A life cycle assessment on the dehairing of rawhides: Chemical treatment versus enzymatic recovery through solid state fermentation

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Abstract

The leather industry needs to switch from the traditional chemically based dehairing process to an environmentally friendly one so that the overall burdens to the environment are reduced. The primary goal of the work was thus to compare the chemical leather dehairing process to an enzymatically based one using the enzymes that are extracted after the application of solid state fermentation (SSF) on hair wastes generated after dehairing. The environmental burdens of the dehairing stage were determined using a life cycle assessment (LCA) approach by comparing the two aforementioned management scenarios. The first scenario was the commonly used technology in which hair is removed via a chemical process and then composted in open piles. This scenario included two sub-scenarios where hair waste is either incinerated or landfilled. In the second scenario, the proteolytic enzymes extracted during the solid-state fermentation of the residual hair are used to dehair the new rawhides instead of chemicals. Industrial and laboratory data were combined with international databases using the SimaPro 8.0 LCA software to make comparisons. The environmental impacts associated to the enzymatic dehairing were significantly lower than the ones associated to the conventional chemical dehairing process. This difference is attributed to the impacts associated to the original production of the chemicals and to the electricity consumed in the conventional method. A sensitivity analysis revealed that the results are affected by the amounts of chemicals used during dehairing.

Keywords: life cycle assessment; solid state fermentation; protease; dehairing; leather industry

Abbreviations

ALO: Agricultural land occupation

BOD: Biological oxygen demand (ppm)

CaO: Calcium oxide

CC: Climate Change

COD: Chemical oxygen demand (ppm)

DM: Dry matter (kg)

FD: Fossil fuel depletion

FE: Freshwater eutrophication

FET: Freshwater ecotoxicity

FU: Functional unit (kg)

HT: Human toxicity

IR: Ionizing radiation

LCA: Life cycle assessment

LCI: Life cycle inventory

LTUI: Leather Tanner's Union in Igualada

ME: Marine eutrophication

MET: Marine ecotoxicity

MRD: Mineral resource depletion

Na_2CO_3: Sodium carbonate

NaHS: Sodium hydrosulfide

Na_2S: Sodium sulfide

NLT: Natural land transformation

OD: Ozone depletion

PMF: Particulate matter formation

POF: Photochemical oxidant formation

SSF: Solid state fermentation

TA: Terrestrial acidification

TET: Terrestrial ecotoxicity

TS: Total solids

ULO: Urban land occupation

WD: Water depletion

1. Introduction

Large amounts of organic wastes are produced worldwide that can be treated by biological treatment technologies under aerobic or anaerobic conditions. The principal aerobic treatment processes are composting and solid state fermentation (SSF). The main aim of composting is to reduce the volume of the wastes, to stabilize organic matter and to generate a compost for agricultural use. Solid state fermentation is a process with the main objective of generating bioproducts (e.g. enzymes), after an extraction procedure, and to generate compost with the fermented solid (Abraham et al. 2014; Abu Yazid et al. 2016). SSF has proven to be a very promising technology in the development of several bioprocesses and products, since it holds tremendous potential for the production of enzymes. It can be of special interest in those processes where the crude fermented product may be used directly as an enzyme source (Doelle et al. 2009). This technique has, therefore, become an attractive alternative for specific applications. In recent years, for example, the production of enzymes from various organic substrates using solid state fermentation has been evaluated. In particular, protease production by SSF under different process conditions, microorganisms and substrates has been demonstrated in different studies (Singhania et al. 2009). Recently, Abu Yazid et al. (2016) presented the protease production and extraction using a pilot-batch mode operation using hair waste from the tannery industry. Also, the yields and recovery achieved on an easily scalable low-cost downstream process have been presented (Abraham et al. 2014), with an obtained recovery of 74%.

