LIFE CYCLE ASSESSMENT OF POLYPHENOL EXTRACTION FROM WASTEWATER: CRITICAL REVIEW AND UPDATE[1]

GERMANA OLIVIERI (*) - ANNALISA ROMANI (**) - PAOLO NERI (***)

Abstract

The aim of this study was to carry out a survey and critical analysis of the Life Cycle Assessment study on polyphenol extraction from wastewater in the olive oil system, in order to continue and improve research on the methodology. The analysis treats the complete cycles of use, reuse and recycling of waste and scrap processing as "secondary raw materials" or as "innovative raw materials".

Data obtained from LCA screening of a process of polyphenol extraction by an adsorption/desorption resin mechanism were used in the study. Improvements to update Life Cycle Inventory (LCI) data using a multi-method approach of impact assessment and process modelling development have been proposed.

Riassunto

L'obiettivo del lavoro è di condurre una ricognizione ed un'analisi critica dell' applicazione di LCA all'estrazione di polifenoli dalle acque reflue di

[1] Paper presented at the XXIV National Congress of Commodity Science, Torino-Alba, June 23-24, 2009.

(*) Laboratory of Commodity Sciences and Quality of Resources, Economics, University of Florence, P.za Ugo di Toscana, 50100, Firenze, Italy . E-mail: germana.olivieri@enea.it
(**) Department of Pharmaceutical Sciences, University of Florence, Via U. Schiff, 6, 50019 Sesto F.no, Firenze, Italy. E-mail: annalisa.romani@unifi.it
(***) LCA-lab srl, spin off ENEA, c/o ENEA, Via Martiri di Montesole 4, 40129 Bologna, Italy. E-mail: paolo.neri@enea.it

vegetazione nel settore olivicolo-oleario per continuare e migliorare il filone di ricerca sulla valutazione di cicli completi per l'uso, il riuso e il recupero di reflui e scarti di lavorazione come materie prime seconde o materie prime innovative. Sono stati ripresi e riconsiderati dati ottenuti in uno studio preparatorio di un processo di estrazione di polifenoli mediante adsorbimento/desorbimento su resine e proposti miglioramenti in termini di aggiornamento dati di Life Cycle Inventory (LCI), approccio multi-metodo di valutazione del danno e avanzamento in termini di modellizzazione dei processi.

Keywords: Life Cycle Assessment, polyphenols recovery, multi-method approach, wastewater treatment.

Introduction

The present study is part of a PhD research project concerning Life Cycle Assessment (LCA) applications on the new agri-food and agri-industrial fields as an example of production of "novel food"[2] from wastes and wastewater recovery.

The aim of the research is to provide added value to environmental, energetic and economic aspects of innovative products manufactured by high technology.

LCA applications can evaluate the effects of the complete life cycle products, in terms of potential impact, on human health, ecosystem quality, depletion of resources and climate change. The recovery of scraps or waste material, for instance olive oil wastewater (OOWW), pulp, marc, leaves and branches as "secondary raw materials" or "new raw materials" is the basis of this work.

The first steps in the study were
1) to consider the problems of the olive oil sector, such as the disposal of olive oil wastewater and olive pulp;
2) to consider the optimization process of recovery of bio-components; and consequently 3) to obtain "green energy" as biomass.

Olive oil wastewaters are a source of pollution and their disposal is very difficult; olive pulp may be further processed and therefore be a source of economic revenue. Since polyphenols have a polar characteristic, during processing they undergo transformation, dissolving in much smaller quantities in the oil than in the wastewater.

[2] REG. CEE n.258/97.

Currently, agricultural and production waste from the olive oil sector are, in part, used in fertigation and the remaining portion is disposed of, requiring considerable economic expense for firms and severe environmental impact.

Italian law bans the discharge of olive oil wastewater into municipal sewerage systems, even though all municipalities are equipped with waste-water treatment plants. Olive oil wastewaters (OOWW) are characterized by high acidity, high values of BOD5 (Biological Oxygen Demand) and COD (Chemical Oxygen Demand), and by a high content of polyphenols and organic substances, thus the law prohibits discharge of these waters to avoid damage to municipal wastewater plants.

OOWW are acidic (pH 5-5.5) liquids which contain mineral salts, organic substances such as fats, proteins, sugars, organic acids, pectins, gums, and polyphenols, thus they are easily subject to decomposition.

The polyphenolic fraction of OOWW contains "free phenols" which are formed mainly by enzymatic hydrolysis of glycosides and esters naturally occuring in the pulp of olives. Some studies have shown that the polyphenols in wastewater have strong antimicrobial as well as antioxidant action, along with other actions.

