Carbon Footprint and Toxicity Indicators of Alternative Chromium-free Tanning in China

by

Xiaoying Xu,[1] Grau Baquero,[2] Rita Puig,[2]* Jiabo Shi,[1] Jun Sang[1] and Wei Lin[1]*

[1]*Department of Biomass and Leather Engineering, Key Laboratory of Leather Chemistry and Engineering of Ministry of Education,* Sichuan University, Chengdu, 610065 , China

[2]*Universitat Politècnica de Catalunya, Igualada School of Engineering (EEI)* Igualada, Barcelona, Spain

Abstract

This paper analyzes, from a life cycle perspective, the environmental performance of a newly developed chromium-free tanning process compared to the conventional one, in China. Both processes were evaluated by using carbon footprint, energy consumption and toxicity indicators. Chromium-free tanning process has been found to significantly reduce the considered impact categories compared to conventional tanning. The impact contribution of each process step was calculated, with the tanning step being the major contributor. Results show that the production of chemicals used in the tanning process, have a significant effect on the impacts evaluated. Some of these chemicals have been substituted with similar ones (used as proxies) when no manufacturing-data was available in the databases. Thus, it is important for future and more precise LCA studies to develop databases on the specific chemicals used. This study is a first estimation of the impacts and will help on the decision of expending time and efforts on developing and optimizing the new technology. The results show that it is interesting to use this LCA methodology to environmentally evaluate new research processes and products, before industrial scaling and implementing them, to optimize research time and efforts towards the most environmentally promising products and processes.

Introduction

The main environmental burdens of a tanning process derived from the consumption of chemicals and the emissions of solid waste and wastewaters. In the tanning process, the collagen fiber is stabilized by the tanning agents, which change the hide properties, being no longer susceptible to putrefaction or rotting.[1]

The most commonly used tanning agent is basic chromium sulphate ($Cr(OH)SO_4$). A high proportion (80 – 90%) of all the leather produced worldwide is currently tanned using chromium (III) salts according to the EU-Joint Research Center.[1] However, only 60% of the total chromium salt reacts with the hides. Thus, about 40% of the chromium reagent remains in the solid and liquid wastes (especially in the spent tanning solutions). The presence of chromium (III) and salts in the sludge from both the wastewater treatment plants and the spent-tanning-liquors-recycling plants represents an inconvenience for the safe reuse of this sludge.[2]

Chromium (III) is not listed in Annex X of the Water Framework Directive 2000/60/EC following its amendment by the Directive 2008/105/EC on Priority Substances. Therefore, tannery wastes containing chromium (III) are not classified as a hazardous waste, although chromium is one of the major concerns of tannery industries. In this context, the chromium reduction in tanning processes is addressed in many research projects and different authors are working on chromium-free tanning alternatives.[3-6]

In line with the trend of the world leather industry, the Chinese leather industry suffers from some threats: pressure on environmental protection, increase of labor costs, shortage of raw hides and chemicals and slow development of technologies, among others. Concerning environmental protection, wastewater from tanneries is a major concern of the tanning process according to Houzhen Zhou, et al.[7] Firstly, due to the large quantity of waste water generated, which is a consequence of the large amount of water used in leather tanning processes. Secondly, due to the heavy load in the wastewater, including chemical oxygen demand (COD) and biological oxygen demand (BOD) charges, protein, fat, dyestuff, suspended solids, chromium salts and sulphide salts among others. In 2012, the discharged waste water was 26.5 million ton from the making of leather, fur, feather and related products and footwear, which includes 62115 ton COD, 6051 ton ammonia nitrogen,[8] 73.9 ton chromium (39.2% of total chromium discharged), 77.2 ton heavy metal (15.1% of total heavy metal discharged).[9]

*Corresponding authors; Rita Puig, Tel: +34 (93) 803-53-00, email: rita.puig@eei.upc.edu and Wei Lin, e-mail: wlin@scu.edu.cn.
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From this point of view, it's a tough thing to completely solve this environmental problem. As the environmental requirement not only concerns the control of the pollution caused by leather production, but also takes into account the chemicals used which may have a bad effect on human bodies or environment, such as chromium in finished leathers.[10] Thus, the use of chromium in tanning processes is also a major concern in China and research on chromium free tanning alternatives is being performed. One of these alternatives developed in Sichuan University, using a modified glutaraldehyde agent instead of chromium, will be environmentally evaluated in the present paper.

