Life Cycle Assessment (LCA) of the Oxidative Unhairing Process by Hydrogen Peroxide*

by

Domenico Castiello[1], Monica Puccini[2], Maurizia Seggiani[2], Sandra Vitolo[2]**, Francesco Zammori[3]

[1] *Po.Te.Co. Scrl - Polo Tecnologico Conciario,*

Via Walter Tobagi, 30 56022 Castelfranco di Sotto Pisa, Italy

[2] *Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali - Università di Pisa,*

Via Diotisalvi, 2 56126 Pisa, Italy

[3] *Dipartimento di Ingegneria Meccanica, Nucleare e della Produzione - Università di Pisa,*

Via Bonanno Pisano, 25/B - 56126 Pisa, Italy

Abstract

The ever increasing attention to the environmental impact of the process industries imposes an obligation to constantly improve the global sustainability of the leather tanning process. Among the numerous phases of the tanning process, the beamhouse accounts for most of the total polluting charge, due to the use of sodium sulfide and lime during the manufacturing process of hides. Hence, the authors have recently developed an alternative unhairing process that eliminates the use of sulfides. The actual reduction of the environmental impact of this process, in relation with the traditional one, was evaluated performing a Life Cycle Assesment (LCA) using SimaPro 6, one of the most used software for LCA analysis. Environmental impacts were finally rated using "EDIP 97" assessing methodology. Since impact assessment methodologies were mainly developed for the manufacturing field, EDIP 97 was slightly modified and adapted to fit with the tannery industry.

Resumen

La siempre creciente atención prestada al impacto ambiental en la industria de transformación impone la obligación de crear una mejora contínua en la sostenibilidad global del proceso de curtición. Entre las numerosas fases de la curtición, la ribera genera la mayoría de la carga contaminante total, debido a uso del sulfuro de sodio y cal durante el proceso de manufactura de pieles. Tal cual entonces, los autores han recientemente desarrollado un proceso alternativo de apelambrar que elimina el empleo de sulfuros. La real merma del impacto ambiental debido a este proceso comparado con el tradicional, se evaluó por medio del Cateo del Ciclo de Vida (LCA) utilizando SigmaPro 6, uno de los más empleados softwares en el análisis LCA. Impactos ambientales fueron finalmente valorados por uso de la metodología de valoración "EDIP 97". Como las metodologías de valoración del impacto ambiental fueron desarrolladas principalmente para el ramo de la manufactura, EDIP 97 se modificó ligeramente y se adaptó para cuadrarse a la industria curtidora.

Introduction

The tanning industry generates great amount of wastes and causes several negative effects on the ecosystem. Considering the ever increasing attention toward environmental themes, it is necessary to minimize the pollution charge of effluents and to decrease production of wastes.

Among the several phases of the tanning process, the beamhouse is responsible for most of the overall impact, as it generates 83% of BOD_5, 73% of COD, 60% of suspended solids, 68% of salinity and 76% of total polluting charge produced during the manufacturing process of hides. This is because the traditional unhairing process requires sodium sulfide and lime in the beamhouse phase. Besides, the fleshing operation that follows the unhairing phase generates a waste (mainly constituted by collagen) whose reutilization and valorization, as a valuable protein source, may be precluded by the presence of sulfides. Consequently, the development of an alternative unhairing process, with an environmental impact lower than the traditional one, represents a priority. To the scope, a recent research activity has been conducted by the authors (S. Bronco *et al.*, 2005). The obtained alterative unhairing process is based on the use of hydrogen peroxide and makes it possible to avoid sulfides utilization. To assess the quality of the finished leather (obtained through the oxidative unhairing process), several experimental activities have been performed, both on a laboratory and on an industrial scale. Results have shown that the finished leathers are comparable to that obtained by the traditional process in terms of physical-mechanical and technical properties. In addition, the process has proved to be practical and economical to be implemented, because it is compatible with the existing machineries installed in the plant.

* A **Technical Note** based on a presentation at the XXIX IULTCS Congress and103[nd] annual meeting of the American Leather Chemists Association at the JW Marriott Hotel, Washington, DC, on June 22, 2007

** Corresponding author - E-mail: vitolo@ing.unipi.it

Manuscript received June 21, 2007, accepted for publication July 12, 2007

Given the technical and the economical feasibility of the oxidative unhairing process, the objective of the present work consists in the evaluation of the actual reduction of the environmental impact in relation with the traditional one. To the scope, a Life Cycle Assesment (LCA) was made.

