Environmental assessment of enzyme application in the tanning industry

Per H Nielsen from Novozymes makes an environmental comparison of chemical and enzyme-assisted bovine leather soaking and unhairing/liming processes in a Chinese tannery

Introduction

Enzymes have been used in the tanning industry for centuries because they are efficient in degrading protein and fat. In early times, the enzymes were derived from animal excrement and later on from the pancreas of cattle. Nowadays, the enzymes are almost entirely produced by microbial fermentation.

Microbial enzymes are highly specific and fast in action and are used in the tanning industry in soaking and unhairing processes because they can replace chemicals and shorten processing time, thereby reducing production costs.

Novozymes is a major supplier of enzymes to the tanning industry and has collaborated with a Chinese customer to assess the environmental implications of enzyme application in soaking and unhairing as an integrated part of the companies' environmental responsibility strategies.

The purpose of this paper is to share the results with a broader audience and to communicate the message that enzymes not only add to the tannery's bottom line through chemical savings, increased yield and improved quality of the final product, but also to the company's environmental profile.

Enzymes are biological catalysts with an enormous capacity to increase the speed of biochemical reactions. They have evolved over millions of years and are found in any living organism. In our own bodies they play an essential role, for instance in degrading the food we eat.

Enzymes are proteins not living organisms. They are everywhere in nature and can be easily degraded in natural environments as well as in wastewater treatment facilities.

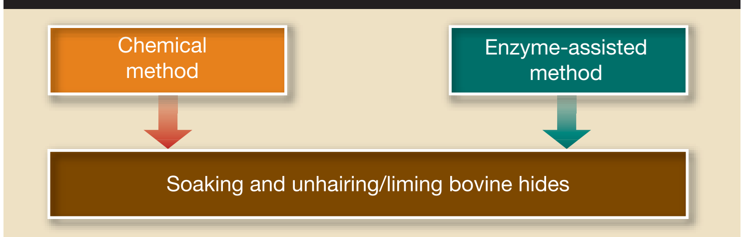
Enzymes are produced industrially today and are used in many industries to take advantage of nature's own workmanship.

The tanning industry is a diverse industry with a variety of production methods reflecting the diversity of hides and tanneries and the individuality of tanners. This study has focused on a single tannery in China and it should be recognised that the results might have come out differently if the study had been carried out in other tanneries elsewhere in the world.

Method

The assessment is basically a comparison of two different ways of achieving the same result in the tanning industry, namely soaked and unhaired/limed bovine hides using either an entirely chemical method or using an enzymatic method with reduced chemical consumption. (see Figure 1).

Figure 1: The study compares chemical and enzyme-assisted soaking and unhairing/liming processes



Lifecycle assessment (LCA) has been used as an environmental analytical tool and, in practice, the study has addressed the changes in enzyme and chemical consumption that occur when switching from the chemical method to the enzyme-assisted method.

Information about changes in chemical consumption related to soaking and unhairing processes was collected from the Chinese

Principle of lifecycle assessment (LCA)

LCA is an holistic environmental assessment tool which addresses raw material uses and emissions in all processes in the product chain from raw material extraction through production to use and final disposal (Wenzel *et al* 1997)

The environmental impact potential of substance i emitted to the environment from a process is calculated as:

$$EP(j)_i = Q_i \cdot EF(j)_i$$

Where

Q_i is the emitted quantity of substance i
j is the environmental impact (eg global warming)
i is CO_2, CO, CH_4, N_20, NO_3, PO_4, SO_2 etc
EF is an effect factor

EF (global warming)$_{CO_2}$ = 1g CO_2 equivalent per g
EF (global warming)$_{CO}$ = 2g CO_2 equivalents per g etc