1.1 The leather processing industry

Leather processing involves a series of unit operations that can be classified into three groups:

I. Pre-tanning or "beamhouse" operations
II. Tanning
III. Post-tanning and finishing operations

Pre-tanning includes different steps such as soaking, fleshing, dehairing and liming, deliming, bating and pickling. During pre-tanning, the previously dehydrated raw material (the rawhides) must be carefully rehydrated before it can be subjected to mechanical action. The flesh layer (meat) is removed to aid in the penetration of chemicals. Fleshing can be done after slaughter, after soaking or after liming. Then, conventionally, the hides or skins are treated with different chemicals to destroy the keratinous material of the epidermis and to remove hair. During this process, hair roots and pigments are removed. Pickling increases the acidity of the hide to a pH of 3, and salts are added to prevent the hide from swelling. For preservation purposes, fungicides and bactericides are applied to the dehaired leather. The hair waste (solid residue) is produced at this stage (Thanikaivelan et al. 2004).

According to studies as Saran et al. (2013) or George et al. (2014), the pre-tanning operations uses chemicals that may have hazardous effect to tannery workers and to the environment. Almost 70% of the total pollution of the process is produced in these operations (Thanikaivelan et al. 2004). The use of proteases in this step can be a viable and green alternative to the conventional chemical process that can lead to substantial reduction of the amount of effluent and its toxicity (Kamini et al. 1999).

Daddi et al. (2016) and Laurenti et al. (2016) showed that the use of chemicals in the tanning process contributes more than 60% to the environmental impact in the leather industry. Chemicals' usage and water resources depletion are the main environmental impacts of the whole tanning process.

Composting is traditionally used to treat hair residues (hair wastes) generated during the conventional dehairing process in the leather industry. SSF, a process similar to composting, could be applied to extract enzymes (mainly proteases) that can replace chemicals in the original dehairing process. The use of extracted enzymes in the dehairing process can result in: a) shorter processing (dehairing) time, b) practical elimination of chemicals and c) lower amount of wastewater generated (Valeika et al. 2009). In fact, the efficiency of proteases extracted during the SSF of hair waste to replace typical chemicals used to dehair rawhides has been well demonstrated in recent studies (Abraham et al. 2014; Abu Yazid et al. 2016).

The proteases can be excellent alternatives to decompose hair keratin. Around 40% of keratin has been found to be decomposed through digestion with protease after 10 minutes (Park et al. 2004.) In recent studies, it has been demonstrated that after 24h of incubation, between 90% and 95% of hair was removed from raw hides following treatment with proteases, which is a value similar to that obtained with the common chemicals (Abu Yazid et al. 2016).

1.2 Gaps in knowledge and scope of work

The use of SSF as an enzymatically sustainable process has rarely been studied. In particular, the use of LCA to assess the environmental impact of this technology has never been reported. Hence, the main objective of this study was to compare the two principal scenarios for dehairing in a typical leather industry, namely:

- The existing chemical dehairing process in which hair waste is then composted to provide a potential soil amendment
- An enzyme driven dehairing process, in which enzymes are extracted during the SSF of the hair residues and used to fully replace the traditional chemicals used in dehairing. The resulting SSF solid end product, after the enzyme extraction, is also directed to composting (or other treatment techniques such as landfilling or incineration).

A LCA-based comparison was performed to quantify direct and upstream environmental burdens for both scenarios (chemical vs enzymatic dehairing), including three sub-scenarios for the traditional method, in order to investigate the optimum treatment (composting, landfilling, incineration) of hair wastes. It is clarified that our study focused only on the dehairing stage and the composting of the removed hair (hair waste). That is, we did not focus on the whole leather processing life cycle (Figure 1), since this was beyond the scope of our work. We chose the dehairing stage, however, since it contains the two main stages in a leather industry that are responsible for the high usage of chemicals. A sensitivity analysis was performed for both main scenarios to study the effect of key parameters on the outputs.

2. Methodology and case study

To better study the process, we considered a tannery industry located in North Catalunya, Spain, as a typical model industry. Operating data were collected from that industry that currently adopts the conventional chemical based dehairing process to remove hair. Data related to the environmental burdens of the SSF were based on pertinent laboratory experiments.

2.1. The conventional chemical dehairing process

The first scenario consists of the conventional chemical process as depicted in Fig. 1 and described below.

