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**Energy and Environmental Tools
for Process Sustainability Evaluation**

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*Quod est inferius est sicut quod est superius,
et quod est superius est sicut quod est inferius,
ad perpetranda miracula rei unius.*

*Ciò che è in basso è come ciò che è in alto,
e ciò che è in alto è come ciò che è in basso,
per fare i miracoli della cosa una.*

*That which is below is like that which is above,
and that which is above is like that which is below,
to do the miracles of only one thing.*

-Hermes Trismegistus: Tabula Smaragdina-



-Camille Flammarion: Universum-

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Abstract

The aims of this thesis are the development of theoretical approaches and their application to real cases in order to assess the sustainability of production processes. Adopting an approach of Life Cycle Thinking allows to compare different technologies, both traditional and innovative ones, evaluating the best performance from an energy and environmental perspective. Currently there are many technologies that are presented as sustainable at the theoretical level. However there are actually insufficient tools to verify that technologies are truly sustainable, not only at the theoretical level and considering not only the final stage of the operation, but the entire life cycle. Moreover there are insufficient tools for ranking technologies on the basis of their sustainability. In order to select the most efficient technology, the question is: "Which criteria can be used for selecting the most appropriate technology?". The present thesis proposes instruments to answer that question: the Analogical Model, EROI (Energy Return On Investment) and EPT (Energy Payback Time), SEI (Environmental Sustainability Index). The uncertainty is treated in a dedicated chapter. The first section of the thesis is dedicated to a theoretical analysis of those arguments, which are applied in the second section in four case studies. The first case study is dedicated to the Dark Anaerobic Fermentation in two stages: hydrogen and methane are produced using waste organic materials as substrate. The second one illustrates the comparison between four prototypes of nano-structured heat exchangers and a traditional heat exchanger (Thermonano European Project). The third one shows the design of the artificial leaf by applying a sensitivity analysis to find out the direction to follow for future developments (Solhydromics European Project). Finally, the fourth one describes a study in which energy and environmental impacts of a typical workday are compared by evaluating dietary and transport.

Introduction

We live in a globalized world where a characteristic peculiar of humanity and nature expresses itself always better: interconnection. Everyone has a specific role in society: we live offering our abilities and receiving others' abilities, in an endless interchange.

This continuous energy flow is easily observable looking at the world of work: someone design buildings, someone practically build them, someone else decorate them, and so on. Everybody participates to a part of a project creation (a building in the example) and all together are able to realize it in less time and with more quality. If nowadays we would like to isolate ourselves from the rest of the world and to live in a autarkic way, this would be maybe possible but extremely difficult.

Observing the nature, interconnection arises with more evidence: just think of food chain in order to realize how each animal species is fundamental for the existence of all the others.

Let's have a look on the relationship between humankind and nature: the equilibrium is definitely compromised as a detriment for both of them. Pollution is today a global problem, ozone depletion and global warming are common concepts also outside the scientific circle. However also humans emerge as losers: of course from a physical perspective, as pollution affects directly their health; moreover, losing their connection with nature, humans have lost the connection with themselves, with their spiritual self. A global confusion is enfolding the West, although right there science has its zenith.

It is time to act, recognizing our real needs and those of society and environment.

In a so interconnected world, going up till the origin of a problem for developing changes is really arduous. Finding out the effects is easy, as for example the increase in autoimmune diseases or the disappearance of some animal species;

being able to go up along the cause-effect chain till the origin point for producing an action which will change the route, this is more difficult.

The science world often has the propensity to look faraway, to great innovations of the future, and it forgets the present, when some problems are requiring to be solved with urgency.

Old generations have given a fundamental contribution to the today world. However it is evident that something has not worked.

Let new generations free to RESEARCH, outside and inside themselves!

I wish that the present thesis may be a little piece in helping the change that is in the air since a long time to be concretized. The invitation that I feel to aim to you, Reader, is: "Let's act!".

In the present Thesis I intend to deepen some tools for studying the burdens of anthropic processes and activities on environment and humankind.

In the **Part I** decision-making tools are proposed in order to identify feasible solutions to a given problem from a sustainability perspective. Obviously it is necessary that some actions will follow the analysis, otherwise time is wasted in useless habits of mental nature: knowledge permits to decide at best how to act, and it has its natural conclusion in a practical realization. Some tools of environmental sustainability are suggested.

At first in **Chapter 1** a methodology of detailed analysis is described: the Life Cycle Assessment (LCA). Starting from a macrosystem, we come down to each little particular during the step of Inventory Analysis; subsequently the perspective is extended again till embracing all the system in the final step assigning a global judgment.

In **Chapter 2** the Analogical Model is described: it is useful for graphically summarize the energy flows of a generic process, starting from the energy theoretically available till the useful energy. This term is designed for representing the effective amount of energy delivered to the society. The Analogical Model has been developed using a LCA approach: each energy contribution is included, with both direct and indirect features.

Chapter 3 is dedicated to two tools: Energy Returned On Investment (EROI) and Energy Payback Time (EPT). They were primarily used in economic evaluations and subsequently they were introduced in energy estimations. Here they are described on the basis of the useful energy for a sustainability assessment.

Chapter 4 proposes the quantification of the environmental loads of a generic process with a sustainability index: the Sustainability Environmental Index (SEI). It aims to facilitate the interpretation of many indicators summarizing them and offering to the reader a quick and comprehensible response.

In **Chapter 5** the uncertainty topic is examined. It is a fundamental element in a LCA in order to assure a good comprehension about the quality of results.

After illustrating the theoretic tools, the **Part II** of the Thesis is dedicated to study cases, for underlain the importance of concretizing the theoretical studies. During my research I have investigated many cases. In the next four chapters the major ones among them are presented.

In **Chapter 6** the Anaerobic Digestion process in two stages is explored: the Life Cycle Assessment described in Chapter 1 is here practically applied, as well as the Analogical Model (Chapter 2). Moreover the sustainability of the process is verified using EROI and EPT tools (Chapter 3), and a sensitivity analysis is performed (Chapter 5).

In **Chapter 7** a Life Cycle Assessment (Chapter 1) concerning four new prototypes of nanofilled-polymer-based heat exchangers and a traditional heat exchanger is developed and modelled.

In **Chapter 8** the Artificial Leaf is studied in order to enlighten the hot spots of the process and to propose some technological improvements for reaching sustainability. A Life Cycle Assessment (Chapter 1) is performed, as well as the EROI and EPT tools (Chapter 3) and the sensitivity approach (Chapter 5).

In **Chapter 9** the environmental impacts of individual consumers during a normal work day is investigated, offering concrete data in order to promote pondered behaviour, in order to enhance consumers' global awareness of their responsibility towards the ecosystem. Two main topics of daily life are considered: dietary and transport. The Sustainability Environmental Index (SEI) (Chapter 4) is here practically applied.

The present Thesis is mainly based on the following papers, result of our study conducted during my PhD course in Chemical Engineering under the helpful and essential supervision of Prof. Bernardo Ruggeri:

- Sanfilippo S., Raimondi A., Ruggeri B., Fino D. (2012) *Dietary vs. transport: an analysis of environmental burdens pertaining to a typical workday*. In: International Journal Of Consumer Studies, vol. 36, pp. 133-140. ISSN 1470-6423
- Tonia Tommasi, Bernardo Ruggeri, Sara Sanfilippo (2012) *Energy Valorization of Residues of Dark Anaerobic Production of Hydrogen*. In: Journal Of Cleaner Production, Vol. 34, pp. 91-97. ISSN 0959-6526
- Ruggeri B., Sanfilippo S., Tommasi T., Fino D. (2011) *Process Energy Sustainability evaluation trough a LCA approach*. In: PRES'11, AIDIC (ITA), 14th International Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction, Florence (Italy) 8-11 May, pp. 6, 2011, Vol. 25, pagine da 629 a 634, DOI: 10.3303/CET1125105
- Tommasi T., Ruggeri B., Sanfilippo S. (2011) *On Energy Sustainability of Dark Anaerobic fermentation of biohydrogen*. In: PRES'11, AIDIC, 14th International conference on Process Integration, Modelling and Optimisation for energy saving and pollution reduction, Florence (Italy) 8-11 May, pp. 6, 2011, Vol. 25, pagine da 1073 a 1078, ISBN: 9788895608167, DOI: 10.3303/CET1125180
- Raimondi A., Sanfilippo S., Ruggeri B. (2011) *Towards the Assessment of an Ecological Index for Quantifying Sustainability of Day Life. A Case Study of the Environmental Consequences of Dietary and Transport in a Standard Work Day*. The 1st World Sustainability Forum (WSF-2011) Available on: <http://www.sciforum.net/presentation/744> Published: 2 November 2011
- Sanfilippo S., Tommasi T., Bernardi M., Sassi G., Ruggeri B. (2010) *Energy Return On Investment (EROI) and Energy Payback Time (EPT) Evaluaiton on Anaerobic Technology Producing Bio-H₂ and Bio-CH₄*. In: WasteEng10, 3rd Int. Conf. On Engineering for Waste and Biomass Valorization, Ecole des

Mines d'Albi-Carmaux, WasteEng10, Beijing, China 17-19 May, 2010, 2010, ISBN: 9782951159181

- Tommasi T., Sanfilippo S., Bernardi M., Sassi G., Ruggeri B. (2010) *Optimal Working Temperature of Bio-H₂ and Bio-CH₄ from Psychrophilic vs. Thermophilic Regime*. In: WasteEng10, 3rd Int. Conf. On Engineering for Waste and Biomass Valorization, Ecole des Mines d'Albi-Carmaux (FRA), WasteEng10, Beijing, China 17-19 May 2010, 2010, ISBN: 9782951159181
- Sanfilippo S., Ruggeri B. (2009) *LCA Alimentazione: stima del consumo energetico per la produzione, il trasporto e la preparazione del cibo in Italia*. La Rivista di Scienza dell'Alimentazione, 38(4):1-16, ISSN 1128-7969

PART I

Chapter 1

Life Cycle Assessment (LCA)

This chapter has the aim to introduce some features of the Life Cycle Assessment (LCA). This method is largely discussed in literature, so just the main topics are here treated for giving to the Reader the ability to easily understand next chapters. Many practical application are reported in the Second Part, dedicated to cases studies.

1.1. Introduction

Based on the definition of Life Cycle Assessment (LCA) given by SETAC (Society for Environmental Toxicology and Chemistry, 1991), LCA is a *“Technique of objective evaluation that allows quantifying environmental loads of a product or process along all life cycle phases, through the systematic measurement of all physical exchanges from and towards the eco-system”*.

Environmental burdens have to include the use of natural resources, as well as generation of waste and release of harmful substances into the eco-system. In general every anthropogenic activity can be generalised by a LCA. Parameters of environmental impacts, must be identified and quantified through a systematic and objective technique in all phases of the life cycle.

The first definition of LCA given by SETAC in *“Guidelines for Life-Cycle Assessment: a code practice”* was implemented by ISO 14040 (2006) international standard from which the following statement was drawn: *“LCA studies analyse the environmental*

aspects and potential impacts throughout the product's life cycle (from-cradle-to-grave) from raw material acquisition, through production, use and disposal" (Fig. 1.1).

LCA can therefore address production and consumption of goods towards better standards of human and environmental health, as well as natural resources saving. As it allows an objective and meaningful measurement of the product's eco-profile, LCA methodology is worldwide accepted and appreciated.



Figure 1.1: Life Cycle Assessment (LCA) framework

According to ISO 14040 (2006), an LCA comprises four major stages: *goal and scope definition*, *life cycle inventory*, *life cycle impact assessments* and *interpretation of the results* (Fig. 1.2).

1. **The Goal and Scope Definition** phase defines the overall objectives, the boundaries of the

system under study, the sources of data and the **functional unit** to which the achieved results refer.

2. **The Life Cycle Inventory (LCI)** consists of a detailed compilation of all the environmental inputs (material and energy) and outputs (air, water and solid emissions) at each stage of the life cycle.
3. **The Life Cycle Impact Assessment (LCIA)** phase aims at quantifying the relative importance of all environmental burdens obtained in the LCI by analysing their influence on selected environmental effects.
4. **In the Interpretation phase and improvement**, (not mandatory) as the last step of an LCA study, the results from the LCI and LCIA stages must be interpreted in order to find hot spots and compare alternative scenarios.

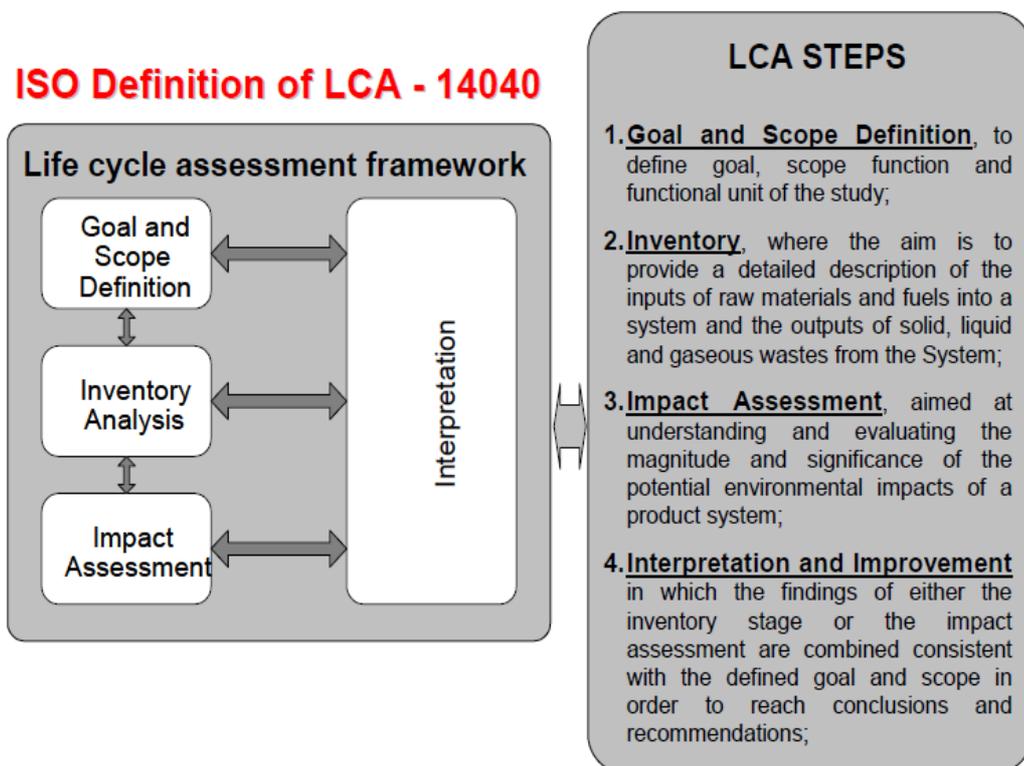


Figure 1.2: Life Cycle Assessment (LCA) structure according to ISO 14040 (2006)

The LCA approach is currently wide accepted by the scientific basis, to describe several environmental sustainability indicators, as well as a tool for supporting green communication and green marketing instruments.

For these reasons, among other methodologies, Life Cycle Assessment (LCA) is increasingly being

used as an objective and credible tool to measure the environmental performances of products and understand the environmental sustainability of the production chain.

The ISO 14040/44 standards (2006) provide the general framework for Life Cycle Assessment. However, the ISO framework leaves the practitioner with a range of choices that can change the results and conclusions of an LCA study and therefore affect its legitimacy. While flexibility is essential in responding to the large variety of questions addressed, further guidance is needed to support consistency and quality assurance.

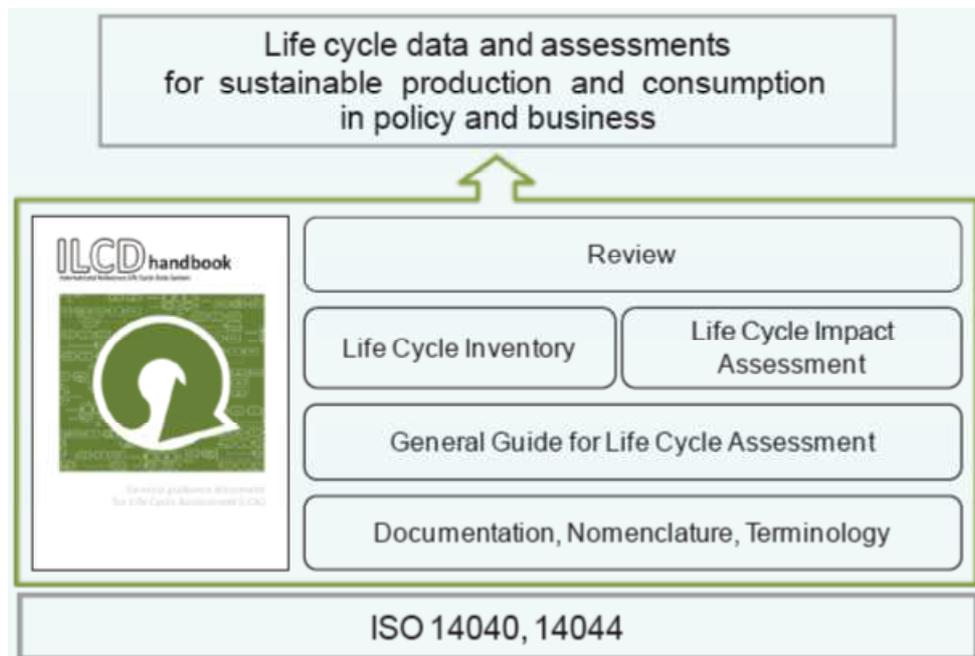


Figure 1.3: The structure of the ILCD Handbook (European Commission, Joint Research Centre, Institute for Environment and Sustainability, 2010)

For this reason, the Joint Research Centre (JRC) of the European Commission has set up an International Reference Life Cycle Data System (ILCD), which provides a common basis for consistent, robust and quality-assured life cycle data and studies.

The ILCD Handbook (European Commission, Joint Research Centre, Institute for Environment and Sustainability, 2010), which is available online at <http://lct.jrc.ec.europa.eu/pdf-directory/ILCD-Handbook-General-guide-for-LCA-DETAIL-online-12March2010.pdf>, aims to improve the compatibility and consistency of data generation and reporting requirements, as well as it aims to increase stakeholder acceptance of the tool LCA and its results.

1.2. Goal and scope definition

In the first step of an LCA the system under study and its boundaries, the functional unit to be used and the procedure to be followed for the assessment are explicated. In particular, the goal of the LCA study must define the aim of the study, the future use of the results and the people to which the study is addressed.

The scope of the study must clearly describe the system of the studied product or process and its boundaries, the included items and the items to be evaluated, the system functions, the functional unit, the calculation unit, the impact categories, the methodology applied, and finally, the necessary assumptions and restrictions.