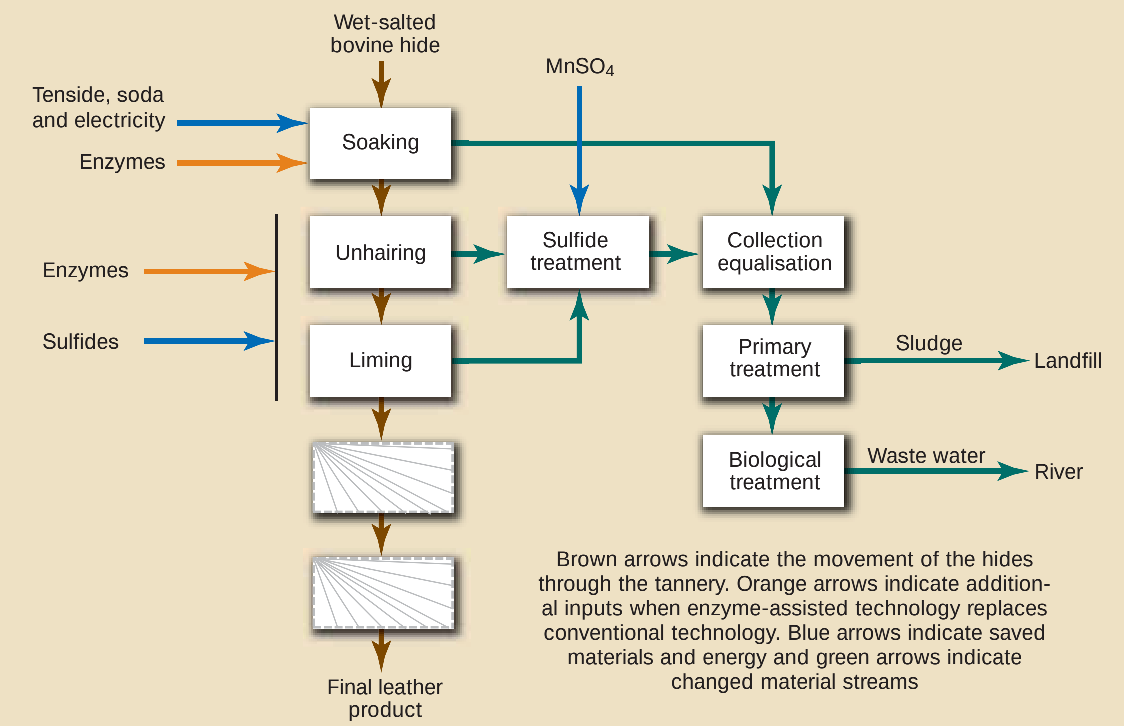
The environmental impact potential of a product

$$EP(j)product = \sum(Q_i \cdot EF(j)_i)$$

See www.howproductsimpact.net for a quick introduction to the LCA concept

Modelling has been facilitated in SimaPro 6.04 LCA Software

Figure 2: System boundaries of the environmental assessment



Brown arrows indicate the movement of the hides through the tannery. Orange arrows indicate additional inputs when enzyme-assisted technology replaces conventional technology. Blue arrows indicate saved materials and energy and green arrows indicate changed material streams

tannery which uses chemical as well as enzyme-assisted production methods.

It was originally envisaged that information about changes in chemical use when enzymes are introduced to the soaking and unhairing/liming processes could be obtained by comparing the tannery's enzyme-assisted process with the chemical processes. However, early in the project it turned out that this was not possible because other differences between the two process lines would overshadow the differences caused by the application of enzymes.

It was, therefore, decided to base the study as far as possible on true production records and to supplement these with the production manager's changes in recipe if he should switch between chemical and enzymatic processes. The study refers to a hair-saving process.

System boundaries of the study

The main system boundaries of the environmental assessment are shown in Figure 2.

Soaking enzymes are active against fat and proteins and they reduce the required soaking time and the tenside and soda requirements for the process. Reduced soaking time leads to electricity savings in turning the drum.

Unhairing enzymes are active against proteins and reduce the sulfide requirements for the process but do not influence processing time. However, a lower level of sulfide application reduces the sulfide content of the wastewater, and some $MnSO_4$ used in sulfide treatment can, therefore, be saved.

Enzymes do not influence the temperature requirements for the processes and no changes in terms of heat consumption are considered in the environmental assessment. Application of enzymes may increase the area of the final leather product to some extent. However, this increase is difficult to quantify exactly and has been ignored in this assessment.

