Life cycle assessment of Italian and Spanish bovine leather production systems

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Análisis del ciclo de vida de la curtición de piel bovina en Italia y España

Anàlisi del cicle de vida de l'adobament de pell bovina a Italia i España

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RESUMEN

El objetivo de la investigación aquí descrita fue era estudiar el perfil ambiental de dos sistemas de fabricación de cuero vacuno (el italiano y el español), para identificar sus puntos débiles y para averiguar si las distintas tecnologías y soluciones de gestión cooperativa adoptadas llevan a importantes diferencias ambientales en los dos sistemas analizados.
Se analizan los impactos ambientales por medio de la metodología de análisis del ciclo de vida (ACV). A nivel macro-fase, el proceso de curtición resultó ser la fase más ambientalmente significativa en casi todas las categorías de impacto en ambos sistemas. A nivel de las etapas específicas del proceso de curtición, las más impactantes son las etapas de curtición, tintura, recurtición y remojo en el sistema italiano y el remojo, encalado, curtido y recurtido en el español.
Las principales diferencias entre los dos sistemas y algunas opciones de mejora se identificaron a tres niveles: el mix energético, el proceso industrial y la gestión de los residuos sólidos. A pesar de la disparidad tecnológica y de gestión de residuos de los dos sistemas, su carga ambiental total apareció bastante similar. Sin embargo, en este trabajo se destacan las diferencias relevantes en las fases, operaciones y sustancias de más carga ambiental.
Las mejoras en ambos sistemas pasan por una optimización del proceso de curtición y por una reducción de los productos químicos utilizados. Se recomienda realizar estudios de inventario de ciclo de vida para los procesos de valorización y eliminación de residuos.

Palabras clave: cuero, industria de curtidos, matadero, Análisis del Ciclo de Vida, ACV, Ecología Industrial.

RESUM

L'objectiu de la recerca aquí descrita era estudiar el perfil ambiental de dos sistemes de fabricació de cuir boví (l'italià i l'espanyol), per identificar els seus punts febles i per esbrinar si les diferents tecnologies i solucions de gestió cooperativa adoptades porten a importants diferències ambientals en els dos sistemes analitzats.
S'analitzen els impactes ambientals per mitjà de la metodologia de l'anàlisi del cicle de vida (ACV). A nivell macrofase, el procés d'adobament de pells va resultar ser la fase més significativa ambientalment en gairebé totes les categories d'impacte en ambdós sistemes. A nivell d'etapes específiques dins el procés d'adobament, les més impactants són les etapes d'adobament, tintura, readobament i remull en el sistema italià i el remull, calciner, adobament i readobament en l'espanyol.
Les principals diferències entre els dos sistemes i algunes opcions de millora es van identificar a tres nivells: el mix energètic, el procés industrial i la gestió dels residus sòlids. Tot i la disparitat tecnològica i de gestió de residus dels dos sistemes, la seva càrrega ambiental total va sortir bastant similar. No obstant això, en aquest treball es destaquen les diferències rellevants en les fases, operacions i substàncies de més càrrega ambiental.
Les millores en ambdós sistemes passen per una optimització del procés de curtició i per una reducció dels productes químics utilitzats. Es recomana realitzar estudis d'inventari de cicle de vida per als processos de valorització i eliminació de residus.

Paraules clau: pell adobada, escorxador, Anàlisi del Cicle de Vida, ACV, Ecologia Industrial.

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SUMMARY

The objectives of the research here described were to put in evidence the eco-profiles of two product-systems concerning bovine leather manufactured in Italy and Spain, to identify their hot spots and to find out if the different technologies and cooperative management solutions adopted led to significant environmental differences in the two systems analysed.
The environmental impacts of two systems were analysed by means of the life cycle assessment (LCA) methodology. At the macro-phase level, tanning resulted to be the most burdensome phase for almost all impact categories in both systems. At the level of the specific tannery phases, the main hot spots were tanning, dyeing-retaining and soaking in the Italian system, soaking-liming, tanning and retanning in the Spanish one.
The main differences between the two systems and a few options for improvement were identified at three levels: energy mix, industrial processes and solid waste management. Despite the technological and waste management dissimilarity of the two systems, their total environmental burdens appeared quite similar. However, relevant differences in the most burdening phases, operations and substances are highlighted in this paper.
Improvements in both systems should be aimed at by means of an optimisation of tanning processes and reduction of chemicals use. Further studies dealing with inventories of recovery processes and landfill disposal of wastes are recommended.

Keywords: leather, tanning industry, slaughtering industry, Life Cycle Assessment, LCA, Industrial Ecology

INTRODUCTION

This paper refers to a Life Cycle Assessment (LCA) (Finnveden et al., 2009) that is part of a research programme called 'Cicle Pell: Industrial ecology in the animal-to-leather chain' funded by the EU in the framework of the Interreg III C Community Programme, Regional Framework Operation 'Ecosind'. The main aim of Ecosind was to define the basis for the implementation of a new strategy of industrial sustainable development in the Southern Europe regions (Catalonia, Abruzzo, Tuscany, Peloponnese).
According to the Italian National Statistics Institute in 2004 Italy has been the leading country in the leather sector in Europe and in the World, with 65% of the EU production and 13% of the world one, and with an average production of more than 135 million m^2 of leather and hides. Italy is followed by Spain with an average production of about 28 million m^2, which accounts for approximately 13% of the EU production and for about 3% of the world production. However it must be considered that in both countries more than 75% of chrome-tanned leather (commonly referred to as "wet blue") is imported from developing countries. This sector essentially consists of small- and medium-sized enterprises, gathered in districts, each with a specific kind of processing methodology and product destination.
Recently, the European leather industry has been facing a number of challenges, including the massive imports of raw materials from various countries, the size of companies, the increasing competition from the transition economies and developing countries and the environmental impact of the industry itself. In an international context, where the competition of the developing countries in the traditional industrial sectors is becoming stronger and stronger, the survival of the European industrial districts is threatened by low price policies due to low labour costs and to the lack of environmental constraints, which make the delocalisation of processing plants and facilities very attractive from an economic point of view. It is therefore important to study in depth the European (especially Italian and Spanish) leather processes, in order to identify the notable differences and the environmental improvements which could transform constraints into opportunities for improving the environmental performance and competitiveness of the leather enterprises, as well as avoiding the relocation of firms which has already taken place in other sectors.
A number of studies were found on life cycle assessment of leather or leather products, as well as on clean technologies and environmental improvements in the leather industry. The previous LCA studies were aimed at: identifying the hot-spots of the leather production in the cradle-to-gate life cycle (agriculture, cattle rising, slaughtering and tanning) (Milà et al. 1998a); defining the ecolabeling criteria for leather products (Milà et al. 2002); assessing the environmental improvements achieved by specific factories in developing countries (such as Chile or India) with the application of specific best available technologies (Rivela et al. 2004; Kurian et al. 2009). In these studies major attention is given to water and energy consumption, while the inventoried chemicals remain limited in number. Moreover the growing awareness of a high environmental impact of the tanning process has led to the research of new environmentally-friendly processes. Different authors have analysed the characterization of fluxes in large tanning districts (De Nicola et al. 2007; Lofrano et al. 2008) and the technological improvements of the tanning manufacturing cycle (Counts et al. 1996; Tünay et al. 1999; Sundar et al. 2002; Thanikaivelan et al. 2003; Raghava Rao et al. 2003; Sivakumar et al. 2005; Morera et al. 2007; Oral et al. 2007).
The aim of this LCA study is manyfold: a) to put in evidence the eco-profile of two tanning process life cycles in Italy and Spain from an industrial ecology perspective (Ayres and Ayres, 2002; Korhonen, 2004, Graedel and Allenby, 2010), considering above all the cooperative systems of solid and water waste management; b) to identify their hot spots and the differences in the process performance, as well as to find out if the diversity in the adopted technologies and cooperative management solutions have led to significant environmental differences; c) and, finally, to identify improvement possibilities in the case of two developed countries where environmental regulations are very strict.