In order to environmentally evaluate the presented alternative, carbon footprint (using global warming potential indicator (GWP) and energy consumption) and toxicity indicators are used in this work to assess both current tanning process and chromium free alternative. Carbon footprint is chosen as it is probably nowadays the most relevant indicator of environmental impacts. Toxicity indicators are selected because toxicity is one of the major problems when using chromium and to take into account the effect of other chemicals used in the process.

Aim of the Study

The objective of this LCA study is to determine the environmental advantages of using chromium free tanning process in China, in terms of carbon footprint (using global warming potential indicator (GWP) and energy consumption) and toxicological indicators for humans (Human Toxicity Potential, HTP) and marine water (Marine Aquatic Ecotoxicity Potential, MAETP). Inventory data has been collected at laboratory scale from a chromium free tanning process and from a traditional one. This data has been completed with data from energy production and use in industrial leather tanning processes in China.

Thus, the aim of the study is to quantify the environmental benefits and compare the environmental performance of the proposed chromium free tanning process with the conventional tanning process in China. The comparison is made specifically in the tanning step of the process, which traditionally comprises pickling, tanning, retanning and neutralization processes. This comparative study will provide a more clear idea on the reductions of environmental burdens achieved. A second aim is to identify the contribution to environmental impacts of each specific tanning step (pickling, tanning, retanning and neutralization).

Methodology

First of all inventory and process data comprising inputs and outputs of the tanning step were collected and reviewed with mass balances. No industrial scale data information was available; therefore inventory data was collected at laboratory scale. Then, the carbon footprint, the energy consumption and the toxicological impacts of the tanning step were calculated using the Life Cycle Assessment methodology.

Life cycle assessment (LCA) has been chosen as the methodology to implement this study and quantitatively evaluate the environmental burdens. LCA is a methodology used to assess the environmental impact of a product, process or activity which tracks all the steps from the extraction of the raw materials, resources and energy inputs into a defined system and waste streams flowing out of the system. This methodology is regulated by the international standard ISO 14044 (2006).[11]

The studied process has been modeled using GaBi 4 software from PE International (Stuttgart, Germany). The global warming potential (GWP) index used to calculate the carbon footprint of both processes is measured in kg of CO_2 equivalent emissions using the impact factors of Centrum voor Milieukunde Leiden (CML) developed by the Leiden University Centre of Environmental Science, which was updated in 2009.[12] As a measure of energy efficiency, the primary net energy used to process 1000 kg of raw salted hides using both conventional and chromium free tanning processes are compared. To evaluate the burdens of the chromium avoidance and the use of alternative chemicals, Human Ecotoxicity Potential (HTP) and Marine Aquatic Ecotoxicity Potential (MAETP) impacts are used when comparing both processes to evaluate their toxicological effects.

Inventory Data and Modeling

In this section the life cycle inventory (LCI) is detailed and the model of the processes is presented. To this end all the processes in the system boundaries are analyzed along with their inputs and outputs. Model description and assumptions are also presented.

Functional Unit and System Boundaries

The functional unit used in the study is 1000 kg of raw salted cattle hides to be processed using both conventional and chromium free processes. Inventory data of the process was obtained from bibliographical sources and from experiments in a laboratory scale. Data on upstream processes, such as production of electricity and thermal energy or manufacture of chemicals used was provided by databases (ELCD, Plastics Europe and Ecoinvent databases from GaBi4).

This study is focused on the Chinese leather industry, which is mainly developed in the eight provinces shown in Figure 1. Data from these provinces has been considered to establish the particular electricity and thermal energy mixes mainly used for the leather industry in China.

Tanning industry conventionally comprises three main steps, namely beamhouse, tanning and post-tanning steps. Beamhouse step includes soaking, liming, unhairing, deliming and bating processes. The conventional tanning step is comprised by pickling, tanning, retanning and neutralization processes. Retanning and neutralization are made together with the tanning in the same bath, and this is why they didn't show up in the diagram. Finally, the post-tanning step begins with the fatliquoring. The tanning steps in chromium free tanning process includes also a de-pickling process. It is thus clear that both conventional and chromium free tanning processes have common steps, comprised in the beamhouse and post-tanning steps, as shown in Figure 2. The system boundaries of this comparative study comprise only the tanning step as long as the products and energy used in it, which is the step where differences in conventional and chromium free tanning processes are found.