1.2.1. Software

The software used by the analyst to perform an LCA must be clearly declared. In This thesis all the results obtained for the cases study are elaborated using the SimaPro v7.2 software (Pré, 2010).

1.2.2. Functional Unit

The main target of a functional unit is to constitute a reference unit to which all the inputs and the outputs of the system are referred. This reference unit is necessary in order to ensure the possibility of comparison between the results of a LCA study; the existence of a common base is essential in order to compare different systems.

1.2.3. System Boundaries

The definition of system boundaries of the study is one of the most important step of a LCA. The determination of the system boundaries concerns the selection of the processes or units in sequence (subsystems) that will be included in the studied system; they must be always determined in accuracy and remain stable during the whole study. In addition, the boundaries of a study are drawn so as to include all relevant impacts.

1.3. LCA Inventory

Life Cycle Inventory (LCI) analysis involves creating an inventory of flows from and to nature for a product system. Inventory flows include inputs of water, energy, and raw materials, and releases to air, land, and water. To develop the inventory, a flow model of the technical system is constructed using data on inputs and outputs. The input and output data needed for the construction of the model are collected for all activities within the system boundary.

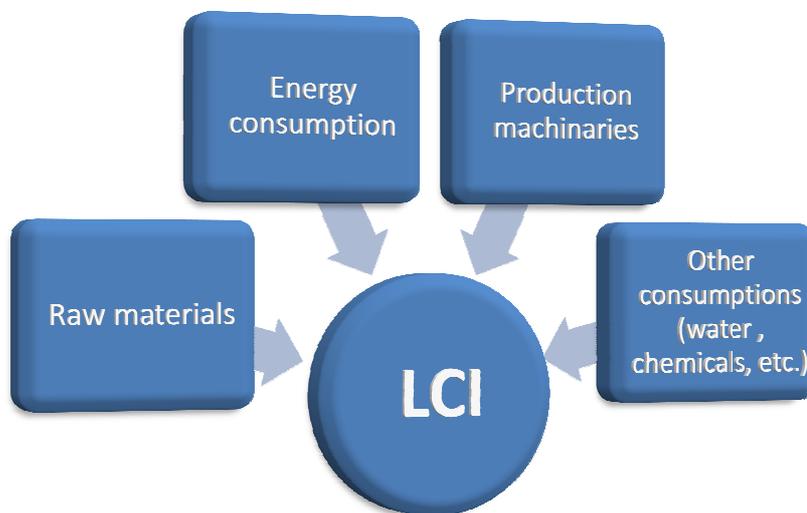


Figure 1.4: Life Cycle Inventory model.

1.3.1. Primary and secondary data

There are numerous types of data that can be acquired for conducting LCI studies, and it is important to distinguish between primary and secondary data. Primary

data are those obtained from the specific facilities that are the subject of the LCI. Secondary data are those included in the product system life-cycle inventory that have been obtained from published sources.

Examples of secondary data sources include published literature, other LCI studies, emissions permits, and general government statistics (e.g., mineral industry surveys, Bureau of Labor statistics, and Energy Information Administration data). All data should be identified as being either primary or secondary as part of routine data documentation. The most representative and reliable data should always be used, with the proviso that critical reviewers should be able to verify that the data is current and that it reasonably represents relevant aspects of the unit process under study.

1.4. Impact categories

In order to expose results and make comparisons between different kind of products, categories of impacts and related indicators must be identified. These indicators summarize environmental effects connected with energy and mass flows in input and output from the system.

In this Thesis the phase of impact assessment considers the following indicators.

Table 1.1: Indicators list

Global Energy Requirement (GER)	MJ eq
Global Warming (GWP)	kg CO ₂ eq
Ozone Layer Depletion (ODP)	kg CFC-11 eq
Photochemical Oxidation	kg C ₂ H ₄ eq
Acidification (AP)	kg SO ₂ eq
Eutrophication (EP)	kg PO ₄ ³⁻ eq
Carcinogenics	kg benzene eq
Non carcinogenics	kg toluene eq

1.4.1. Global Energy Requirement

The use of raw materials with energy content will be dealt by calculating the Gross Energy Requirement as the total primary energy extracted from the Earth:

$$GER = \sum (\text{Gross heat content})_i * m_i$$

Such indicator is obtained by the product of quantities m_i of all raw materials with energy content (both non renewable and renewable) by their gross heat value. The GER impact indicator, expressed in MJ, can further be divided according the non renewable (NRER) and renewable (RER) contributions.

1.4.2. Global Warming

It is caused by the increase of atmospheric temperature following the massive increase of greenhouse gases such as CO₂ and water vapour which are able to absorb the infrared radiation emitted from the Earth. This contributes to global warming and consequently to climate change.

The category indicator is the GWP (Global Warming Potential) and the characterization factor is represented by kg of carbon dioxide equivalent; the corresponding quantities of the various greenhouse gases are converted through the global warming potentials (GWP's) in common units of kg of carbon dioxide equivalent. The GWP's are normally calculated for an exposure period of 100 years.

1.4.3. Ozone Layer Depletion

Ozone is the gas that characterizes the stratosphere and its function is to shield the Earth from ultraviolet rays of the sun, CFCs (chloro-fluoro-carbons) affect the ozone molecules and over time have created the well known "Hole". The major consequences of this phenomenon regard especially human health (carcinomas, decrease in immune system function).

It is quantified by kg CFC-11 equivalent; the ozone-depleting potential (ODP), that is based on the number of reactions of ozone molecule breakage, is used to standardize the values for the various substances.

1.4.4. Photochemical Oxidation

It is an environmental effect caused by the presence of unburned hydrocarbons and nitrogen oxides in the flue gases of oil and derivatives. They react with each other in the presence of sunlight and produce ozone (tropospheric level), highly toxic to humans because of the high chemical reactivity.

The category indicator is ethylene, to which all the various substances values are related through the photochemical ozone formation potential (POCP). The unit of measurement is the kg of ethylene (C₂H₄) equivalent.

1.4.5. Acidification

It consists in decrease of the pH of lakes, rivers, forests and soil: this leads to serious consequences for humans and environment. The main causes are emissions from fossil fuels combustion, particularly those with a high content of sulfur.

It is expressed in terms of kg of SO₂ equivalent or moles of H⁺ equivalents through the standardization system that considers the acidification potential (AP).

1.4.6. Eutrophication

The massive injection of substances such as phosphorus and nitrogen causes a decrease of oxygen content in soils and surface water lakes. Effect is evident due to the formation of supernumerary algae.

BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand), both of them expressed in kg of O₂, represent the measurement units that quantify the oxygen demand necessary to achieve the natural purity. The kg of NO₃⁻ or PO₄³⁻ equivalent are obtained through the eutrophication potential (EP).

1.4.7. Carcinogenics and Non Carcinogenics

The toxicological impacts on both humankind and environment depend on the characteristics of chemical substances and other factors such as the ability to degrade or to accumulate.

Since the influence area is local, it is very difficult to quantify the various contributions to the overall effect, which can involve any organism or ecosystem. They are expressed respectively in kg of benzene equivalent and in kg of toluene equivalent.

Environmental impacts can affect the environment and ecosystems at different scales such as global, local, regional. Table 1.2 reports the main impact categories and their scale of damage.

Table 1.2: Main impact categories with their scale of damage

Environmental Effect	Scale Of Influence
Resources depletion	Global
Global warming	Global
Ozone depletion	Global
Acidification	Regional
Eutrophication	Regional/local
Photochemical smog	Regional
Human toxicity	Regional/local
Eco-toxicity	Regional/local
Waste generation	Regional/local
Visual impact	Local
Surface water pollution	Local
Land use	Local
Water resources use	Local
Dust emissions	Local
Noise / vibrations	Local
Traffic	Local

Results can be supplied as midpoint indicators or can be converted into damage indicators. Both midpoint and endpoint indicators can be normalised to the per capita yearly impacts of one European citizen, thus expressing the results as person-year equivalents. After normalisation, indicators might be added up using the default weighting factor (all weights = 1) or other socially-driven weighting values. In Figure 1.5 the mid-point categories reside in the centre of the figure and are linked on the right to attributes, which are in turn linked to the life cycle stages. On the left, mid-point categories are aggregated into damage categories, which are then aggregated into a single score index. The mid-point category values are created through classification and characterisation of the inventory of attributes, an objective process. Conversely, some form of subjective weighting (w_1 - w_4) is required to calculate the damage category and single score index values.

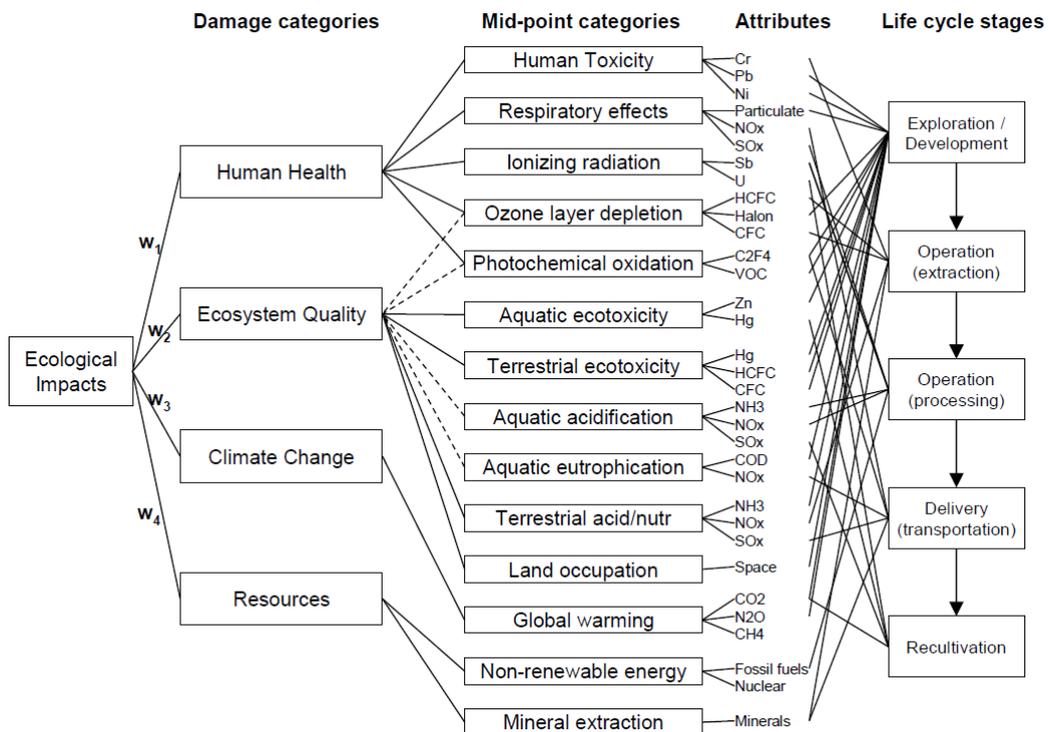


Figure 1.5: correlation of ecological impacts to LCA considering impact categories

The model used for indicators calculation is EPD 2008. It is an environmental declaration defined in ISO 14025 (2010) as quantified environmental data for a

product with pre-set categories of parameters based on the ISO 14040 (2006) series of standards, but not excluding additional environmental information. Some EPDs are available on www.environdec.com and they are free to download.

1.5. Allocation criteria

A process providing more than one function, is called “multifunctional” and usually its output comprises more than one single product. Moreover, raw material inputs often include intermediate or discarded products.

An appropriate decision must therefore be made as to which of the economic flows and environmental impacts associated with the product system under study are to be allocated to that system.

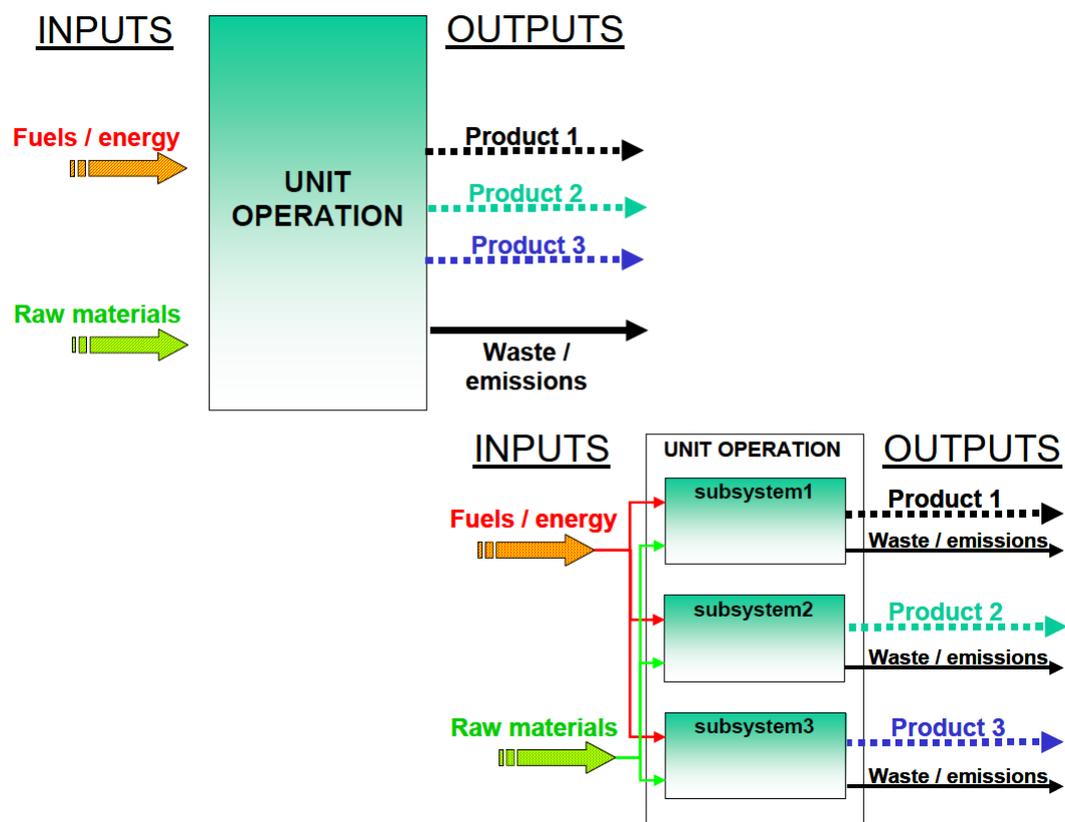


Figure 1.6: Allocation or partitioning operations in LCA framework (Badino, 1998)

“Allocation”, or “partitioning”, solves the multifunctionality by splitting up the amounts of the individual inputs and outputs between the co-functions according to some allocation criterion, being a property of the co-functions (e.g. element content, energy content, mass, market price etc.).

The environmental burdens must be assigned to all economic valuable product, that imply that industrial rejects are not claimed to be responsible of any environmental load (this latter has to be

discuss while dealing with recycling). To assign environmental loads in the right proportion, different criteria can be chosen. On the basis of the exact knowledge of the industrial system under study, allocation can be performed according to physical criteria such as mass or volume or energy.

Normally, physical allocation must be preferred to economic allocation due to the fact that environmental loads are associated to industrial operations and use of materials and energy, and these are not forcedly connected to the formation of economic value of products.

In any case ISO 14041 (1998) and ISO 14040 (2006) supply guidelines on allocation criteria. According to them, wherever possible, allocation should be avoided by:

- dividing the unit process to be allocated into two or more sub-processes and collecting the input and output data related to these sub-processes;
- expanding the product system to include the additional functions related to the co-products.

Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between its different products or functions in a way which reflects the underlying physical relationships between them. This allocation will not necessarily be in proportion to any simple measurement such as the mass or molar flows of co-products.

Finally, where physical relationship alone cannot be used for allocation, the inputs should be allocated between co-products and functions on the basis of other relationships between them, such as the economic value of the products.

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Chapter 2

Analogical Model

In this chapter the Analogical Model is presented and described from a theoretically perspective: it is useful for graphically summarize the energy flows of a generic process, starting from the energy theoretically available till the useful energy. The Analogical Model has been developed using a LCA approach: each energy contribution is included, with both direct and indirect features. This method is practically applied in Chapter 6.

2.1. Introduction

Sustainable development is a fundamental topic for the future. Scientific literature is filled with papers concerning the importance of energy and energy as tool to support the historical development of human civilization (Smil, 2011) from the control of the fire to the use of fossil resources. The energy assessment of a process by LCA involves the entire life cycle of the process, including: raw material extraction and processing, manufacturing of the plant and its assembly, transportation, energy use for the operation of the plant, such as electrical energy and heat, multiple use of the plant, if it is necessary, and recycling and/or final disposal in the so called decommissioning phase. It is important to point out the three blocks in an energy chain: the *energy source*, the *energy transformation* technology, and the *energy service* which is able to supply the well-being of a society.

LCA has gained wider acceptance as a quantification method of environmental impacts (Dewulf and van Langenhove, 2006) but it can also be considered as

candidate for process selection, design and optimization (Jolliet et al., 2003). In the present chapter, the energy metrics of LCA is used to quantify all the energy flows.

2.2. Analogical Model description

A deep theoretical formalization of the approach here is shown and each energy flow is analyzed in detail, focusing particularly on Indirect Energy Consumed which is often not considered in the literature; disregarding it is a theoretical and a practical error, because it has a great impact as quantitative term.

The analysis of energy flows must be referred to a defined time period (e.g. 1 year or entire plant life) and to a functional unit, in the LCA words, according with the specific process under study (e.g. 1 m³ of volume for a reactor). In Figure 2.1 a diagram of the energy terms encountered in the energy analysis of a generic process is reported.