METHODS

The LCA methodology has been applied according to the ISO 14040 (ISO, 2006a) and ISO 14044 (ISO, 2006b) standards except for what concerns to comparative assertions intended to be disclosed to the public, as the results are not to be intended for comparison, but just for learning purposes. Several steps of the LCA methodology, as applied to this study, are described below.

Function of the systems, functional unit and reference flow.

Function 1: 'Delivery of chrome-tanned leather for women's shoes through regional slaughtering and tanning in Italy'.
Function 2: 'Delivery of chrome-tanned leather for women's shoes through regional slaughtering and tanning in Spain'.

The function is linked to the surface area of the leather. Therefore, the functional unit should be chosen as the delivery of the surface area of leather needed to make a certain quantity of shoes or the surface area of a typical delivery of leather to a shoe company, etc. The chosen reference flow to which all other flows within the study are normalized was the delivery of 2,000 square feet (or 185.8 m^2) of chrome-tanned bovine leather with a thickness of 1.3 mm to be used for the manufacture of woman's shoes, which is equivalent to a leather mass of 200 kg (Grasso et al. 1990).

System boundaries

Both systems include the following phases: production and supply of electric energy, production of the main chemicals, slaughtering, raw hides storage, beam house, tanning, dyeing, finishing, wastewater and solid waste management, and transports. The agricultural phase and cattle-breeding were kept out of the system, as it was defined by the 'Cicle Pell' research project, which was mainly focused on the environmental implications of the slaughtering and tanning processes. The further steps of leather processing and woman's shoes production, as well as the use and disposal life-cycle phases are outside the system boundaries. The systems include all the inputs that cumulatively account for more than 80% of the total mass of the inputs used in the life cycle.

The slaughtering and tanning processes of the Italian foreground system (Guinée, 2002; Bauman and Tillman, 2004) are respectively located in the Abruzzo region and in the tanning district of Santa Croce sull'Arno in Tuscany, while those of the Spanish one in the tanning district of Igualada in Catalonia. The background reference systems (Guinée, 2002; Bauman and Tillman, 2004) are located all over Italy for the Italian system and in Catalonia for the Spanish one, with the exception of chromium ore supply, which comes from South Africa and Russia and chromium sulphate supply which comes from Italy, Germany and Romania.

Data quality

For each process throughout the analysed life-cycles, the collected data refer to the most widespread relevant technologies . The foreground data were obtained from industrial sites and compared with literature data (EC 2003a, EC 2003b, UNIC 2005, Bieankiewicz 2006, Covington 2009), while the background data were mainly taken from literature. In particular, slaughtering data were taken, for the Spanish system, from one slaughterhouse, while, for the Italian system, two slaughterhouses, representative of the Abruzzo region situation, were considered. Tanning data were collected from one tannery in each of the two countries. The input/output balance of slaughterhouses and tanneries was calculated as the average consumption of the specific process in the last available year. As a common assumption, depending on the geographical background of the study, the electricity mix of the Catalan and the Italian systems was considered. The Italian electricity mix was obtained from governmental databases (Map 2004), whilst the Catalan one was adapted from Milà et al, 1998b. The assignment of environmental loads to energy sources was made by using data from ETH database (Frischnecht et al. 1996). Data for auxiliary materials and chemicals were found in the literature and reported in Table 5. Data quality and data consistency analysis were carried out. When only low quality data were found, a sensitivity analysis was carried out whenever possible. The allocation of co-products from slaughtering and tanning was determined by following the causality principle on the basis of mass and economic criteria (Bauman and Tillman, 2004, ISO 2006a and 2006b).

Impact assessment

The impact assessment method used was the 'problem-oriented' one CML 2000 (Guinèe et al., 2000). The impact categories to which the inventory data refer were chosen on the basis of those more burdened by the environmental interventions of the systems. These are the following: primary energy consumption (EC), abiotic resource depletion potential (ADP) global warming potential (GWP), acidification potential (AP), photochemical oxidant creation potential (POCP), human toxicity potential (HTP), fresh aquatic eco-toxicity potential (FAETP), terrestrial eco-toxicity potential (TETP), nutrification potential (NP). The characterisation factors for all the impact categories, with the exception of the energy consumption, were taken from the CML 2000 Guide. For the energy consumption category, the values of primary energy (on a LHV basis) were taken into account.

RESULTS

Life cycle inventory

The inventory is comprised of the following five macro phases of the life cycle: slaughterhouse, storage, tannery, tannery solid waste management, tannery wastewater treatment.

Slaughterhouse

The slaughtering data are referred to one head of cattle with an average live weight of 425 kg for the Spanish system, and 478 kg for the Italian one. The import of raw hides from abroad was taken into account. The two systems respectively include the following phases. Spain: transport of cattle to the slaughterhouse by 16-tonne truck, slaughtering, wastewater treatment and disposal of the related sludge in landfill, disposal in landfill of solid waste; Italy: transport of cattle to the slaughterhouse, slaughtering, wastewater treatment, recovery and disposal of the solid waste.

The average distance travelled by the cattle from the breeding farm to the slaughterhouse is assumed to be 100 km in the Spanish system; in the Italian one the employed means of transport are considered, as well as the different size of the trucks, their load, and the specific distances from the breeding farms to the slaughterhouses. By considering all these variables, the average distance of the Italian system corresponds to 90 km. The slaughtering residues were classified into three categories, according to European Council Regulation 1774/2002 (EC 2002), which specifies health rules concerning animal by-products not destined to human consumption and were treated accordingly. In particular, in the Italian system, for sick organs from slaughtered cattle (Category 1 materials) the phases of transport to the treatment sites, of processing into animal meal and fat and the incineration of these materials were taken into account. For manure and digestive tract content (Category 2 materials), their transport to the sites of spreading nearby the slaughterhouse was considered. Other edible parts (Category 3 solid materials) are directed to rendering plants for material recovery. Blood (Category 3 liquid residue) is sent to treatment plants to be converted into blood meal. The Spanish slaughtering residual waste was considered to be disposed of in landfill due to lack of data on their specific treatment while most of residues is considered edible part and allocated, therefore leaving the system. The allocation of the slaughtering co-products was managed by following the causality principle on the basis of economic and mass criteria with the following percentage rates: 8% leather, 92% meat and other edible parts. Whereas economic criteria were used, the trend of price variability of the related prices was taken into account. In Table 1 the inputs and outputs concerning the Spanish and Italian slaughterhouses are shown (for further details on the collection of the slaughtering data of the Spanish and Italian systems, see: Milà et al. 1998b, Raggi et al. 2006). In Table 1 the mass could be balanced if the physiological loss from the dead cattle were considered.