The antimicrobial action makes OOWW disposal difficult, while the antioxidant action justifies in part OOWW recovery processes (1).

Material and Methods

The Life Cycle Assessment

Life Cycle Assessment is an objective evaluation procedure to examine the energetic and environmental impact related to a product, process or activity.

This procedure is carried out by identifying and quantifying energy and materials used and the amount of waste released into the environment.

The evaluation covers the entire life cycle of the product, process or activity and includes the extraction and treatment of raw materials, manufacturing, transport, re-use, recycling, and waste treatment.

Traditional methods focus on single elements of the production processes while LCA considers the entire system ('from cradle to grave') in which all phases of transformation are taken into account as they participate in the realisation of the production process.

In 1998 European environmental legislation introduced the ISO (International Standard Organisation) regulations with series 14040-44 related to LCA, which were then updated in 2006.

The phases for ISO LCA are:

1) Goal and scope definition, the preliminary stage where the purpose of the study, the functional units, system boundaries, the quality data, the assumptions and limitations are defined.

2) Life cycle inventory analysis (LCI), where input and output of the system are identified and quantified, giving as a result an eco-balance that considers energy, resources consumption, emissions to air, water and soil.

3) Life cycle impact assessment (LCIA) is carried out using indicators that quantify the impacts and that allow comparison of the different options. LCIA is divided into different stages: classification, the qualitative phase where the inventory data are divided into general damage categories such as Human Health, Ecosystem Quality, Resources and Climate change; characterization (of substances and impact categories), which identifies and weighs, within a single category, the type of damage related to the substance emitted or resource used; normalization, which allows comparison of damage categories that have different unit of measurement; evaluation, which assigns a value, in terms of importance to each environmental impact through an overall indicator (the point).

4) Life cycle interpretation and improvement. In this phase results are interpreted to identify critical environmental phases and to suggest technical and managerial improvement for process and product life cycle.

Damage evaluation method and indicators

In the present LCA study a multi-method approach of impact assessment was chosen since the evaluation methods have different substance characterization factors. The evaluation method IMPACT 2002+ (2) and some indicators chosen by CML method (3) and other sources (4-9) were used. The Impact 2002+ method inlcudes four damage categories: Human Health, measured in DALY (Disability Adjusted Life Year); Ecosystem Quality, measured in PDF*m^2*yr (Potentially Disappeared Fraction); Climate Change, measured in kg of CO_2 equivalent in air, that derives from impact category Global warming; Resources, in MJ, starting from midpoint categories; Non renewable energy and Mineral extraction.

The other set of indicators used for the sensitivity analysis (to compare results obtained with the application of the Impact 2002+ method) are: Global Warming (GWP 100) (3-4), Ozone layer depletion (5), Acidification (6), Photochemical Ozone Creation Potentials (7), and Eutrophicating compounds (8). The results of these indicators are expressed in equivalent substances (midpoint).

Results and discussion

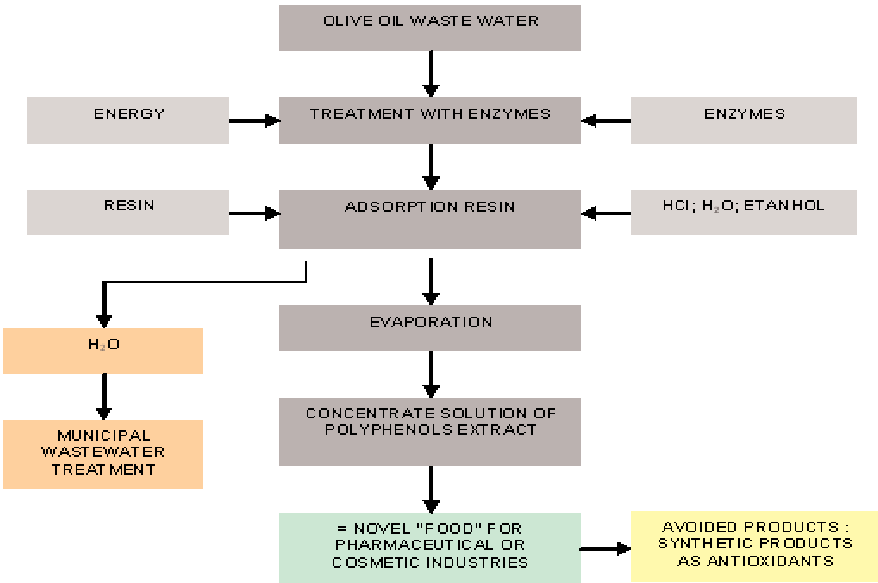
The preliminary study

Data obtained in a LCA screening study (9) of a process of polyphenol extraction from OOWW by adsorption/desorption resin mechanism (10) were used.