When comparing both conventional chrome tanning process and chromium free tanning process, it is worth noticing that the proposed chromium free process includes a de-pickling procedure, not present in the conventional tanning process. This step is to adjust the pH of the bath to the optimal one for modified glutaraldehyde tanning agent, which is pH around 4 instead of the conventional value of 3. As its name implies, chromium powder is used in the conventional tanning process and thus chromium is present in the effluent of the process. On the other hand, chromium free tanning process uses a modified glutaraldehyde compound instead of chromium. Consequently, its effluents do not contain any chromium.

The comparative model must consider the energy inputs and waste water treatment. Figure 3 shows electricity consumption, thermal energy consumption and also wastewater treatment amounts. The energy consumption in glutaraldehyde tanning is higher than that of chrome tanning because the time needed for the operation is nearly double (see a summary of both processes recipe in the following sections, Figure 4 and 5).

In both tanning processes the relation between electricity and thermal energy consumption is in average 20:80 as described in the literature.[13] This is the relation also used in the model. Chinese electricity mix and thermal energy mix are not available in GaBi4 database; therefore they were developed from the former Chinese tanning regions and presented in later section; "Chinese electrical power grid mix and thermal energy mix."

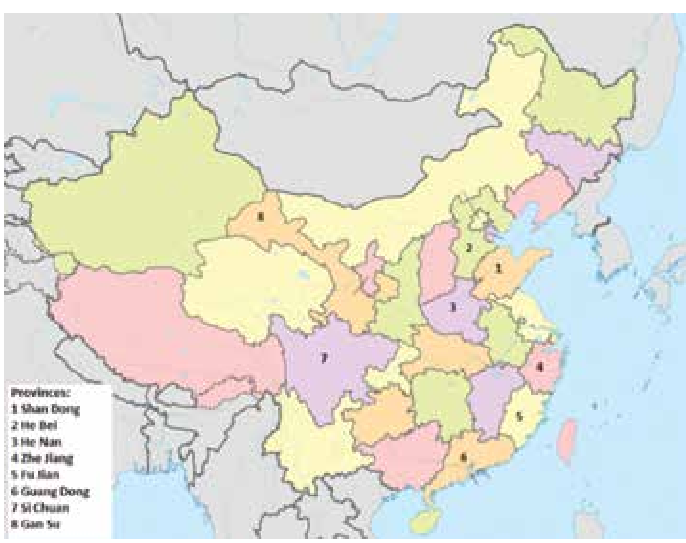

Figure 1. China provinces with leather industries.

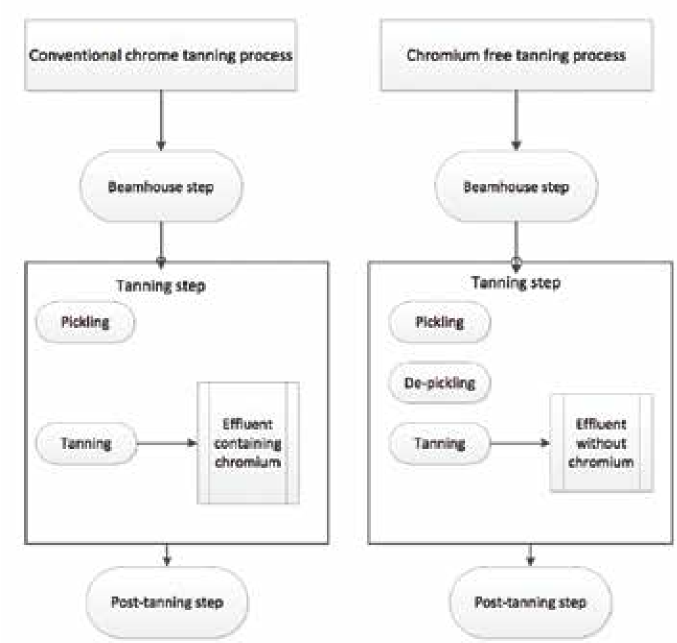

Figure 2. System boundaries of the comparative life cycle study of conventional chrome and chromium free tanning processes.