LCA is a methodology that provides a quantitative basis to assess the environmental performance of a product and/or a process. The most important applications are: (*i*) analysis of the contribution of the life stages to the overall environmental load, and (*ii*) comparison of products and/or processes designed to fulfill the same function. First applications of LCA took place in the early nineties and nowadays LCA studies are receiving an increasingly deal of attention, especially to compare products such as: paper/ceramic/plastic cup, polyetilene/cardboard packages, plastic/mirror bottles, paper/cloth diapers, paper/plastic/durable shopping bags (Matthews *et al.*, 2002). Other typical applications concern the agri-food industry, and the energy production field. Excellent applications can be found in: Andersson *et al.* (1993), Koroneos *et al.* (2003), Ardente *et al.* (2005), Finnveded *et al.* (2005). On the contrary, fewer applications directly address chemical processes (Munoz *et al.*, 2006), and the tanning process in particular (Rius *et al.* 2002).

In the present work, the oxidative unhairing process is compared to the traditional one focusing in particular on the life cycle stages that account for most of the environmental loads: *(i) Na_2S production, (ii) H_2S production, (iii) H_2S waste treatment, (iv) unhairing*. LCA was accomplished by aim of SimaPro 6, one of the most used software for life cycle analysis in the industrial field. Environmental impacts were finally rated using EDIP 97 assessing methodology. Since impact assessment methodologies were mainly developed for the manufacturing field, EDIP 97 was slightly modified and adapted to fit with the requirements of the tannery industry.

LCA DESCRIPTION

LCA is a quantitative and objective technique for assessing the environmental performance of a product and/or a process over its life cycle (Wenzel *et al.* 2000). The basic concept is that the impact an item has on the environment does not depend exclusively on the manufacturing process, but begins with the design and ends with the final disposal (Zabaniotou, Kassidi, 2002). For this reason, all the inputs (i.e. energy, material, etc.) and the outputs (i.e. products, waste materials, emissions, etc.) must be identified and quantified for each life stage of a product. Only in this way it is possible to objectively evaluate its impact on the environment. According to the definition given in the international standard ISO 1400, LCA is based on four sequential steps. These are listed below:

Aim and Scope definition (ISO 14040).

The *aim* is a brief description of the reasons for using LCA, while the *scope* is a clear definition of the main choices, assumptions and limitation of the analysis. The main issues to be addresses are the following ones. *Functional unit* that is the reference quantity used to evaluate, in relative terms, two alternative products. To keep the comparison fair the functional unit should refer to the function fulfilled by each product. *System boundaries* that specify which unit processes (i.e. life stages) are included in the analysis. Three alternative approaches are possible: (*i*) first order (i.e. only production and transportation of material are considered), (*ii*) second order (i.e. all process are included, but equipments and ancillary goods are not considered), (*iii*) third order (i.e. also equipment are taken into account). *Allocation rules* are used whenever a process realizes more than an output, or performs more than a function. Under these circumstance it must be defined how the environmental loads of a process are allocated among its several outputs.

Life Cycle Inventory (ISO 14041).

During LCI, a model is made to represent the technical system used to produce, transport, use and dispose of a product. This results in a flow diagram containing all the unit processes of the entire life cycle. Furthermore, for each unit process, all the inflows and outflows must be quantified (on a volume or mass basis) and listed into different environmental categories, relevant to resource use, human health and ecological areas.

Life Cycle Impact Assessment (ISO 14042).

To determine which flows are significant and how great is their contribution, data contained in the LCI must be interpreted. To do that, a model of environmental mechanisms is used to establish a connection between the environmental loading and

TABLE I
Input - Output of the unhairing processes

		Oxidative Unhairing	Traditional Unhairing
Input	Na_2S	0 [kg]	0.043 [kg]
	$Ca(OH)_2$	0 [kg]	0.04 [kg]
	NaOH (50%)	0.096 [kg]	0 [kg]
	H_2O_2	0.09 [kg]	0 [kg]
Output	COD	85.9 [kg]	106 [kg]
	suspended solids	58.73 [kg]	59.9 [kg]
	Nitrogen (as NH_4+)	0.8 [kg]	0.6 [kg]
	Sulfides (as S_2-)	0 [kg]	4.6 [kg]