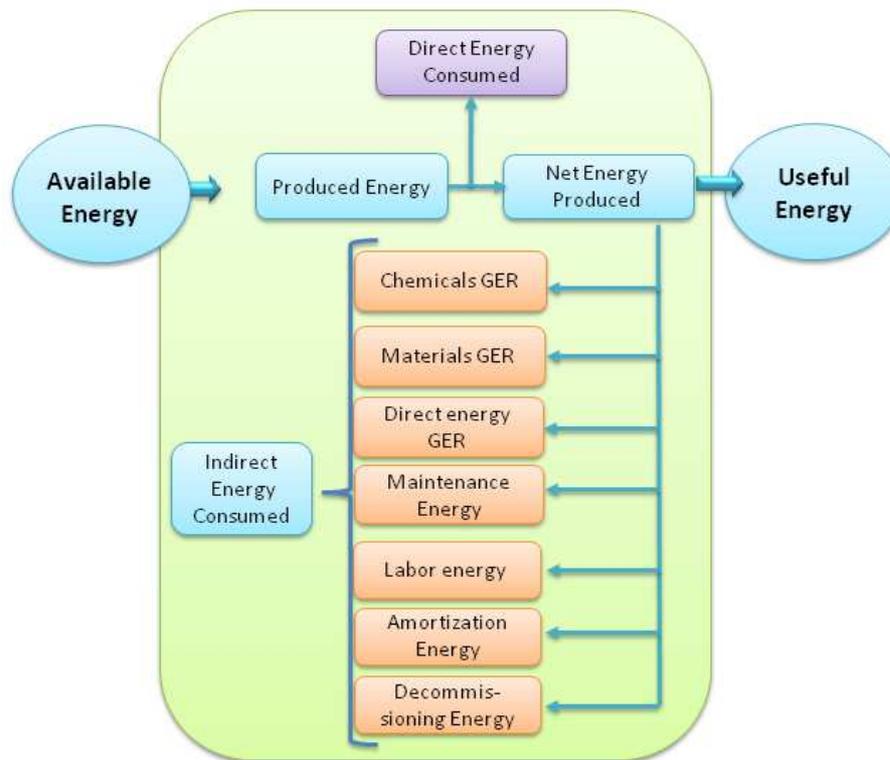


Fig. 2.1: Energy terms involved in a generic process

The term “useful” is for the energy delivered into the society and the term “net” is for the energy produced by the process minus the energy necessary to run the

process itself. Performing a Useful Energy Analysis (UEA) offers several advantages over the standard economic analysis: primarily because it assesses the change in the physical scarcity of energy resources, then because it is a measure of the potential of such a technology to work in a sustainable way, and finally because it is possible to rank alternative energy supply technologies according to their capacity to produce useful energy. All these properties are able to support the decision towards sustainable technologies.

This methodology is applied in Chapter 6 to evaluate the sustainability of Dark Anaerobic Fermentation (DAF) using organic waste materials as a substrate to produce biohydrogen plus biomethane.

2.2.1. Available Energy

Following the schematization reported in Figure 2.1, the first term to evaluate is the Available Energy: it represents the theoretical energy that the process may produce. Considering a DAF technology as example, the Available Energy may be calculated referencing to the Low Heating Value of the substrate.

2.2.2. Produced Energy

The produced Energy is the energy that the process under study is actually able to extract from the source. Going on with the DAF technology as example, the Produced Energy may be calculated referencing to the Low Heating Value of the produced gases.

2.2.3. Direct Energy Consumed

The direct energy is the fuel and/or the electricity directly used to run the process *in gate* including the energy necessary for the facilities.

2.2.4. Net Energy and Useful Energy

The difference between Produced energy and Direct Energy Consumed is the Net Energy in the classical term of energy analysis. The Useful Energy is the difference between Net energy and the Indirect Energy Consumed.

It is important to introduce the concept of energy service, here intended as the amount of energy required by the end user as Useful Energy; when this approach is adopted it is of great importance to take into account the final form in which the energy is used to support the needs of society and to maintain civilization. Among the many issues that are of primary importance for society (e.g. human culture, nutrient cycling and entropy), the key is not the energy itself but the *surplus energy* produced by means of each energy technology. Wealth, survival, art, army and even civilization itself is a product of surplus energy. The issue is not simply whether there is surplus energy but also *how much, what kind (quality), and at what rate* the energy is delivered. The interplay of these three factors determines the *useful energy* and hence the ability of a given society to divert attention from life-sustaining needs towards luxuries, such as art and scholarships including research and innovation for the exploitation of different energy sources.

According to the concept introduced by Georgescu Røegen, in order to have energy sustainability of such an energy technology, it is necessary for the technology to be vital (*viable*) (Røegen, 1976). Like a biological system, an energy technology must be able to produce at least a quantity of energy that is able to sustain itself in order to sustain "others". It necessarily needs to use only a part of the energy source for its operational necessities and reproduction, and the remaining part will be used to feed civilization in an appropriate form. In other words, a technology is sustainable if more and more produces a surplus energy as useful energy.

2.2.5. Indirect Energy Consumed

Indirect energy is the energy used for many purposes and it is constituted by seven items: Chemicals GER, Materials GER, Direct Energy GER, Maintenance Energy, Labour Energy, Amortization Energy and finally Decommissioning Energy. The sum of all the indirect energy is called the *energy embedded* in the technology.

Chemicals and Materials GER represent the amount of energy necessary for producing both chemicals and materials necessary for operating the plant. It is important to remark that indirect energy need to be measured in an energetic physical unit as well as direct energy, in order to have data coherence. Hence it is necessary to convert all the material flows in energy unit. To do this we use the

Global Energy Requirement (GER) evaluated by the software SimaPro 7.2.4 (2010) and Ecoinvent database (2007).

Direct Energy GER is the energy necessary to produce a unit of direct energy.

Maintenance Energy is the energy required by the process for its maintenance during its lifetime.

Labour Energy is the energy necessary for guarantee the presence of workers for the process running. The energy spent for labor has an intrinsic difficulty to be evaluated (Brown and Herendeen, 1996) and it is often disregarded, but it could be of utmost importance in comparing different labor and capital intensive technologies. A paragraph is dedicated to this topic because of its importance.

Amortization Energy is the energy necessary to rebuild (*reproduce*, according to the biological mimic suggested by Røegen (1999)) the plant at the end life taking into account the recycling or re-use options.

Finally Decommissioning Energy is the energy that has to be spent for decommissioning the plant at the end of its operational life.

2.2.6. Labour

The labour energy consumption deserves particular attention. It can be separated into three components: i) the caloric value of food for the biological support of life; ii) both direct and indirect energy consumption necessary to produce, transport, conserve and prepare food; iii) all the other direct and indirect forms of energy consumption linked to daily activities (clothing, appliances, fuel for transportation from the house to the factory etc.). The energy spent on labour is intrinsically difficult to evaluate, in particular as far as the last contribution is concerned (Brown and Herendeen, 1996; Cleveland and Costanza 2010). The labour contribution is often disregarded, but it could be of utmost importance when comparing different labour vs. capital intensive technologies, for example gasification vs. energy crop cultivation. We suggest only evaluating the energy related to the biological support of the labour via the computation of the first two components of above. Considering the third term, some errors are introduced, it could be evaluated as pro-capita energy consumption of the Nation. Using the pro-capita energy a false energy charge is calculated, either in the case the nation produces the plant or

imports it: higher in the first case and lower in the second one, respectively. The pro-capita energy consumption depends to a great extent on the salary of the workers operating in the plant, and this can introduce a false energy charge on the technology under study.

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Chapter 3

Energy Return On Investment (EROI) & Energy Payback Time (EPT)

In this chapter to environmental indexes for sustainability evaluation are presented from a theoretically perspective: Energy Return on Investment (EROI) and Energy Payback Time (EPT). Many practical application are proposed in the Second Part of this thesis.

3.1. Introduction

The present energy crisis together with environmental issues, such as global warming, has persuaded men to search new energy sources (Balat, 2008). Different renewable sources are now being exploited. Energy crops, wind power, water power, solar energy and organic refuse from the food chain could offer possible solutions (Angenent et al., 2004). Over the last few decades many technologies have been suggested in order to use alternative energy sources through research as well as practical applications. However, we believe that it is also important to introduce the concept of energy service, here intended as the amount of energy required by the end user as useful energy, i.e. the energy necessary to support human life, as outlined in Figure 3.1. Therefore it is of great importance to take into account the final form in which the energy is used to support the needs of society and to maintain civilization. Surplus energy flowing from each block in Figure 3.1 depends from the technology used, and it

is of primary importance for society. Wealth, survival, art, army and even civilization itself is a product of surplus energy. The interplay of how much, what kind (quality), and at what rate the energy is delivered determines the useful energy. It gives the ability to the society to divert attention from life-sustaining needs towards luxuries, such as art and scholarships including research and innovation for the exploitation of different energy sources.

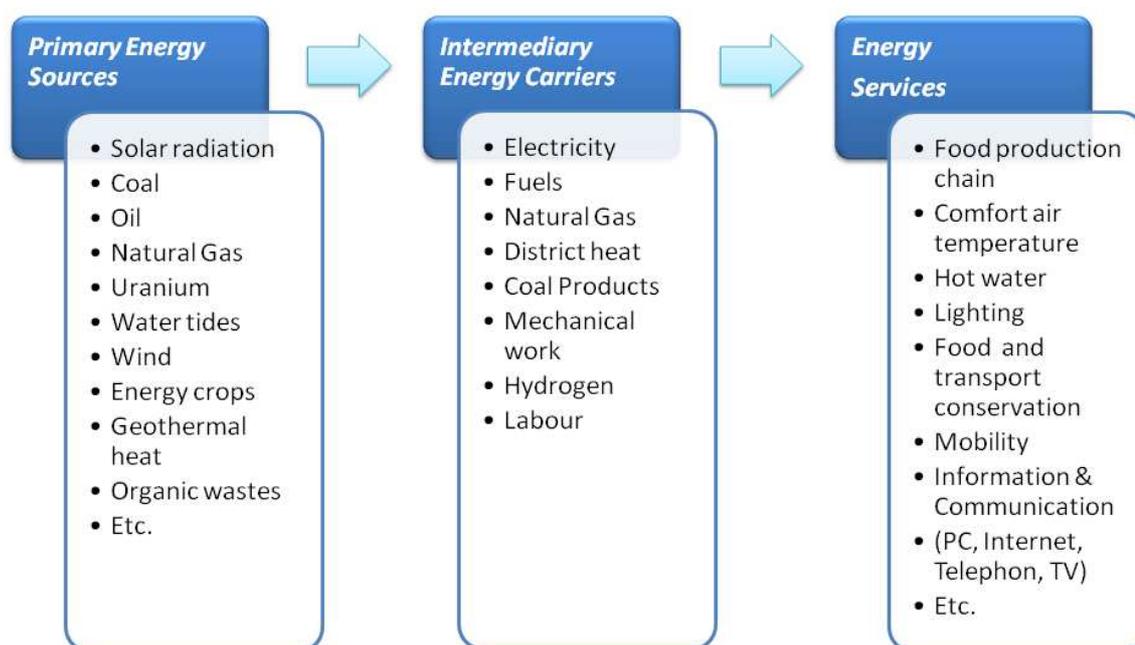


Figure 3.1: General layout of energy flow

Among the primary energy sources organic waste material (Evans, 2001) is approximately 60% of daily refuse production. The technology pallet to use organic waste (referring to Figure 3.2) ranges from biological processes (Pfeffer and Lieman, 1976) to thermal methods, such as gasification, pyrolysis and incineration (Guéhenneux et al., 2005) including the direct conversion of organic matter into electrical energy through the use of Microbial Fuel Cell (Tommasi et al., 2012; Logan, 2008; Aelterman et al., 2006).

In order to select the most appropriate technology, it is necessary to establish which criteria should be used to valorize the sources (Sentimenti and Biorgi, 2006). In this context, economic criteria on their own appear to be inappropriate, because data can

easily be manipulated according to the working hypothesis and the conclusions might not be completely reliable (Cleveland et al., 1984).

Economists argue that the price of a technology or a fuel automatically captures all the relevant features, but in a finite resource scenario this at least appears to be questionable.

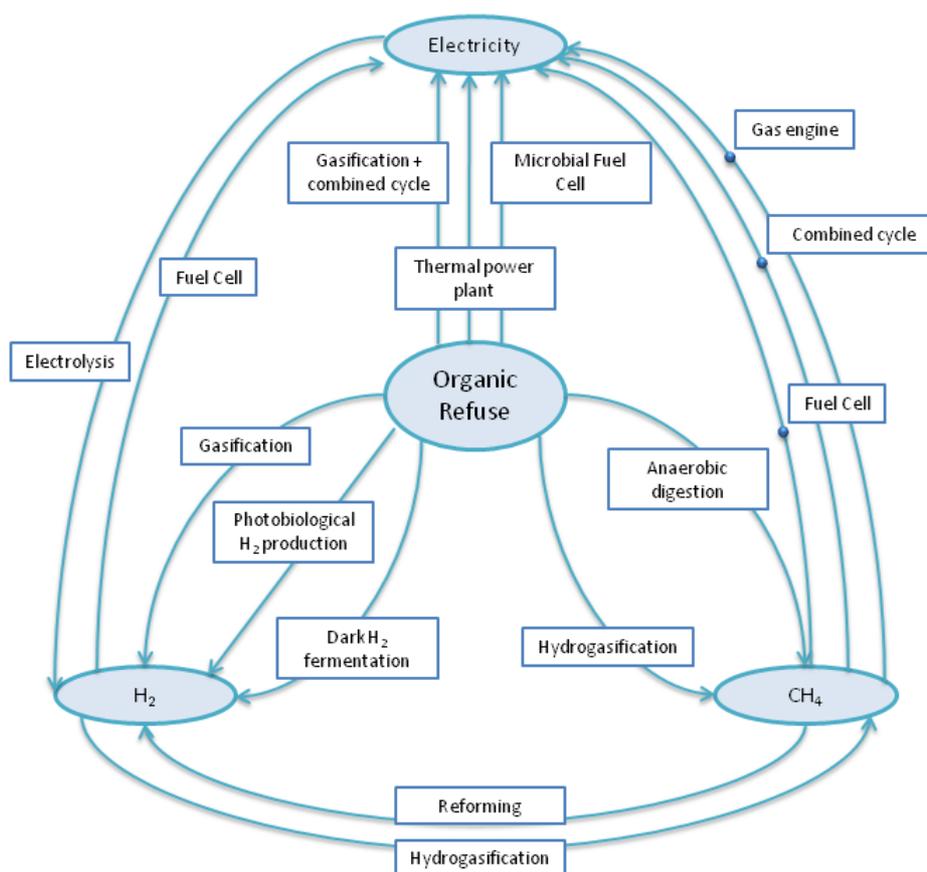


Figure 3.2: Technologies able to produce energy using Organic Wastes

The Life Cycle Analysis (LCA) (SETAC, 1993), which takes into account all the aspects of such a technology (e.g. environmental impact, safety, toxicity, energy use and social issues together with economics), is an alternative to a conventional economic analysis. One of the difficulties of selecting a technology in order to produce an energy carrier or an energy service concerns the need to measure the sustainability level of it. It is even more important the search for an effective scoring tool in order to compare several technologies. To this aim, several approaches, ranging from a thermodynamic one (de Swan et al., 2004) to a more industrial oriented alternative (Apazagic and Perdam, 2000; De Simone and Popoff, 1997) have been put forward in recent years for

the selection of the sustainability (Apazagic, 1999; Laws et al., 1984). Hall et al. (2009) with reference to energy sustainability, proposed that the most appropriate way to judge the relative merits of different energy sources is to evaluate the ratio between the amount of energy produced and the energy needed to produce it known as the Energy Return on Investment (EROI). EROI, in its simplest form, measures the output energy at the point of production or “mine mouth” (Murphy et al., 2011). The evaluation of the EROI of such an energy source away from “mine mouth” needs to compute the energy consumed to deliver and to use it at the point of energy utilization, this causes a decrease of EROI. In order to have some idea about this concept, it can be considered that the EROI for oil at “mine mouth” is about 20: this means that for 1 unit of energy consumed for extraction from reservoirs, well-head treatments and new exploration, 20 units of energy are available to society. Hall et al. (2009) estimated at the end user level, EROI would need to be at least 10 to cover the needs of society/civilization to support an energy service. The EROI for ethanol derived from maize was instead estimated to be at best 1.3 (Cleveland and Costanza, 2010) and according to some authors (Patzek and Pimentel 2006; Patzek 2004) less than 1. This implies that maize-based ethanol requires some other energy source, subsidy for its production.

According to the concept introduced by Georgescu Røegen (1976), in order to have energy sustainability of such an energy technology, it is necessary that the technology must be vital. Like a biological system, an energy technology must be able to produce at least a quantity of useful energy that is able to sustain itself in order to sustain “others” energy service. It necessarily needs to use only a part of the energy source for its operational necessities and reproduction, and the remaining part will be used to feed civilization in an appropriate form. In other words, a technology is sustainable if produces a surplus energy as useful energy.

Energy Payback Time (EPT) is a related concept to EROI. It permits to score such technology against the time parameter. It is the time necessary to the plant to produce the energy necessary to rebuild the plant itself.

Unlike other researches in which EROI was used to evaluate the net energy of such energy sources (Cleveland and O’Connor, 2011; Guilford et al., 2011; Brand, 2009), we

used EROI and EPT to evaluate the sustainability of a technology; the approach is quite similar, but some differences exist linked to the use of useful energy.

3.2. EROI definition

EROI is the ratio between the total amount of net energy delivered to society by a technology during its working lifetime and the amount of total indirectly energy in such process to produce energy (Murphy et al., 2011). It is a ratio between two energy quantities, and is therefore dimensionless. In mathematical terms, EROI is:

$$\text{EROI} = \text{TNEP} / \text{TIES} \quad (3.1)$$

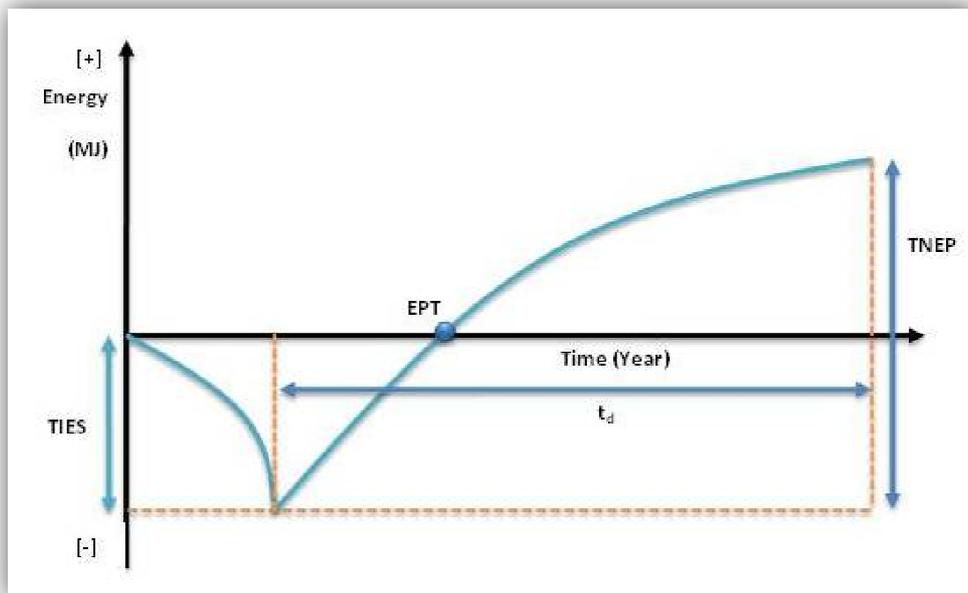


Figure 3.3: EROI and EPT

TNEP is an acronym for Total Net Energy Produced: it represents the energy generated minus the direct energy necessary to run the plant itself. Direct energy, in general terms, is the electrical energy which should be produced in loco or taken from the grid and fuel (solid, liquid or gas) to produce heat. According to Murphy et al. (2011), TIES is the Total Indirect Energy Spent elsewhere in the economy for the construction of the plant and for its operation. It includes the following energy headings: to produce the plant sections (vessel, pumps, valves etc.), to produce the consumables, to prepare the

site, to assemble the plant, for maintenance to replace parts or to upgrade and, finally, the energy spent for decommissioning. In addition, as indirect energy we have to take into account the energy used to support the labour force in charged to the plant and the amortization energy. The higher the EROI value, the higher the sustainability of the technology. If EROI is less than 1, sustainability is certainly not guaranteed as the energy gained from the process is lower than the expended energy.