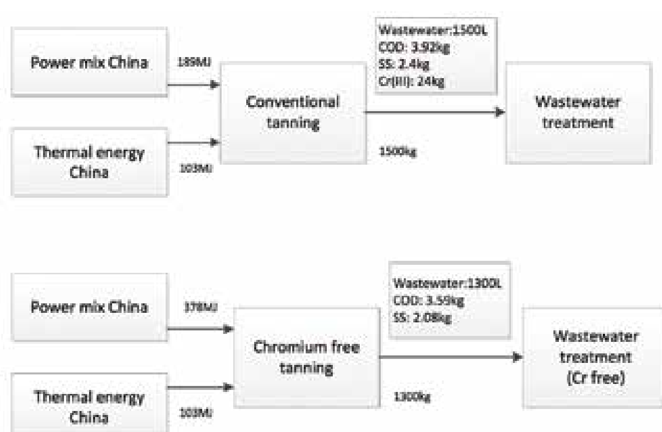

Figure 3. Comparative model of both conventional and Chromium free processes.

Conventional Tanning Process Model and Inventory Data
Conventional tanning step comprises pickling, tanning, retanning and neutralization processes. Pickling and chrome tannning are conventionally performed within one bath. The float is 800 Kg for pickling and additional water (200 Kg) will be added for tanning. The pickling and early chrome tanning are firstly performed at room temperature, then temperature rise to 38-42 ºC. Energy and inputs for the 4 processes in this step are shown quantitatively in Figure 4. The tanning operation shown in this figure, includes tanning, retanning and neutralization. Process time and final temperature are also shown, as well as wastewater characteristics and quantity. Data on this step has been obtained from laboratory scale experiments at Sichuan University (2014) and completed with data from bibliographical sources.[14,15]

According to LCA methodology, the production impacts of the intermediates and chemicals used in the evaluated process have also to be taken into account. Thus, all intervening products have to be characterized, or if no data is available, the product is usually substituted by similar ones (used as proxies). Accordingly, and due to the lack of some chemicals in GaBi 4 database, the following proxies have been used:

- Acetic acid instead of formic acid.
- Acetic acid instead of sodium formate.
- Sodium carbonate instead of sodium bicarbonate.
- Ferro chrome mix (60% chrome) instead of chromium Cr_2O_3.
- Ammonia and sodium carbonate (stoichiometric amounts) for ammonia bicarbonate.

As already stated, the relation between electricity and thermal energy consumption in this step is considered as 20:80 as described in the literature.[13]

Chromium Free Tanning Process Model and Inventory Data
The proposed leather tanning process that avoids the use of chromium has its difference with the conventional process only in the tanning step as stated before. The chromium free tanning process consists on using a yellowish-clear-bright-liquid polymer-modified glutaraldehyde (without free formaldehyde) instead of the traditional chromium(III) salt (Cr_2O_3).

Referring to the pickling process, the same products are used in both conventional and chromium free tanning process. The next step in the chromium free process is depickling, which does not exist in the conventional tanning process. Depickling process implies the consumption of Na_2CO_3 to raise the pH from around 3 to 4 (the optimal for glutaraldehyde modified-polymer). The following process is tanning, where glutaraldehyde compounds are used to replace the chrome powder used in the conventional process. The use of glutaraldehyde instead of chromium, leads to a chromium free wastewater, which is the main purpose of this alternative tanning procedure. On the other hand, effluents contain a slightly higher amount of total organic carbon (TOC) and less COD than in conventional chrome tanning process. These different wastewater-pollutant concentrations (i.e. COD, SS, etc.) are related to the use of different type of chemicals in the recipe and their different absorption by the hide.

The chromium free tanning process is shown in Figure 5. Energy and chemical inputs, process time and temperature are shown in the figure.

As can be observed, the time needed for tanning is around 10.5 h, nearly twice the time of the conventional tanning, for a correct penetration to assure the quality of the final leather. Data on this step has also been obtained from laboratory scale experiments at Sichuan University (2014) and fulfilled with data from bibliographical sources[14,15] as is the conventional process.

Due to the lack of some chemicals in GaBi 4 database, the following proxies have been used:

- Acetic acid instead of formic acid.
- Sodium carbonate instead of sodium bicarbonate.
- Acetaldehyde instead of modified glutaraldehyde polymer.

Glutaraldehyde and acetaldehyde toxicity could be considered more or less similar, although glutaraldehyde has probably slightly higher toxicity, according to descriptions and details found about both chemicals in the literature.[16,17] Nevertheless, specific data for glutaraldehyde modified-polymer would be advisable for a more rigorous assessment.