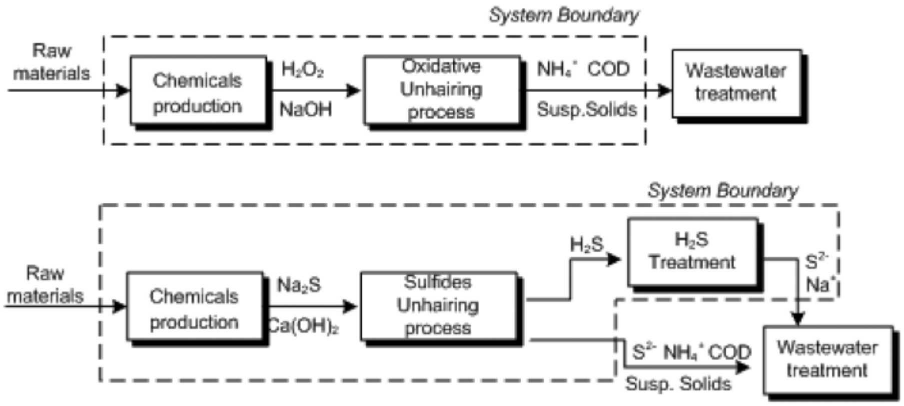

Figure 1: Processes flow diagram

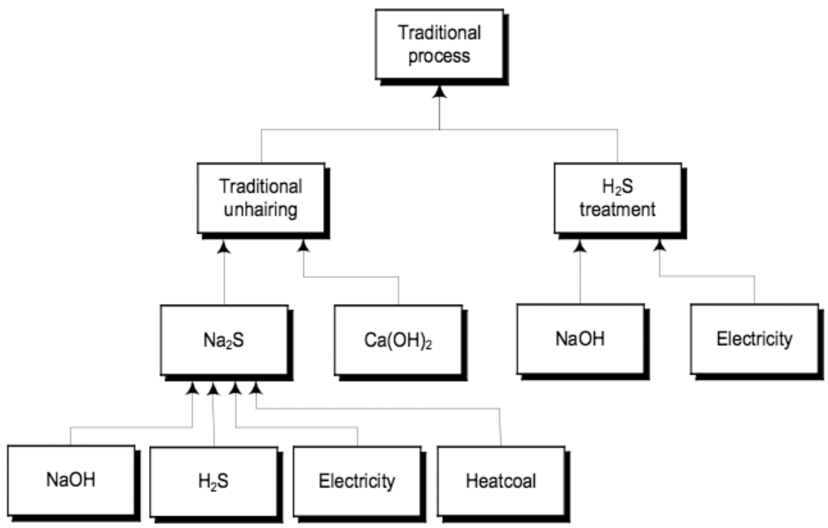

Figure 2: Life cycle of the traditional unhairing

known exposure pathways to humans and ecology. Using several environmental mechanisms, LCI results can be translated in a number of environmental issues of concerns (i.e. impact categories) such as: acidification, ozone depletion, climate change, eutrophication etc... The contribution of a parameter to a certain impact category is then evaluated through an equivalence factor that expresses its effects in relation with a reference parameter. For example CO_2 is the reference parameter for the "climate change" category and the equivalence factor for CH_4 is 42 (i.e. contribution of 1 Nm^3 of CH_4 is 42 times as high as the emission of 1 Nm^3 of CO_2). Clearly, determination of equivalence factors is the most difficult and controversial step of the process, but can be often overcome applying standard procedures (CML2, EDIP, ECO-Indicator) purposely developed to the scope.

Results are finally normalized to describe their magnitude in relation to a background impact that is generally expressed as the average impact per person.

Interpretation and improvements (ISO 14043).
The last step mainly consists in the validation of the obtained results and in the development of feasible solutions intended to reduce the overall impact.

Methodology

Considering that the objective of the present work consists in an environmental comparison of two alternative processes, LCA have been accomplished in relative terms using a third order approach, and considering only inputs and outputs that change with the alternative. This is clearly represented in Figure 1 that shows the main phases considered in the analysis.