From the analysis it emerges that the two systems reveal some differences, especially with regards to water consumption, which in the Spanish slaughterhouses is 5 times higher than in the Italian ones. As far as energy use is concerned, the Spanish system shows a 1.3 times higher consumption than the Italian one. There are also some differences in the by-products, as a result of the different method of classification of waste and co-products due to the fact that the data for the two systems refer to different time periods. The Italian one refers to the classification of the European Regulation 1774/2002 which had not yet come into force when the data collection of the Spanish system was carried out. In Table 2 the inputs and outputs of the solid waste treatments are shown. In this Table the mass balance could be reached if the wastewater and the evaporated water in the thermal treatments were considered.

Table 1: *Slaughterhouse inputs and outputs in the Spanish and Italian systems (per head of cattle)*

		Spain	**Italy**
Inputs			
Live cattle	kg	425	478
Water	L	840.5	180.4
Natural gas	MJ	56.7	70.0
Diesel	MJ	28.3	-
Fuel oil	MJ	28.3	-
Electric energy	kWh	0.52	4.5
Outputs			
Wastewater	L	840.5	180.3
Sick organs from slaughtered cattle	kg	-	45.4
Manure and digestive tract	kg	31.9	38.6
Other edible parts	kg	71.2	60.8
Residual solid waste	kg	31.9	-
Blood	kg	13.8	20.0
Meat	kg	225.0	248.0
Skin	kg	31.9	35.7

Storage

For both systems, salting was considered as the storage process. The two systems include the following phases: transport from the slaughterhouse to the storage site, storage treatment, input procurement (salt), wastewater treatment, landfill disposal of solid waste. The average distance travelled to transport raw hides from the slaughterhouse to the storage (nearby the tannery) is 100 km for Spain and 50 km for Italy (the Italian slaughtering foreground system was conventionally localized in Abruzzo, because of project constraints; however skins come from local firms in the real situation). The data sources for all the phases are Mila I Canals et al., (1998b) for the Spanish system and industrial plants for the Italian one. Data are very similar for the two systems; in particular, per 1,000 kg of raw salted hides the following inputs and outputs were quantified for the Spanish and Italian system, respectively: raw hides: 1140 kg and 1160 kg; electric energy: 15.6 kWh and 15.5 kWh; wastewater: 312 L and 237 L ; solid waste: 12 kg and 16.1 kg.

Table 2: *Inputs and outputs of industrial plants processing sick organs from slaughtered cattle (Category 1) and other edible parts (Category 3 animal solid residues).*

		Cat. 1 plant	Cat. 3 plant
Inputs			
Sick organs from slaughtered cattle	t	20,000	-
Other edible parts	t	-	47,500
Water	m3	13,000	36,000
Detergents	kg	1,800	11,500
Disinfectants	kg	6,000	5,500
Industrial salt	kg	-	30,000
Electric energy	MWh	1,800	2,500
Natural gas	m3	550,000	3,300,000
Outputs			
Animal meal	t	7,000	13,775
Animal fat	t	3,000	13,775

Tanning

The considered tanning process is exclusively the one using chromium. The two systems include the following phases: transport of the salted raw hides from the storage site to the tannery, procurement of chemicals, all the tanning phases – soaking, liming, fleshing, splitting, deliming, pickling/tanning, draining, shaving, re-tanning, neutralization, dyeing/re-tanning/fat-liquoring, pressing, drying, trimming, finishing – wastewater treatment, landfill disposal and/or recovery of solid waste. The average distance travelled to transport the raw hide from the storage to the tannery is 10 km for both systems. The allocation between crusts and leather is the same for both systems with the following percentage: 5.5% crusts, 94.5% leather. Where economic criteria were used, the trend of price variability over time was taken into account. In Figure 1 and Figure 2 the tanning flowcharts of the two systems are shown. By analysing the tanning operations of the Spanish and Italian systems, one can see that the two processes are very similar.

In Table 3 the thermal and electric energy uses for the various phases are reported for both systems (Puig et al. 2005; Notarnicola et al. 2006). From Table 3 one can see that the Italian system requires more thermal energy than the Spanish one; this is due to a lower energy use in the beam house operations but a larger one in the tanning and post-tanning operations. Since thermal energy is mainly used for heating water, its use is linked to the consumption of warm water, which, in the Italian system, is higher in the cited phases. The electric energy use is almost the same in the two systems with small differences in the various phases which derive from different machinery power, drums speed, duration of operations; in both systems the main consumption derives from pickling, tanning, drying and finishing.

Water consumption amounts to 21.4 m^3 and 16.3 m^3 for the Spanish and the Italian system, respectively (Table 4). It is mainly associated with the first phases of beam house; the Italian system uses less water than the Spanish one in the soaking, un-hairing and liming operations (10.4 m^3 vs 17.5 m^3); on the contrary, the Italian tannery uses much more water in the tan yard and post-tanning operations (5.9 m^3 vs 3.9 m^3). In particular, the reasons for the different