Regarding the electricity consumption, chromium free tanning process has a higher consumption compared to the conventional process, because the time needed for each process step is higher (see Figure 5). In this step the relation between electricity and thermal energy consumption is also considered as 20:80 as described in the literature.[13]

Chinese Electrical Power Grid Mix and Thermal Energy Mix
Chinese electrical mix has been developed with data obtained from the national bureau of statistics of China.[18] In China, there are four main power generation plant types that produce electricity, namely hydroelectric (17.31%), thermal (79.85%), nuclear (1.77%) and wind power plants (1.07%).

Thermal power plants are the main source of electrical power in China and are usually coal-fired power plants. Currently, two types of coal are used, namely anthracite and lignite. Anthracite is used in 20.4% of the total thermal power production in China, whereas lignite is used in 79.6% thermal power plants according to Hezhong Tian et al.[19] Hydro power plants are used as a proxy for wind power plants, as no data from wind power plants is available in GaBi 4 database.

Regarding thermal energy, 99.68% of thermal energy is obtained from coal in China according to the national bureau of statistics of China.[16] However, detailed data on the "thermal consumption for manufacture of leather, fur, feather and related products" is also available and shows the different sources of thermal energy, namely coal (72.48%), coke (0.21%), crude oil (0.05%), gasoline (8.11%), kerosene (0.23%), diesel oil (13.22%), fuel oil (5.66%) and natural gas (0.04%). To model the thermal energy production, only the four main sources are considered (coal, gasoline, diesel and fuel oil). Thermal energy from diesel has been used as a proxy for gasoline, as no data from gasoline thermal production is available in GaBi 4 database.

Wastewater Treatment

Data on wastewater treatment and waste management has been used according to bibliographical data.[14,15] Figure 6 shows the considered treatment for leather industry wastewater (data is for 1000L wastewater treated). The treatment for chromium-containing wastewater includes a precipitation step (as also shown in Figure 6), which is not necessary in the chromium free alternative presented in this work. Thus, the chromium free tanning process avoids the use of some energy and chemicals.

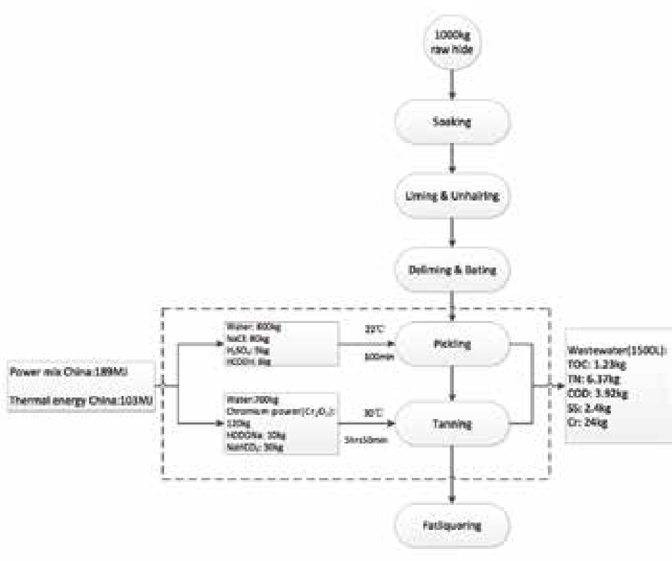

Figure 4. Chinese conventional chrome tanning process. The system modeled includes only pickling and tanning operations, from the production of chemicals and energy used to the wastewater treatment.

RESULTS AND DISCUSSION

This section presents and analyzes the LCA comparative results of the conventional and the chromium free tanning processes. The processes have been modeled using GaBi4 software following the descriptions and schemes shown in the above section INVENTORY DATA AND MODELING, where the assumptions made and the proxies selected have been detailed.

The results are given in terms of GWP to calculate the carbon footprint, the energy consumption to evaluate the energy efficiency and finally HTP and MAETP to assess the toxicological effects of both presented processes. Results are presented grouped for each category evaluated (GWP, energy consumption, HTP and MAETP) into four impact contributors, namely tanning, power, thermal energy and WWT processes contribution.