Insert Figure 1

Conventionally, hair removal is carried out by chemical and mechanical means. The keratinous material and fat are removed from the pelts mainly with sulphides (NaHS or Na_2S) and lime. In the first stage, soaking is performed to allow hides to re-absorb any water that may have been lost after flaying to clean the hides, and to remove inter-fibrillary material. The data included in the first scenario considered in this study and the system boundaries are from the Leather Tanner's Union in Igualada, Spain (LTUI 2015) for 100 kg of initial leather after the salting stage and before rehydration/soaking (i.e. referred to as rawhide); these 100 kg of rawhide were defined as the functional unit (FU) in this work.

The sequential chemical treatment of raw cow hides consists of the soaking, liming and dehairing stages, namely:

1. In the soaking stage, the following reagents are added and stirred over 30h: 600 kg H_2O at 25ºC, 0.2 kg surfactant, 0.5 kg Na_2CO_3, 0.25 kg NaHS and 0.1 kg NaOH.
2. In the liming and dehairing stages, the following reagents are added and mixed over a 5h period: 700 kg H_2O, 3.3 kg CaO, 0.3 kg NaOH, 0.8 kg NaHS and 0.5 kg Na_2S. This step produces 13 kg of solid (mainly hair waste) and 703 kg of liquid residues.

The water effluent generated by the whole process (from both steps combined) contains a high inorganic and organic polluting load. The soaking stage is the most polluting stage of the tanning process since it contributes up to 50-55% of the total polluting loading (Chowdhury et al. 2015). This is due to the inorganic chemicals that are used for the treatment of the hides, such as lime, sodium carbonate and sodium hydroxide. In the liming stage, hair, skin and emulsion fats (i.e. a mixture of sodium soap and fat) are removed from the hides, are released to the effluent and increase its total solids (TS) content (Chowdhury et al. 2015). Wastewater is normally treated by an on-site or central wastewater treatment plant and the treated effluent is discharged to surface water. According to Chowdhury et al. (2015), the principal pollutants in tannery wastewater is increase sulfates, chlorides and sodium cations, as well as chemical oxygen demand (COD) (between approximately 4000 to 5000 mg/L for each of the above four parameters), whilst a typical BOD_5 is around 900 mg/L (Chowdhury et al. 2015). These literature values are in agreement with the corresponding field values provided after the personal communication with LTUI (2015). The hair residues obtained after dehairing become solid waste that is normally treated via composting or disposed of to a landfill. Composting takes place either in turned windrows or in-vessel. At this point, the main environmental emissions of the process are primarily ammonia due to the high nitrogen content of hair waste (Barrena et al. 2007). Alternative techniques to treat hair waste is landfilling and incineration (sub-scenario 1: landfill; sub-scenario 2: incineration) as illustrated in Figure 2. However, the dominant techniques are composting and landfilling (LTUI 2015).

More detail about the conditions and the operations, during all stages, in a beamhouse that utilizes the conventional dehairing process can be found in Thanikaivelan et al. (2004) and Ramasami et al. (1999).

Insert Figure 2

2.2. The enzymatic based dehairing process

The hair waste is a good source of protein with a content of 65-95% DM (Dawber 1996). Recent studies have proven the efficiency of SSF to produce alkaline proteases from hair waste. These enzymes could be used in the dehairing process of new rawhides instead of chemicals (Abu Yazid et al. 2016). This enzymatic dehairing was tried at laboratory scale (Abraham et al. 2014) and is briefly described below: Fermented solid material was mixed thoroughly with buffer HCl-Tris (tris(hydroxymethyl)aminomethane) according to Abu Yazid et al. (2016). The incubation for dehairing performed is using the protease extract in the hides according to the method of Abraham et al. (2014).