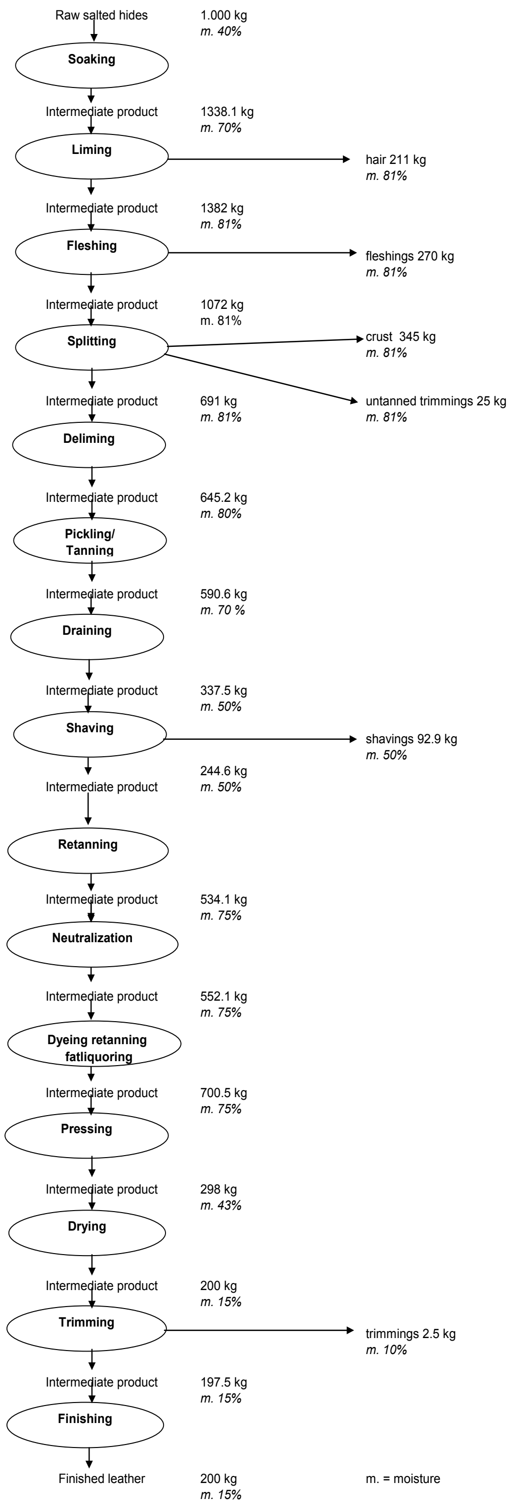


***Fig.1**: Spanish tanning flowchart*

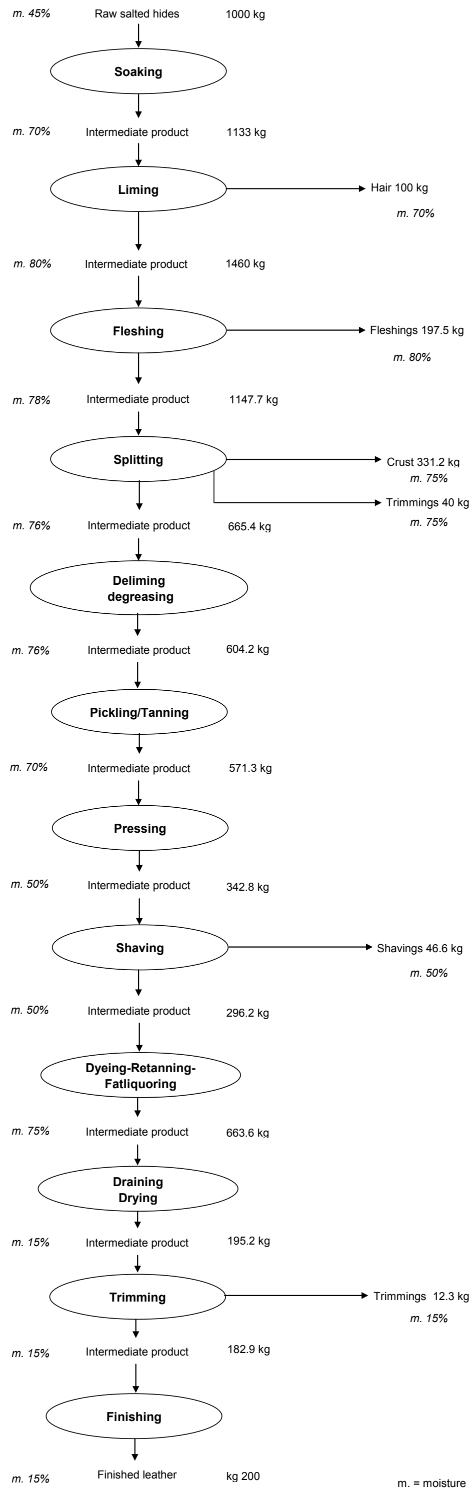


***Fig.2:** Italian tanning flowchart*

water consumption in the two systems are the following: in the soaking phase the Italian tannery spends, for desalting, only 150% water (based on raw skin weight before soaking) vs. 300% of the Spanish one; in the liming phase it uses the same bath coming from soaking and only 300% cold water for the final washing against 600% warm water of the Spanish system; also in deliming the Italian system spends in general less water and, above all, much less warm water. This explains the higher thermal energy consumption in these phases of the Spanish system. In pickling/tanning operations the Italian tannery spends more cold water for washing; much higher water consumption takes place in the Italian system for neutralization, dyeing, retanning, fatliquoring because of a higher chemicals consumption which needs much more operations of float discharge and consequent water renewal. Moreover the operation temperatures for these phases are on average 35-40 °C in the Spanish system and 55-60 °C in the Italian one, with consequent higher consumption of thermal energy in the latter system. Lastly, the higher moisture percentage of the product to be sent to drying is the reason for higher thermal energy consumption in this phase in the Italian system. The quantity of discharged wastewater is linked to the fresh water used in processes; consequently the Spanish system releases a higher volume of wastewater.

Table 3: *Thermal and electric energy use in the two systems*

	Thermal energy (MJ)		Electric energy (kWh)	
	Spain	Italy	Spain	Italy
Soaking	250	228.6	4.11	5.53
Liming	334	---	13.3	10.14
Fleshing	---	---	24.4	14.36
Splitting	---	---	8.66	4.41
De-liming	308	168.7	5.11	7.19
Pickling/tanning	70.8	45.2	21.4	29.31
Draining	---	---	21.4	8.8
Shaving	---	---	15.2	24.35
Re-tanning	69	---	6.17	---
Neutralization	97.4	---	1.51	---
Dyeing/re-tanning/fat-liquoring	124.8	529.3	6.92	14.68
Pressing	---	---	21.4	67.04
Drying	418	856	42.3	
Trimming	---	---	7.63	5.41
Finishing	314	485.4	84.1	103.7
Total	**1,986**	**2,313.2**	**283.61**	**294.92**

The chemicals used in the two systems are reported in Table 5, together with the indication of whether their input/output balance is included in the inventory and the relevant bibliographic data source. In the Italian system, compared to the Spanish one, larger amounts of chemicals are used in all the operations (483 kg vs. 346 kg), above all in the post-tanning and finishing operations. The main emissions to air in both systems derive from the finishing operations and are related to VOCs emitted during solvents use. Since the Italian system uses more chemicals and solvents in this phase, the result is comparatively higher than in the other system. Moreover, for the same reason, the concentration of polluting substances in the Italian wastewater is significantly higher; also the total emissions to water of suspended solids, COD, TKN, sulphides, sulphates, chromium (III) and chlorides is higher than in the Spanish system. As regards the solid waste produced in the two systems we can say that the Spanish tannery produces about 50% more waste than the Italian system (especially: hair, fleshings and shavings).

Table 4: *Water balance in the two systems (in L)*

Water balance	Spain		Italy	
	IN	OUT	IN	OUT
Soaking	5,000	4,460	3,500	2,860
Liming	7,500	7,150	3,000	2,855
Fleshing	400	432	150	265
Splitting	400	410	330	440
De-liming	4,150	4,111	3,400	3,450
Pickling/tanning	981	1,160	1,660	1,720
Draining	--	245	--	230
Dyeing/re-tanning/fat-liquoring	2,943	2,542	4,000	3,650
Drying	--	397	--	185
Finishing	21	28	210	207
Total	21,395	20,935	16,250	15,862

In Table 6 the summary data of the tanning inputs and outputs of both systems are reported; in this Table the mass balance could be respected if the evaporated water in the drying phase, the salt eliminated during soaking and the quantity of chemicals not fixed in the final product were considered.

Table 6: *Tannery main inputs and outputs of the two systems*

		Spain	Italy
Input			
Raw salted hides	kg	1,000	1,000
Thermal energy	MJ	1,986	2,313.2
Electric energy	kWh	283.6	294.9
Water	L	21,395	16,250
Auxiliaries	kg	345.7	483.2
Output			
Wastewater	L	20,935	15,862
Hair	kg	211	100
Fleshings	kg	270	197.5
Untanned trimmings	kg	25	40
Shavings	kg	92.9	46.6
Tanned trimmings	kg	2.5	12.3
Tanned leather	kg	200	200
Crust	kg	345	331.2

Tannery solid waste management

The two systems include the following phases: transport of the solid waste to the respective disposal/recovery plants, disposal/recovery treatment, final disposal of the treated solid waste. The respective percentages of disposal/recovery of the different waste fractions produced in the tanning phase by the two systems are reported: both systems send hair to landfill (100%); in Spain the recovery percentages are 94.9% for fleshings, 69.1% for untanned and tanned trimmings, 93.0% for shavings; in Italy the recovery percentages are 99.4% for fleshings and 98.0% for all the other residues (Puig et al. 2003; UNIC 2005). The Italian system shows greater recovery rates compared to Spain for all the waste fractions.