The use of enzymes in the soaking and unhairing/liming processes does not influence other processes in leather-making and processes after liming are disregarded, as indicated by dotted boxes. Details on changes in chemical use and electricity consumption induced by enzyme application are specified in Table 1.

Chemicals and enzymes used in production are transported from various suppliers to the tannery and a rather rough transportation scenario for the most important process has been included in the study. However, transportation turned out to be quite insignificant for the overall outcome of the study and has not been given further attention here.

Table 1 shows that a relatively small quantity of enzymes displaces a quite large quantity of

Shopping for leather clothing is a popular pastime

Table 1: Changes in inputs to soaking and unhairing/liming process when enzyme-assisted processes replace conventional processes. All data are provided per ton wet salted hide.

Compound and location of supplier	Soaking	Unhair/ liming	Reference and geographical source of data	Comment
Soda (Na_2CO_3) China	-1.6kg	-	Eco-invent (2003) Europe	Solvay process: $2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$. Both products of the process (Na_2CO_3 and $CaCl_2$) are useful for a variety of purposes, but it is assumed that the marginal $CaCl_2$ is wasted (see Weidema 2003) and all impacts are assigned to Na_2CO_3
Tenside Europe	-0.8kg	-	Eco-invent (2003) Europe	It is assumed that palm oil is the marginal source of oil for tensides and all processes from palm growing through oil pressing, fatty methyl esther production (with methanol produced from natural gas) to ethoxylated alcohol production (with ethylene oxide from mineral oil) are included in the assessment. Co-products are accounted for by system-expansion (Weidema and Wesnæs, 2005)
Sodium sulfide (Na_2S) China	-	-15kg	Zhou (2005) China	Na_2S is produced from anhydrous sodium sulfate by reduction with carbon: $Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$ at 700-900°C. Data refer to conventional production in China. It is assumed that Na_2SO_4 is extracted from the ground. Coal serves as carbon and energy source
Organic sulfides Various suppliers	-	-1.3kg	Ecoinvent (2003) Ullmann's (2005) Europe	Various organic sulfides are used in production. Organic sulfide consumption is only slightly changed when enzymes are applied and for simplicity it is assumed that all applied organic sulfides are mercaptoethanol. Mercaptoethanol is produced industrially by adding H_2S to ethylene oxide under basic conditions. Energy consumption, use of base and catalyst and yields of the process are unknown and only raw material uses based on stoichiometric calculations are included in the study. Data on ethylene oxide: Ecoinvent (2003). Data on H_2S: Ullman's (2005)
Manganese sulfate ($MnSO_4$) China	-	-0.67kg	Ecoinvent (2003) Patyk and Reinhardt (1997) Europe	$MnSO_4$ is produced from MnO: $MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O$. Quantity is small and $MnSO_4$ turned out to be unimportant for the final outcome of the study
Electricity China	-2.1kW	-	Ecoinvent (2003) Europe	When electricity demand for turning the drums in the soaking process decreases as a result of enzyme application, the marginal source(s) of electricity will be influenced. The Chinese electricity network is large and complex and the marginal source is difficult to identify. Based on information provided in 'China Country Analysis Briefs' DOE (2005) electricity produced from coal is considered the most likely marginal source of electricity to the tannery
Greasex 50 L	+0.2kg	-	Nielsen et al (2006)	Enzymes are produced in a three step procedure: fermentation, filtration and formulation at Novozymes' production sites in Denmark, USA and China. Modelling includes all electricity, steam and water consumptions, all waste treatment processes and at least 95% (w/w) of ingredients (primarily, carbohydrates and proteins (fermentation), filtering materials (filtration) and sodium sulfate and kaolin (formulation). Modelling is based on principles described by Nielsen et al (2006)
Novocor S 2500 C	+ 2.0kg	-		
NUE 0.6 MPX	+ 0.25kg			

