the LCA approach takes into consideration the production of the chemicals being used as well as the emissions being generated. This wider view of the process results in a more detailed environmental assessment, quantitatively measuring the effect of the chemicals and energy involved.

In the impact assessment phase the emissions are aggregated into impact categories according to an internationally accepted method. The method chosen in this study is the CML method

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from the Environmental Sciences Institute of Leiden University, because it is the one which has generated the most global consensus and avoids subjectivity.¹⁹ This is a cause-effect method that limits the uncertainty in groups dealing with impact categories.²⁰ This cause-effect methodology analyses the impact of a given pollutant when modifying a variable that its concentration depends on. Therefore it calculates the increase of damage and quantifies its effects.²¹

Material and Methods

Goal and scope

The goal of this study is to assess and compare the life cycle environmental impacts associated with the traditional processes to obtain leather and a new system of dehydration, tanning and post-tanning by immersion. A functional unit is defined to ensure that all comparisons are consistently measurable and correspond to the basic unit that tanneries use for trading. The functional unit is defined as 1000 kg of salted raw hide.

Material

The tests were carried out using hides split at 2.5 mm. In order to finish the preparation before dehydration, the hides were delimed using 1.5% of a commercially available carboxylic acid and were bated using 0.7% of enzymes of 1000 LVU g⁻¹. The pH of the hides was 8.5; the hides were negatively charged since the ionized groups of collagen in this pH are carboxyl groups. In order to reach the isoelectric point of the hide, neutralization has to be carried out using 0.5% of HCOOH, adjusting the pH with NaHCO₃ if it drops below 5.0. The pH obtained is 5-5.5, which is the point at which the ionization of the hides is at its lowest. In this condition, the water present in the hide is less likely to create hydrogen bonds and it is therefore easier to move the water towards the external medium of the solution.

Dehydration Process

The process of dehydration is described in the international patent WO 2010070571 (A2) of the technological center AIICA.²² The industrial scale prototype (Figure 1) to perform the dehydration process consists of a wash drum, two collection tanks for the final floats, a tank to recover the condensed solvent, and a tank for feeding the solvent. As for the recovery of acetone in the final floats, a distiller is coupled to a cooling tower, which also collects the recovered gas emissions. The prototype is made of stainless steel and is appropriately equipped with pumps and valves for the processing of solvents.

The prototype is protected with a cover to prevent possible emanations of acetone in the workplace. The measurements of the device are the following: 3200 mm in width, 2420 mm in length and 2880 mm in height.

Next is a brief description of the units in prototype (1):

- Stainless steel machine (2) with wash drum (2a) with variable rotation speed, of 360 L capacity. Pneumatic valves, full automation of wash process times and subsequent spin cycles to replace the sammying operation. The final floats are collected by the different tanks of the device depending on the concentration of acetone.
- Distillation column (3) to separate the solvent from the rest of the float (fat + water + leather fibers + dissolved salts)
- Condensation unit (6) with a cooling system
- Tank to collect the final floats (4) comprised of different compartments: (4a) tank to collect the solvent condensed during the process of acetone distillation; (4b) collection of centrifugation float and sammying float; (4c) collection of the last wash float with solvent to recirculate it through a first float application; 4(d) feed tank
- Heating units (7) and (9)
- Circulation nozzle (5) of final wash float with acetone
- Nozzle (5a) to circulate the final recovery wash float into the system
- Drum solvent feed nozzle (8)
- Nozzle (10) to circulate solvent vapors into the condensation unit



Figure 1. Dehydration industrial scale prototype.

The working parameters for bovine hides into the prototype are: temperature (25°C), dehydration time (60 minutes) divided in 5 floats, rotation speed (25 min⁻¹), and atmospheric pressure. With the aim of recovering as much solvent as possible, a final centrifuging of 600 min⁻¹ is applied for 5 minutes.

Tanning and Post-tanning by Immersion of Dehydrated Hides

In this stage, a tanning and post-tanning process on dehydrated hides was carried out on an industrial scale by means of a dyeing machine by through feed immersion from GEMATA model Starcolor.