The LCI modelling of the resin adsorption/desorption process has the advantage of establishing an innovative methodological approach and ensuring implementation of further studies, however it has some limitations. The modelling process was over simplified and the specific data were not sufficient. Therefore, the Life Cycle Inventory with a more recent database and Life Cycle Impact Analysis using more recent evaluation methods were used (11). Table 1 presents the flow chart of the olive oil wastewater treatment studied.

TABLE 1

FLOW CHART OF THE PROCESS OF POLYPHENOL EXTRACTION FROM OLIVE OIL WASTEWATER



Updating of LCI

The LCI updates proposed in 2008 (without changing the plant, or quantities of substances and materials in the 2004 case study) were: substitution of materials and substances with the latest database; addition of manufacturing materials; addition of end-of-life treatment of all materials; addition of transport of materials; multi-method approach for impact assessment. The results are shown in Figure 1 and Tables 2 and 3.

Results for equivalent substances (midpoint)

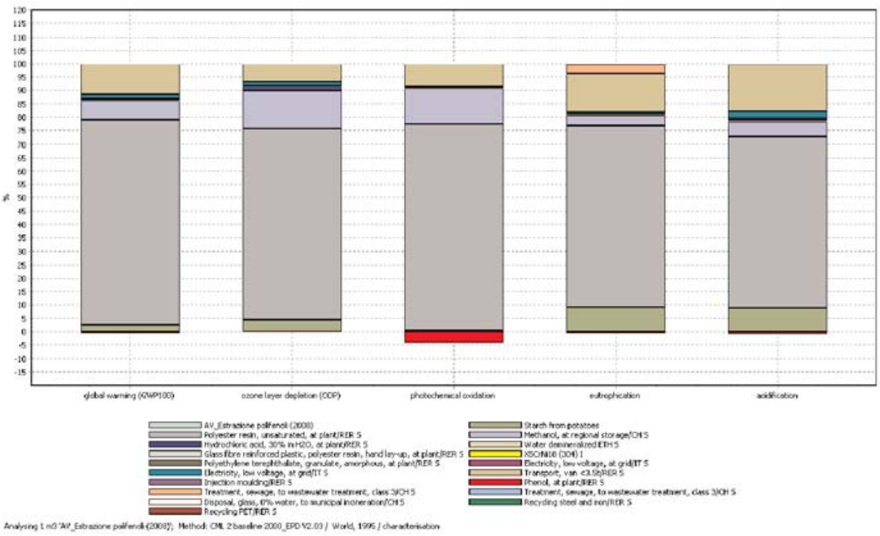


Fig.1 - Characterisation impact assessment results and contribution of processes to the damage [% of equivalent substances. Functional Unit: 1m3 of OOWW]

TABLE 2

CHARACTERISATION IMPACT ASSESSMENT RESULTS [kg OF EQUIVALENT SUBSTANCES AND IMPACT POTENTIAL. FUNCTIONAL UNIT: 1m³ OF OOWW]

IMPACT CATEGORY POTENTIAL	UNIT	TOTAL
GLOBAL WARMING (GWP100)	kg CO_2 eq.	544
OZONE LAYER DEPLETION (ODP)	kg CFC-11 eq.	$9.8 \cdot 10^{-5}$
PHOTOCHEMICAL OXIDATION	kg C_2H_4 eq.	0.07
EUTROPHICATION	kg O_2	16.7
ACIDIFICATION	kmol H+ eq	0.06

The Life Cycle Impact Assessment of olive oil wastewater treatment with polyphenol extraction process (2008 update) reveals several interesting facts.

The characterisation phase points out that the process produces emissions equal to those indicated in Table 1. Resin production (as *Polyester resin, unsaturated, at plant/RER*) is the process with the most important environmental impact contributions for each impact category: 77% for global warming, 71% for ozone layer depletion, 80% for photochemical oxidation, 68% for eutrophication, and 64% for acidification.

The resin transport process (as *Transport, van <3,5t/RER*) contributes for 8-10% of each category, while the avoided use of polyphenols which would otherwise be chemically synthesized (as *Phenol, at plant/RER*) contributes an avoided damage value of -4% for photochemical oxidation (principally due to avoided emission of cumene). Finally, the use of enzyme (as *Starch from potatoes*) contributes 9% to eutrophication and production of ethanol generates 3 to 14% damage for each category.

