

Comparison of the Sustainability of the Vegetable, Wet-White and Chromium Tanning Processes through the Life Cycle Analysis

by

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Abstract

Public concerns about the quality of life of human beings as well as the quality of natural environments and ecosystems have led to the increasing importance of sustainability for governments and for all industries, including the leather industry. In this context, more “ecological” leather goods are being demanded. It should be noted that this concept is often used without a scientific study to support it.

This concept of sustainable or ecological product in the field of leather goods, are mainly associated with chrome-free tanneries (that is vegetable and wet-white), but this association should be backed up or dismissed by scientific evidence. A complete scientific study is required, which takes into account the different stages of leather production, including also the treatment of water and by-products, analyzing in a scientific and systematic way the environmental impact of each of these tanning processes.

This study focuses on the life cycle analysis of the three basic tanning processes: chrome, vegetable and wet-white leather production. It will focus on European manufacturing to have reliable data and reduce uncertainty.

In the tanning stage, the process with the greatest impact is the vegetable one, to highlight its high impact on global warming at 100 years (GWP100). This result is due to the energy necessary for the production of mimosa and quebracho in addition to the energy for the processing of the leather in the drums.

Wet white tanning with glutaraldehyde has lowest environmental results than vegetable tanning.

The chrome tanning process (wet blue) also stands out for its reduced environmental impact.

Subsequently, to have a global view of the entire production, the LCA of the post-tanning stages must be performed to evaluate the impact of each of the systems studied.

Introduction

The life cycle analysis (LCA) is a methodological tool that allows us to evaluate the environmental loads associated with a product, process or activity. To do this, the raw materials, chemicals and energy used as well as the emissions to the environment are identified and quantified in order to quantify the impact of the use of these resources and those emissions to subsequently determine environmental improvement strategies focused on minimization.

This tool takes into account stages of extraction and processing of materials, production, transport and distribution, use, reuse and maintenance, recycling and final disposal.

Its application is standardized by the ISO, International Organization for Standardization, through the following standards:

- UNE EN ISO 14040: 2006. Environmental management. Life cycle analysis. Principles and frame of reference.
- UNE EN ISO 14044: 2006. Environmental management. Life cycle analysis. Requirements and guidelines.

LCA is used in the application of eco-design in products and services, in the elaboration of the criteria for compliance with ecological labels, as a source of information for the implementation of environmental management systems, in comparative studies between similar products (different origin, composition but same function) and any other case related to obtaining information about the environmental behavior of a product or service.

In this work, this tool is used to compare the environmental impact of different tanning processes: vegetable, wet-white (WW) and chrome (wet-blue, WB).

Public concerns about the quality of life of human beings as well as the quality of natural environments and ecosystems have led to the increasing importance of sustainability for governments and for all industries, including the leather industry. In this context, more

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“ecological” leather goods are being demanded. It should be noted that this concept is often used without a scientific study to support them.

This concept of sustainable or ecological product in the field of leather goods, are mainly associated with chrome-free tanneries (that is vegetable and wet-white), but this association should be backed up or dismissed by scientific evidence. A complete scientific study is required, which takes into account the different stages of hide production, including also the treatment of water and by-products, analyzing in a scientific and systematic way the environmental impact of each of these tanneries.

The final objective of this work will be the dissemination of the results of the study in a scientific and pedagogical way.

In the literature comparison works between WB-WW tanning technologies can be found, with results that indicate trends, but always with nuances and uncertainties.

According to Xu et al.,¹ wet-white tanning compared to chrome tanning, has a lower energy consumption so the impact on global warming potential (GWP) is lower. Even so, it should be objected that wastewater treatment should be taken into account.

In a 2016 study² it is identified that chromium derivatives have a problem of depletion of abiotic resources and - at the same time - that the global warming potential (GWP) in the case of wet-white tanning may be higher if some factors are excluded.