The landfill disposal is characterised by airborne and waterborne emissions. The forecasted temporal horizon for the emissions coming from the landfill is estimated in a surveyable time of 100 years. In this period it is assumed that all the organic matter is degraded in anaerobic conditions. The airborne emissions were stoichiometrically calculated starting from the waste composition and by using the chemical formula reported in Mila I Canals et al. (1998b). Biogas capture and its burning were not considered here; obviously this assumption has an effect on the calculation of GWP, and it should be considered as a limitation. The emissions coming from the landfill are essentially CH_4, NH_3, H_2S and non-fossil CO_2 (Nielsen et al. 1998; Ménard et al 2004; Hauschild et al. 2008; Barcelò et al. 2008). For the calculation of metals emissions to water the composition of the waste reported in Mila I Canals et al. (1998b) was the starting point and then the Finnveden

Table 5: *Chemicals used in the tanning phase in the Spanish and Italian systems and their inventory data source*

Process	Used chemicals	Quantity			Total quantity per process			Bibliographic data source
		Spanish system	Italian system		Spanish system	Italian system		
soaking	Humectants	4		kg				not included in inventory
	Sodium carbonate	5		kg				Frischnecht et al. (1996)
	Solvay Soda		3	kg				Frischnecht et al. (1996)
	Sodium hydrosulphide	2.5		kg				Ullmann (2000)
	Sodium sulphide		1	kg				Ullmann (2000)
	Synthetic alcohol		1	kg				not included in inventory
	NaOH (50%)	1		kg				BUWAL 250 (1996)
	NaOH (15%)		8	kg	12.5	13	kg	BUWAL 250 (1996)
liming	Polyalcohol	2		kg				not included in inventory
	Polyphosphate	5		kg				not included in inventory
	Sodium hydrosulphide	7.5	10	kg				Ullmann (2000)
	Sodium sulphide	4.5	21.5	kg				Ullmann (2000)
	NaOH (50%)	3		kg				BUWAL 250 (1996)
	Lime	43.5		kg				Frischnecht et al. (1996)
	Hydrate lime		47.5	kg				Frischnecht et al. (1996)
	Enzymes		1	kg				not included in inventory
	Methylamine		8	kg	65.5	88	kg	not included in inventory
deliming	Ammonium sulphate	3.5	16.6	kg				Ullmann (2000)
	Lactic acid	25		kg				not included in inventory
	Surfactant	0.7		kg				not included in inventory
	Soaking agent	3.5		kg				not included in inventory
	Synthetic alcohol		2.0	kg				not included in inventory
	Oxalic acid		2.7	kg				not included in inventory
	Sodium metabisulphite		2.0	kg				not included in inventory
	Enzymes		1.3	kg	32.7	24.6	kg	not included in inventory
pickling/ tanning	NaCl	34.6	46.6	kg				Frischnecht et al. (1996)
	Formic acid	0.84	3.3	kg				Ullmann (2000)
	Sulphuric acid	1.26	9.3	kg				BUWAL 250 (1996)
	CrOHSO4 33% liquid	66.7	86.5	kg				Ullmann (2000)
	Sodium sulphate	9.22		kg				BUWAL 250 (1996)
	Basic agent	13.8	5.7	kg				not included in inventory
	Sodium phosphate		0.7	kg				not included in inventory
	Sodium formate		2.7	kg				not included in inventory
	Sodium acetate		5.7	kg				not included in inventory
	Greasing agent		3.3	kg				Tenside SD (1995); Nicoletti et al. (2001); BUWAL 250 (1996)
	Bactericide		0.7	kg	126.4	164.3	kg	Ullmann (2000)
retanning	Glutaraldehyde	1.63		kg				not included in inventory
	CrOHSO4 33% liquid	30		kg				Ullmann (2000)
	Sodium sulphate	4.08		kg				BUWAL 250 (1996)
	Formic acid	0.06		kg				Ullmann (2000)
	Degreasing agent	0.12		kg	35.9		kg	not included in inventory
neutralization	Aromatic compounds	4.89		kg				not included in inventory
	Neutralising salts	1.22		kg	6.1		kg	not included in inventory
dyeing/ retan-ning/ fatliquoring	Formic acid	17.1		kg				Ullmann (2000)
	Phenolic tannins	9.78		kg				not included in inventory
	Vegetal tannins	9.78	11.8	kg				Ullmann (2000)
	Anionic dye	7.34	20.7	kg				Ullmann (2000)
	Resin	7.34	26.7	kg				Ullmann (2000)
	Filling agent		11.8	kg				not included in inventory
	Synthetic tannins		22.2	kg				not included in inventory
	CrOHSO4 33% liquid		11.8	kg				Ullmann (2000)
	Greasing agent		42.4	kg				Tenside SD (1995); Nicoletti et al. (2001); BUWAL 250 (1996)
	Degreasing agent		3.0	kg				Ullmann (2000)
	Formic acid		13.3	kg				Ullmann (2000)
	Penetrating agent		3.0	kg	51.3	166.8	kg	not included in inventory
finishing	Aniline	1.34	1.0	kg				Ullmann (2000)
	Casein	1.34	3.6	kg				not included in inventory
	Wax	0.9	0.1	kg				not included in inventory
	Acrylic polymer	6.72		kg				Ullmann (2000); APME (1999)
	Dye	0.67		kg				Ullmann (2000); Nicoletti et al. (2002a)
	Lacquer	4.39	2.4	kg				Ullmann (2000)
	Auxiliaries		5.4	kg				not included in inventory
	Pigments		1.6	kg				Spin (1994)
	Resins		6.0	kg				Ullmann (2000)
	Solvents		6.4	kg	15.4	26.5	kg	APME (1999)
				total	**345.7**	**483.2**	**kg**	

model was applied (Finnveden 1996). Trivalent chromium is the main heavy metal released to water. The average distance travelled to transport the waste from the tannery to the landfill is 20 km for both systems.

Fleshing is the main waste in quantitative terms. In both the considered systems the fleshing is directed to the process of hydrolised matter production utilised as organic matrix to formulate customised organic-mineral fertilisers. Due to the lack of specific plant and literature data, only the energy use was estimated for the fleshing processing. The recovery treatment of the other waste in the two systems presents some differences: in the Spanish system the untanned trimmings are processed in order to obtain fertilizers, while regenerated leather is obtained from the shavings and from tanned trimmings. In the Italian system all the remaining tanned and untanned residues are utilised for the production of fertilisers. Both Spanish and Italian data are plant-specific; due to the lack of data for the process of leather regeneration, only the flow of chromium was followed for this process. The quantity of chromium assigned to the system as a release to the environment was calculated as half the input quantity; this is due to the fact that this chromium is embedded in the regenerated leather, therefore it can be considered to be used twice. The average distance travelled to transport the solid waste from the tannery to the treatment plants is 50 km for both systems.