It is important to point out that EROI should not to be confused with energy efficiency conversion, which is well depicted by First and Second Laws of classical thermodynamics, i.e. going from one form of energy to another one, such as upgrading oil in a refinery or converting diesel oil to electricity. EROI is only loosely related, at least in the short term, to the concept of return of monetary investment, but this aspect has not been considered in the present contribution.

3.3. EPT definition

A mathematical formula for EPT is:

$$EPT = TIES / (TNEP/t_d) \quad (3.2)$$

TNEP and TIES have the same meaning as that of EROI; t_d is the operation time of the facility. Straight lines are usually used in the a priori estimation of EPT. For the evaluation of EPT we have considered all the indirect energy including the amortization term, as spent during the construction time. Different assumptions can be made depending on the technology under study.

EPT permits to score a technology against the time parameter. It represents the time necessary to the plant to produce the energy necessary to rebuild the plant itself. The higher the EPT value, the lower the annual rate of useful energy, and hence the lower the sustainability of the technology. In other words EPT is the time of the operational lifetime of the plant necessary to reach the sustainability condition i.e. the time in which the technology starts to feed the society.

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Chapter 4

Sustainability Environmental Index (SEI)

In this chapter a new environmental index for sustainability evaluation is presented from a theoretical perspective. It aims to summarize the results of the LCA and it represents a simple and understandable tool to the decision makers and single consumers, influencing their decision towards the sustainability. A practical application is reported in Chapter 9, regarding the topics of dietary and transport.

4.1. Introduction

The effectiveness of the Life Cycle Approach is well accepted to quantify correctly the impacts and its potentiality of supporting the sustainable development is out of the question. However a global consensus about the interpretation of results is not yet achieved. It is, as example, not still unanimously accepted which impact categories should receive more attention and higher priority from decision makers (Miettinen et al., 1997). Eshun et al. (2011) criticized how almost the totality of methods that aims to quantify the environmental impacts evidence the limit to evaluate these problems only considering how they manifest themselves in the western world, instead than globally, and cannot be easily adapted to different realities like the African countries. They particularly underline how critical aspects such as biodiversity loss or wood waste, that severely affect many countries of the third world, are scarcely considered by the most of the LCA studies. Moreover a second goal of the LCA would be the detection of social impacts on communities along the whole chain, which represent a very complex problem to be evaluated by

the analytical approach of a standard LCA (Dreyer et al., 2006; Jørgensen et al., 1997; Weidema et al., 2006).

In reason of these aspects the LCA itself can be often not sufficient, at the moment, to support proficiently the best decisions. In addition the results of a LCA alone require a high level of competencies to be comprehended and can be often difficult to be correctly interpreted by final users or decision makers. In reason of that, the possibility to integrate the LCA study with additional information, complementary to the standard evaluation methods, can be a very effective tool. In regard of that Cunningham et al. (2003) have recently developed an internal criterion at the Shell Group, associating their products with a score that summarises and quantify the high quantity of information, taking in consideration the environmental, the social and the economical aspects, that are provided by a life cycle analysis, in order to support the final decisions of their management.

The present chapter proposes the quantification of environmental loads with a sustainability index, which aims to summarize the results and offers to the reader a quick and comprehensible response. The possibility to associate a mark, that synthesises the results of the LCA, can represent a simple and understandable tool to the decision makers and single consumers, influencing their decision towards the sustainability. Moreover when sustainability indexes can be internationally accepted and they will be known to the large population not only the expertise of LCA analysis, the possibility to promote or reject a product or a behaviour as sustainable will be easier.

4.2. SEI description

The stage of interpretation and implementation of results represents the final additional phase of a LCA study. The possibility to have a subsequent critical analysis of the results, possibly involving subjects with a different know-how, is a milestone for implementing and proficiently using the high number of information coming from the LCA, with the purpose to save energy and raw materials as well as to identify possible risks for the environment and human health.

This chapter aims to focalize its attention to this stage, and proposes an index to assess the sustainability of a process assigning to each option a mark as Sustainability Environmental Index (SEI). The possibility to present the environmental load with a simple index can be easy and quick understood by decision makers and single consumers. With an internationally-accepted simplification of the results of the LCA, it would be easier to identify the products which promotes or not sustainability and force institutions and companies to go through the route of sustainable development. Table 4.1 presents the environmental index: it offers a simple and quick interpretation, and it assesses a scale of sustainability.

Table 4.1: Sustainability Environmental Indexes (SEI) descriptions

SEI	Description
1	Very low impact
2	Low impact
3	Medium impact
4	High impact
5	Very high impact

Table 4.1 presents the environmental indexes proposed that offers a simple and quick interpretation, and assesses a scale of sustainability.

An impact achieving 1 or 2 as SEI can be considered as a sustainability promoter, 3 represents the sufficiency while 4 or 5 are considered do not promote sustainability.

The following expression has been used in order to assign a global environmental index SEI which takes into account all the environmental stressors for a generic process:

$$SEI = \frac{1}{n} \sum_{i=1}^n (I_i * w_i) \quad (4.1)$$

where I is the indicator (like GER, GWP and others) expressed in SEI terms as explicated in Table 4.2, w is the weight factor, n is the total number of i indicators.

Table 4.2: Indicator values expressed in SEI terms

I_i	Description	Percentage
1	Very low impact	0% - 15%
2	Low impact	15% - 40%
3	Medium impact	40% - 60%
4	High impact	60% - 85%
5	Very high impact	85% - 100%

The indicators values expressed in SEI terms have been assigned on the basis of the percentages obtained dividing each impact value by the highest one of the same category.

It is possible to consider each w_i equal to 1: this means that all the indicators concur equally to the SEI. Otherwise different w_i values could be considered. If the goal of a project is, for example, the evaluation of environmental burdens on a global scale, a good choice is to define w_i of Global Warming Potential greater than w_i of Eutrophication, which has a local effect (see Table 1.2 in Chapter 1). If the focus of the study are the environmental burdens on regional scale, higher w_i values are given to Acidification, Eutrophication and Photochemical Smog rather than to Global Warming, Ozone Depletion and Gross Energy Requirement. However the choice at moment remains subjective. It is important that the hypothesis are clearly explicated by analyst before applying the SEI.

The Sustainability Environmental Index (SEI) may moreover be used for integrating different options together. In Chapter 9 there is reported a study in which dietary habits and transport means are correlated each other in order to find the best combination from a sustainability perspective. The following linear combination equation was used in that case in order to score the environmental impact of the combination of transportation means and menu:

$$SEI = \frac{1}{2} (SEI_{mi} + SEI_{ti}) \quad (4.2)$$

where the subscripts m and t are referred respectively to menu and transport option.

Other correlation may be used and clearly defined before calculation.

4.3. Conclusion

This chapter proposes a theoretical description of the Sustainability Environmental Index (SEI), practically applied in Chapter 9. It is a simple and quick presentation of the LCA results with specific marks, which can facilitate the interpretation of many indicators.

A scale to quantify the environmental burdens resulting from a LCA analysis is proposed, believing how the establishment of internationally-accepted parameters defined by well known and respected institution, such as International environmental agencies, or governments agreement, will facilitate the penetration of the LCA adoption within companies and productive realities as well as increase the idea of sustainable development in the public opinion.

4.4. References

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Chapter 5

Uncertainty in LCA

In this chapter the uncertainty in Life Cycle Assessment is treated. Input data are often affected by uncertainty, and so are the models used for sustainability evaluations. Here a theoretical approach is adopted, while practical applications are reported in Chapter 6 and in Chapter 8.

5.1. Introduction

Uncertainty is a fundamental element in a LCA in order to assure a good comprehension about the quality of results. A LCA is constituted by four phases, and each of them presents significant associated uncertainties. Decisions made on the basis of a LCA results relating to a process (or an activity) design or improvement may be erroneous without including uncertainty. Uncertainty quantification permits to increase the transparency of LCA data and results. Nevertheless an uncertainty assessment has still not a standard feature (Heijung and Huijbregts, 2004). Looking back in LCA history, we find already in 1992 a SETAC workshop (SETAC, 1993) dedicated exclusively on including uncertainty in LCA (Fava et al., 1994). Scientific papers were produced afterwards (Heijungs et al., 1992; Heijungs, 1994), but were not practically used for two main reasons: first because of a gap in knowledge of uncertainty values relating input data, and moreover because of a deficiency of an apposite software (Heijung and Huijbregts, 2004). These two reasons were strictly correlated: uncertainty data were not collected since no software was available for elaborating those, on the other hand an opportune

software was not developed since there were no data available to be processed. In the last years, this correlation is breaking: Monte Carlo analysis is becoming a standard feature of software and moreover the Swiss Ecoinvent data source, one of the most famous one in use, has begun to collect uncertainty data (Heijung and Huijbregts, 2004).

Uncertainty is intrinsically present in the LCA phases, and a dedicated assessment is desirable to ensure good results. Comparing two processes, evident variation in impacts values may misinform if impacts uncertainty is significant enough to overwhelm any relative differences between alternatives. Uncertainties quantification will sustain informed decision making (Basson and Petrie, 2004; Cowell et al., 2002; Lenzen 2006). If uncertainty has a significant weigh in alternatives estimation, it is really complicated to determine which alternative scenario is the best choice: apparent differences in impacts values may be neglectable compared to uncertainties.

LCA loses credibility if uncertainty is present but it hidden or ignored by the analyst.

5.2. Uncertainty definition

A general definition of uncertainty is “any departure from the unachievable ideal of complete determinism” (Walker et al., 2003) with three dimensions: location, nature and level; the evaluation of the level concerns the quantification of the uncertainty.

Measured values often differ from the true values: this is described by the concept value of *uncertainties*; these are probabilistic errors of quantitative values (Ciroth et al, 2004).

The definition of an error is: the difference between the measured value and the true value; a simple formula may expressed it:

$$\Delta x = x - x_t \quad (5.1)$$

where:

- Δx is the error in x
- x is the measured value for variable x
- x_t is the true value for x.

The single *random error* is not of much relevance in order to evaluate the uncertainty: in fact it will differ in each calculation due to its random nature. Instead it is of great interest the evaluation of *average error* or *mean error*. The standard mean error of a variable x is calculated as the standard deviation s of the random errors Δx_i , obtained from a series of calculations (Wolf , 1979; Höpcke, 1980):

$$s = \sqrt{\frac{1}{m-1} \sum_{i=1}^m (x_i - x_t)^2} \quad (5.2)$$

where:

- s is the standard deviation
- x_i is the observed value for variable x
- x_t is the true value for x
- m is the number of evaluations performed.

The use of the mean \bar{x} as an estimation for the unknown true value (that is unknown) is quite common practically (Höpcke, 1980):

$$x_t \cong \bar{x} = \frac{1}{m} \sum_{i=1}^m x_i \quad (5.3)$$

The uncertainty analysis in LCAs may be conducted paying attention on three levels:

- estimating errors in input data;
- estimating the propagation of errors in the calculation;
- estimating errors in the calculation's outputs, interpreting outcomes with errors and uncertainties.

The propagation of errors in the calculation may be calculated using many methods: interval calculation (Le Téno, 1999), fuzzy logic approaches (Pohl and Ros, 1996), Gaussian error propagation formulas (Heijungs, 1996), and Monte Carlo Simulation (Huijbregts, 2001; Canter et al., 2002; McCleese and LaPuma, 2002). This latest captures the main attention of analysts.

5.3. Confidence and reliability

Confidence and reliability are two strictly correlated concepts: if we state that the study results have a reliability of 90%, this means that there is a confidence of 90% in our results (Norris GA, 2002). If the final results present an insufficient reliability

for the decision-making needs expressed in the beginning of the study, uncertainty analysis represents a good help in identifying which data are most significant. It can be moreover helpful in defining the levels of reduction in data uncertainty required to achieve the attended level of results reliability.

Norris (2002) asserts that an uncertainty analysis in a LCA presents two main difficulty.

The first one is the necessity to integrate dimensions of data quality and data elements. There are different dimensions of quality and reliability in data, as indicated by many authors (Funtowicz and Ravetz, 1987; Funtowicz and Ravetz, 1990; Pate-Cornel, 1996; Cullen and Frey, 1999). If just a half of the data is of good quality, and the other half is not, this does not permit to the analyst to tell something about the quality of results.

The second one is the weight of context (*usage*) upon uncertainty. Uncertainty is an intrinsic characteristic of data itself, and it is moreover dependent from the *usage*, through the use in a specific modelling application.

5.4. Uncertainty dimensions

Norris (2002) proposes a classification of LCI results in six categories, using two dimensions, scope and form (see Figure 5.1).

There are three levels for the scope dimension: process level, tree level and life cycle level.

In the process level results are referred to a single unit of the process. The tree level concerns a *driving process*: it is under study the full set of processes whose outputs are exploited by a given driving process, directly or indirectly. An example may clarify this concept: if the driving process is electricity production, then the tree is the whole chain of processes whose outputs are needed, as coal mining, petroleum extraction, petroleum refining, transport, etc.; outputs are used directly by the generating plant, or indirectly by suppliers. There are two types of trees: *cradle-to-gate* and *gate-to-grave* trees. The first ones are *upstream*, while the last ones *downstream*. The life cycle level is constituted by sets of multiple tree-level results.

Then, there are two levels for the form dimension: single and comparison. Results are expressed in terms of statement about a single process, tree or life cycle, or as a comparison between two processes, trees or life cycles.

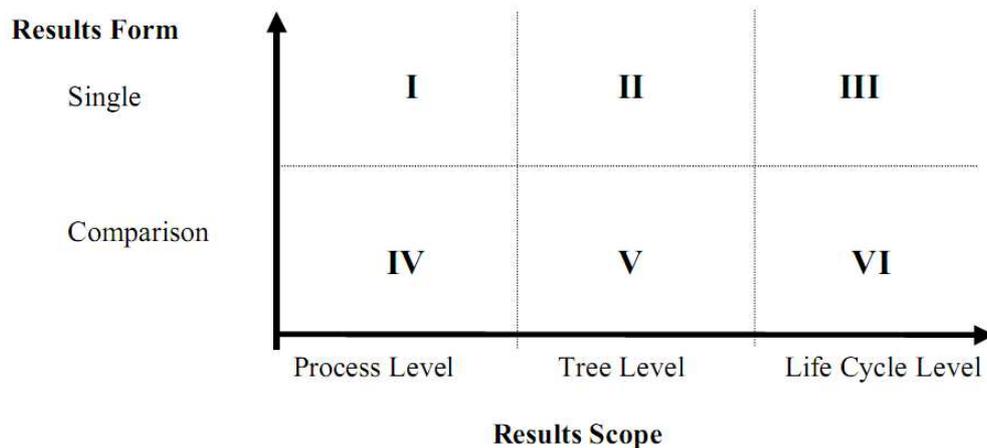


Figure 5.1: Six dimensions of LCA results (Norris GA, 2002)

5.5. Error types

According to Norris (2002), there are different types of error in a LCA. If we study a specific process, an hydroelectric power plant located in Turin (Italy) for example, we collect data about inputs, outputs and releases. The results may be affected by two types of error: measurement and aging errors. *Measurement errors* depend to the fact that data collection may be not perfectly accurate. *Aging errors* depend to the continuous changing of the process over time, while the model remains unchanged unless we update it constantly.

The process under study belongs to many process classes: electric power plants in Turin, hydroelectric power plants in North Italy, power plants in Europe and so on. The model of the specific process of the hydroelectric power plant in Turin may be used as a substitute for modelling other processes belonging to related classes. It is possible to model a class of process instead of a specific process: many processes belonging to a class are studied and main results are evaluated. The use of the sample mean as an estimator or model of the class mean may conduct to a *sampling error*, due to the technological distance between data subject and model object. It is quite uncommon having data for a selected sample of the class, so the

arithmetic mean parameters of the subset are used for estimating the class, with some error: the *subset error*.

Moreover, according to Weidema and Wesnaes (1996), when data of a class are used for modelling another one there are errors due to *technological distance* and *temporal distance* between the subject of the data and the object of the modelling. Huijbregts (1998a) introduces the concept of *spatial variability*: most LCA studies present all environmental interventions summed up not considering the spatial context of the intervention and this implies uncertainty in the model. Results may be more suitable making some distinction, for instance between outdoor versus indoor emissions, or between emissions to land versus emissions to sea (Potting and Blok, 1994). In order to take into consideration the spatial variability it is possible to distinguish compartments by choosing appropriate sub-areas for LCA purposes. So there is the necessity to modify both inventory analysis and impact assessment: in this way the appropriate spatial variability is incorporated for the interpretation of environmental interventions. The feasibility of using spatial variability in LCA studies is limited. There are many reasons: firstly because a detailed regional context of emissions is sometimes not known. Moreover there is the need to have detailed environmental information, such as ecological properties, for evaluating local factors. This information is normally available for Europe (Potting et al., 1997), but it is often lacking for other continents. Finally, detailed information related to some impact categories, such as human toxicity and ecotoxicity, may not be available.

Huijbregts (1998b) continues his variability study analysing the *temporal variability*, that is present in both the inventory and the impact assessment of LCA studies. LCA emission data are usually evaluated dividing yearly emission by yearly production: in this way variations of environmental interventions over a relatively short time period are not considered. It is possible to take into account temporal variability over the years, if inventory data are collected for several years (Hanssen and Asbjornsen, 1996), though yearly variations in environmental interventions are quite difficult to be acquired. Moreover data can be collected with unreliable or inaccurate measurements and this can be the origin of the variation: it is necessary to pay attention on interpretation of the yearly variation.

It is quite hard including temporal variability in inventory data, however not including it involves consequences for the operationalisation of temporal variability in the impact assessment.

Variables like wind speed and temperature are substance-independent, and they are utilized for evaluating characterisation factors, such as toxicity potentials (Guinée et al., 1996). These variables vary over time, but it is not possible to match their temporal variation with the inventory data, due to the fact that temporal variation is not made operational in the inventory analysis over short time periods.