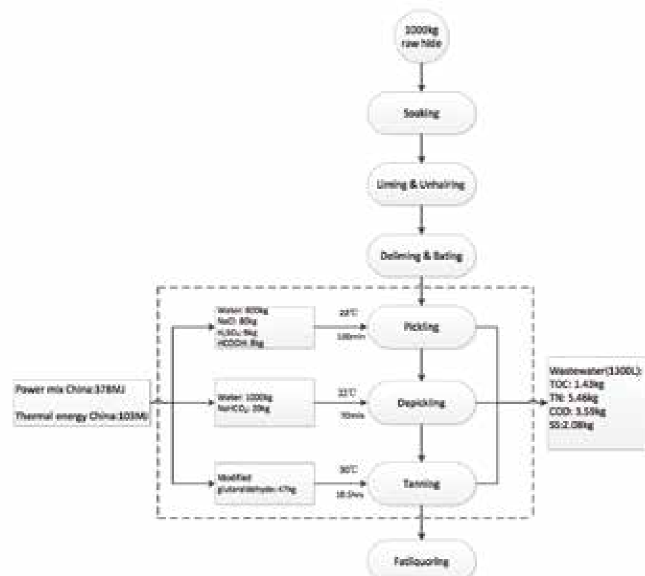

Figure 5. Proposed Chinese chromium free tanning process. The system modeled includes only pickling, depickling and tanning operations, from the production of chemicals and energy used to the wastewater treatment.

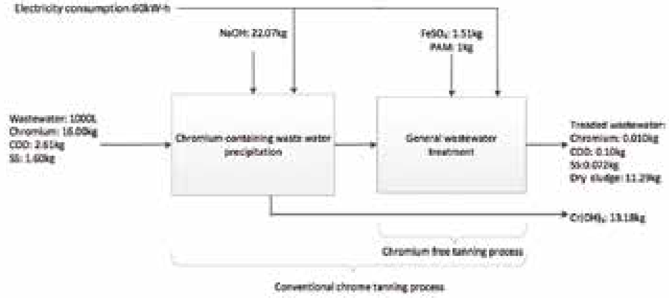

Figure 6. Wastewater treatment for leather industry.

Evaluation of the GWP Index

Carbon footprint of both processes is calculated using the Global Warming Potential index (GWP 100 years), calculated in kg of CO_2 equivalent with CML 2001 methodology (revised on November 2009). Comparative results are shown in Figure 6 for the conventional and the chromium free tanning processes. Results present a clear preference for Chromium free tanning process, which reduces the GWP impact a 42% compared to the conventional tanning process.

Comparing the four impact contributors of each process, it is clear that the main contributor to GWP impact category is the tanning process, due to the production of the chemicals used. Following this contributor, electricity (or power) is the second more important to Chromium free process and the wastewater treatment (WWT) is the second for the conventional one.

Figure 6 also shows that, from conventional to Chromium free tanning process, whereas GWP due to WWT is reduced a 66%, GWP due to power consumption increases a 100%. GWP due to Thermal energy consumption does not change from conventional to chromium free tanning process. The GWP results show that although the energy use is higher in the new process (Cr free), the production of chemicals used in tanning and the wastewater treatment are less polluting and compensate this increase (at least in this impact category).

Evaluation of the Energy Consumption

As a measure of energy efficiency, the energy is calculated as the net calorific value (in MJ) used to process 1000 kg of raw salted hides.

Figure 7 shows the comparative energy consumption results for both considered processes. Energy consumption in chromium free tanning process is a 21% lower than in conventional one. This decrease is mainly due to the reduction in the WWT process (66%), which is the main contributor to this category. On the other hand, chromium-free-tanning-process energy consumption increases (+100%) when considering power contribution. However, the increase in the power contributor is diluted in terms of energy consumption, as it only represents a 6% in the conventional tanning process and a 15% in the Chromium free tanning process.

Thermal energy contributor in terms of energy consumption shows no difference between conventional and chromium free tanning processes.

Evaluation of the Toxicological Impacts to Humans and Freshwater

To evaluate the toxicological effects of both processes, human (HTP) and marine (MAETP) toxicity impact categories are calculated in kg of DCB equivalent with CML 2001 methodology (revised on November 2009). HTP and MAETP impact results show a great preference for Chromium free tanning process, reducing a 59% and a 58% when comparing to conventional tanning process. This reduction is mainly due to the decrease in the impact from the tanning contributor, followed by the decrease in WWT.