In the light of the previous data and assumptions one can note that the Italian system is characterised by a higher rate of matter recovery from tanning solid waste. This implies two types of environmental (and economic) advantages: firstly, less waste to be disposed of in landfill, which means, consequently, lower emissions of NH_3 and CH_4 due to the anaerobic degradation of the organic component of waste; secondly, the recovery, in an industrial ecology perspective, implies a lower need of virgin raw materials in other productive systems, as fertilisers etc. These results, based on the inputs and outputs of the recovery options included, show that the cooperative management of the solid waste in the district of Santa Croce sull'Arno, with higher recovery rates, permits to reach environmental (and economic) advantages.

Tannery wastewater management

The two systems include the following phases: water collection to be directed to chromium recovery, chromium treatment, water purification, disposal and/or treatment of the purification sludge. The data source for all phases were Mila I Canals et al. (1998b) for the Spanish system and industrial plants for the Italian one.

In the Spanish system only the tanning water is directed to chromium recovery, while in the Italian one also the re-tanning water is. For this reason the recovery rate is 4% in weight for the Spanish system and 2% for the Italian one.

In both systems the waste water treatment plant is a centralised unit belonging to the district consortium. Both the waste water coming from the tannery which is not directed to chromium recovery and the waste water coming from chromium recovery are directed to the water purification plant. The plants include: a mechanical treatment, whose aims are to separate the solid parts of the different waste releases, to homogenize the waste release, to separate the finest particulates (hair, fibres, lime), and those which are sedimentable; a chemical-physical treatment, with the aim of coagulating and precipitating chromium, iron and the part of hydrocolloids (proteins, tannins, fats); a biological treatment, with the aim of aerobically biodegrading the organic matter still present, which is removed as gelatinous flakes (active sludge).

Sludge with different composition is an outflow from the wastewater treatment plants; in the Spanish system the sludge outflow has a moisture of 80%, in the Italian one it is very liquid with a moisture of 96%.

In the Spanish system, the sewage sludge is disposed of in landfill; the organic component was assumed to be released to the atmosphere, as it had been assumed for the landfilled solid waste. In the Italian system, the purification sludge is directed to an exploitation treatment. The treatment consists of a mechanical dehydration of the liquid waste to obtain a sludge with a 30% of dry substance, which successively undergoes a thermal treatment (drying, pyrolysis and sintering) in order to obtain, finally, an inert material that could be reused in the bitumen and asphalt industry, by mixing it with other elements (Nicoletti et al. 2002b). The sludge part which is not thermally treated is disposed of in landfill. The transport distance of the sludge from the wastewater treatment plant and/or from the sludge treatment site to the landfill is 20 km for both systems.

Figure 3 shows the wastewater management flow charts of the two systems (amounts are expressed per functional unit); since the quantity of wastewater discharged is linked to the fresh water used in the processes, the Spanish system releases a higher volume of wastewater due to a higher water consumption. In the wastewater treatment one can note the following differences: the Spanish system produces a higher

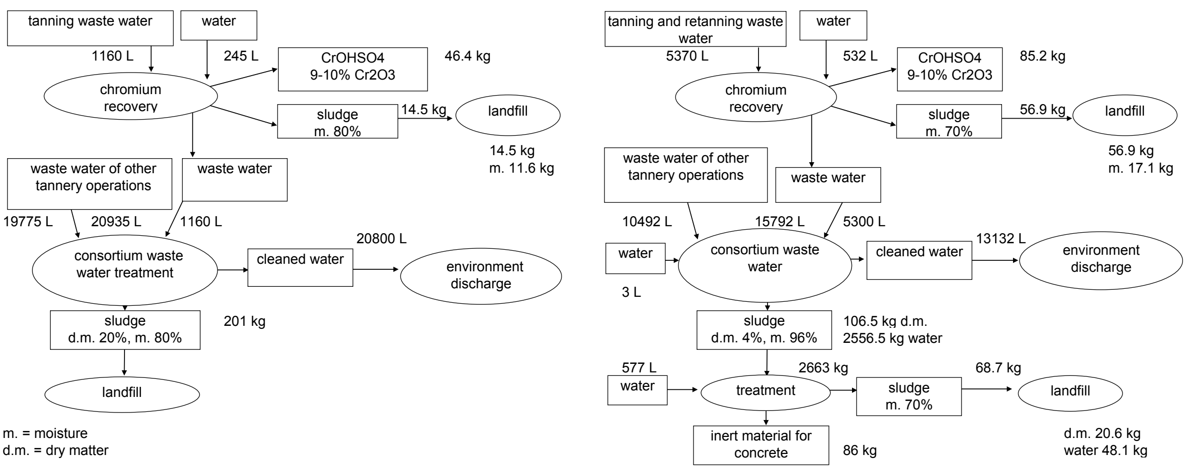
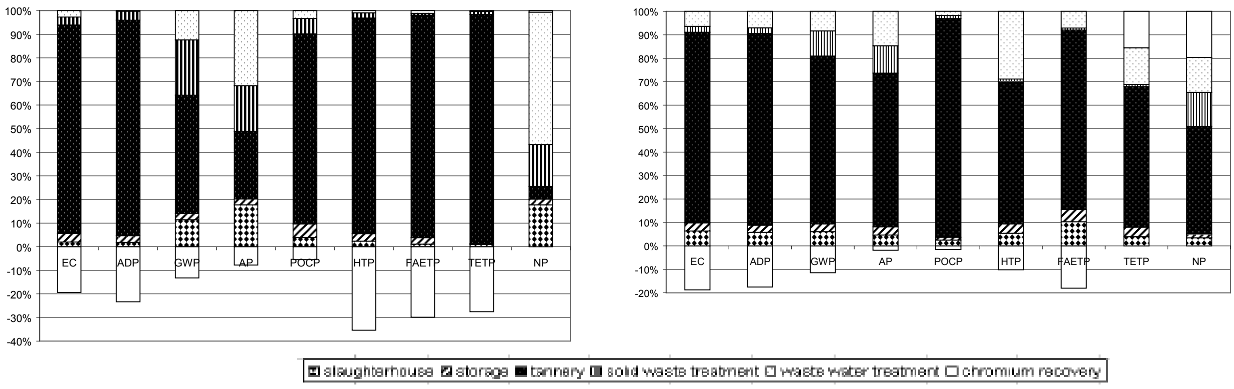


Fig. 3: *Spanish (left) and Italian (right) tannery wastewater management*



EC	ADP	GWP	AP	POCP	HTP	FAETP	TETP	NP
MJ LHV	kg Sb eq	kg CO2 eq	kg SO2 eq	kg C2H4	kg 1,4-DB eq	kg 1,4-DB eq	kg 1,4-DB eq	kg PO4--- eq
1,54E+04	6,81	1,43E+03	21,1	1,74	161	17,7	2,45	5,42

EC	ADP	GWP	AP	POCP	HTP	FAETP	TETP	NP
MJ LHV	kg Sb eq	kg CO2 eq	kg SO2 eq	kg C2H4	kg 1,4-DB eq	kg 1,4-DB eq	kg 1,4-DB eq	kg PO4--- eq
21400	12	1660	15,3	5,1	508	44,5	9,39	2,67

Fig. 4: *Characterisation of the Spanish (left) and the Italian (right) system per phase*

Table 7: *The chemicals supply, energy and other emission factors for the tanning process.*