Another type of temporal variability in the impact assessment is operational. The values of some impact potentials, as global warming potentials (GWPs), ozone depletion potentials (ODPs) and photochemical ozone creation potentials (POCPs), are strictly correlated to the chosen time horizon (Albritton et al., 1996; Solomon et al., 1994; Andersson-Skold et al., 1992). The temporal variability is due to the difference in life times between the reference substance, selected per impact category, and the remaining substances. In order to overpass this problem, model outputs may be compared for several chosen time horizons, changing temporal variability in uncertainty due to choices.

5.6. Uncertainty from data and from models

According to many authors, uncertainty may be derived from two main sources: from data and from models.

Data may present five typologies of uncertainty (Finnveden et al., 2009): variability (e.g. different electricity use of various similar boilers and, considering just one boiler, the use may change over time or depend on the conditions), miss-specificity (e.g. data for the electricity use of a 75 L boiler in Germany in 2006 are used instead of a 80 L boiler in France in 2007), error (e.g. a typo, a mistake in the units, or a decimal point confused for a thousands separator), incompleteness (e.g. data on emissions of dichlorobenzene from the incinerator under study are missing), round-off (e.g. entering 0.3 instead of 0.342 introduces an error higher than 10%).

While uncertainty from data is quite clear to be understood, it is more complicated the comprehension of uncertainty from models. The study conducted by Winkler

(2004) and Winkler and Bilitewski (2007) highlights a large discrepancy in results starting from the same inputs but using different models. They compared LCA models for waste management (ARES, EPIC/CSR, IWM2, MSW-DST, ORWARE and UMBERTO) assessing the waste management scenario of the city of Dresden (Germany). The analysis of Winkler and Bilitewski (2007) was the first one to underline differences among different LCA models, quantifying these differences up to 1400%. Results so different from the six models lead to contradictory results.

An important study was conducted by Rimaitytė et al. (2007): results obtained from the LCA-IWM model relative to incineration were compared with measured emissions data. A large difference between estimated data and measured data is underlined.

Another study was performed by Gentil et al. (2010) on waste management LCA models: eight models were used to compare the functional unit, system boundaries, energy modelling, and process models including collection, transport, separation, material reprocessing, thermal and biological treatment, and landfilling. Results have shown that comparability of models may be affected by the assumption of the time horizons for landfill emissions. Moreover the date of development and the current level of knowledge at that time are correlated to different hypothesis applying the models. Further, the models have the tendency to be most suitable for studies in the country where they have been developed: it is important to consider the fact that some country-specific data might be used in the LCI, and this can lead to models differences if the study is conducted on another country.

5.7. Uncertainty tools

Accordingly to Bjorklund (2002), some tools for the evaluation of data quality and uncertainty are needed, but they must not be too complex. Sometimes the time and the resources required for collecting data are so high that it is not practically feasible and consequently the tools are not applied. It is important that tools are developed with the feature of generating impressive reports of data quality and uncertainty and moreover of making analysts helped to used them. A tool may be defined good if it permits to reach four goals: improving data inventory routines,

model insight and results presentation, and lastly being an help for decision makers. If a tool is quite simple, it may be rejected if it does not guarantees enough accuracy; otherwise, especially if its use is very practically, it is a good choice. Focusing on areas where large improvements can be reached more easily permits to maximize the work, avoiding to waste time in superfluous calculations.

The most popular approach in LCA is the **Monte Carlo simulation**. Some software, as SimaPro and Umberto, offer the opportunity to evaluate uncertainty using the Monte Carlo analysis. The Ecoinvent database provides uncertainty data in many of its processes.

Another approach is an **approximate analytical method** (Baker and Lepech, 2009): results can be presented as linear relationships between input and output variables, which can be approximated with the application of Taylor Series expansion in the First-Order Second-Moment method. This approach is less diffused than the Monte Carlo one, due perhaps to its more complex mathematics. On the other hand, it is less computationally expensive than Monte Carlo analysis: this is profitable if any part of the model required complex numerical modelling (Baker and Cornell, 2003). The third approach that is here illustrated is the **sensitivity analysis**, though it is not a complete uncertainty propagation procedure. However it is functional for the comprehension of a system, and moreover it represents an helpful tool in finding input parameters those can be omitted in the simulation, as they are quickly recognized to be insignificant to the final results. The sensitivity analysis consists of systematically varying input parameters in order to determine how sensitive the outputs are to each input.

Heijungs (1996) proposes to carry out firstly a general sensitivity analysis using standard uncertainty estimates: this permits to discover parameters with the higher contributes in uncertainty of environmental profiles. Then the priority for more accurate measurements or better uncertainty estimates is given to those parameters which together cover a specific percentage of the sensitivity range, 90% for instance. Using one standard sensitivity range has however a negative feature: parameters which are initially thought to present a minor contribution to LCA

results, but has an expected large unknown uncertainty range, are eliminated from the analysis ahead of time.

In LCAs it is not feasible to study the effects of all possible combination of choices, to highlight the uncertainty ranges of all the input data used in the inventory, and to perform an extensive parameter uncertainty analysis in the characterisation phase (Huijbregts, 1998b).

Making choices in a LCA is inevitable and it implies uncertainty in outcomes. Huijbregts (1998b), partly basing on Kortman et al. (1996) recommendations, suggests a procedure suitable for reducing the number of choice combinations in LCAs: after producing many options for each LCA choice, find the two extreme ones among them; then create two extreme combinations of options and finally evaluate the effect of them on the LCA results.

Huijbregts (1998b) suggests another strategy to simplify the uncertainty analysis: implementing uncertainty ranges for accumulated environmental interventions rather than individual parameters in LCA inventories (Kennedy et al.,1996).

5.8. Monte Carlo simulation

A Monte Carlo analysis is a method for uncertainty analysis: some parameters are selected and then their influence on cumulative results is calculates due to their uncertainties. A large number of simulations is performed with the same model in subsequent series using each time a different set of model input parameters. The procedure is constituted by four steps: firstly uncertainties, width and probability distribution are explicated for each input datum; then the variable values are selected from the probability distribution; subsequently results are calculated using the selected input values; the first three steps are iterated until mean and distribution do not change anymore, and finally the probability distributions of the output data are calculated. The Monte Carlo method permits to evaluate a large number of scenarios.

For a function $f(x) = y$, one run of the simulation may be expressed as (Ciroth et al, 2004):

$$f(x) = f(x_t + \Delta x) = y_t + \Delta y = y \quad (5.4)$$

where:

- x_t is the true value for x
- Δx is the error in x
- y_t is the true value for y
- Δy is the error in y
- y is the observed value for variable y .

The Monte Carlo simulation is widely used for performing error propagation for model parameters (Lo et al., 2005; McKone, 1989; Bergin et al., 1999; Hertwich et al., 2000; Huijbregts et al., 2000; Goovaerts et al., 2001; Dubus et al., 2003).

However, the simulation cannot correct ill-specified input uncertainties and it does not tell what to do with the uncertainty it calculates.

The Monte Carlo method presents as a negative feature the time required for computing data. Morgan and Henrion (1990a and 1990b) state that reliable results are obtained in 10,000 runs. The software for uncertainty analysis must calculate the inventory analysis and the impact assessment for 10,000 times. If we hypothesize that a single run needs 1 second, some 3 hours are required for calculation (Heijungs and Kleijn, 2001).

The Monte Carlo simulation is nowadays the most common method for studying the propagation of input uncertainties into output uncertainties (Lloyd and Ries, 2007). However it has been admitted that its application to large systems may be too computationally intensive (Ciroth et al., 2004; Heijungs and Frischknecht, 2005; Hong et al., 2008).

5.9. Approximate analytical method

Heijungs (2010) proposes its solution for uncertainty analysis, basing on analytical error propagation.

The theory of analytical error propagation has been recommended in LCAs using Taylor series expansion by many authors (Heijungs, 1994; Giroth et al., 2004; Hong et al., 2008).

Taylor series expansions are based on the approximation formula for calculating the variance of a stochastic result using stochastic data (Bevington and Robinson, 1994;

Morgan and Henrion, 1990a and 1990b). For a system of the form $z=f(x,y)$ it assumes the form:

$$\text{var}(z) = \left(\frac{\partial f}{\partial x}\right)^2 \text{var}(x) + \left(\frac{\partial f}{\partial y}\right)^2 \text{var}(y) + 2 \frac{\partial f}{\partial x} \times \frac{\partial f}{\partial y} \text{cov}(x,y) \quad (5.5)$$

where:

- $\frac{\partial f}{\partial x}$ is derivative of f in function of x
- $\text{var}(x)$ is the variance of the variable x
- $\frac{\partial f}{\partial y}$ is derivative of f in function of y
- $\text{var}(y)$ is the variance of the variable y
- $\text{cov}(x,y)$ is the covariance between the stochastic variables x and y.

In most cases the formula is simplified not considering the term related to covariance: this is due to the fact that data are not available, or its value can be assumed negligible as the uncertainties are in many cases independent.

5.10. Sensitivity analysis

The sensitivity analysis is defined for a continuous function $y=f(x)$ by its derivative $\frac{\partial y}{\partial x}$, where:

- y is the result
- x is the input parameter.

The parameter y changes in function of x accordingly to the derivative. In LCAs, functions are usually linear expressions, so the derivatives are constant. We have non-linear expressions when a input parameter x represents an emission that causes an effect with a threshold. In this case the sensitivity may be defined for ranges of x, and it works when there are few such ranges or independent non-linear parameters. In fact if the expression for sensitivity calculation becomes too complex, it loses its information capability (Steen, 1997).

5.11. Uncertainty in SimaPro software

The software SimaPro (Pré, 2010) permits to use some databases. One of them is the Ecoinvent database (Ecoinvent Centre, 2007), released in two versions: one with unit processes, and the other one with system processes. The unit process version

data are provided with a specification of uncertainty: a mean value is accomplished by uncertainty information, always assumed as a lognormal distribution that is characterized by a standard deviation. A lognormal distribution has the property that the square of the geometric standard deviation covers the 95% confidence interval: a square geometric standard deviation of 1.2 means that 95% of all values lies between the best mean value times 1.2 and the best mean value divided by 1.2. It is obvious that, if the square of the geometric standard deviation is equal to 1, there is no uncertainty.

The estimation of the geometric standard deviation presents some problems, due to the fact that data often are obtained from a limited number of measurements. In Ecoinvent this problem is overcome by using a Pedigree matrix, originally developed by Weidema and Wesnaes (1996).

Six criteria plus a so-called Basic uncertainty factor are taken into account in order to assess each data point. The squared geometric standard deviation is calculated accordingly to the following formula (PRé, 2010):

$$SD_{g95} = \sigma_g^2 = \exp^{\sqrt{[\ln(U_1)]^2 + [\ln(U_2)]^2 + [\ln(U_3)]^2 + [\ln(U_4)]^2 + [\ln(U_5)]^2 + [\ln(U_6)]^2 + [\ln(U_b)]^2}}$$

(5.6)

where:

- U_1 is the uncertainty factor of reliability
- U_2 is the uncertainty factor of completeness
- U_3 is the uncertainty factor of temporal correlation
- U_4 is the uncertainty factor of geographic correlation
- U_5 is the uncertainty factor of other technological correlation
- U_6 is the uncertainty factor of sample size
- U_b is the basic uncertainty factor.

The meaning of the factors from U_1 till U_6 is expressed in Table 5.1 together with numerical values.

Table 5.1: Description and quantification of the factors (from U_1 till U_6) used in geometric standard deviation formula in Ecoinvent database

Score:	1	2	3	4	5
U1 Reliability	Verified data based on measurements	Verified data partly based on assumptions OR non-verified data based on measurements	Non-verified data partly based on qualified estimates	Qualified estimate (e.g. by industrial expert); data derived from theoretical information (stoichiometry, enthalpy, etc.)	Non-qualified estimate
	1.00	1.05	1.10	1.20	1.50
U2 Completeness	Representative data from all sites relevant for the market considered over an adequate period to even out normal fluctuations	Representative data from >50% of the sites relevant for the market considered over an adequate period to even out normal fluctuations	Representative data from only some sites (<<50%) relevant for the market considered OR >50% of sites but from shorter periods	Representative data from only one site relevant for the market considered OR some sites but from shorter periods	Representativeness unknown or data from a small number of sites AND from shorter periods
	1.00	1.02	1.05	1.10	1.20
U3 Temporal correlation	Less than 3 years of difference to our reference year (2000)	Less than 6 years of difference to our reference year (2000)	Less than 10 years of difference to our reference year (2000)	Less than 15 years of difference to our reference year (2000)	Age of data unknown or more than 15 years of difference to our reference year (2000)
	1.00	1.03	1.10	1.20	1.50
U4 Geographical correlation	Data from area under study	Average data from larger area in which the area under study is included	Data from smaller area than area under study, or from similar area		Data from unknown OR distinctly different area (north America instead of middle east, OECD-Europe instead of Russia)
	1.00	1.01	1.02		1.10
U5 Further technological correlation	Data from enterprises, processes and materials under study (i.e. identical technology)		Data on related processes or materials but same technology, OR Data from processes and materials under study but from different technology	Data on related processes or materials but different technology, OR data on laboratory scale processes and same technology	Data on related processes or materials but on laboratory scale of different technology
	1.00		1.20	1.50	2.00
U6 Sample size	>100, continuous measurement, balance of purchased products	>20	> 10, aggregated figure in environmental report	>=3	unknown
	1.00	1.02	1.05	1.10	1.20

Table 5.2 shows factor U_6 characterization, that has been parameterized basing on expert judgement.

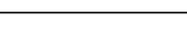
Table 5.2: Description and quantification of the factor U_b used in geometric standard deviation formula in Ecoinvent database

Input / output group	U_b	Input / output group	U_b
Demand of:		Emission to air of:	
thermal energy	1.05	CO ₂	1.05
electricity	1.05	SO ₂	1.05
semi-finished products	1.05	combustion: NOX, NMVOC total, methane, N2O and NH ₃	1.50
working materials	1.05	Combustion: CO	5.00
transport services	2.00	Combustion: individual hydrocarbons, TSM	1.50
waste treatment services	1.05	Combustion: PM10	2.00
Infrastructure	3.00	Combustion: PM2.5	3.00
Resources:		combustion: polycyclic aromatic hydrocarbons (PAH)	3.00
primary energy carriers	1.05	Combustion: heavy metals	5.00
metals, salts	1.05	process emissions: individual VOCs	2.00
land use, occupation	1.50	process emissions: CO ₂	1.05
land use, transformation	2.00	process emissions: TSM	1.50
Waste heat:		process emissions: PM10	2.00
emission to air, water, and soil	1.05	process emissions: PM2.5	3.00
Emission to water of:		from agriculture: CH ₄ , NH ₃	1.20
BOD, COD, DOC, TOC	1.50	from agriculture: N2O, NOX	1.40
Inorganic compounds (NH ₄ , PO ₄ , NO ₃ , Cl, Na etc.)	1.50	Radio nuclides (e.g., Radon-222)	3.00
individual hydrocarbons, PAH	3.00	process emissions: other inorganic emissions	1.50
heavy metals	5.00	Emission to soil of:	
from agriculture: NO ₃ , PO ₄	1.50	oil, hydrocarbon total	1.50
from agriculture: heavy metals	1.80	Pesticides	1.20
from agriculture: pesticides	1.50	heavy metals	1.50
Radio nuclides	3.00	Radio nuclides	3.00

In Ecoinvent unit process, each process presents in the comment field a list of six figures, like 1.2.1.5.1.3: trough these numbers the uncertainty estimation is explained using the pedigree matrix.

The SimaPro software offers four different distribution for applying the Monte Carlo method, as listed in the Table 5.3 (PRÉ, 2010).

Table 5.3: List of different distributions offered by the SimaPro software

Distribution	Data needed	Graphical presentation
Range	Min and Max value	
Triangular	Min and Max value plus best guess value	
Normal distribution	Standard deviation and best guess value	
Lognormal distribution	Standard deviation and best guess value	

The **range distribution** is used when there is an equal probability that a value lies between a minimum and a maximum value. The **triangular distribution** is sometimes used as a substitute for the normal one: there is the advantage that

extremely high or low values cannot occur. In order to perform an uncertainty assessment in SimaPro it is necessary to specify the range and the best guess value: this permits to find out the point with the highest probability. So there is the possibility to specify an asymmetrical distribution that can also be used to simulate a lognormal distribution. The **normal distribution** needs that both the best guess value (the centre) and the standard deviation (SD) are specified; in SimaPro, however, it is required to specify the 2xSD value. This is functional as the 95% confidence interval lies between 2xSD and +2XSD. This practically means that the 95% of the data points lie between these points, and that just the 2.5% lie above or below these points. If there is an estimate for the upper and lower value, they can often use be used to estimate 2xSD. Finally the **lognormal distribution** occur when values with a normal distribution are multiplied. This is very common in LCAs, so this distribution can be considered as the default. The 95% confidence interval is defined by dividing or multiplying the best guess value with the squared geometric standard deviation. SimaPro requires to specify this square of the standard deviation, often written as σ^2 .

In order to perform a Monte Carlo calculation in SimaPro, it is necessary to specify some important parameters:

- the impact assessment method used
- the criteria to stop the calculations
- a fixed number of runs
- a stop criterion.

The stop criterion has the aim to stop the Monte Carlo calculation when the standard error of mean reaches the specified level. The lower the standard error of mean, the more reliable your results are. It is moreover possible to stop the calculation at any time, though the stop criterion or the maximum number of runs is not yet reached.

5.12. Uncertainty diffusion in LCA studies

Uncertainty is a useful tool in LCAs, however it is often disregarded. Ross et al. (2002) have analyzed LCAs published post-1997. They included in their review only

those studies in which inventory and impact assessment are accomplished accordingly to standard LCA methodology, and moreover only those studies assessing a mix of environmental burdens (global warming, ozone depletion, acidification, eutrophication, photochemical oxidation, eco-toxicity and human-toxicity). After this selection the number of studies to review was 30. They found that very few LCAs performed a qualitative analysis of uncertainty associated to the impact assessment: the 53% of the studies did not mention uncertainty at all. The remaining 47% of the studies referred to uncertainty problems, but just the 13% did it explicitly.

In my opinion this lack in uncertainty assessment, though it is clearly recommended by the ISO methodology, it is due to an intrinsic difficulty rather than to a negligence of the analysts. Performing a Monte Carlo analysis requires the knowledge of a range of data for a single input, and practically this occurs quite rarely. Nowadays databanks often offer data with uncertainty information: these data are however secondary data. If we want to perform a LCA with primary data, we are often divided between the desire of using real data and that of evaluating their uncertainty. Which one is the best choice: using data with uncertainty information from databanks or using data measured from the specific process under study but without uncertainty information? I chose this second option for my studies, integrating results, when it is possible, with a sensitivity analysis (see Chapters 6 and 8).