A solution of 10% of chromium salt with a basicity of 45°Sch was prepared. The solution was deposited in the immersion compartment of the roller machine. The speed of the rollers was 4.4 m/min while the speed of the conveyor was 3.3 m/min. The process time of tanning by immersion was 13 seconds. In order to obtain a good tannage, two applications were performed. Once the tannage by immersion was finished, the hides were left to rest for 24 hours.

After tannage, a solution with 10% of synthetic retanning product, 2% of dyestuff, 3% of soya lecithin, 2% of sulfonated beef tallow, and 4% of oxisulfated marine oil was prepared. The solution was deposited in the immersion compartment of the roller machine. The speed of the rollers was 4.4 m/min while the speed of the conveyor was 3.3 m/min. The process time of post-tanning by immersion was 13 seconds. In order to obtain a good post-tannage, two applications were performed.

Once the tannage and post-tannage by immersion were finished, the hides were left to dry piled flat on a plate for 12-14 hours.

The new leather processing, called BCD (bovine ketone dehydration), as well as the traditional leather processing are both shown in Figure 3.

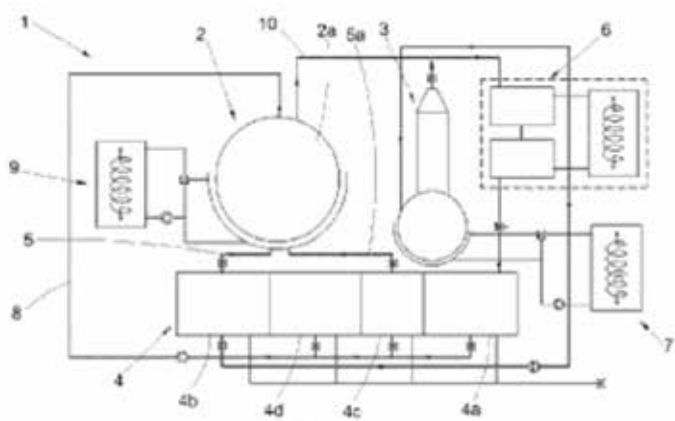


Figure 2 shows the different parts of the dehydration prototype.

Life Cycle Assessment Methodology

In order to carry out a study of the environmental feasibility of the new system, the Life Cycle Assessment (LCA) methodology has been chosen to provide a reliable and quantifiable environmental comparison between both traditional and new tanning processes.

The first step involved performing a life cycle inventory analysis. Following the flow diagram shown in Figure 3, all the inflows and outflows were quantified for each unit process. The GaBi 4 software from PE International (PE International, 2009) has been used to perform this LCA.

Primary data and product information (including material types and quantities, manufacturing processes and associate parameters) were provided by A3 Chair in Leather innovation and its suppliers. Complementary data were obtained from the GaBi 4 database and from the literature, including energy production patterns and raw material production, among others. Proxies for materials not found in databases were also selected.

To determine which flows are significant and how great their contribution is, data contained in the life cycle inventory must be interpreted. Therefore, a model of environmental mechanisms is used to establish a connection between the environmental loading and known exposure pathways to humans and ecology