For what concerns the leather productive process, the main differences can be found in the inputs required at the unhairing stage. On the contrary, energy flows, required machineries and ancillary goods remain unchanged. Another major difference is due to the fact that the traditional process requires a system to eliminate H_2S generated during the unhairing process, while this step is completely eliminated through the adoption of the oxidative process that uses oxygen peroxide instead of sodium sulfide. Please note that the boundary of the system here considered includes the production of chemicals used for the unhairing process. In fact, accordingly to the main principles of LCA, all the environmental impacts occurring during the life cycle of an item must be taken into account. If this was not made, the comparison would not be made on an equal base because environmental loads upstream the unhairing process would be neglected.

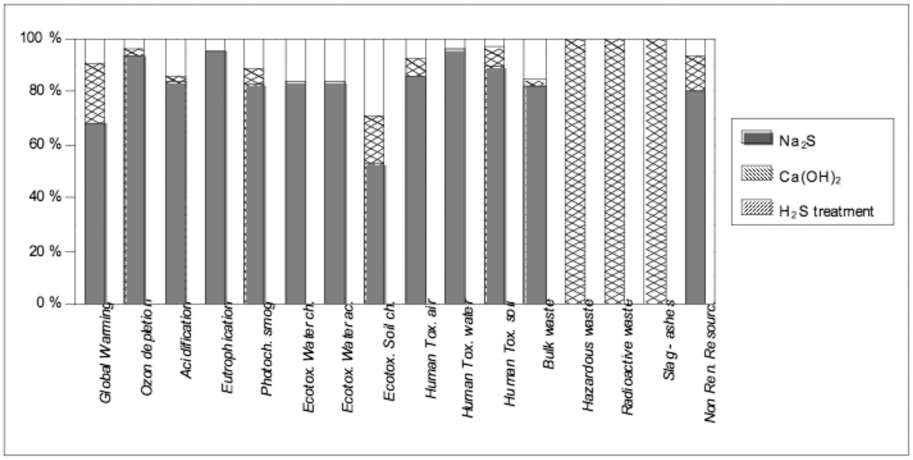

Figure 3: Relative contribution of the inputs of the traditional unhairing proces

TABLE II
Normalized Results Per Impact Category

Impact Categories	Oxidative Unhairing	Traditional Unhairing
Global warming	1.96E-05	1.43E-05
Ozone depletion	1.08E-07	3.65E-07
Acidification	9.73E-06	8.80E-06
Eutrophication	9.32E-03	6.90E-03
Photochemical smog	7.12E-06	7.69E-06
Eco-toxicity water chronic	3.73E-04	7.00E+01
Eco-toxicity water acute	3.68E-04	3.36E+02
Eco-toxicity soil chronic	6.11E-05	4.34E-06
Human toxicity air	2.46E-06	1.29E-06
Human toxicity water	3.11E-05	3.49E-04
Human toxicity soil	4.77E-05	2.44E-05
Bulk waste	7.91E-06	3.44E-06
Hazardous waste	1.68E-07	1.43E-09
Radioactive waste	1.27E-04	4.78E-06
Slag/ashes	4.38E-06	7.01E-10
Non Renewable Resources	1.00E-08	1.00E-08

This is especially true in the present case. In fact, if the boundary was not extended to include the production of chemicals, the impact of the oxidative process would obviously yield results lower than the traditional one for the absence of sulfides in the wastewater and in the emissions.

Input flows and emissions at the unhairing phase were collected directly on the field, and are listed in Table I. Please note that the amount of each pollutant is evaluated per kg of salted hides that represents the functional unit adopted for the present work.

Other data were taken from the Buwal and the Ecoinvent Database, both included in the library of the software SimaPro 6, which has been used to develop the LCA model. This is clearly shown in Figure 2, which displays the life cycle of the traditional unhairing process, defined in SimaPro 6.

In order to evaluate the environmental impact of both processes, taking into account the effect on the ecosystem and on the human health, the following impact categories have been considered: (*i*) global warning, (*ii*) ozone depletion, (*iii*) acidification, (*iv*) eutrophication, (*v*) photochemical smog, (*vi*) eco-toxicity water chronic, (*vii*) eco-toxicity water acute, (*viii*) eco-toxicity soil chronic, (*ix*) human toxicity air, (*x*) human toxicity water, (*xi*) human toxicity soil, (*xii*) bulk waste, (*xiii*) hazardous waste, (*xiv*) radioactive waste, (*xv*) slag and ashes, (*xvi*) non renewable resources.