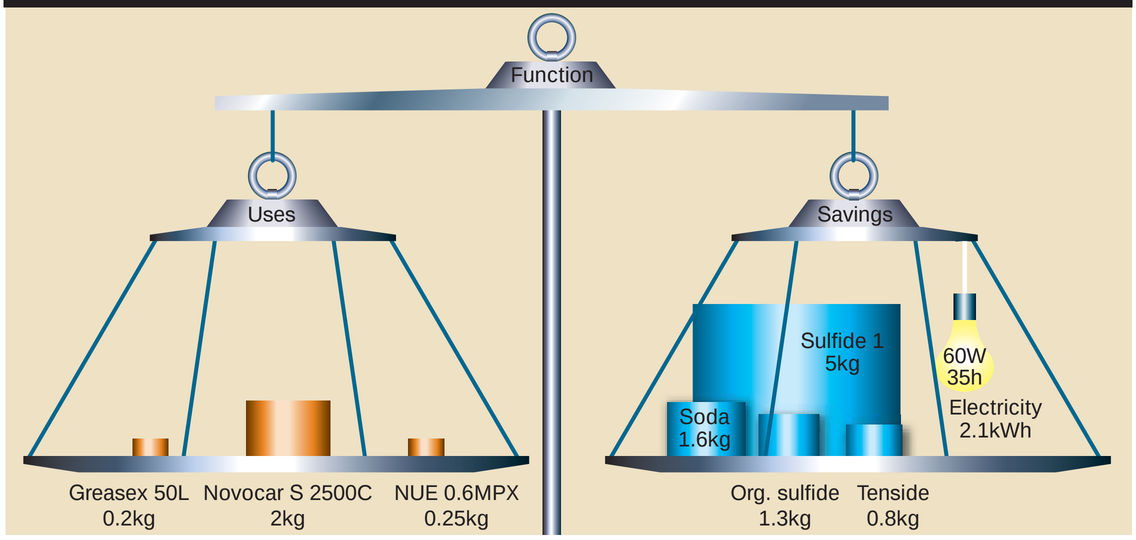
chemicals. The same is illustrated in Figure 3.

Data quality assessment

Soaking and unhairing/liming: Quality of data derived directly from the tannery on soaking and unhairing/liming is generally considered high, although it must be acknowledged that some data are based on the tanner's experience and not records of a full-scale production process in operation.

Production of displaced chemicals: Many of the chemicals which are replaced as a result of enzyme application are produced in China. However, LCA databases in China are very limited and with a single exception (Na_2S), all data on the production of chemicals refer to European production processes. The fact that the modelling of

Figure 3



A relatively small quantity of enzyme products (orange cans) provide the same function in the tannery as a relatively large quantity of chemicals (blue cans) and some electricity. Saved electricity is equivalent to using a 60W light bulb for 35 hours. The volume of cans provides an indication of quantity in terms of weight. All figures are given per ton of wet-salted hide

displaced chemicals is largely based on European data instead of true Chinese data, contributes to the uncertainty of the study. It is, however, worth noting that the uncertainty is likely to favour the chemical process because the Chinese chemical industry is generally less efficient and more polluting than the European industry. This results in an underestimation of the environmental impacts from the production of chemicals when basing it on European data. The final results of the study are, therefore, likely to underestimate the environmental advantage of the enzymatic solution.

Production of enzymes: Modelling is based on very detailed production information. Modelling is scientifically documented (see Table 1) and the quality of data is considered high.

Results

The environmental impacts of producing and delivering the enzymes to the tannery on the one hand and saving chemicals and electricity on the other have been evaluated (see Table 2) and the results in terms of energy consumption and contribution to global warming are shown in Figure 4.

Figure 4 shows that a small 'investment' in energy and CO_2 emission in enzyme production results in considerable savings when the products are replacing chemicals and electricity in the soaking and unhairing/liming processes.

Contributions to other environmental impacts (acidification, nutrient enrichment and smog formation) follow the same pattern (data not shown) and it appears that environmental impacts induced by enzyme production are at least 20 times lower than avoided impacts obtained by chemical and electricity saving. Data quality assessment suggests that environmental impacts of saved chemicals is prone to be underestimated and it is likely that real savings are even higher.

Sulfide saving in the unhairing/liming process is considerable compared with other chemicals and, since a large quantity of coal is used to produce sulfides and a large quantity of CO_2 is emitted during production, the saving of sulfide turns out to be the most important environmental effect of enzyme use (see Table 2).