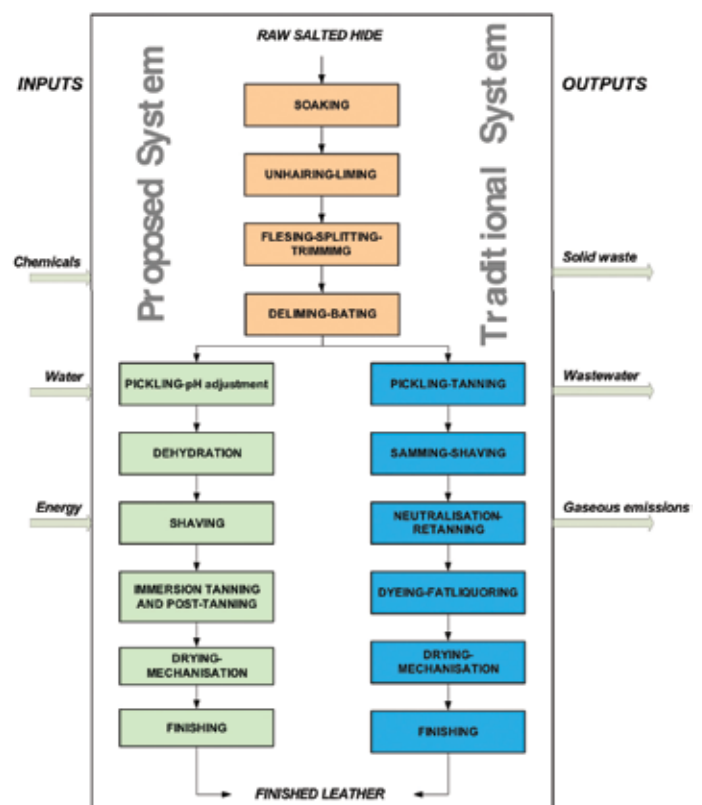


Figure 3. Proposed and traditional system stages.

(i.e. acidification, ozone depletion, climate change, eutrophication, global warming potential, etc.). CML methodology has been chosen to perform the Life Cycle Assessment. CML 2001 is an impact assessment method, which restricts quantitative modelling to early stages in the cause-effect chain to limit uncertainties. Results are grouped in midpoint categories according to common mechanisms (e.g. climate change) or commonly accepted groupings (e.g. ecotoxicity).

Environmental impact categories including human health impacts are evaluated. Furthermore, additional scenarios are considered (reducing acetone emissions) to assess the sensitivity of the results. The last step consists in the validation of the obtained results and the proposal of feasible solutions intended to reduce the overall impact.

The 11 impact categories considered in this LCA comparison are listed in Table I with the acronyms used and their units. Energy is also considered in terms of net calorific value, calculated in MJ.

The non-toxicological categories related to Ecosystem Quality considered for this LCA are: abiotic depletion (ADP elements and fossil), acidification potential (AP), eutrophication potential (EP), ozone layer depletion potential (ODP) and photochemical

Table I
Impact categories.

Abiotic Depletion (ADP elements) [kg Sb-Equiv.]
Abiotic Depletion (ADP fossil) [MJ]
Acidification Potential (AP) [kg SO ₂ -Equiv.]
Eutrophication Potential (EP) [kg Phosphate-Equiv.]
Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB-Equiv.]
Global Warming Potential (GWP 100 years) [kg CO₂-Equiv.]
Human Toxicity Potential (HTP inf.) [kg DCB-Equiv.]
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB-Equiv.]
Ozone Layer Depletion Potential (ODP, steady state) [kg R11-Equiv.]
Photochem. Ozone Creation Potential (POCP) [kg Ethene-Equiv.]
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB-Equiv.]

ozone creation potential (POCP). The non-toxicological category related to climate change impact used is global warming potential (GWP), which is probably the most known and used impact category in environmental studies. They are evaluated using CML 2001.

On the other hand, 4 toxicological categories (covering water, soil and human affectation) are also evaluated CML 2001, namely Freshwater Aquatic Ecotoxicity Potential (FAETP), Human Toxicity Potential (HTP), Marine Aquatic Ecotoxicity Potential. (MAETP) and Terrestrial Ecotoxicity Potential (TETP).

The emissions and resources are assigned to each of these impact categories. They are then converted into indicators using impact assessment models. Different emissions and resources consumed, as well as different product options, can then be cross-compared in terms of the impact indicators.²³

In this context, a broad range of impact categories has been selected to evaluate widely the burdens of the compared production systems.

Results and Discussion

Life Cycle Inventory Analysis

A broad analysis of the input/output flows (I/O) was carried out for both the traditional tanning system and the new tanning system being proposed in this study. Table II shows all the inflows and outflows for each unit process quantified per 1000 kg of raw salted hide with the traditional tanning system.

Similarly, Table III shows all the inflows and outflows for each unit process quantified per 1000 kg of raw salted hide in the new tanning system.

The inventory data were calculated for processing an average of 1000 kg rawhides per day. The total water, energy, chemicals, thermal and electrical energy, as well as emissions generated in the production have been taken into account to assess the environmental burdens as well as the total energy consumption. In addition, different scenarios were studied with the aim of improving the impact reduction of the new system being proposed. The proxies considered in the traditional and the BCD tanning systems were acetic acid, as formic acid, and CrOHSO₄, as chrome salt. Retanning agents, dyes and fatliquor agent production energy were taken into account. Production data were obtained from product manufacturers.