SSF was performed out in pilot-scale reactors (10-50 L) that worked under near-adiabatic conditions and a continuous aeration regime (Abraham et al. 2014; Santis-Navarro et al. 2011). Those experiments provided all the necessary data (emissions, enzyme activity) to carry out the LCA study describe here. Fermented solid material, after reaching the thermophilic phase, was mixed with buffer for 1 hr. The enzyme extract was separated by centrifugation and filtration through a 0.45 mm filter. The complete description of the SSF based enzymatic dehairing process, including operational conditions, material conditioning, quality of final product, etc., can be found, in Abraham et al. (2014) and Abu Yazid et al. (2016). It is noted however that the enzymatic dehairing process does not exist yet in the field scale. Thus, all data necessary to perform our LCA were obtained from the aforementioned references performed at laboratory scale.

To apply the enzymes, wet-salted cow hides were washed and cut in similar shapes (approximately 15 cm^2), then they were incubated with enzymatic crude extract at 37ºC for 24 hours on a rotatory shaker. After 24 hours of incubation, the hides treated with these specific proteases showed an easier removal of hair when mechanically scraped compared to the chemical dehairing process (Abraham et al. 2014). This modification in the process implies a likely less water consumption, decreased to negligible chemical usage and likely less wastewater emissions. For example, BOD and COD loadings from the effluent during enzymatic processing of buffalo hide skins is reduced by 82% and 85% respectively when compared to conventional processing thought chemicals (Saran et al. 2013). A scheme of the enzymatic dehairing process is presented in Figure 3, which also shows the internal loop of the enzyme generation, during SSF, and the reuse of the enzymes during dehairing of new leather. It is this loop that this work attempts to compare, on an LCA basis, with the conventional chemical dehairing process.

Insert Figure 3

2.3. Functional unit (FU)

The FU in LCA provides a reference to related inputs and outputs and to allow comparisons among systems (International Organization for Standardization, 2006). In this study, the functional unit was determined to be the 100 kg of rewetted (soaked) hide, which have resulted from the salting stage of 95 kg of initial hide. That is, the 5kg gain is due to the rehydration (soaking) that follows the salting performed during storage. Since several coefficients in the tannery industry are based on an area basis (m^2), the coefficient of 7.5 kg/m^2 was used to convert units of kg to m^2 and vice versa, where necessary (LTUI, 2015).

2.4. LCA software and inventory data per scenario

SimaPro® v.8 and the Ecoinvent v.3 database were used to perform the LCA based comparison. In addition, the ReCiPe methodology (ReciPe 2016) was adopted to calculate the environmental impacts. ReCiPe is a follow up of the Eco-Indicator 99 and the CML method and has two levels of indicators, namely: i) Midpoint indicators ii) Endpoint indicators. At the midpoint level, which was adopted here, there are 18 impact categories. The 18 midpoint impact categories of Recipe are presented in Table 1.

Insert Table 1

In the present study, the life cycle inventory (LCI) original data with regard to the conventional process were obtained by the Leather Tanner's Union in Igualada (Catalunya). Additional data were obtained from the literature especially regarding the enzyme dehairing process that is still in an experimental stage. The main inputs and outputs that are common in both processes are given in Table 2. Water consumption is presented in supplementary Table S1. All data have been converted to correspond to the functional unit used here (100 kg of rawhide prior to soaking).

Insert Table 2

a. Base scenario: conventional chemical dehairing

The flow diagram of the typical dehairing process that uses chemicals (herein referred to as chemical process) was presented in Figure 1. This case is characterized, apart from the use of chemicals, by a relatively high water consumption. According to the collected data, not all of the used water is fresh water: 75% of the water usage is actually recycled water. After the process, wastewater is treated in a wastewater plant. In the case of Igualada, which was the model tannery industry in our case (LTUI, 2015), wastewater treatment takes place in a central wastewater plant located in the industrial site. The hair waste is stabilized via composting with bulking agent to produce compost with a high nitrogen content (Barrena et al. 2007). The main inputs and outputs for the chemical process are shown in supplementary Table S1.

b. Alternative scenario: Use of extracted enzymes to perform dehairing

The alternative enzymatic based dehairing scenario is shown in Figure 3 and the specific data used are displayed in supplementary Table S2. It is noted that the water used to perform the enzyme extraction was considered equal to the water necessary to perform the soaking step that is included in the traditional process. For this reason, the soaking step does not appear in the enzymatic process (see Figure 3). In addition, due to the lack of field data, we considered that the enzymatic process has the same electricity consumption as the traditional process, during soaking/dehairing.