As indicated by Laurenti et al.,³ the variability in the results obtained through a study-survey of several tanneries regarding the consumption of water and energy (electrical and thermal) demonstrates that the data for the tanning process should be used with caution in a context of decision making. The need for a more specific study, focusing on comparable products and specific productions, is detected since, according to the same author, the location and production methods greatly influence the use of water and energy, highlighting the importance of wastewater treatment in the own tannery, if it exists.

It should be noted that in the studies found in the literature, it has not been considered that part of the chromium used in the stores would be a byproduct of the pharmaceutical industry. For this reason, in an environmental study the use of a byproduct can greatly affect the comparative result.

A comparative study has not been found a priori that includes WW, WB and vegetable tanning but due to the own experience in different studies,⁴⁻⁶ it can be affirmed that vegetable tanning has an energy consumption and a GWP greater than the other types of process. They should be studied in other environmental impacts and take into account the stages to be compared for a complete comparative study.

According to the compilation of Dixit et al.,⁷ the negative impact associated with the leather industry requires the so-called Green Technology, which can be divided into two methods: waste reduction or improvement in technology that reduces the toxicity of waste and wastewater treatment and solid waste processing. These concerns are not new, for example, there are studies of recovery of chromium salts from wastewater 20 years ago.⁸

Unlike the basic material and energy balances, the LCA approach takes into account the production of the chemicals that are used, as well as the emissions that are generated. This broader vision of the process leads to a more detailed environmental assessment, quantitatively measuring the effect of chemicals and energy involved.⁵

It should be noted that the use of incomplete data, data from technologies experienced only in pilot tests but not validated in the industry, or the omission of any part of the process (or subprocess) can lead to biased comparative results. For this reason, it is preferable to specify in product, type of tanning and stages of the process to be compared in order to obtain specific and unquestionable results.

Experimental – Scope and limits of the system

The study focuses on the production of leather for bovine leather items for footwear and leather goods. It will focus on European manufacturing to have reliable data and reduce uncertainty.

It should be considered that a comparative generalist study of tanning processes covers a huge number of variables and it is necessary to begin by limiting its scope.

The comparative result will show the impact of producing leather considering the products used and their origin and production, as well as emissions to the environment through standardized impact indices.

Production depends on the type of factory and its location, but above all it is important to define the product that is produced and for this, this comparative study will focus specifically on the processes of:

- WB: Chrome tanning process (wet-blue)
- WW: Wet-white tanning process (by glutaraldehyde and by tara)
- Vegetable: Vegetable tanning process

Chrome tanning is the most widely used globally, due to its speed and savings in water and products, which make it very economically competitive. According to the latest report of best available techniques (BAT, Best Available Techniques), 80-90% of the world would use chromium III salts in their tanning processes.⁹

It should be taken into account that the first stages of the tanning process (previous operations and beamhouse process) are common in the different processes considered in this study. In the stages of tanning and post-tanning it is where the main differences between the different tanning processes are found. However, in this study

the post-tanning process and the finishing stage have not been considered in this study.

Each product used has a different environmental impact associated due to its own production and the treatment required by the waste generated by its use (in this particular case mainly wastewater), an effect that will be taken into account in the study of life cycle analysis.

Wastewater treatment is considered a necessity in a study of this nature. It is possible to consider the process for each type of wastewater, considering the energy, and products necessary to obtain water with the necessary characteristics for its return to the environment without negatively affecting it.

In addition to the treatment of wastewater baths, the specific risks of each process must be taken into account in accordance with the corresponding wastewater treatment.

This study includes this treatment, however, the relative low impact in the results shows no influence from the wastewater treatment on the conclusions.

Experimental – Inventory

The inventory includes the inputs and outputs in each process of energy and matter, which will be considered generation, production, transport and management of waste generated. Tanning formulas considered conventional for each process are reflected in this study.