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PART II: Case Studies

Chapter 6

Two-Steps Anaerobic Digestion

In this chapter the environmental impacts of the Anaerobic Digestion process in two stages are evaluated. The Life Cycle Assessment described in Chapter 1 is here practically applied. Moreover a sensitivity analysis is performed, and the sustainability of the process is verified using EROI and EPT tools, theoretically described respectively in Chapter 5 and in Chapter 3.

6.1 Introduction

Anaerobic Digestion (AD) is a naturally occurring decomposition process, by which organic matter is broken down to its simplest chemical components under anaerobic conditions. This process can be very useful to treat organic waste such as: sewage sludge, organic farm wastes, municipal liquid/solid wastes, green/botanical wastes as well as organic industrial and commercial wastes.

The overall of anaerobic digestion process can be schematically divided into 4 sections, as shown in Figure 6.1: pre-treatment, digestion, gas upgrading and digestate treatments. The level and type of pre-treatment depends on the type of feedstock. The key point is the digestion unit, which can work at different conditions, e.g. pH, temperature and hydraulic retention time and one or more stages.

Before being digested, the feedstock has to be pre-treated. Various types of pre-treatment can be adopted depending on the feedstock; the addition of water or on towing away undesirable materials such as large items and inert materials (e.g. plastic, glass and metals) to allow a better digestate quality are generally applied.

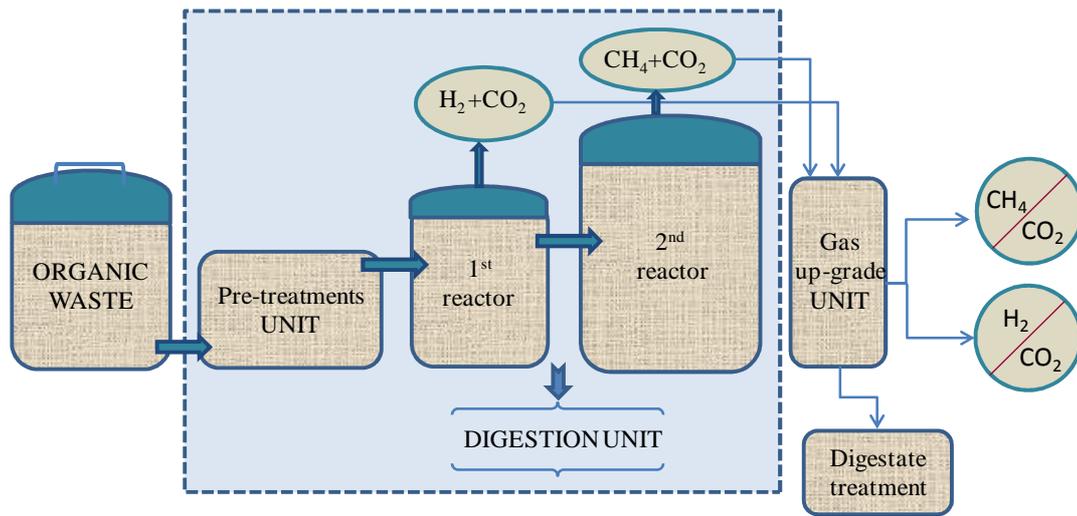


Figure 6.1: Schematic view of the process involved in AD technology. The AD stages taken into consideration for the sustainability evaluation are shown inside the block: pre-treatment unit and digestion unit (two stages in series for the production of biohydrogen and biomethane, respectively)

A more efficient digestion and higher energy production are obtained by means of acid or base as well as thermal pre-treatments (Kim et al., 2009; Wang and Wan, 2008a; Yang et al., 2007; Mu et al., 2006; Chen et al., 2002). The digestion process itself takes place in a digester, which can be classified in relation to the temperature, the water content of the feedstock, the number of stages (single or multi-stages) and the type of biogas produced, that is methane or hydrogen (Ueno et al., 2007; Kraemer and Bagley, 2005). During the natural anaerobic digestion process, some bacteria convert the organic material present in the digester into hydrogen, carbon dioxide and water-soluble metabolites, such as ethanol, acetic, butyric and propionic acids (Tommasi, 2011 and 2012). These bacteria usually live in close proximity to other bacteria that consume these metabolites, including hydrogen, and produce final products such as methane and CO_2 . If the differences

between *hydrogen forming bacteria* HFB which produce H_2 and *hydrogen consuming bacteria* HCB are known, it is possible to design a two-stage operation condition process (Lakaniemi et al., 2011). The combination of multi-stage processes with the production of two high value gases, such as hydrogen and methane, is a solution which leads to several energy and environmental advantages: two separate fluxes of high energy value gas (H_2 and CH_4), optimization of the AD process for the treatment of refuse and an improvement in the control process (Monnet, 2003). The anaerobic digestion, biogas by-product (CH_4 and/or H_2) can be used to create a source of income: biogas can be upgraded removing carbon dioxide and water vapour, and then, for example, used in a cogeneration unit as Combined Heat and Power (CHP) to produce electricity and heat. The digestate either liquid or solid can instead be used as a fertilizer, or further processed into compost or high value products, as bioproducts, e.g. acetic and butyric acids (Angenent et al. 2004).

6.1.1 Hydrogen and methane production in two-steps AD

Anaerobic digestion, from a biological point of view, is a multistep process that involves the action of various microbial species (Lyberatos, 1999). Usually, such a process contains a particular step, the so-called rate-limiting step, which, being the slowest, limits the rate of the overall process (Hill, 1977). However, the limiting step is not always the same over a wide range of operating conditions. It depends on the waste characteristics, hydraulic retention time, temperature and many others (Speece, 1983). The two-steps AD process is a process in which hydrogen and methane are produced in two separate bioreactors through the separation of hydrogen forming bacteria from methane forming bacteria (Tommasi, 2011; Gómez et al., 2011) working in different conditions such as pH and hydraulic retention time. This partition, optimizing the fermentation process, permits the production of two high value gases by splitting acetogenesis from methanogenesis, and increases the overall energy production (89%) compared to one-step processes (only hydrogen production ~33%, only methane production ~84%) as can be seen in Table 6.1.

Table 6.1: Stoichiometric energy efficiency of the reaction involved in H₂ and CH₄ production from AD with respect to the energy contained in 1 mol of glucose

Theoretical reaction involved in two-stage AD process	Energy yield (kJ/mol glucose)			
	H ₂	CH ₄	Total	Comparison
Energy content in glucose	-	-	2,872	100%
Theoretical maximum H₂ yield C ₆ H ₁₂ O ₆ + 6H ₂ O → 12H ₂ + 6CO ₂	2,870.4	-	2,870.4	99.9%
Maximum H₂ yield from acidogenesis (1st step) C ₆ H ₁₂ O ₆ + 2H ₂ O → 4H ₂ + 2CO ₂ + 2CH ₃ COOH	956.8	-	965.8	33.3%
Maximum CH₄ yield from standard AD C ₆ H ₁₂ O ₆ → 3CH ₄ + 3CO ₂	-	2,400	2,400	83.3%
Maximum yield from two-steps (H₂+CH₄) C ₆ H ₁₂ O ₆ + 2H ₂ O → 4H ₂ + 2CH ₄ + 4CO ₂	956.8	1,600	2,556.8	89%

For a sustainable energy point of view, it is necessary to energetically valorize the Volatile Fatty Acids (VFAs) and other residue compounds present at the end of the first anaerobic step, which produces H₂ and Volatile Fatty Acids as acetogenic fermentation. This valorization also permits the waste materials to be degraded as much as possible; the most adequate way is to use VFAs as a substrate for methanogenes to produce methane. The energy analysis can be applied for only the H₂ or CH₄ production or for both AD processes in series to produce H₂ and CH₄, respectively. The results of these analyses show that the net energy balance of a bioreactor producing H₂ in almost all conditions is never in the positive range (Ruggeri et al., 2010). On the contrary, two-steps (H₂ plus CH₄) in series show an increase in the produced energy and, consequently, the net energy balance becomes positive. In fact, from a thermodynamic point of view, during H₂-fermentation from glucose, only 1/3 of the energy available is converted to H₂, the other 2/3 remains occluded in the form of fatty acids. Therefore one can obtain a positive net energy balance from an energy valorization of the end-liquid

metabolites that accompany the H₂ production, due to the increment in the energy production. Temperature and pH play an important role on fermentative hydrogen production. Many studies (Akutzu et al., 2009; Wang and Wan, 2008b, Mu et al., 2006; Zhang and Shen, 2006; Nath and Das, 2004; Hawkes et al., 2002; Lee et al., 2006) have shown that, in an appropriate range, increasing the temperature can increase the ability of hydrogen forming bacteria and archaea bacteria to produce hydrogen and methane, during fermentation; a much higher temperature level (40÷50 °C) provokes a decrease in the hydrogen production and shifts the biological pathways towards the production of other compounds, such as lactic acid. Temperature is the most important parameter, from an energetic point of view, because it influences not only the energy produced, but also the energy necessary to run the bioreactor. Therefore the temperature is the key parameter in the net energy balance of the technology. In the present sustainability analysis of the AD of organic refuse, the produced H₂ and CH₄ were experimentally evaluated by conducting test runs with market refuse pre-treated with 2N NaOH (Bettoli, 2010).

6.2. Net Energy in Anaerobic Digestion process

The net energy produced in an anaerobic digestion process is the difference between the energy produced in the form of biofuels (H₂ and/or CH₄) and the direct energy used to run and maintain the system. The production of renewable energy (e.g. biofuels) in fact requires energy expenditure, as any other process. Pretreatment units also represent an expensive energy cost. To perform the energy balance in the present case, all the energy quantities have been evaluated in energy units per unit volume of bioreactor (MJ/L). Many factors can influence the net energy balance of anaerobic digestion such as the type of feedstock, environmental, geographical and operational conditions.

In order to calculate the net energy, it is necessary to consider the energy balance of the anaerobic bioreactor, including the thermal and the electrical energy necessary to run the bioreactor. A detailed analysis of the net energy production of

two-steps AD can be found in (Ruggeri et al., 2010). The net energy production E_{net} may be calculated as:

$$E_{net} = E_{H_2+CH_4} - (E_h + E_{hp} + E_l + E_m + E_p) \quad (6.1)$$

where:

- $E_{H_2+CH_4}$, Energy produced [MJ/L]
- E_h , Heating energy necessary to reach the working temperature [MJ/L]
- E_{hp} , Heating energy necessary to reach the pre-treatment temperature [MJ/L] if the pre-treatment is present
- E_l , Thermal energy loss, which depends on the outdoor ambient temperature and the duration of the fermentation [MJ/L]
- E_m , Electrical energy consumed for mixing [MJ/L] if a mixing system is present
- E_p , Electrical energy consumed for pumping [MJ/L]

The calculation of the net energy production requires the evaluation of the heat necessary to pre-treat the organic refuse and the heat needed to keep the system at the working temperature. The heat required to keep the fermenting broth at the working temperature (T_w) is the sum of the heat necessary to warm up the feeding biomass from the ambient outdoor temperature (T_a) to T_w and the heat lost from the digester walls, which depends on the geography of the plant location, seasonal variations and obviously on the night/day oscillations. Figure 6.2 offers an overall view on the energies involved in the balance of an AD reactor, which is valid either in the case of producing H_2 or CH_4 .

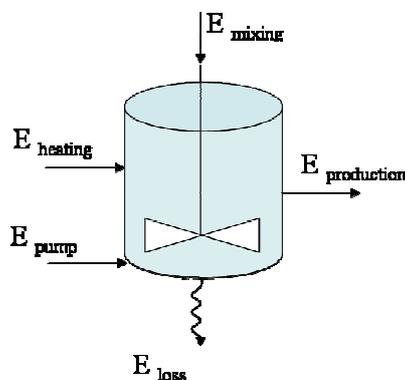


Fig. 6.2: Global view on the energies involved in the balance of an AD reactor

The energy balance of full-scale AD should be conducted in order to evaluate the quantity of net energy produced from a carbonaceous substrate as a function of two parameters namely: working temperature and the diameter of a stated construction material of bioreactor. In the following sections each term of equation (6.1) will be explained.

6.2.1 Energy production

The produced energy is the total energy embedded in the produced gas, i.e. the energy contained in the amount of hydrogen and/or methane retrieved from a single batch run, with reference to the reactor volume and it can be calculated as:

$$E_{produced} = F * (P_{H_2}(T_w) * H_{H_2} + P_{CH_4}(T_w) * H_{CH_4}) \quad (6.2)$$

where:

- $P_{H_2}(T_w)$ and $P_{CH_4}(T_w)$ are the specific productions of H_2 and CH_4 , respectively, and refer to the amount of gas produced during a single batch run. They are expressed as Nm^3 of H_2/CH_4 per unit of fermenting broth, which depends strongly on the working temperature.
- H_{H_2} and H_{CH_4} are the Low Heating Values (10.8 MJ/ Nm^3 and 36.18 MJ/ Nm^3 , respectively)
- F is the filling coefficient of the reactor, which is usually equal to 90% of the available volume.

6.2.2 Heating energy

The energy required to warm up the fermenting broth mainly depends on its specific heat, the difference between the outdoor ambient and the working temperature of the bioreactor, and the efficiency of the heating system. The heating energy per unit volume of bioreactor can be calculated as:

$$E_h = (\rho * c_p * \Delta T * F) / \eta \quad (6.3)$$

where:

- ρ is the biomass density [kg/m^3]
- c_p is the specific value of fermenting broth heat [$kcal\ kg^{-1}\ ^\circ C^{-1}$]

- $\Delta T = (T_w - T_a)$ according to the season [°C]
- η is the global efficiency of the system to furnish heat taking into account η_{comb} and $\eta_{\text{heat exc}}$

ρ and c_p have been considered equal to those of water. The difference between the working temperature and the outdoor ambient ΔT was considered for different seasonal conditions, i.e., summer and winter conditions. A combustion boiler was considered to calculate the global efficiency of the warming system η : combustion efficiency ($\eta_{\text{comb}} \approx 0.8$) and heat exchanger efficiency ($\eta_{\text{heat exc}} \approx 0.6$) were multiplied to obtain the global efficiency ($\eta \approx 0.48$) necessary to furnish the heat required.

6.2.3 Thermal energy loss

The difference between the working temperature of the digester T_w and the pervading outdoor ambient temperature T_a . It is responsible for the heat loss from the fermenting broth. The amount of energy lost should be supplied from such a temperature control system and it depends on the insulation of the fermenting broth, the surface area exposed to the ambient and the duration of the batch run. The energy loss per unit volume of reactor can be calculated as:

$$E_l = (4.5 * k/s * \Delta t(T_w) * \Delta T/D) / \eta \quad (6.4)$$

where:

- k [$\text{Kcal h}^{-1} \text{m}^{-1} \text{°C}^{-1}$] is the thermal conductivity of the digester walls (e.g. material such as concrete or steel, coupled with an insulator, such as polystyrene)
- s is the thickness of the reactor/insulating walls
- $\Delta t (T_w)$ is the total duration of fermentation [h]
- $\Delta T = T_w - T_a$, according to the season [°C]
- D is the diameter of reactor

The resistance to heat transport is here only considered for the insulating material (k/s). This assumption leads to an overestimation of the insulator thickness for the same energy loss. Some explanations are given here about the above assumption.

The heat flux from the bioreactor crosses three heat resistances in series. Therefore, the global thermal resistance U^{-1} is:

$$U^{-1} = 1/h_i + s/k + 1/h_e \quad (6.5)$$

where h_i and h_e are the internal and external convective heat transfers. A very thick insulator leads a higher resistance, due to a series of phenomena (Rohsenaw and Hartnett, 1973) and both the convective coefficients, h_i and h_e can be disregarded; the situation graphically reported in Figure 6.3 occurs, hence the controlling resistance will be that of the insulator, in term of thickness s and heat conductivity k .

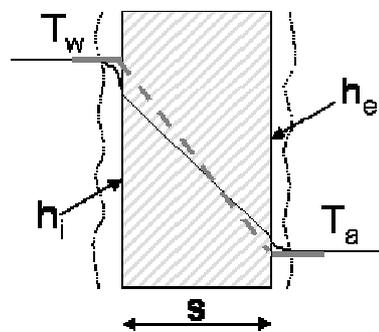


Fig. 6.3: Assumption used for the evaluation of heat loss across bioreactor wall

6.2.4 Focus on a thermal insulator

The insulating material is responsible for the main influence in the energy balance of AD for several reasons. It plays a particular role in limiting the heat loss and, at the same time, it contributes as GER to the total indirect energy consumed for construction materials. Insulating materials are solid and usually non homogeneous materials, characterized by a very low thermal conductivity value k , mainly due to the air enclosed in the pores of the material itself. The value of the coefficient of conductivity k [W/(m*K)] indicates the degree of ease with which a material allows the transport of energy, through collisions at the molecular level: apart from the nature of the material, it also depends on the considered medium (solid, liquid or gas), the crystal structure, if it is a solid, the temperature and pressures and the

degree of homogeneity of materials (Cocchi, 1993). Thermophysical properties of some insulating materials are mentioned in section 6.4.3 (Table 6.7).

6.2.5 Electrical energy

Apart from the minor energy necessary for control the whole system, the larger quantity of electrical energy to run a bioreactor is consumed for mixing E_m and pumping E_p . A small energy input is necessary for E_p for pH control. Working in batch mode, the electrical energy is spent for filling and emptying the bioreactor by a pump. In this case, it is possible to consider, as a first approximation, $E_p \sim 0$, compared with the electrical energy consumed for the agitation, considering the duration of the process of the order of weeks or months. However, E_p depends on the electric power of the pump:

$$E_p = P_{wpump} * \Delta t \quad (6.6)$$

The evaluation of the energy necessary to mix the fermenting broth could be computed by applying a turbulence scale-up criteria, taking into account a constant Reynolds number vs. diameter. If one considers the constant ratio between the diameter of the bioreactor and that of the impeller as a geometrical scale-up, the following relations can be used to estimate the electrical power necessary to mix the broth (Nagata, 1975):

$$Re \approx N_1 D_1^2 = N_D D_D^2 \quad (6.7)$$

$$P_W = (P_n * \rho) / (8 * g * \pi) * N_1^3 * D_1^6 * D_D^{-4} \quad (6.8)$$

where:

- 1 and D refer to the bench scale and actual bioreactor respectively
- P_n is the power number and it can be evaluated by applying the procedure reported in Bailey and Ollis (1986) considering the Re of the bench scale bioreactor
- P_w is the power required to have a defined Re in order to evaluate the energy consumed for mixing

It is necessary to take into account the running time, which depends on T_w :

$$E_m = P_W * \Delta t(T_w) / \eta_{el} \quad (6.9)$$

An efficiency factor of electrical energy conversion into mixing energy equal to 0.75 was considered. All the above mentioned Equations could be implemented in an Excel sheet to perform the energy balance for each situation.