2.5. Technical assumptions and system boundaries

The characterization of each raw material, energy and water consumptions have been mainly obtained from the Ecoinvent database v3. As the main goal of this paper is to analyze and compare the environmental impacts of the dehairing process for the two selected dehairing scenarios (conventional chemical, enzymatic based), within the boundaries of the systems, the following sub-systems have been included: i) the production of the hair via the dehairing process, ii) the treatment of hair wastes: composting or solid state fermentation and iii) the treatment of exhaust gases emitted during the previous stage. In this study, the LCI includes the consumption of chemical products, energy, and water during each process. In the evaluated scenarios, the treatment of wastewater is considered to lie outside the limits of the system, while any transport of raw materials and products into or outside the system is also not taken into account.

3. Results and discussion

3.1 Environmental impacts assessment of the conventional chemical and the enzymatic dehairing processes

The environmental impacts associated to both processes are presented in Figure 4. For each process, both direct and indirect emissions are presented. The environmental impacts due to direct emissions are those associated to the dehairing process per se, while the environmental impacts associated to indirect emissions are, for example, those that come from the production of wood chips, the production of the chemicals, or the electricity production that highly depends on the local grid and the specific usage of fuel. In our case, the (medium voltage) electrical grid of Spain was used as this is defined in the Ecoinvent® database. To facilitate the comparison between the impact categories, all results are normalized so that all category indicators have the same units (see Figures 4, 5 & 6). Normalized units are calculated by the division of the actual impact emission, at each category by a reference emission. A commonly used reference coefficient, for example, is the average yearly environmental (pollutant) load in a country or continent, divided by the number of inhabitants. There are various methodologies to perform normalization. The ReciPe methodology was utilized here. A detailed explanation of the normalization procedure can be found in Sleeswijk et al. (2007).

Figure 4 (top) shows that the main direct environmental impacts (red color) in the conventional chemical method are, in hierarchical order, freshwater ecotoxicity, marine ecotoxicity, human toxicity and terrestrial ecotoxicity, which are mainly due to the wastewater discharge.

Regarding the indirect impacts associated to the conventional chemical method, the highest ones are related to electricity consumption, and the production of sodium sulphite and sodium hydroxisulfide that are used in chemical dehairing. The categories with the highest impact were marine ecotoxicity, freshwater ecotoxicity and natural land transformation. It is noted that the electricity consumption shown (yellow color) is the sum of the electricity consumption at the dehairing stage (LTUI 2015) and in the composting facility (Colón et al. 2011).

The negative values observed are due to the beneficial use of the compost that can partly replace some chemical fertilizer, due to its nitrogen content. The negative values imply environmental benefits rather than net burdens since environmental burdens associate to the production of the chemical fertilizer are now reduced due to compost usage.

According to the results shown in Figure 4 (bottom) for the enzymatic scenario, the impacts related to fresh water ecotoxicity, marine ecotoxicity and fresh water eutrophication, had positive values, which means high environmental loads. These burdens are due to the high electricity consumption, mainly due to the usage of an in-vessel system in both the composting and SSF systems (the same reactor is assumed to be used in both technologies).

The direct impacts associated to the enzymatic based dehairing process are relatively low and are basically caused by the ammonia emissions during the SSF. In this case, obviously, no indirect emissions are observed from the usage of chemicals, since they are not used anymore. As observed in Figure 4 (bottom), most of the environmental impacts are negative, due to the benefits gained by the compost application that partly replaces some chemical fertilizer (Sánchez et al. 2016). Another way to analyze the environmental impacts is to study at which stage the main impacts are created in both scenarios. It is revealed from Figure 4 that the highest contribution to each impact category is due to the direct emissions (mainly as wastewater effluent) during the chemical dehairing (red bars) and the electrical energy consumption (yellow bars), with regard to the indirect emissions. In the case of the enzymatic process (Figure 4 bottom), the electrical energy consumption justifies most of the emissions.