The specific data considered in the reference formulation of each of the processes considered are those shown in the tables:

Table I: Chrome tanning process (wet-blue)

Table II: Wet-white tanning process using glutaraldehyde

Table III: Wet-white tanning process incorporating tara

Table IV: Vegetable tanning process using mimosa and quebracho

Considerations for all processes in this initial study:

- It is considered a maximum use of tanning products, assuming optimal process conditions in terms of time, temperature and application of the products.
- A medium thickness (3.5mm) for split hides is selected for the initial comparison between processes, which involves similar penetration times and fixation of the tanning products. In the case of tanning with vegetable extracts, for articles of greater thickness (eg, sole, belt) it will be necessary to increase the amount of extracts and consequently the processing time for complete penetration and fixation.
- Water heating for the processes was obtained by means of a gas boiler. The thermal energy input into the system has not been considered, but it is considered that the temperature is maintained within the drum due to the mechanical effect itself.

- In the case of the wet white process, the tanning stage will be referred to as pre-tanning since it is essential to retan the wet white hide obtained for its complete stabilization. In the other tanneries, post-tanning confers certain characteristics, but the hide is already stabilized with the tanning stage.
- If we do not have in the database to calculate a specific product, a product with similar characteristics (called proxies) has been selected.

Table I

Inputs and outputs for the chrome tanning process (wet blue)

TANNING			
Inputs			
Pickled hide	Mass		1000 kg
Chromium salt 33°Sch	Mass		65 kg
Water 20°C	Mass		500 kg
Energy for drum (1565 kg, 120 min)	Electric energy		169 MJ
Thermal energy (agua 20 → 45°C)	Thermal energy ^a		96.86 MJ
Magnesium Oxide	Mass		3.5 kg
Fungicide	Mass		1 kg
Energy for drum (1569.5 kg, 480 min)	Electric energy		678.02 MJ
Outputs			
Wet blue hides	Mass		1069.5 kg
Chromium tanning process wastewater	Mass		500 kg

^aNet calorific value.

Remark: kg = kilograms; min = minutes; MJ = megajoules.

Table II

Inputs and outputs for the wet-white tanning process using glutaraldehyde

PRETANNING			
Inputs			
Pickled hide	Mass		1000 kg
Water 20°C	Mass		50 kg
NaCl	Mass		3 kg
Energy for drum (1053 kg, 15 min)	Electric energy		14.22 MJ
Glutaraldehyde	Mass		25 kg
Energy for drum (1078 kg, 210 min)	Electric energy		203.74 MJ
Phenolic syntan	Mass		50 kg
Energy for drum (1128 kg, 300 min)	Electric energy		304.56 MJ
Water 20°C	Mass		300 kg
Fungicide	Mass		1 kg
Energy for drum (1428 kg, 20 min)	Electric energy		25.70 MJ
Outputs			
Wet white hides	Mass		1078 kg
Wet-white tanning process wastewater	Mass		350 kg

Remark: kg = kilograms; min = minutes; MJ = megajoules.

Table III

Inputs and outputs for the wet-white tanning process using glutaraldehyde and tara

PRETANNING			
Inputs			
Pickled hide	Mass	1000	kg
Water 20°C	Mass	50	kg
NaCl	Mass	3	kg
Energy for drum (1053 kg, 15 min)	Electric energy	14.22	MJ
Tara	Mass	90	kg
Phenolic syntan	Mass	20	kg
Ferric pyrophosphate	Mass	40	kg
Sulfited oil	Mass	20	kg
Energy for drum (1223 kg, 480 min)	Electric energy	528.34	MJ
Formic acid	Mass	40	kg
Energy for drum (1563 kg, 240 min)	Electric energy	337.61	MJ
Drain			
Water 20°C	Mass	300	kg
Fungicide	Mass	1	kg
Energy for drum (1447 kg, 20 min)	Electric energy	26.05	MJ
Outputs			
Wet white with tara hides	Mass	1147	kg
Wet white with tara process wastewater	Mass	960	kg

Remark: kg = kilograms; min = minutes; MJ = megajoules.

As can be seen, the amount of water used is much higher when using vegetable tanning products. Likewise, it should be noted that the fixation of the tanning principle in vegetable products is less than in the case of chromium salts or glutaraldehyde.