Impact 2002+ method application results

TABLE 3

CHARACTERISATION OF IMPACT ASSESSMENT RESULTS [kg OF EQUIVALENT SUBSTANCES AND IMPACT POTENTIAL, IMPACT 2002+ METHOD. FUNCTIONAL UNIT: 1m³ OF OOWW]

IMPACT CATEGORY	UNIT	TOTAL
CARCINOGENS	kg C_2H_3Cl	10
NON-CARCINOGENS	kg C_2H_3Cl	3.8
RESPIRATORY INORGANICS	kg $PM_{2.5}$	0.3
IONIZING RADIATION	Bq C-14	9837
OZONE LAYER DEPLETION	kg CFC-11	$6.97 \cdot 10^{-5}$
RESPIRATORY ORGANICS	kg ethylene	0.4
AQUATIC ECOTOXICITY	kg TEG water	32434
TERRESTRIAL ECOTOXICITY	kg TEG soil	7762
TERRESTRIAL ACID/NUTRI	kg SO_2	8.7
LAND OCCUPATION	m^2org.arable	2.7
AQUATIC ACIDIFICATION	kg SO_2	2
AQUATIC EUTROPHICATION	kg PO_4 P-lim	0.16
GLOBAL WARMING	kg CO_2	460.5
NON-RENEWABLE ENERGY	MJ primary	10944
MINERAL EXTRACTION	MJ surplus	5.8

Conclusions

An initial comparison of the two evaluation methods reveals that the impact categories measured with the same indicators (global warming in kg of CO_2 eq. and ozone layer depletion in kg of CFC-11 eq.) gave similar results (see Tables 2 and 3).

The process damage contribution is also the same: resin production is most impacting of all the processes followed by ethanol production and transport of the resin. The Impact 2002+ method has a greater number of indicators, i.e. land occupation, non renewable energy consumption and climate change.

The recovery of polyphenols from olive oil wastewater is important to add value to this waste as these substances can be an important source of new antioxidant products in the "novel food" fields (e.g. phytotherapy, cosmetics). Moreover, the recovery of polyphenols helps to avoid phytotoxicity in soil.

Further LCA analysis will be developed to improve methodology application and to quantify the potential environmental impact of alternative uses of these wastes.

REFERENCES

(1) ROMANI A., BALDI A., MULINACCI N., VINCIERI F.F., MANCINI P., "*Acque reflue di frantoio: studio di composti polifenolici per un eventuale uso alternativo" in Atti del XVII Congresso Nazionale di Merceologia Merci e cicli produttivi nel settore agroindustriale alle soglie del 21° secolo, Vol. 1*, Adriatica Editrice Salentina, Lecce, 1996.

(2) JOLLIET O., MARGNI M., CHARLES R., HUMBERT S., PAYET J., REBITZER G., ROSENBAUM R., Impact 2002: A new Life Cycle Impact Assessment Methodology, Lausanne, 2003.

(3) GUINÉE ET AL., CML, 2002.

(4) IPPC (Intergovernmental Panel on Climate Change) 1996, Climate Change 1995, Cambridge University Press, Cambridge, 1996.

(5) SOLOMON & ALBRITTON, *Nordic Guidelines on Life Cycle Assessment*, Nord 1995:20, Nordic council of Ministers, Copenhagen, 1992.

(6) STEFAN UPPENBERG, IVL AB.

(7) R.G. ET AL., "Photochemical Ozone Creation Potentials for Organic Compounds in Northwest Europe calculated in a Master Chemical Mechanism", in *Atmospheric Environment*, Vol. 32, Elsevier Science Ltd., Great Britain, 1998, n°14/15, 2429-2441.

(8) LINDFORS, L-G. ET AL., *Nordic Guidelines on Life Cycle Assessment, Nord 1995:20*, Nordic council of Ministers, Copenhagen, 1995.

(9) G.OLIVIERI, SETTI L., NERI P., MULINACCI N., ROMANI A., "Life Cycle Assessment (LCA) for Olive Oil Waste Water", in *Ricerche e Innovazioni nell'industria alimentare*, Vol. VI, Chiriotti Editore, Pinerolo (Torino, Italy), 2004, 1219-1224.

(10) L. SETTI, D. ZANICHELLI, A. ROMANI, N. MULINACCI AND E. BADIALI, "Recovery of antioxidant compounds from olive milling wastes using an integrated valorisation process" in *Atti del 9th FECS Conference and 2nd SFC meeting on Chemistry and the Environment (FECS)*, Bordeaux (France), August 29-September 1, 2004, pagg. 52.

(11) ECOINVENT: Database, The Swiss centre for Life Cycle Inventories, Swiss, 2000.