Since in the typical chemical dehairing method, there were much more available wastewater effluent data than in the enzymatically based dehairing process, the LCA simulation was run by using COD as the only effluent parameter which is the common available wastewater parameter from both processes. The chemical dehairing process was proven to be still the one with the highest environmental impacts. This indicates that it is the production of chemicals and the electrical energy consumed in the chemical dehairing process that are mostly responsible for the overall emissions of the (base) chemical dehairing scenario. The wastewater does contribute in the environmental impacts, but not as much as the chemical production and the electrical energy.

3.2 Comparison of three hair waste traditional treatment techniques in the conventional chemical dehairing process.

Hair waste generated in the leather industry can be treated via composting, although landfilling and incineration are two viable treatments options too. Figure 5 shows the comparison to the possible three sub-scenarios. According to Figure 5, composting has the lowest environmental impacts for almost all categories. Incineration, for example, is the most environmentally polluting with regard to freshwater and marine ecotoxicity, likely due to the generation of the acidic off-gases CO_2, NO_x and SO_x, (Assamoi et al. 2012) that lower the pH of aquatic systems. Landfilling follows as the second most polluting method. In conclusion, in-vessel composting is the method that generates the lowest environmental impacts. For this reason, it was considered in this work as the optimal hair waste treatment method.

Insert Figure 5

3.3 Comparison of the conventional chemical dehairing process with the enzymatically driven dehairing process.

Figure 6 shows the comparison of the conventional chemical dehairing process with the enzymatic dehairing process via the use of SSF. This figure shows the total emissions, namely the sum of direct and indirect environmental impacts per category and per scenario. No categorization per type of parameter is done as was done in Figure 4. According to Figure 6, it can be clearly observed that the conventional chemical process has significantly higher environmental impacts than the enzymatic dehairing process via the application of SSF. This difference is mainly attributed to the avoidance of the chemicals during dehairing, when SSF is applied, and to the reduction of the electrical energy consumption. Table 3 clearly shows that there is significant reduction in all impact categories when the dehairing is changed from chemically induced to enzymatically induced, proving the benefit of adopting this technology in the dehairing stage. The range of reductions is from 20% (Ionizing radiation) to up to 1942% (Metal depletion).

Insert Figure 6

Insert Table 3

These results agree with the study of Nielsen (2013) who performed an LCA to compare the environmental impact of conventional soaking and liming processes against enzyme assisted processes. Their work showed that environmental impacts of producing the enzyme were much smaller compared to the impacts of the traditional method (Nielsen 2013). It is noted that although the functional unit and all calculations used in this paper is per FU of 100 kg of rawhide, the environmental impacts are expressed on a per kg basis due to SimaPro® limitations (see Figures 5 and 6).

Based on the above results, the impacts of four categories under each scenario are specifically discussed below:

Human toxicity: Figure 6 demonstrates that the enzymatic process has a negative impact on human health indicating environmental benefits. A detailed analysis of the results confirms that the impact of all stages equals $6.12 \cdot 10^{-5}$ kg of 1,4-DCB eq/kg rawhide for the chemical process.

Freshwater aquatic ecotoxicity: Both analyzed systems show positive values here; yet, the impact of the chemical process is again much higher. This is mainly attributed to the high amounts of chloride and sulfate contained in the effluent from the chemically based dehairing process. In the enzymatic process, energy production emission is the most important contributor associated at indirect production. The contribution of this impact in the conventional chemical process is 43% more than that in the enzymatic process.

Marine ecotoxicity: In the conventional chemical process, the largest positive contributions to the marine ecotoxicity impact category are from effluent emissions, mostly due to emission into water; the consumption of electrical energy (indirect emissions) and to the chemicals production (indirect emissions). In the case of the enzymatic process, agricultural compost application is responsible for avoided marine ecotoxicity impacts due to compost application that replaces chemical fertilizer (which explains the negative impact in this category).