It can be also observed the consumption of electrical energy considered in terms of the load and process time, a prominent contributor of electrical consumption in tanning processes. Also highlight the need for thermal energy for the wet blue process and to a lesser extent in vegetable tanning.

Wastewater treatment energy is considered 8.41MJ/m³ according to data from the reference Wastewater treatment plant of IDR in Igualada, which treats the effluents from the tanneries grouped in the Leather Cluster Barcelona from Igualada.

Experimental – Characteristics of the wastewater of the different processes

The characterization of the wastewater for each process is shown in Table V. The data shown are analysis of floats obtained in tests performed at A3 leather innovation center.

As it is observed, there are parameters that only affect some of the processes (Chromium and glutaraldehyde). The chromium oxide value

Table IV

Inputs and outputs for the vegetable tanning process

TANNING			
Inputs			
Pickled hide	Mass	1000	kg
Water 20°C	Mass	600	kg
Phenolic syntan	Mass	50	kg
Energy for drum (1650 kg, 60 min)	Electric energy	89.10	MJ
Mimosa extract	Mass	160	kg
Energy for drum (1810 kg, 180 min)	Electric energy	293.22	MJ
Water 25°C	Mass	50	kg
Thermal energy (water 20 → 25°C)	Thermal energy ^a	15.94	MJ
Quebracho extract	Mass	120	kg
Sulfited oil	Mass	7,5	kg
Energy for drum (1987.5 kg, 560 min)	Electric energy	1001.70	MJ
Drain			
Water 20°C	Mass	1000	kg
Energy for drum (2226.5 kg, 25 min)	Electric energy	50.10	MJ
Fungicide	Mass	1	kg
Drain			
Outputs			
Vegetable hide	Mass	1226.5	kg
Vegetable process 1 wastewater	Mass	762	kg
Vegetable process 2 wastewater	Mass	1000	kg

^aNet calorific value.

Remark: kg = kilograms; min = minutes; MJ = megajoules.

Table V

Comparison of the pollutant load in the tanning stage in the processes considered

Parameter	WB Cr	WW Glut.	WW Tara	Vegetable	Units
pH	3.8	4.3	3.8	4.5	-
Suspended matter	793	9097	7976	9105	mg/L
COD	11320	32550	25560	153600	mg O ₂ /L
Total Nitrogen ^a	1380	362	390	3280	mg N/L
Conductivity	11255	78315	69855	26522	μS/cm
Chromium Oxide	111	0	0	0	mg/L Cr ₂ O ₃
Glutaraldehyde ^b	0	300	0	0	mg/L glutaraldehyde

^aOrganic and Ammoniacal Nitrogen.

^bEstimation from experimental data.

Remark: DQO = Chemical oxygen demand; mg/L = miligrams/liter; mg O₂/L = oxygen miligrams/liter; mg N/L = Nitrogen miligrams/liter; μS/cm = microsiemens/centimeter.

shown is a value corresponding to a residual bath in a process with moderate exhaustion. High float exhaustion (high use of chromium salts) can be obtained by optimizing the tanning process and consequently lower values of this parameter can be obtained. In the case of glutaraldehyde, it is an estimate based on experimental data.

In the suspended matter parameter, for the analysis shown high values are detected in the tanning using glutaraldehyde due to the phenolic syntan use. In the process of tanning using tara, it is also a high parameter due to its high content of non-soluble substances. In the case of mimosa and quebracho (considered vegetable tanning) it is also high.

Also comment on the high COD and total nitrogen values in vegetable tanning, since most of the suspended matter in this bath is organic matter.

Results

The results of the life cycle analysis are shown based on the impacts considered (impact categories). Each impact takes into account different consumptions and emissions with respect to the environment to a different extent according to pre-established scales by recognized research institutions or centers. They are collected as analysis of life cycle impacts (from LCIA, Life Cycle Impact Assessment).