6.3 Indirect energy in Anaerobic Digestion process

When performing a sustainability analysis of a technology, great care should be taken in the evaluation of the energy and materials flows. The net energy and useful energy differ from each other because of for the contribution of the total indirect energy (refers to Figure 6.6 in section 6.4.1). In mathematical terms, the useful energy can be evaluated from the difference between the net energy and the indirect energy. Equation (6.10) expresses, in mathematical terms, each contribution that should be considered to evaluate the total indirect energy having taken into account the Global Energy Requirement (GER), i.e. the sum of all the contributions of the energy life cycle (direct, indirect, capital and feedstock energy):

$$E_{ind} = E_{chem} + E_{mat} + E_{dir\ en} + E_{main} + E_{decomm} + E_{amort} \quad (6.10)$$

where:

- E_{chem} is the GER of chemicals [MJ]
- E_{mat} is the GER of construction materials [MJ]
- $E_{dir\ en}$ is the GER of direct energy [MJ]
- E_{main} is the energy for maintenance [MJ]
- E_{lab} is the energy for labour [MJ]
- E_{decomm} is the energy for decommissioning [MJ]
- E_{amort} is the energy for amortization [MJ]

As previously stated, both direct and indirect energy need to be measured in a physical energy unit; hence it is necessary to convert all the material flows into energy units. In the process, materials that were produced elsewhere are usually used. This leads to a higher consummation of energy, but without it the process cannot take place. The GER allows one to convert and evaluate the energy content in each kilogram of material and is evaluated in energy units per unit mass of

material. E_{chem} and E_{mat} were evaluated by utilizing the SimaPro 7.2.4 software (Pré, 2010) and the Ecoinvent database (Ecoinvent, 2007) (Table 6.2).

Table 6.2: GER values of the construction materials and chemicals

Steel	29,630 kJ/kg	(DeBenedetti et al., 2007)
Polystyrene	105,800 kJ/kg	(Buwal 250, 1996)
NaOH	4.578 kJ/kg	(Ecoinvent, 2007)
Water	6.169 kJ/kg	(Ecoinvent, 2007)

An analogous discussion should be made about direct energy: the scheme process should be followed for direct energy. The direct energy such as, e.g., electricity could be taken off from the grid; each unity of electricity has determined an energy expenditure that occurs elsewhere in order to be produced it (power plant construction, grid maintenance etc.). The indirect contribution of direct energy is calculated using a GER value expressed in an appropriate unit, e.g. kJ/kWh in the case of electricity. In the AD process here analyzed, the term $E_{dir\ en}$ is zero because the energy is produced in loco with a cogeneration plant using a quote of the biogas produced by the AD process itself. In the calculation of Equation (6.10), E_{decomm} is the energy consumed for decommissioning: it was considered that a workman works for 2 months to disassemble the plant. The energy consumed for maintenance operation (E_{main}) is evaluated as 15% of the total energy expenditure for construction materials.

It is intrinsically difficult to evaluate the energy consumed for labour E_{lab} and this parameter is often disregarded. In this case, the scoring procedure is only valid for comparisons of technologies in the same category i.e. capital intensive or labour intensive. It is calculated considering the GER of a typical meal in the industrial word: a worker needs to eat twice a day each workday in order to have the power necessary to work on the AD process, this was considered for 365 days per year.

Finally E_{amort} is the energy necessary for amortization and it is evaluated as the energy necessary to reconstruct the plant.

6.4 Sustainability Evaluation

In this section the results of the evaluation of the net and useful energy of the two-stages anaerobic fermentation process producing H_2+CH_4 is reported by evaluating the above energy terms. All the energy terms are expressed as energy unit per volume evaluated over the operation time.

6.4.1. Net Energy and Useful Energy production for two main cases

Table 6.3 shows results of the evaluation of the net energy for the case study considering diameters of 4 m and 10 m. Regarding the volume of bioreactors we considered one of 1.3 m where hydrogen was produced, and the second of 4 m diameter as CH_4 producer; the volume where hydrogen was produced was considered 1/20 of the volume of CH_4 producer bioreactor for all the situations, results refer to the diameter of methane bioreactor.

Table 6.3: Net Energy evaluation in the case of 4m and 10m diameter respectively

	D= 4m	D= 10m
$E_{H_2+CH_4}$ [kJ/L]	1,123	1,123
E_{dir} [kJ/L]	171	161
E_{net} [kJ/L]	952	962

The useful energy production E_u can be calculated as:

$$E_u = E_{net} - E_{ind} \quad (6.11)$$

where E_{ind} is the total indirect energy consumed.

Results of the calculation of the useful energy for the same situation is reported in Table 6.4.

Table 6.4: Useful Energy evaluation in the case of 4m and 10m diameter respectively

	D= 4m	D= 10m
E_{net} [kJ/L]	952	962
E_{chem} [kJ/L]	120.5	120.5
E_{mat} [kJ/L]	90	36
$E_{dir\ en}$ [kJ/L]	0	0
E_{main} [kJ/L]	18	7
E_{amort} [kJ/L]	210.5	156.5
E_{lab} [kJ/L]	29	1.8
E_{decomm} [kJ/L]	0.3	0.002
E_{ind} [kJ/L]	468	322
E_u [kJ/L]	484	640

From Table 6.4 one can see that the increase of the Useful energy E_u along the diameter from D =4 m to D= 10 m is of 32%.

In order to show the linkage between all the energy terms as contributions to the sustainability of AD, an analogical model of the process considering a 4m diameter reactor is presented in Figure 6.4. This figure highlights the linkage between: i) the energy production due to the knowledge of the technology; ii) the direct energy consumption necessary to run the technology; iii) the indirect energy; iv) the useful energy i.e. the energy that the technology gives to society in a sustainable way.

It is interesting to conduct a detailed examination of the percent values: the theoretical available energy evaluated as the LHV of organic waste is 100 %. The percent value drops to 48.1% as produced energy. This depends on the present knowhow on the fundamentals of AD technology or, in other words, the current knowledge on biochemistry and microbiology does not permit better results to be obtained. The percent value further decreases to 40.8% as net energy, considering that the present technology of heat exchanger and electricity production technology have lead to an optimization of the system, the 7.3% is consumed as

direct energy. In the classical energy analysis approach, 40.8% of energy is delivered to society and no other aspects need to be considered.

From a global point of view, in terms of energy sustainability, it is also necessary to take into account the energy expenditure necessary for the production of materials and the energy flows in different part of the World. In this context, the useful energy effectively available from society adopting the AD technology is 20.7%: at this point it is clear that the complete ignorance of indirect energy is not justified.

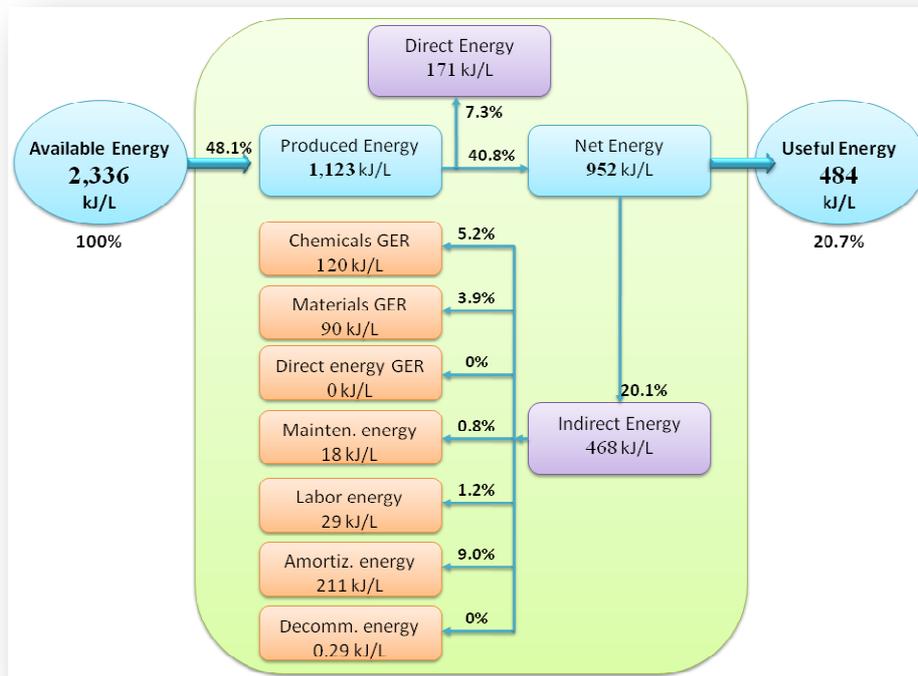


Fig. 6.4: Analogical model of the H₂ and CH₄ technology process at T=35°C with heat recovery and a diameter of the bioreactor equal to 4m

One consideration should be made regarding the modality of supplying direct energy to run the plant: we have considered that the energy is produced through the cogeneration of a part of the produced methane. This energy can be furnished from different sources, for example, from a renewable one, such as solar energy or wind power. In this case, the degree of sustainability would not change because the use of renewable sources to furnish direct energy is removed from a different energy service in society. In other words, the quality of the energy to produce direct

energy in such a technology has no influence in the energy sustainability. In fact, with the present approach the useful energy remains constant.

6.4.2 The evaluation of EROI and EPT

In this section the sustainability of AD is evaluated by EROI and EPT. In this manner it is possible to score the H₂+CH₄ produced by the AD against other energy technologies; the AD is equivalent to “mine mouth” for fossil energy sources.

EROI and EPT are evaluated using the Equations (6.12) and (6.13). The results are shown in Figures 6.5 and 6.6, considering two cases: with or without the contribution of labour in the Total Indirect Energy. The EROI and EPT values vs. the reactor diameter, which is the scale-up parameter for this kind of technology, are reported. The sustainability of the technology increases with the dimensions: without the labour contribution, EROI is always higher than 1; with the labour contribution, the technology is sustainable for higher diameters than 1.5m.

$$EROI = E_{net} / E_{ind} \quad (6.12)$$

$$EPT = t_d / EROI \quad (6.13)$$

In Table 6.5 the values of EROI and EPT are reported for the two diameters considered in previous paragraph for the evaluation of useful energy.

In spite of the fact that the energy labour as only food contribution in this analysis, a great effect of labour on the EROI for low diameters of the bioreactor was found.

Table 6.5: EROI and EPT evaluation for different diameters

Diameter [m]	EROI [#]	EPT [yr]
4	2.03	9.84
10	2.99	6.69

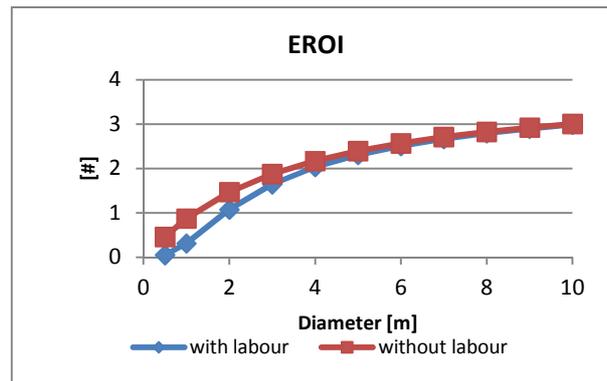


Figure 6.5: EROI of an AD process with and without the labor contribution

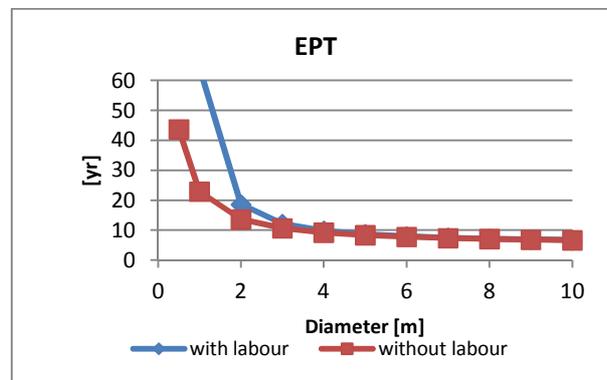


Figure 6.6: EPT of an AD process with and without the labor contribution

Table 6.6: EROI of several energetic technologies (Sentimenti and Biorgi, 2006)

Technology	EROI (Elliot)	EROI (Hore-Lacy)
Hydroelectric	50-250	50-200
Mini hydroelectric	30-270	-
Oil XIX century	50-100	-
Oil today		5-15
Wind turbine	5-80	20
Nuclear Power	5-100	10-60
Photovoltaic Si	3-9	4-9
Photovoltaic Film		25-80
Natural gas	-	5-6
AD (present estimation)		0-3

A comparison of the evaluated EROI and EPT of H_2+CH_4 values with other energy technologies ranks the AD technology in a good position among renewable and fossil energy sources (see Table 6.6).

6.4.3 Sensitivity of EROI and EPT

The sensitivity of EROI and EPT to the indirect energy of materials has been investigated: the main case previously described, with polystyrene foam as the insulator, is compared with other cases, varying the kind of insulating material. In order to permit a comparison between different insulating materials. Physical and thermophysical properties are reported in Table 6.7. In the sensitivity evaluation net energy value has been kept constant, i.e. $k/s=\text{cost.}$, which means that the thickness of the insulating walls varies according to thermal conductivity value.

Table 6.7: Physical and thermophysical properties of different materials

Insulation materials	k [W/(m*K)]	d [kg/m ³]
polyurethane	0.03	35
polystyrene foam	0.035	25
Cork	0.04	100
sheep wool	0.04	28
lime foam	0.045	100
Straw	0.058	175
recycled paper	0.07	400
raw clay	0.132	700

Figure 6.7 and 6.8 show the EROI and EPT for different insulating materials: polyurethane, cork and sheep wool permit similar performances to those of polystyrene foam, while better results could be achieved using lime foam, straw and raw clay; the use of recycled paper as an insulating material has the worst impact on both the EROI and EPT.

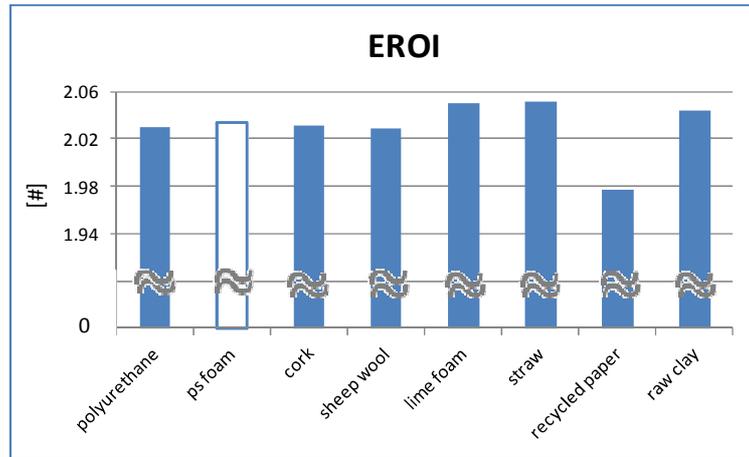


Fig. 6.7 EROI evaluation of different insulation materials

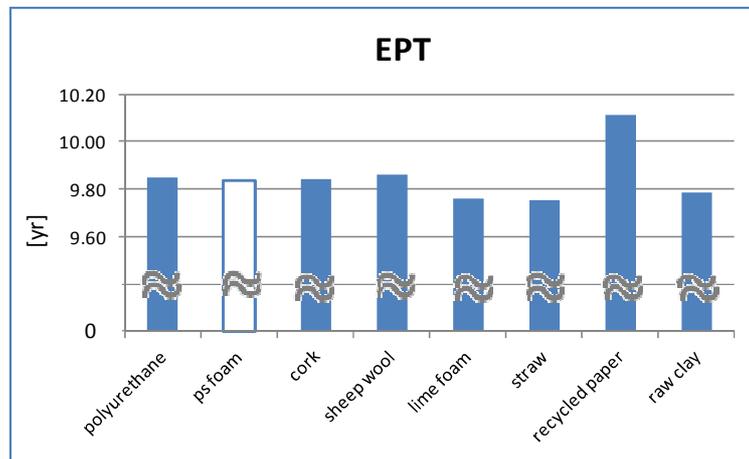


Fig. 6.8 EPT evaluation of different insulation materials

6.4.4. Sensitivity of substrate

Figure 6.9 shows the Analogical Model applied at the same process using glucose as substrate instead of Organic Waste Materials. Pre-treatments are not required.

It is interesting to conduct a detailed examination of the percent values: the theoretical available energy evaluated as the LHV of glucose is 100% the percent value drops to 72.9% as produced energy. This depends on the present knowhow on the fundamentals of AD technology. The percent value further decreases to 67.6% as net energy considering that the present technology of heat exchanger and electricity production technology have lead to an optimization of the system, the

5.3% is consumed as direct energy. In the classical energy analysis approach, 67.7% of energy is delivered to society and no other aspects need to be considered.

From a global point of view, the useful energy effectively available from society adopting the AD technology is 53.3%.

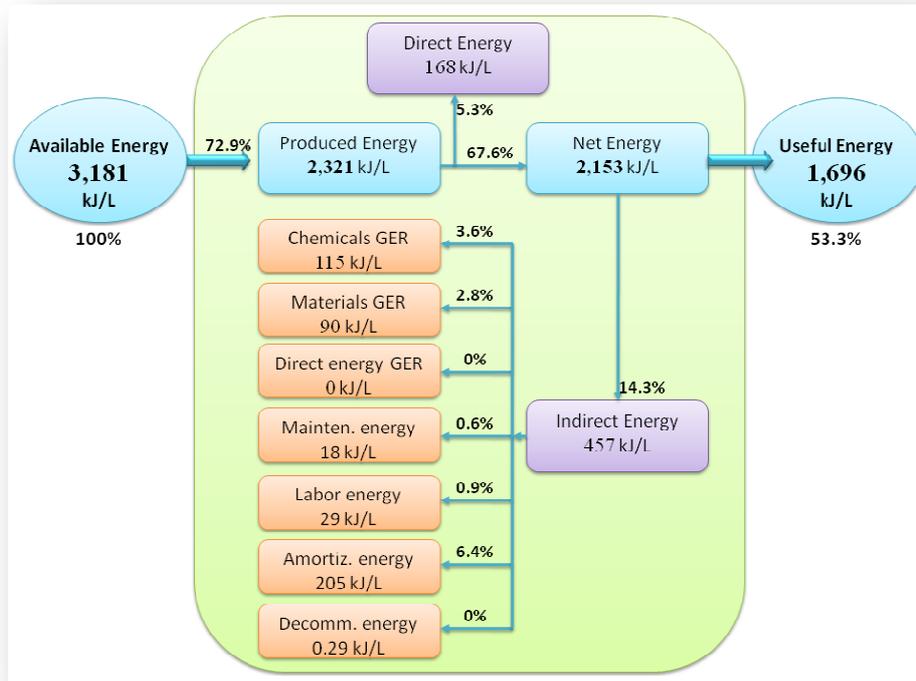


Figure 6.9: Analogical model of the glucose test

A comparison of the results permits to underlain that the best case is the one using glucose: this is predictable as the glucose has a higher LHV. The glucose test is interesting as a comparison with the OWM, that is the real object of the study. An AD technology can be considered renewable using waste materials, not refined materials which also need to be produced by a process that consumes other energy and materials.