Life Cycle Impact Assessment

The analysis of the environmental burdens of both types of leather production is required to detect the hot spots.

Table II**Traditional tanning system inflows and outflows.**

Process	Traditional system	
	Inflows	Outflows
Pickling-tanning	60% H ₂ O 6% NaCl 0.5% HCOOH 0.7% H ₂ SO ₄ Drum T 20°C, running 2h30' (348.75MJ) 50% H ₂ O 2% Chrome salt 33°Sch 5.5% Chrome salt 66°Sch 0.15% MgO Drum T 50°C, running 8h (1080MJ)	Wastewater with salts and chrome
Shaving	Shaving (72MJ)	
Neutralization – Retanning	150% H ₂ O 4% Retanning agent 1.5% Sodium formiate 1% Soya Lecithin 1.5% Sodium bicarbonate Drum T 40°C, running 2h (256.5MJ)	Wastewater with salts
Dyeing - fatliquoring	50% H ₂ O 4% Retanning agent 2% Dye 3% Naphthalene-sulfonic syntan Drum T 50°C, running 2h (256.5MJ) 150% H ₂ O 3% Soya Lecithin 2% Sulfonated beef tallow 4% Oxisulfated marine oil 0.7% HCOOH Drum T 60°C, running 1.5h (192.37MJ) Dryeing of fatliquored hides (thermal energy from Natural Gas, 2309.2MJ)	Wastewaters with salts, dyes and fats

Table III**Proposed tanning systems inflows and outflows.**

Process	New System	
	Inflows	Outflows
Pickling-pH adjustment	70% H ₂ O 1.5% HCOOH 4% NaCl 0.75% NaHCO ₃ Drum T 20°C, running 2h, 281.25MJ	Wastewater with salts
Dehydration	Acetone (5 floats) Patented dehydration machine, running 1h, (18.75MJ)	Loss of 5% of acetone
Shaving	Shaving (72MJ)	
Immersion tanning and post-tanning	Water solution containing: 10% Chrome salt at 45% Basicity Immersion 13 seconds Water solution containing: 10% Retanning agent 2% Dye 3% Soya Lecithin 2% Sulfonated beef tallow 2% Oxisulfated marine oil 2% Sulphited natural oil Immersion 13 seconds Dryeing of hides (thermal energy from Natural Gas, 1130.2MJ)	

Comparative results for CML impact categories are shown in Figure 4. They indicate better performance with the proposed system. Yet, three categories show better results in the traditional tanning system, namely abiotic depletion (fossil)s (ADPf), freshwater aquatic ecotoxicity potential (FAETP) and photochemical ozone creation potential (POCP).

Reductions in GWP (15%) and energy consumption (5%) were estimated according to the material and energy balances presented. Though these amounts are significant, the decrease in energy consumption presented in the basic energy balance was expected to be larger. Therefore, as the major contributor to energy consumption in the new tanning process is acetone, a

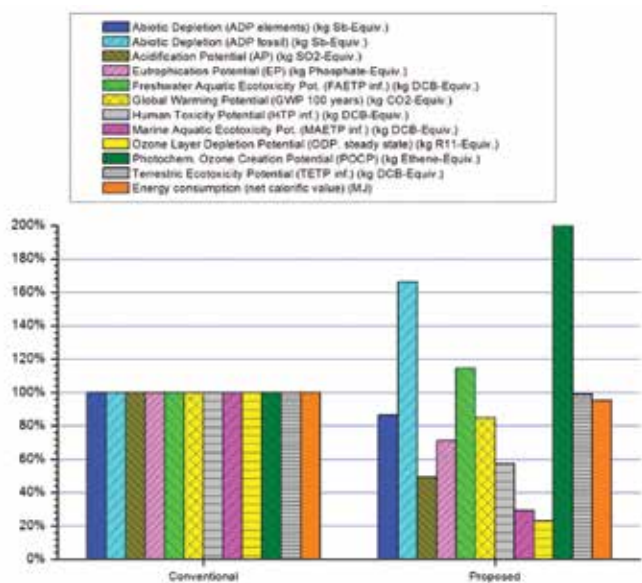


Figure 4. Contribution from acetone emission and acetone production to the CML impacts evaluated for the proposed tanning system.

sensitivity analysis of this particular chemical was needed to assess its effect on the results.