Next, to evaluate contributions to each environmental issue of concern, EDIP 97 impact assessment methodology was selected. This choice was motivated by the fact that EDIP 97 is probably the impact assessment methodology more suitable for an application concerning a chemical process. In particular there is a perfect matching between the parameters for which EDIP 97 provides an equivalence factor, and the chemicals included in the LCI of the unhairing process. The only inconvenient was that, unfortunately, EDIP 97 in its standard way, does not take into account COD as parameters affecting the eutrophication impact category. However, COD is one of the main parameter used to characterize wastewaters of a chemical process, as the one here considered. To fulfill these requirements, a specific equivalence factor was computed in order to express the environmental load of COD in relation to the reference parameter (i.e. nitrates). The equivalence factor was evaluated in 0.23 point, making an interpolation of all parameters that characterize the eutrophication impact category in EDIP 97 and CML'96 impact assessment methodologies.

RESULTS

Results of the impact assessment step are graphically shown in Figure 3 and Figure 4. The bar chart of Figure 3 shows the relative contribution of the inputs of the traditional unhairing process for each environmental impact category. It is evident

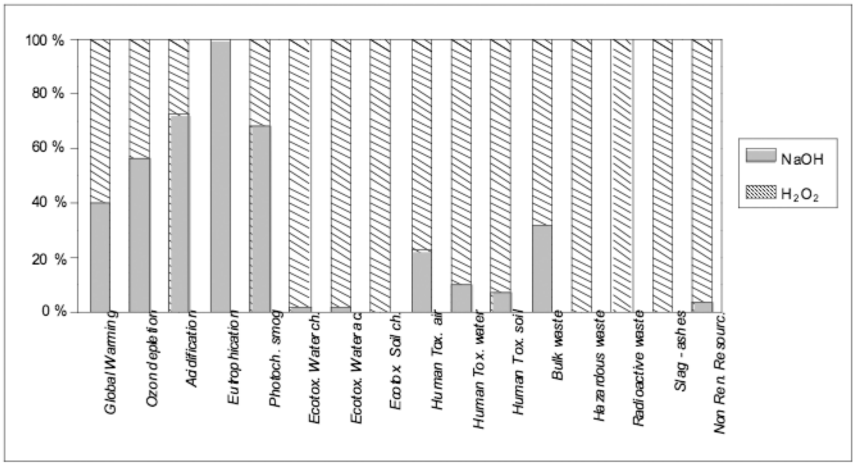

Figure 4: Relative contribution of the inputs of the oxidative unhairing process

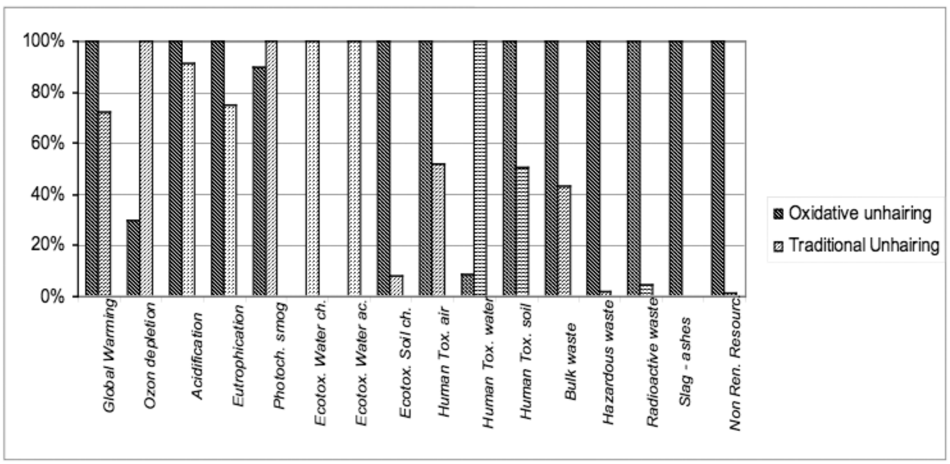

Figure 5: Impact assessment results

that the life cycle of Na_2S accounts for most of the whole environmental impact. Therefore the elimination of Na_2S from the unhairing process appears to be necessary to reduce the environmental impact. Please note that the environmental impact of Na_2S is due to the sulfides released in the wastewaters and also to its productive process.