Natural land transformation: This is the natural land transformed and occupied for a certain time. The unit is $m^2 \cdot$year (PRé Consultants 2015). As a reference, in the case of the conventional chemical method, the land transformation (a positive impact) is associated to the energy production and the sodium sulfite production used in the chemical dehairing.

3.4 Sensitivity analysis

Given the uncertainties that characterize the LCA phases, the final outcomes of a LCA should be tested via sensitivity and uncertainty analysis to improve its robustness and transparency (Guo et al. 2012). A sensitivity analysis was therefore performed to determine the effects of changing selected model or assessment parameters on the results. In the sensitivity analysis, three alternative scenarios were formed, as described below:

- Alternative 1: Doubling of the amount of chemicals used in the conventional chemical process.
- Alternative 2: Removing the fertilizing ability of the produced compost in both processes (chemical and enzymatic).
- Alternative 3: Use of the turned windrow system instead of the in-vessel system during composting. The energy requirements of the turned windrow system were based on Colón et al. (2011).

Alternative 1 observes the effect of the use of the chemicals used in the conventional dehairing step. Specifically, under this alternative scenario, we doubled the quantity of the chemical substances compared to the base scenario. Results are depicted in supplementary Figure S1 (top). The first thing that can be observed is a marked increase in the final environmental impacts under all categories. This is expected, since major impacts associated to the chemical process involve the production of the specific chemicals. A notable increase (more than double compared to the base scenario) is observed in the human toxicity scenario. By noticing the other impact categories too, it is observed that an increase does occur when doubling the use of chemicals, but this does not necessarily lead to a corresponding doubling of the environmental impacts in all categories.

In the case of the 2nd alternative, Figure S1 (bottom) demonstrates that the application of compost to replace a chemical fertilizer is also important. When the compost "looses" its fertilizing abilities, all impact categories have higher values compared to those of the base scenario. In particular, the impacts under the freshwater and marine ecotoxicity are now mostly increased and have the higher values among all 3 scenarios. Figure S1 (bottom) also confirms the importance of the land application of compost even with the enzymatic dehairing process. That is, the environmental impacts in all categories highly increase when compost looses its fertilizing ability in the enzymatically based dehairing system as well. Figure S1 (bottom) also reveals that certain categories are actually not influenced by the application of compost. For example, categories such as ozone depletion, ionizing radiation and agriculture and urban land occupation are not affected at all. Another important aspect to take into account is the wastewater obtained. In the enzymatic process, this wastewater implies a significant reduction of the environmental impact in different categories. But it should be kept in mind that in the enzymatic process, there were available values in the literature only for BOD and COD loadings in the wastewater and not for the other parameters as occurs for the chemical dehairing process. It should be also pointed out that the highest reduction is observed in the fresh water ecotoxicity follow the marine water ecotoxicity.

Regarding alternative 3, Figure S2 reveals that by changing the composting system to turned windrow slightly reduces the environmental impacts. This is because the turned windrow system consumes less electricity than the in-vessel system (which traditionally operates on electricity) despite its higher usage of diesel. Actually, Colón et al. (2011) have shown that the total energy consumption in the turned windrow system is 16% less than that in-vessel system, which accounts for the combined use of electricity and diesel. That is, although the turned windrow system has a higher diesel consumption than the in-vessel, the overall impacts of the turned windrow technology are lower than those of the in-vessel system.

The sensitivity analysis of the LCA methods shows that water ecotoxicity (fresh water and marine), and terrestrial acidification are the impact categories that are mostly affected by the chemical process. The enzymatic process leads, for all impact categories, to lower environmental burdens rendering it as an environmental friendly alternative that needs to be tried and practiced in full scale by tannery industries.