	Spain					Italy				
	Unit	Characterization factor	chemicals supply	energy	other	Unit	Characterization factor	chemicals supply	energy	other
EC	MJ LHV	16,850	68%	32%	0%	MJ LHV	21,427	72%	27%	1%
ADP	kg Sb eq	8.1	81%	19%	0%	kg Sb eq	11.9	75%	24%	1%
GWP	kg CO2 eq	827.6	80%	4%	17%	kg CO2 eq	1,344.5	67%	19%	15%
AP	kg SO2 eq	6.5	88%	4%	8%	kg SO2 eq	10.2	74%	22%	4%
POCP	kg C2H4 eq	1.5	39%	1%	60%	kg C2H4 eq	4.8	18%	4%	77%
HTP	kg 1,4-DB eq	227.5	91%	8%	1%	kg 1,4-DB eq	342.2	67%	32%	1%
FAETP	kg 1,4-DB eq	23.8	84%	16%	0%	kg 1,4-DB eq	41.5	61%	39%	0%
TETP	kg 1,4-DB eq	3.3	95%	5%	0%	kg 1,4-DB eq	5.6	66%	34%	0%
NP	kg PO4--- eq	0.3	82%	7%	11%	kg PO4--- eq	1.2	89%	7%	4%

amount of sludge to be disposed of in landfill; the Italian system is characterised by a higher rate of materials recovery.

Impact assessment

Figure 4 shows the characterisation results for each macro phase of the system life cycle (slaughterhouse, storage, tannery, tannery solid waste management, tannery wastewater treatment, chromium recovery) together with the total characterization amount. In both systems, tanning is the most burdening phase in almost all the impact categories (with the exception of AP and NP only in the Spanish system), while the impact of slaughterhouse and storage is low. The chromium recovery leads to an environmental credit in both systems. In both systems, the tanning impact is mainly due to the chemicals supply, and to a lesser extent to the energy load, as can be noted from Table 7, where the impact percentages of chemicals supply, energy and other emission factors for the tanning process are shown. Among the raw materials for tanning, the most relevant ones in all the impact categories are basic chromium sulphate ($CrSO_4^+$:OH^-) and formic acid (HCOOH) for the Spanish system, and basic chromium sulphate and greasing agents for the Italian one. This is an important element to be considered; with the inclusion in the inventory of the inputs that cumulatively account for more than 80% of the total mass of the inputs used, it can be noted that the chemicals supply is the main responsible for environmental burdens while energy use plays a secondary role. Chemicals are also responsible for the impact during their use phase because they cause a higher demand for water treatment and higher emissions to air, such as solvents in finishing which contribute for respectively 60% and 77% to the Photochemical Oxidation Potential in the Spanish and Italian system.

In order to deepen the evaluation profile of the two systems, an analysis was carried out, in which the environmental impacts of all the activities related to tanning were directly related to the single tanning operation to which they are functional. Therefore, the impact of the chemicals procurement or of the energy used in the different operations was completely attributed to the relevant phases; the impact of the treatment of wastewater coming from a given tanning phase was completely attributed to that phase; the impact of chromium recovery was assigned to those phases which generate chromium discharge into water; the impact of solid waste treatment was assigned to those phases which produce solid waste. The impact of slaughtering and storage was attributed to soaking. In this way it was possible to correlate the results coming from possible environmental improvements occurring in tannery (i.e. water or energy use reductions, or solid waste addressed to recovery rather than to disposal) directly to the single tannery phase where the improvement is introduced.

Table 8: *Characterisation of the Spanish system per tannery phase*

	Energy consumption	Abiotic depletion	Global warming	Acidification	Photochemical Oxidation	Human toxicity	Fresh aquatic ecotoxicity	Terrestrial ecotoxicity	Nutrification
soaking	11%	10%	22%	31%	12%	12%	11%	4%	30%
liming	8%	7%	31%	30%	9%	7%	9%	7%	36%
fleshing	6%	5%	5%	4%	1%	3%	1%	2%	6%
splitting	1%	0%	2%	2%	0%	1%	1%	1%	3%
de-liming	3%	4%	3%	2%	1%	2%	2%	1%	7%
pickling/ tanning	15%	16%	10%	10%	5%	27%	21%	33%	5%
draining	2%	0%	0%	0%	0%	0%	1%	0%	0%
shaving	1%	0%	3%	4%	1%	0%	1%	0%	3%
re-tanning	17%	21%	11%	8%	4%	37%	29%	32%	2%
neutralization	1%	1%	1%	0%	0%	0%	1%	0%	0%
dyeing/ re-tanning/ fat-liquoring	14%	20%	6%	4%	13%	4%	10%	10%	5%
pressing	2%	0%	1%	1%	0%	0%	1%	0%	1%
drying	6%	5%	2%	1%	1%	3%	4%	1%	0%
trimming	1%	0%	1%	1%	0%	0%	0%	0%	1%
finishing	14%	10%	4%	1%	52%	5%	9%	9%	1%
Total characterization load	15,385	6.81	1,433	21.1	1.74	161	17.7	2.45	5.42
Unit	MJ LHV	kg Sb eq	kg CO2 eq	kg SO2 eq	kg C2H4	kg 1,4-DB eq	kg 1,4-DB eq	kg 1,4-DB eq	kg PO43- eq

Table 9: *Characterisation of the Italian system per tannery phase*

	Energy consumption	Abiotic depletion	Global warming	Acidification	Photochemical Oxidation	Human toxicity	Fresh aquatic ecotoxicity	Terrestrial ecotoxicity	Nutrification
soaking	16%	15%	15%	13%	5%	20%	23%	13%	9%
liming	6%	5%	17%	15%	4%	10%	6%	5%	16%
fleshing	3%	3%	3%	2%	0%	2%	2%	2%	1%
splitting	1%	1%	1%	1%	0%	2%	1%	1%	1%
de-liming	5%	5%	5%	7%	1%	12%	4%	6%	6%
pickling/ tanning	30%	31%	26%	31%	5%	32%	29%	31%	15%
draining	1%	1%	1%	1%	0%	1%	1%	1%	0%
shaving	2%	2%	2%	2%	0%	2%	3%	2%	1%
dyeing/ re-tanning/ fat-liquoring	16%	19%	12%	16%	8%	4%	6%	25%	45%
drying	8%	7%	8%	5%	1%	6%	10%	5%	1%
trimming	0%	0%	0%	1%	0%	0%	1%	0%	0%
finishing	13%	12%	10%	7%	74%	9%	15%	9%	2%
Total characterization load	21,400	12	1,660	15.3	5.1	508	44.5	9.39	2.67
Unit	MJ LHV	kg Sb eq	kg CO2 eq	kg SO2 eq	kg C2H4	kg 1,4-DB eq	kg 1,4-DB eq	kg 1,4-DB eq	kg PO43- eq

The results of this approach are reported in Tables 8 and 9. In both systems some phases result in negligible impact in all the considered impact categories. In the Spanish system the phases of splitting, draining, shaving, neutralization, pressing, trimming result negligible. Other phases result less burdening: fleshing, with a maximum 6% contribution to EC and NP, deliming with a maximum 7% contribution to NP, and drying with a maximum 6% contribution to EC. The most burdening phases in the Spanish system are: soaking, liming, pickling/tanning, re-tanning, dyeing, , fat-liquoring, and finishing.
As far as the Italian system is concerned, the negligible phases are fleshing, splitting, draining, shaving and trimming.
The phases with a minor impact are: deliming, with a maximum 12% contribution only to HTP and drying, with a maximum 10% contribution to FAETP. The most burdening phases are: soaking, liming, pickling, tanning, dyeing, re-tanning, fat-liquoring, finishing.
It is possible to note some similarities between the two systems. In fact, the tanning phases with higher or lower impacts are substantially the same in the two systems, even if they have a different impact profile (different impact categories involved, different impact percentages). The less burdening phases are obviously the ones without thermal energy consumption, without chemicals use and with a modest water consumption; on the contrary, the most burdening phases result the ones with higher energy, chemicals and water consumptions and the consequent wastewater treatment.