In this study, the group of impact categories according to CML (baseline), version 4.4 (January 2015), developed by the Institute of Environmental Sciences of the University of Leiden, has been used. It is considered a classic method of impact evaluation, which quantifies the stages of the cause-effect chain of the process considered. The results are grouped into the so-called mid-point impact categories. Themes are common mechanisms for the impact considered. For example, the one with the most consensus among different calculation methods is the impact of global warming (GWP) associated with the topic "Climate change", expressed in kg of CO₂.

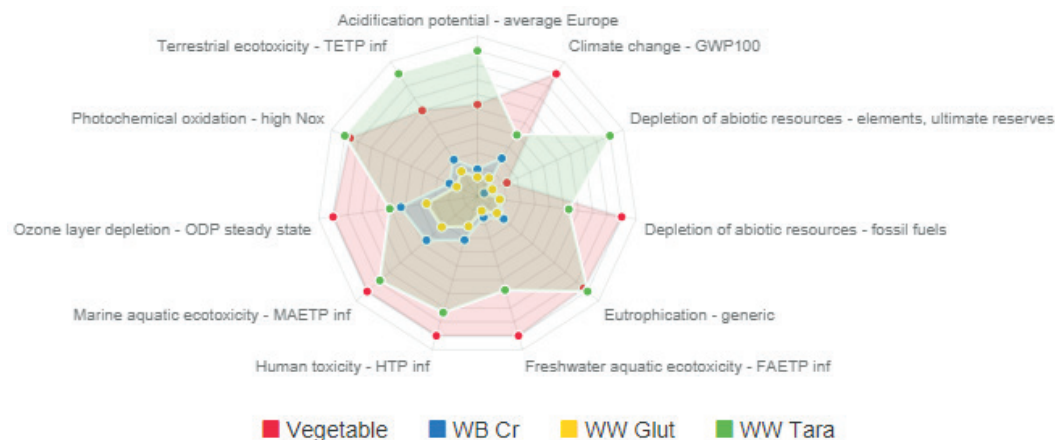


Figure 1. Comparative environmental results of the life cycle analysis of the wet blue, wet white and vegetable tanning processes

Table VI

Impact categories considered
(CML baseline, v4.4, January 2015)

Impact categories	Units
Acidification potential – average Europe	kg SO ₂ eq.
Climate change – GWP100	kg CO ₂ eq.
Depletion of abiotic resources – elements, ultimate reserves	kg antimony eq.
Depletion of abiotic resources – fossil fuels	MJ
Eutrophication – generic	kg PO ₄ ³⁻ eq.
Freshwater aquatic ecotoxicity – FAETP inf	kg 1,4-dichlorobenzene eq.
Human toxicity – HTP inf	kg 1,4-dichlorobenzene eq.
Marine aquatic ecotoxicity – MAETP inf	kg 1,4-dichlorobenzene eq.
Ozone layer depletion – ODP steady state	kg CFC-11 eq.
Photochemical oxidation – high Nox	kg ethylene eq.
Terrestrial ecotoxicity – TETP inf	kg 1,4-dichlorobenzene eq.

The study also includes the impacts from the Cumulative Energy Demand (CED) impact categories, Version 2 (based on the method published by Ecoinvent (Swiss Centre for LC, Duebendorf, CH).

Table VI shows the environmental impact categories used in this preliminary study as well as the reference units with which their impact is measured.