The analogous evaluation for the oxidative unhairing process is shown in Figure 4, which shows how the life cycle of H_2O_2 accounts for most of the whole environmental impact.

Finally, Figure 5 shows, in relative term, which one of the alternative processes has the greatest impact for each impact category.

Take for instance the photochemical smog category. In this case, the oxidative process has an impact 0.9 times lower than the traditional one. As can be seen from Figure 5, the oxidative unhairing has an environmental impact greater than the traditional one in several impact categories. This is due to the production of oxygen peroxide that accounts for more than the 50% of the overall environmental impact.

As previously noted, for a fair assessment of results, data must be normalized to express their actual magnitude in relation to a known reference value that is the equivalent impact per person (i.e. the average annual impact generated by the ordinary activities performed by an individual).

Normalized data are listed in Table II.

As clearly shown in Table II, the impacts categories most significantly affected are "*Eco - Toxicity water chronic*" and "*Eco Toxicity water acute*". It is also evident that the adoption of the oxidative process makes it possible to greatly reduce impact in both these environmental impact categories. As far as the other categories are concerned, even if several impacts of the oxidative unhairing are greater than the traditional one, their normalized magnitudes may be considered not significant in terms of effects on the ecosystem and on the human health.

CONCLUSIONS

An alternative oxidative unhairing process has been previously developed by the authors. Given its technical and economical feasibility, the objective of the present work consists of the evaluation of the reduction of the environmental load, in relation with the traditional process.

To assess the environmental sustainability, LCA was used to compare the traditional and the oxidative unhairing process. The life cycle model for both processes has been implemented using the software SimaPro 6. Results show that "*Ecotoxicity water chronic*" and "*Ecotoxicity water acute*" are the most effected impact categories and that, damages on both these impact categories are greatly reduced through the adoption or the oxidative unhairing process.

At the moment, the process was investigated leaving the wastewaters treatment out of the boundaries of the system. Considering the results obtained, revealing that the main impact does effect water pollution, it seems desirable to extend the systems boundaries to also include the treatment of the wastewaters in the analysis. We intend to include this in our further research work.

Bibliography

1. Andersson, K.,Ohlsson, T., and Olsson, P., (1993), Life Cycle Assessment of food products and production systems, Part 1: LCA methodology, a literature review. *SIK - Report 599: I*, Swedish Institute for Food and Biotechnology.
2. Ardente, F., Beccali, G., Cellura, M., Lo Brano, V., (2005), Life Cycle Assessment of solar thermal collector, *Renewable Energy* **30**, 1031-1054.
3. Bronco, S.,Castiello, D., D'Elia, G., Salvadori, M., Seggiani, M., Vitolo, S., (2005), Oxidative Unhairing with Hydrogen Peroxide: Development of an Industrial Scale Process for High-Quality Upper Leather, *JALCA* **100**, 45-53, 2005
4. Koroneos, C., Roumbas, G., Gabari, Z., Papagianniodou, E., and Moussiopoulos, N., (2003), Life cycle assessment of beer production in Greece, *Journal of Cleaner Production* **13**, 433-439.
5. Finnveded, G., Johansson, J., Lind, P., Moberg, A., (2005), Life cycle assessment of energy from solid waste, *Journal of Cleaner Production* **15**, 2005.
6. Matthews, H., S., Lave, L.,Maclean, H., (2002), Life Cycle Impact Assessment: A Challenge for Risk Analysts, *Risk Analysis* **22** (5) 853-860.
7. Munoz, I., Rieradevall, J., Torrades, F., Peral, J., Domenech, X., (2006), Environmental assessment of different advanced oxidation process applied to a bleaching Kraft mill effluent, *Chemosphere* **62**, 9-16.
8. Rius, A., Hidalgo, R., Canela, J. M., Milà, L., Domènech, X., Rieradevall, J., and Fullana, P., (2001), Use of LCA for the comparison of different strategies in the tanning process, *Setac Europe*.
9. Wenzel, H., Hauschild, M. Z., Alting, L., (2000), Environmental assessment of products, volume 1: Methodology, Tools and Case Studies in Product Development, *Springer*.
10. Zabaniotou, A., Kassidi,E., (2003), Life cycle assessment applied to egg packaging made from polystyrene and recycled paper, *Journal of Cleaner Production* **11**, 549-559.