3.5 Preliminary economical assessment

In this section is an account of the initial exploration in ongoing work on the economic impact of conventional chemical dehairing process into account the cost of chemicals, hair waste treatment and wastewater treatment. The objective of this preliminary estimation is to calculate the potential economic savings after using the proteases obtained through SSF that replace chemicals. by hair waste thanks to save these costs. The preliminary economic assessment has shown that nearly 7 million € per year can be saved due to avoidance of chemicals and due to reduced cost of wastewater treatment compared to conventional dehairing. The unit typical costs encountered in conventional treatment are: chemicals: 0.168 €/m^2 leather, hair waste treatment: 0.043 €/m^2 leather, wastewater treatment: 1.07 €/m^2 leather (LTUI 2015). No actual data exist for the enzymatic dehairing process, since this technique has not been applied to the field yet.

4. Conclusions

There is already enough knowledge on the environmental impacts associated to the production of using the conventional chemical dehairing process. Resource consumption (chemical or water usage mainly) and residue treatment are the principal contributors to the overall environmental impacts of the process. In this work we attempted to integrate this knowledge and the broader perspective offered by LCA into waste management so that to compare conventional dehairing techniques with greener alternatives that abide to the principles of circular economy. Thus, we analyzed an alternative of how to valorize a residue produced by the process (hair waste) so that to recover a compound (protease) that can replace the chemicals used typically in dehairing.

The conclusions from this study are:

- The LCA results show that the substitution of chemicals by enzymes obtained from SSF of hair wastes leads to substantially lower environmental impacts compared to the conventional chemical method during leather dehairing as revealed in Figure 6 and Table 3. The highest reduction was observed in the metals depletion category.

- The categories with the highest impact in the conventional chemical dehairing process were the water ecotoxicity (freshwater, marine), water eutrophication and human toxicity followed by natural land transformation and terrestrial acidification.

- Enzymatic process has a contribution only in five impact categories, namely freshwater eutrophication, marine eutrophication, freshwater ecotoxicity, ionizing radiation and fossil fuel depletion, whilst there is minimal influence on the other thirteen categories.

- Based on the sensitivity analysis, it can be concluded that the overall burdens associated to the enzymatic process are lower compared to those of the conventional process. Therefore, the results demonstrate the eco-efficiency of the hair waste management by the enzymatically induced dehairing, since the enzyme produced in SSF can successfully substitute the chemicals used in dehairing.

- Composting proved to result in the least environmental burdens when treating hair wastes compared to landfilling and incineration.

- Enzymatically induced dehairing can lead to a sustainable production of leather and to the reduction of the overall environmental impacts compared to the traditional chemical dehairing process.

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Legends to figures

Fig 1 Flow diagram to conventional chemical dehairing process it included the composting process to treat hair waste. The flows of the inputs and outputs are shown with dashed lines.

Fig 2 Flow diagram of the conventional chemical dehairing process with landfilling or incineration to treat hair waste instead of composting. The flows of inputs and outputs are shown with dashed lines.

Fig 3 Flow diagram of the enzymatic dehairing process. The flows of inputs and outputs into the system are shown with a dashed line. The enzyme production is not taken into account.

Fig 4 LCA results for the dehairing of 1 kg of rawhides via the conventional chemical process (top) and the enzymatically based process (bottom). Category impacts are based on the ReCipe midpoint method. Units per impact are normalized (i.e. calculated by the division of the impact emission at each category by a reference emission coefficient, according to the Recipe methodology).

Fig 5 LCA results for three hair waste treatment sub-scenarios (composting, landfilling and incineration) based on 1 kg of rawhide dehaired via the conventional chemical process (it is noted that SimaPro® uses 1 kg as the unit basis to express all normalized results). Units per impact are normalized (i.e. calculated by the division of the impact emission at each category by a reference emission coefficient, according to the Recipe methodology)

Fig 6 Overall LCA environmental impacts (presented as a summation) to dehair 1 kg of rawhide via the conventional chemical process and the enzymatic process (it is noted that SimaPro® uses 1 kg as the unit basis to express all normalized results). Units per impact are normalized (i.e. calculated by the division of the impact emission at each category by a reference emission coefficient, according to the Recipe methodology).

Supplementary Figures

Fig S1 Comparison of alternative scenarios 1 and 2 with the base scenario.

Fig S2 Comparison of alternative scenario 3 with the base scenario