The tanning impact reduction in HTP and MAETP is –as expected– in the avoidance of chromium use. Nevertheless, these toxicity results should be revised when specific toxicity data on glutaraldehyde modified-polymer were available, because the actual data was obtained using acetaldehyde as proxy, which has probably a slightly lower toxicity than glutaraldehyde as explained before.[16,17] As seen in the other impact categories comparison, despite power used in Cr free tanning process is higher, its effect on HTP and MAETP is

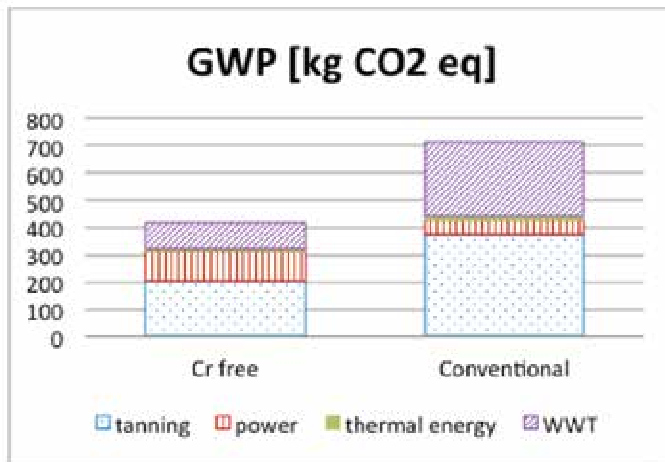

Figure 7. Global Warming Potential results (emissions in kg CO_2 equivalent).

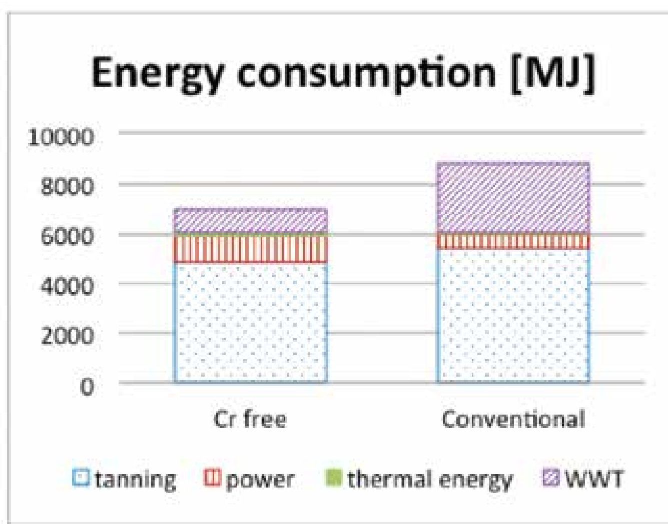

Figure 8. Energy consumption comparative results (MJ, net calorific value).

low. Thermal energy contributor to HTP and MAETP does not differ between conventional and chromium free tanning processes, just as in the other impact categories considered.

Comparative Evaluation of Tanning Steps

To evaluate the contribution of each tanning step to the GWP, the HTP and the MAETP for both conventional and chromium free processes, the cumulative percent graphs in Figure 9 are presented.

As it is shown in Figure 9, the tanning step (tanning, retanning and neutralization) is the major contributor to the calculated impact categories, both in conventional and Cr free tanning alternative.

Considering the steps of the chromium free tanning process, pickling and de-pickling steps represent about 30% of GWP, HTP and MAETP impacts, being pickling more influent to HTP impact and de-pickling more to GWP impact.