The results corresponding to these impacts can be represented in a grouped way in a comparative radar diagram, referenced for each category of impact to the process in which there is a greater impact (100%) and graphically showing the relative impact of the other processes. The environmental results of the tanning processes considered are shown in Figure 1. The results in terms of energy

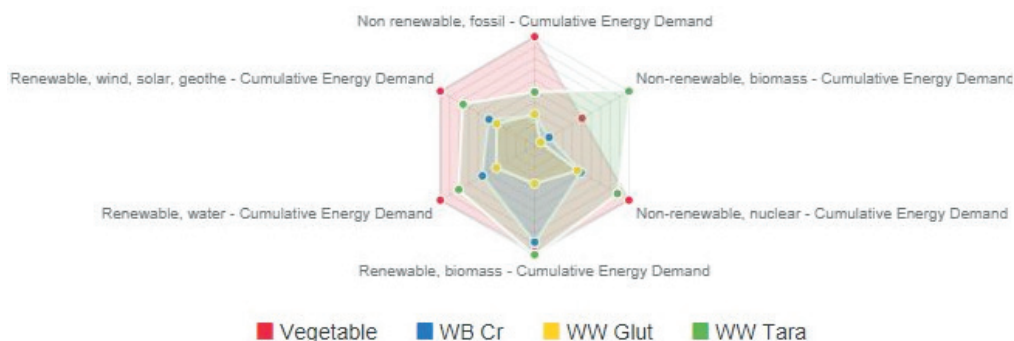


Figure 2. Comparative energy results of the life cycle analysis of the wet blue, wet white and vegetable tanning processes

demand are presented in Figure 2 in order to show basically the energy consumption according to the different origin of the products.

As can be seen in the results obtained, the vegetable process is the one with the greatest environmental impact, clearly noticeable in the high impact on global warming at 100 years (GWP100), stated as climate change in Figure 1. This result is due to the energy necessary for the production of mimosa and quebracho in addition to the energy used in drums. Wastewater treatment has slight significance as its impact is proportionally very low when comparing to other contributors. Namely, the energy contribution of wastewater treatment varies from 3 to 15 MJ depending on the considered process, representing a relative contribution of 0.5% to 1.25% in the energy consumption.

Cumulative energy demand indicators from Figure 2 show, as expected from the formulations a higher energy demand for the vegetable process and the lowest for the WW with glutaraldehyde. However, the production energy from specific products can affect this general layout. In this case, it must be highlighted that the use of tara is revealed as the cause of the comparative increase in non-renewable biomass energy demand for WW using tara process due to the use of pyrophosphate in the formulation, which uses biomass from primary forest.

The wet white tanning process using tara also has high environmental results, greater than vegetable tanning in several impacts. The main contributors are the proxies of ferric pyrophosphate and formic acid, and in some category the production of tara.

Wet white with glutaraldehyde process has the lowest environmental results according to these results.

The chrome tanning process (wet blue) also stands out for its reduced environmental impact, although it should be taken into account that the review of the processes and the validation of the selected proxies or their replacement by specific processes in the final review is pending.

Finally, bear in mind that the extension - already planned for further studies - of the system limits considering post-tanning as well as the treatment of wastewater may affect the result of the analysis.

On the other hand, highlight that it is outside the scope of this work, the life of the tanned product and its end (end-of-life).

For example, the wet white process with glutaraldehyde should also be taken into consideration, since even though it is better at the level of environmental impact in the tanning stage, the amount of products used in the post-tanning process must be increased to obtain a leather with good characteristics. In addition, it should be considered that glutaraldehyde can lead to problems in the biological scrubbers of the water treatment stages.

Conclusions

The study has been focused on the life cycle analysis of the three basic tanning processes: chrome, vegetable and wet-white leather production. Specifically, it has been focused on European manufacturing to have reliable data and reduce uncertainty.

The comparative results have shown the environmental impacts of leather tanning taking into account the products used and their origin and production, including emissions to the environment through standardized impact indices (CML and CED).

From the results obtained, it can be stated that in the tanning stage, the process with the greatest impact is the vegetable one, to highlight its high impact on global warming at 100 years (GWP100). This result is due to the energy necessary for the production of mimosa and quebracho in addition to the energy for the processing of the leather in the drums. Wet white tanning with glutaraldehyde has lowest environmental results than vegetable tanning. The chrome tanning process (wet blue) also stands out for its reduced environmental impact.

Subsequently, to have a global view of the entire production, the LCA of the post-tanning stages must be performed to evaluate the impact of each of the systems studied.

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