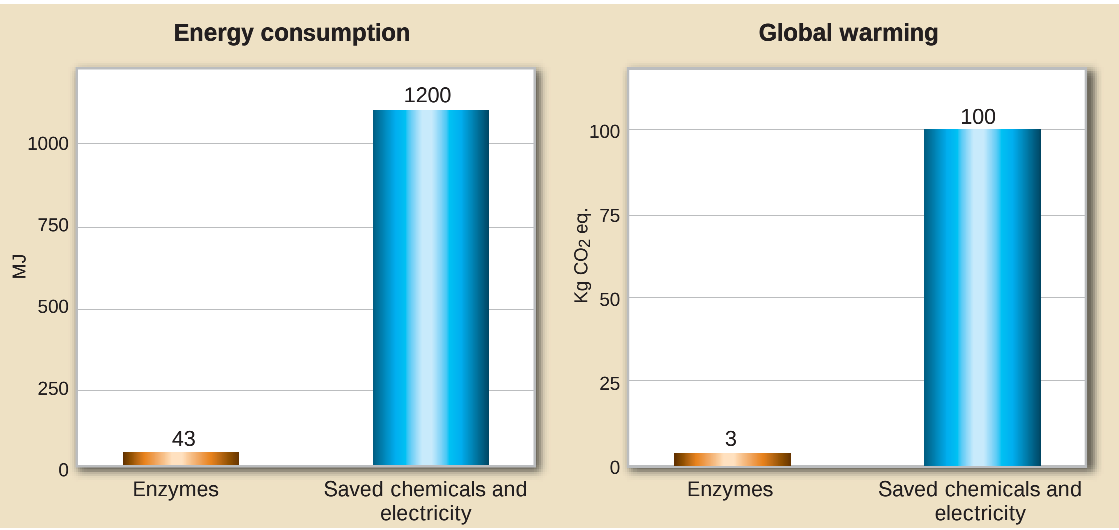


Figure 4: Use of energy and contribution to global warming from enzymes and from saved chemicals and electricity when enzymes are introduced in soaking and unhairing/liming processes. Energy consumption refers to primary fossil energy, ie the low heat value of coal, oil and gas when still in the ground

Table 2: Share of environmental improvements (global warming) when enzymes are introduced in soaking and unhairing/liming processes

Table 2			
Soaking			Unhairing/ liming
Soda saving	Tenside saving	Electricity saving	Sulfide saving
0.5%	0.5%	1%	98%

Agricultural land use

Enzymes are produced by microorganisms fed with carbohydrates produced in agriculture, and the environmental gains in terms of avoided environmental impacts and energy saving may thus have been at the expense of agricultural land use. However, the production of tensides is also based on agricultural crops (palm oil) and an evaluation of the land use indicates that the total area of agricultural land used for enzyme production is around 0.3m^2 in one year, whereas the saved area of land due to tenside saving is about 0.5m^2 in one year.

It is, of course, difficult to compare different types of agricultural land use but the results indicate that in total there is no trade-off in terms of land use when enzymes are used in the tanning processes under consideration – there may even be a small advantage.

Toxicity assessment

Toxic impacts on the environment and human health have not been included in the quantitative assessment because details of the emissions of relevant substances and the fate of these after emission in large parts of the system are not known. Processes that are considered likely to contribute to toxicity have, however, been assessed qualitatively and in summary it is considered likely that the enzymatic solution is far less toxic than the non-enzymatic solution. This is because a relatively small amount of low-toxic enzyme products arising from a low-toxic biological production process and a range of low or non-toxic raw-materials replaces a relatively large amount of toxic materials produced in a range of chemical production processes using a relatively large quantity of mostly coal-based energy.

Sensitivity analysis

This assessment is based on a range of assumptions and simplifications which contribute to the uncertainty of the final outcome of the study. The implications of most of the simplifications and assumptions can only be addressed qualitatively, as has already been done under 'Data quality assessment', but a few remain that will be addressed quantitatively in the following:

Electricity scenario

Enzymes are to a large extent produced in Denmark, whereas replaced electricity in the tannery is produced in China. It is assumed that the marginal electricity is derived from coal-fired power plants in China, whereas it is derived from natural gas-fired power plants in Denmark (see Nielsen *et al* 2006). However, the electricity scenarios have not been established with certainty and it cannot be excluded that it might also be the other way round. Sensitivity analyses where Danish and Chinese electricity scenarios have been reversed (Denmark: from natural gas to coal-based electricity; China: from coal to natural gas-based electricity) have therefore been performed.