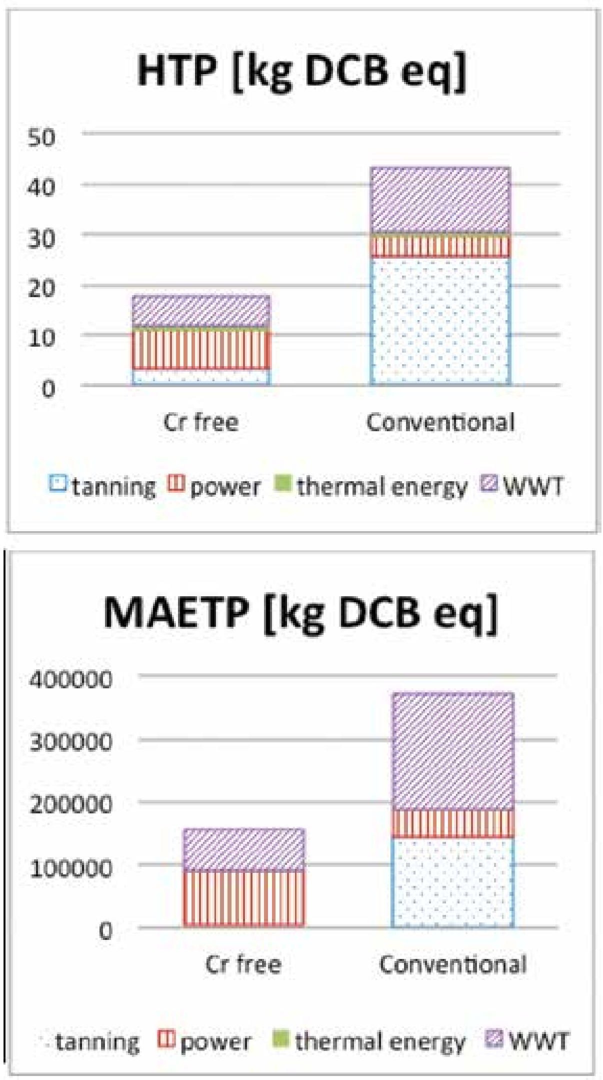

Figure 9. HTP and MAETP comparative results (kg DCB equivalent emissions).

Conclusions

A chromium free process alternative to the conventional tanning in China was evaluated in this work with data at a laboratory scale. Both processes were evaluated by using the framework of LCA. The carbon footprint, energy consumption and toxicity effects were assessed using GWP, net calorific value, HTP and MAETP impact categories.

Chromium free tanning process was found to reduce the considered impact categories compared to conventional tanning process. The main decrease affects the toxicity impacts (HTP and MAETP) with reductions of 59-58% followed by GWP (-42%) and finally, energy consumption (-15%). These results are a first approach because certain hypothesis and considerations were taken due to lack of specific data. The contribution of each tanning step to these impacts (GWP and toxicological categories) was calculated, being the tanning step the major contributor to the impacts.

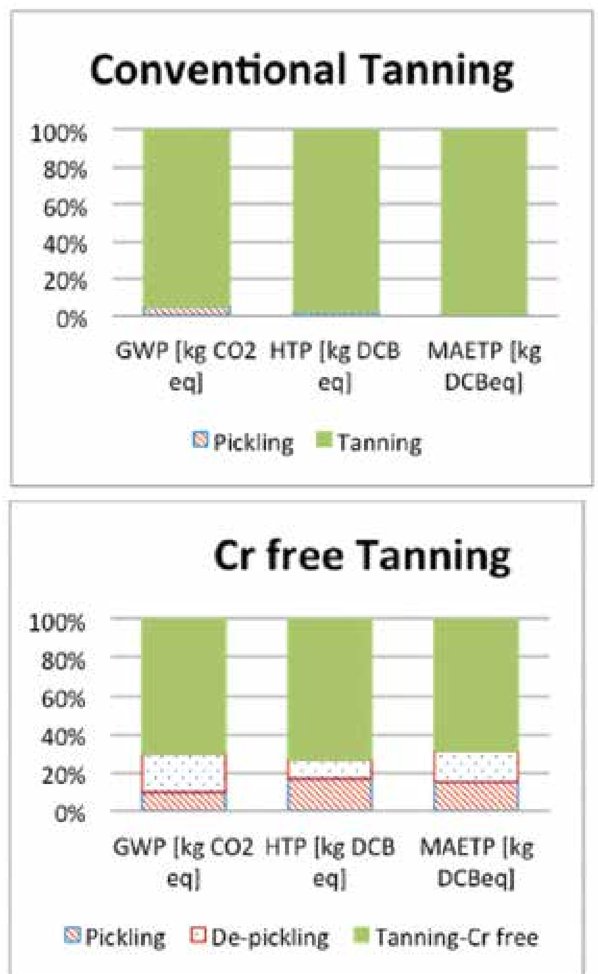

Figure 10. Contribution of each process step to the impact categories (in %).

Results showed that the production of chemicals used in the tanning process have a significant effect on the impacts evaluated. Some of these chemicals were substituted with similar ones (used as proxies) when no manufacturing-data was available in the databases. Thus, it is important for future and more precise LCA studies to develop databases on the specific chemicals used. Nevertheless, from these results one can say that it is interesting, from an environmental perspective, to follow the research on this new process-technology and try to implement it at industrial scale to reduce the environmental impact.

The study shows the usefulness of the LCA methodology to environmentally evaluate new research processes and products, before industrial scaling and implementing them, to optimize research time and efforts towards the most environmentally promising products and processes.

Acknowledgement

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