DISCUSSION

The results relative to the inventory and to the impact assessment shown up to now obviously depend on the data used in the two systems; they basically are environmental data of the processes and system data related to the material and energy flows. In order to make the results consistent with the aim of the study, an analysis of data quality and data consistency was carried out.
Data quality control and system consistency control showed that some elements are uncertain in both systems. Most of these uncertainties do not affect the foundations of the analysis: the absence of data related to the treatment of the fleshing (other than energy use, which was estimated) does not substantially affect the environmental burden of the system. Therefore, the absence of this data is reckoned as not relevant. The same argumentations can be extended to the data related to the treatment of slaughtering solid waste recovery in the Spanish system, which were not collected, and to the data related to the recovery of untanned trimmings and shavings in the Spanish system.
From the application of the above-mentioned model, it emerged that the most uncertain element was the estimation of emissions from the landfill disposal of waste water treatment sludge and the solid waste which is generated by the slaughtering and tannery processes. As far as these emissions are concerned, a sensitivity analysis was carried out, in order to assess the reliability of the results obtained. Landfill emissions were changed as follows:
-CH_4, NH_3 and H_2S emissions were lowered by 10%;
-it was assumed that metal emissions to soil account for 100% of the metals contained in landfill disposed waste.

CONCLUSIONS

The Italian and Spanish tanning systems were analysed in parallel by means of the LCA methodology in order to identify the hot spots and to find where the environmental performance can be improved. The most important hot spots of the two systems are:
1) At the macro phase level (slaughterhouse, storage, tannery, tannery solid waste management, tannery wastewater treatment, chromium recovery): for both systems, the tannery is the most burdening phase in almost all the impact categories (with the exception of AP and NP, only in the Spanish system).
2) At the level of the tannery phases, in decreasing order of importance: tanning, dyeing-retaining and soaking in the Italian system, and soaking-liming, tanning and re-tanning in the Spanish one are the most sensitive phases.
3) At the level of tannery chemicals: basic chromium sulphate is the key impacting chemical, in both systems in all the impact categories.
4) At the level of gaseous emissions: NH_3 and CH_4 from landfill, VOC from the finishing operations, plus energy related emissions are relevant hot spots.
5) At the larger life-cycle level : energy use plays a relevant role in both systems.
Going through the differences between the two systems and the identification of the options for improvement, three levels can be identified: energy mix, industrial processes, solid waste management. The first one really affects the results since the Catalan mix is completely different from the Italian one. The strong share of nuclear in the Catalan mix of course accounts for the difference. Options for improvement should be directed to an increased use of renewable energy sources, especially in the Italian system. The differences in the processes are many, related to energy and water use, chemicals and auxiliaries used, solid waste produced, etc.; sometimes they are negligible, sometimes more important, but this result is in line with what was expected: even if the two technologies are very similar and coherent, they of course feature different product mixtures, water and energy uses, emissions etc., aspects which have been widely discussed. A rationalisation in the energy and water uses during the processes seems to be adoptable in both the systems.
The third difference is the one relative to the exploitation of the solid waste. The Italian system has shown a higher rate of material recovery from solid waste compared to the Spanish system due to a higher adoption of cooperative environmental management solutions occurring in Santa Croce sull'Arno district. This implies two types of environmental (and economic) advantages: the first is related to the lower quantity of waste disposed of in landfill, which means, consequently, lower emissions of NH_3 and CH_4 due to the anaerobic degradation of the organic component of waste; the second is related to the recovery of matter that, from an industrial ecology perspective, implies a lower need of virgin raw materials in other productive systems as, for instance, fertilisers. On this point options for improvement on the basis of the Italian experience could be followed in the Spanish system. The availability of more data on the recovery processes (mass balances, amount of residues going to landfill during the recovery process, energy and water use and chemicals used) would lead to a better comparison of the environmental improvements of the different options.

Finally we can state that all the technological and waste management differences encountered in the two systems have not led to relevant differences, in absolute terms, of the total environmental burden of the systems - which appear quite similar - but to relevant differences in the most burdening phases, tanning operations and substances. In any case, by considering the actual situation of two manufacturing methods in two developed countries in which the strategies of cooperative waste management are already adopted, the environmental impact of wastewater and solid waste treatments are modest in most of the impact categories; moreover this situation can only marginally be improved upon, since high waste recovery rates, in many cases above 90%, and systems of wastewater stream separation for chromium recovery have been already considered, even if this separation could be extended to other tanning phases. It could be stated that the cooperative management of outputs is already showing its positive effects on the environment, already included in the results of this study. If the Spanish and Italian tanning systems would like to further reduce their environmental impact, they should focus on the optimisation of the single tanning operations and in particular on a rational use of chemicals, which result to be the main responsible for the system environmental burden, both in the supply and in the use phase. The numerous experimental processes, proposed to overcome this problem, should be economically viable in order to obtain at the same time environmental and economic advantages so that the linked manufacturing cost reduction could allow the survival of companies in the market without the need for plant relocation.

RECOMMENDATIONS AND PERSPECTIVES

As discussed above, the tanning improvements in the Spanish and Italian systems should be searched in the processes optimisation and the reduction of chemicals use. First of all, closed-loop systems or, at least, systems for water consumption reduction and a rationalised waste treatment could be introduced (Bódalo et al. 2005; Saravanabhavan et al. 2005; Rodrigues et al. 2008; Jian et al. 2008; Kanagaraj et al. 2008). Moreover many process innovations aiming at chemicals use reduction should be considered, following different pathways: reuse of baths containing chemicals (Nazer Dima et al. 2006; Santos et al. 2007), improvements in the adsorption of chemicals (Sivakumar et al. 2001; Bacardit et al. 2008), proposal of new products (Suresh et al. 2001; Dayanandan et al. 2003), proposal of new processes (Aravindhan et al. 2007; Saravanabhavan et al. 2007; Morera et al. 2008; Saravanabhavan et al. 2008; Sivakumar et al. 2009; Valeika et al. 2009). As regards the models and data used in the present study, the availability of more data on the recovery processes (mass balances, amount of residues going to landfill during the recovery process, energy and water use and chemicals used) would lead to a better comparison of the environmental improvements of the different options. Moreover, from the data quality checks it emerged that the most uncertain element concerns the estimation of the emissions from the landfill disposal of both the wastewater treatment sludge and the solid wastes which are generated by the slaughtering and the tannery processes. Further studies dealing with inventories of recovery processes of tanning and slaughtering residues and with the landfill disposal of slaughtering and tannery solid wastes are recommended.

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