A switch from coal-based electricity to natural gas-based electricity in China reduces the contribution to global warming from the non-enzymatic process by about 10%. A switch from natural gas-based electricity to coal-based electricity for enzyme production increases the impacts associated with enzyme production by about 15-20%. In summary, it is justified that enzymatic soaking remains environmentally favourable compared with non-enzymatic soaking, although the difference in environmental impact between the two solutions is reduced slightly.

Sodium sulfide production

Data on sodium sulfide production refer to the current average Chinese production but average Chinese production is not optimised and this means that a highly optimised and modernised enzyme-based production is, in fact, compared with a traditional chemical-based production.

However, Zhou (2005) has analysed the improvement potential in Chinese sodium sulfide production and an optimised process has been applied in the model as an alternative to the conventional process.

Coal consumption for sodium sulfide production is reduced considerably when the optimised sodium sulfide production process replaces the conventional process and impacts on the environment from the sulfide would have been reduced by about 30% if sodium sulfide from an optimised process had been used in the process. This is considerable but it does not alter the overall observation that the enzymatic solution is clearly preferable from an environmental point of view.

Soaking and unhairing technology

The tanning industry is a diverse industry with a variety of production methods reflecting the diversity of tanneries and the individuality of tanners. The present study has focused on a modern process line with hair-saving technology and it is acknowledged that the results might have come out differently if the study had been carried out in other tanneries. To address some of this diversity, a similar assessment has been made in one of the tannery's conventional process lines with hair-burning technology. Inputs of enzyme increased, saving of electricity increased and saving of chemicals changed both up and down compared with the baseline study. The overall observation that enzyme application provides considerable environmental advantages was the same, although the total saving of fossil energy resources and the contribution to global warming was about 30% lower.

Figure 5 (picture): CO_2 emissions corresponding to 170,000 cars' annual emissions could potentially be saved if all bovine hides in the world were soaked and unhaired/limed in enzyme-assisted processes as an alternative to conventional processes. Today, less than 10% of bovine hides are soaked and unhaired in enzyme-assisted processes

Conclusion and outlook

A comparison of conventional and enzyme-assisted bovine soaking and unhairing/liming processes indicates that the application of enzymes in the tanning industry is justified by considerable energy savings and considerable reductions in the processes' contribution to global warming.

The advantages of enzyme application are primarily due to sulfide saving in the unhairing/liming process because a small quantity of enzyme replaces a considerable amount of sulfide, which has a relatively high environmental load.

Data quality assessments indicate that the observed environmental advantages of enzyme application in the soaking and unhairing/liming processes may be underestimated because modelling of many chemical production processes occurring in China is based on European data.

Sensitivity analyses show that the results of the assessment are sensitive to sources of electricity and to sodium sulfide production technology. However, nothing indicates that changed electricity scenarios or changed sodium sulfide production scenarios would change the overall conclusion of the study.

Novozymes is continuously developing enzymatic solutions and it has been envisaged on the basis of preliminary tests that new and further optimised enzymes can virtually replace conventional chemicals in the soaking and unhairing processes. An environmental assessment of a vision for the future indicates that the environmental burden of the soaking and unhairing/liming processes can be reduced even further by implementing increasingly efficient enzymes and replacing conventional chemicals.

The global supply of bovine hides was about 8.8 million tons in 2005 (FAOSTAT, green weight of cattle and buffalo hides), which is equivalent to about 7 million tons of wet-salted hides (about 20% weight loss during salting).

Assuming that the environmental improvements observed in this paper by switching from conventional to enzyme-assisted soaking and unhairing/liming are applicable worldwide, the global saving potential is in the order of 8 million GJ of energy and 0.7 million tons of CO_2 per year. The saved CO_2 emissions are equivalent to the annual load of 75,000 average world citizens or 170,000 cars. ■

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