Figure 5 shows the impact contribution from acetone production and emission. It is thus clear that acetone is the main reason for the higher impact results for the three categories mentioned above as well as a great contributor to energy consumption.

Interpretation and Improvements

The analysis of the data show that a reduction in the use of acetone during the process will lead to significant improvements. In the current results a 5% loss for each of the five baths with acetone is considered. If the 5% acetone losses of the prototype used could be reduced to 2.5%, the energy consumption of the new process would be just 37% of the traditional process. Likewise, this reduction would make the GWP even lower, decreasing the CO₂ equivalent emissions from the initial 15% reduction to a 40% reduction. This scenario reduces the impact categories results significantly, i.e.: FAETP from 114% to 91% and ADP_f from 166% to approximately 100%. Therefore, the same impacts for both the traditional and the new system are achieved.

However, it must be noted that POCP is still several times higher in the new system when compared to the traditional tanning system, as this impact category is virtually only dependent on acetone production, which is nearly absent in the traditional process. This category would therefore only be lowered to 89% in the proposed system in a machine with nearly no acetone losses (in a scenario with 0.03% acetone emission instead of the 5% estimated with the prototype). This scenario would lead to lowered impacts in comparison with the traditional system, i.e.: GWP 36%, FAETP 67% and ADP_f 38%.

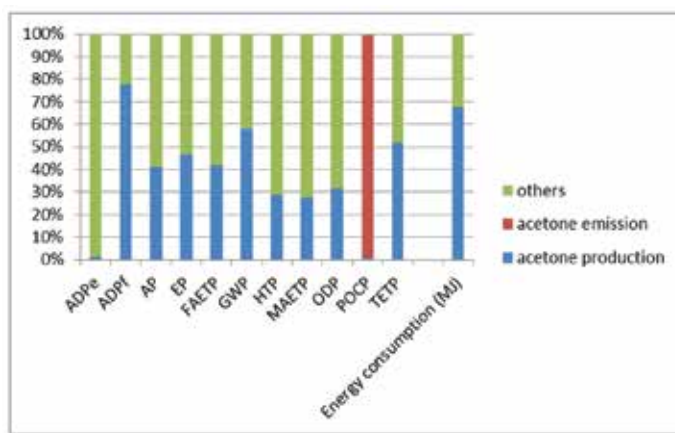


Figure 5. Contribution from acetone emission and acetone production to the CML impacts evaluated for the proposed tanning system.

Conclusions

The dehydrated hides can be transformed into stabilized leather by immersing the hides in an aqueous solution of chemical products after a short period of application. This study includes the relevant life cycle stages of leather processing using the two described methods and explores the environmental evaluation of different scenarios.

When assessing the environmental impact of the new system, it is clear that a reduction in the use of acetone losses during the process will improve the results. The analysis of the data shows reductions of the impacts in eight out of the eleven impact categories as well as reductions in energy consumption.

However, the 5% loss considered for each of the five baths with acetone leads to higher impacts in three specific impact categories compared to the traditional system. These impacts could be improved by lowering acetone emissions by half (up to 2.5%).

Recommendations

The acetone loss considered (5%) led to higher impacts compared to the traditional system in three specific impact categories, which can be improved by reducing the acetone emission to 2.5%. Likewise, this reduction would contribute to decrease the global warming potential (GWP), thus amplifying the reduction in CO₂ equivalent emissions from the initial 15% to a 40% reduction. This scenario reduces impact categories results significantly, i.e.: Freshwater aquatic ecotoxicity potential (FAETP) from 114% to 85% and abiotic resource depletion potential of fossil fuels (ADP_f) from 166% to approximately 100%. Nevertheless, a greater reduction of acetone losses is necessary to decrease photochemical ozone creation potential (POCP), which is directly related to acetone production.

As explained in the Dehydration process section, the prototype used consists of a distiller to separate the acetone in the residual floats produced. The device can also recover the gas emissions of solvent that are released during the dehydrating experiments. For the prototype to be financially and environmentally viable, the recovery of the acetone used to feed the process has to be optimized. More specifically, a modification of the prototype is recommended in order to reduce the acetone emission by means of a vacuum system.

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