6.4.5. Sensitivity of pre-treatments

Figure 6.10 shows the Analogical Model applied at the same process using Organic Waste Materials as substrate with both basic and thermal pre-treatments.

The basic pre-treatment consists in adding 20ml of 2N NaOH per litre of broth, i.e. 1.6g/L. The thermal pre-treatment consists in heating the broth from ambient temperature (5°C and 15°C in winter and in summer time respectively) till 121°C using hot water through a conventional jacket. Then the broth cooling till 35°C (operational reactor temperature) is reached through a natural convection heat transfer.

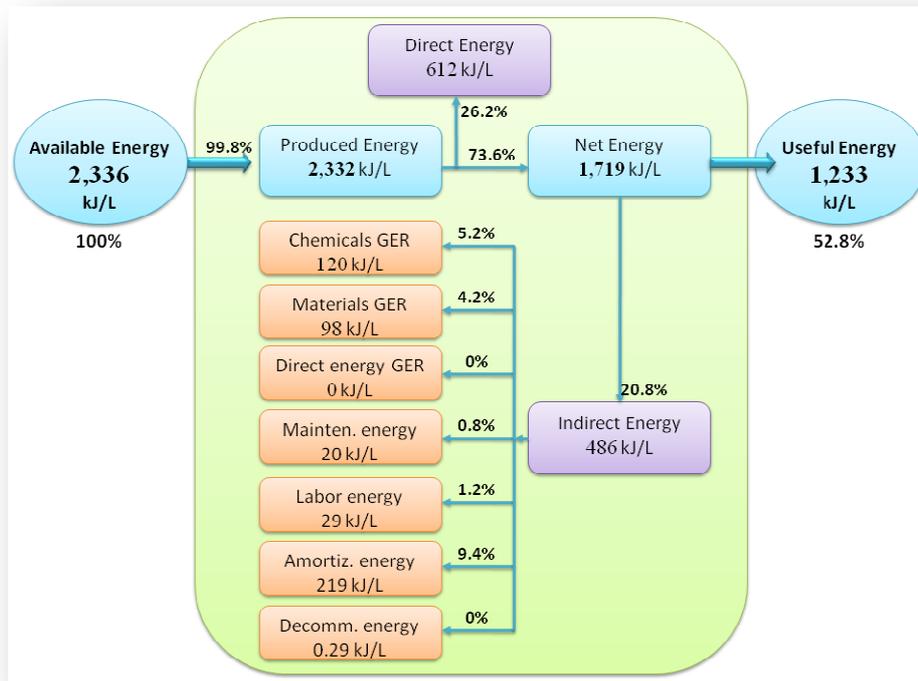


Figure 6.10: Analogical model of the OWM with basic and thermal pre-treatments test

Figure 6.10 shows again the same model previously described applied in the case of OWM with basic and thermal pre-treatment test. The theoretical available energy is 100%, the percent value drops to 99.8% as produced energy and further to 73.6% as net energy; finally the useful energy effectively available from society is 52.8%.

The model of the OWM with basic and thermal pre-treatments test is more optimized: 52.8% as energy effectively available from society against 20.7% of the model with just the basic pre-treatment test.

6.4.6. Final results of sensitivity analysis

Figure 6.11 shows the trends of net energy in the three cases: the base case using OWM with basic pre-treatment, glucose and OWM using thermal and basic pre-treatments.

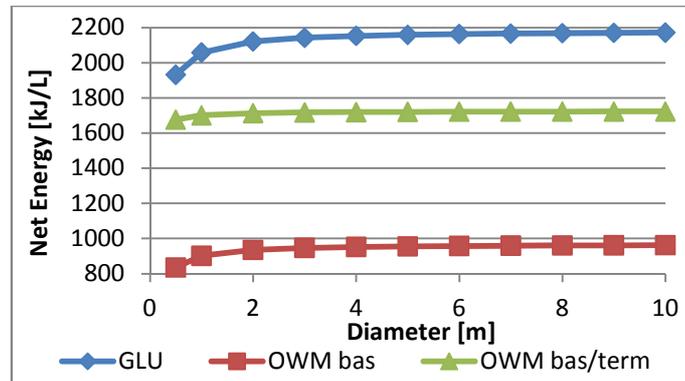


Figure 6.11: Net energy obtained from the three tests: glucose, OWM with basic pre-treatments and OWM with basic and thermal pre-treatments

EROI and EPT are evaluated in the three cases and results are shown in Figure 6.12.

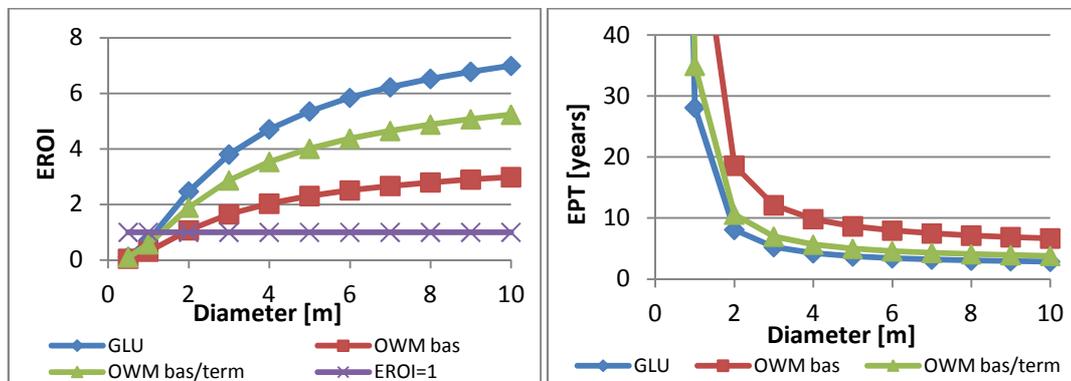


Figure 6.12: EROI and EPT values for the three case studies: glucose, OWM with basic pre-treatments and OWM with basic and thermal pre-treatments

6.5 Conclusion

The degree of sustainability of H₂/CH₄ energy carrier via the Anaerobic Digestion technology has been studied through an evaluation of the useful energy and a determination of the EROI and EPT parameters. The technology resulted to be sustainable for all the diameters higher than 1.5 m; an EROI >10 is never obtained.

The use of an analogical model to evaluate the useful energy of the studied technology has shown that more than 20% of the available energy present in the organic refuse can be furnished to society as useful energy. This value depends to a great extent on the material that is used to insulate the plant. The best case was obtained considering straw, while the worst case was referred to the use of recycled paper for insulating purposes. A comparison of the evaluated EROI values with other energetic technologies places the AD technology in a good ranking position among renewable and fossil energy sources for higher bioreactor diameters.

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Chapter 7

Nanofilled-polymer-based heat exchangers

In this chapter the environmental impacts of nanofilled-polymer-based heat exchangers are evaluated. The Life Cycle Assessment described in Chapter 1 is here practically applied.

7.1. Introduction

The present chapter has the aim to describe an LCA project performed on nanofilled-polymer-based heat exchangers. The project is part of a main project developed for the European Union, called Thermonano.

The European Union is involved in reducing greenhouse gas emissions and in assuring a more secure energy supply: in this perspective, increasing energy efficiency in all areas of consumption is a main topic. Thermonano project originates from this topic, focusing on heating sector.

“Low temperature differences imply large exchange surfaces are required, which are unfeasible from the economic viewpoint because expensive metal is needed to withstand the presence of liquids produced by condensation, as well as from the technical side because the volumes required are too large for specific applications,” explains Guido Saracco, head of the Department of Applied Science and Technology at Politecnico di Torino University in Italy.

The Thermanano project is carried out by a consortium of researchers in order to develop nanofilled-polymer-based heat exchangers that will enable more effective heat conductivity, due to the percolation network of carbon or metal fillers, and to deliver this greater heat recovery efficiency at a much lower cost than using metals such as stainless steel or copper alloys. Other important objects are design flexibility (so that they can be used in a wide variety of applications) and superior resistance to corrosion, which is an intrinsic property of the polymer matrix.

The complete name of the Thermanano project is “Low-temperature heat exchangers based on thermally-conducting polymer nanocomposites”. It anticipates many application areas for these new heat exchangers:

- intercoolers that increase the efficiency of large diesel engines, where heat conductive plastics can provide a cheaper alternative to the very expensive copper alloys which are mandatory when seawater is used as the cooling media (for example, in large naval engines or power plants situated close to the sea)
- spin-off applications in the sea-water-cooled condensers, thermo-electric plants based on the Rankine cycle (a closed-loop, thermodynamic cycle which usually uses water or an organic fluid as the working fluid to convert heat into work)
- heat recovery systems from combustion flue gases acting below 300°C, where commercial metal-based systems lose cost-effectiveness
- applications in the chemical and process industries which have to deal with harsh chemicals or corrosive acid environments, such as biomass furnaces.

The partnership includes two universities (Politecnico di Torino in Italy and TU Bergakademie Freiberg in Germany) and two research centres (the French Atomic Energy Commissariat and the Polymer Institute of the Slovak Academy of Sciences) as well as three small and medium sized enterprises (Astra Refrigeranti SpA of Italy, Nanocyl of Belgium and Starom Group SRL of Romania) and two large companies

(Simona AG and SGL Carbon-GmbH, both of Germany), all of which were selected for their specific expertise in undertaking the project's challenges.

The goal of Thermonano project is for heat conductivity that is at least 10 times greater than that of pure polymers and also exceeds 5 W/mK, due to the percolation network of carbon, such as graphite, carbon nanotubes and graphite particles, or metal fillers with specific loadings not exceeding 10 per cent of the total weight (Han and Fina, 2011).

These new heat-conductive polymers should deliver a 50 per cent cost reduction compared to metals used in such demanding contexts, which should turn into a 20 per cent cost reduction for the complete appliance. They will also enable new heat exchanger designs and manufacturing routes, thereby potentially opening new opportunities for application.

A second work line will look at tailoring existing plastic forming techniques, such as injection moulding, pressing and extrusion. According to Professor Saracco, "this experimental and modelling work line, performed with world-class equipment by leading companies in the field, will aim at preserving excellent thermal conductivity properties within differently shaped products, such as corrugated plates and tubes". Finally, a third work line will manufacture and test up to two proof-of-concept heat exchangers.

A task of the Thermonano project is the LCA of the new developed heat exchangers in comparison with the traditional one. The overall objective of the LCA study is to evaluate environmental impacts related to the whole lifecycle of the ThermoNano Prototypes of nanofilled-polymer-based heat exchangers. The analysis has been performed considering standard indicators such as Global Warming, Acidification, Eutrophication, Human Toxicity, Energy Resources.

In the evaluation of the impact assessment of the prototypes and the reference heat exchanger, the process of manufacturing as well as materials for the apparatus

have been considered. The processes have been deeply investigated on the basis of the available information; a conceptual model for the LCA analysis has been created, paying particular attention to the environmental consequences of the use of electricity, heat, and auxiliary utility consumes (process water, steam,...).

7.2. Goal and scope definition

The goal of the present LCA is to define the environmental burdens associated to the industrial production of four new prototypes of nanofilled-polymer-based heat exchangers and to make a comparison with a traditional heat exchanger produced by Astra Refrigeranti S.p.A. The analysis is performed considering standard indicators such as Global Warming, Acidification, Eutrophication, Human Toxicity, Energy Resources.

LCA is applied to a reference heat exchanger and to four prototypes with different performance data:

- Reference heat exchanger: a classic heat exchanger produced by Astra Refrigeranti S.p.A. with a power of 96 kW and a volume of 0.065 m³
- Prototype 1 (P1): a nanofilled-polymer-based heat exchanger produced through an injection moulding process with a power of 16 kW and a volume of 0.007 m³
- Prototype 2 (P2): a nanofilled-polymer-based heat exchanger produced through a compression moulding process with a power of 16 kW and a volume of 0.005 m³
- Prototype 3 (P3): a nanofilled-polymer-based heat exchanger produced through a compression moulding process with a power of 95 kW and a volume of 0.03 m³
- Prototype 4 (P4): a nanofilled-polymer-based heat exchanger produced through a tube extrusion process with a power of 2.6 kW and a volume of 0.01 m³.

Table 7.1: Performance data of the heat exchangers under study

Heat exchanger	Power [kW]	Volume [m ³]
Reference	96	0.065
P1	16	0.007
P2	16	0.005
P3	95	0.030
P4	2.6	0.010

7.2.1. Software and database

The software SimaPro 7.2 (Pré, 2010) is used in order to perform the present study. Primary data are collected from Thermonano's partners, while secondary data are derived from databases, particularly Ecoinvent v2. The support of the industrial partners Astra Refrigeranti S.p.A., Nanocyl S.A., Omnistamp s.r.l., and SGL Carbon AG was important to implement a LCA model based on actual industrial processes and production chains and therefore consistently estimate the impacts.

7.2.2. Functional Unit

Functional unit is the reference unit, to which environmental indicators are associated. In this study the unit chosen is: 1 GWh/m³.

This choice permits to make a comparison among heat exchangers with different properties without losing important information. The energy term at the numerator is obtained multiplying the power of the heat exchanger and its lifetime expressed in hours. The denominator is the volume of the heat exchanger. A long argument has been made about it: the question was if volume or surface should be taken into account, neglecting the other one. The surface option seemed the best choice from a theoretic point of view, but volume is preferable from an operational perspective. Our partners has strongly required to privilege volume, since the surface estimation may presents difficulties due to the complexity of the prototypes.

7.2.3. System Boundaries

The definition of system boundaries of the study is one of the most important step of a LCA. This study provides five eco-profiles, starting from the extraction of raw materials, until the heat exchangers are ready to be used.

7.3. LCA Inventory

Life Cycle Inventory (LCI) analysis involves creating an inventory of flows from and to nature for a product system. Inventory flows include inputs of water, energy, and raw materials, and releases to air, land, and water. To develop the inventory, a flow model of the technical system is constructed using data on inputs and outputs. The input and output data needed for the construction of the model are collected for all activities within the system boundary.

Next paragraphs present in detail the flow models and the inputs of each heat exchanger.

7.3.1. Astra Reference

Data about the reference heat exchanger produced by Astra Refrigeranti S.p.A. are known in detail. An analogical model of the process is presented in Figure 7.1: there are two main inputs, materials and amortization energy. Materials are described in the blue box: each of them should be produced in a manufacturing process using raw materials and energy. Amortization energy is the energy required by the process: it includes the environmental loads of the machines that produce energy.

Some hypothesis are taken: the heat exchanger has a life of 20 years and it works for 300 days in a year, final disposal is not considered and the machines live for 20 years too.

The energy mix considered for this study is the italian one (medium voltage).

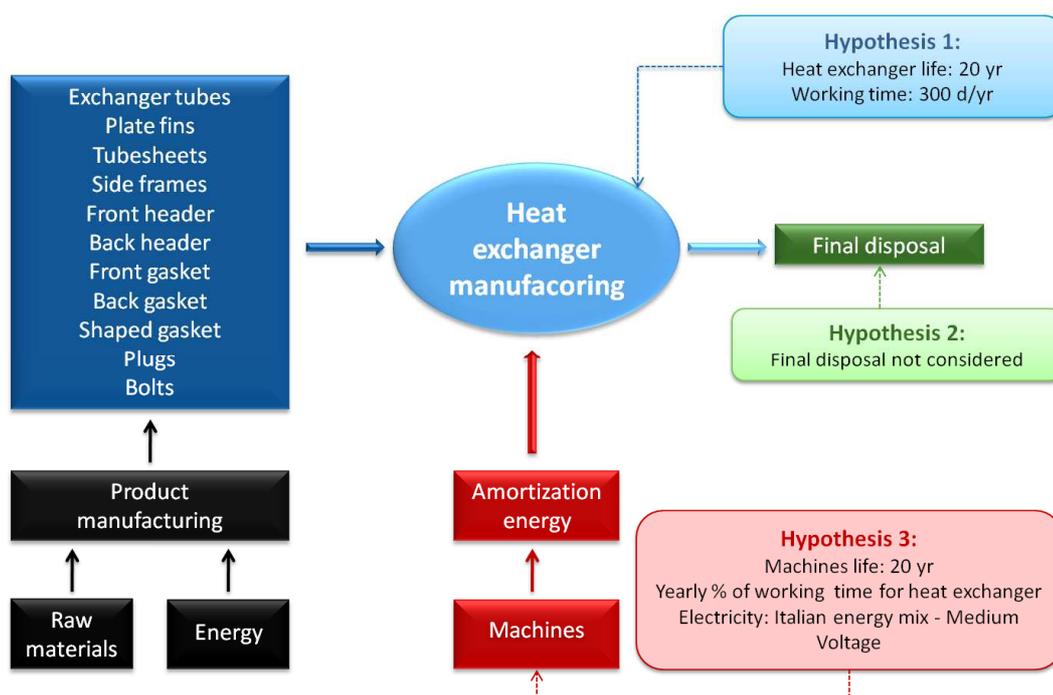


Figure 7.1: Flow model of the reference heat exchanger produced by Astra Refrigeranti

7.3.2. Prototype 1

The Prototype 1 is a nanofilled-polymer-based heat exchanger produced through an injection moulding process with a power of 16 kW and a volume of 0.005 m³.

The CNT tubes are produced by Nanocyl and used to form the compound (20 kg) in a quantity of 1.53 kg together with 16.91 kg of PVDF and 2.05 kg of graphite. This operation requires the use of two machines: a pellettizer (4 kWh) and an extruder (38.6 kWh).

The compound is used to produce the plates of the heat exchanger through injection moulding. For each plate (57.6 g) the indirect contribution of machines can be summarised in 1.904 g of steel, 0.04 g of copper, 0.04 g of HDPE and 0.606 mL of oil; moreover 327.83 Wh of electricity is required.

The tooling operation requires 0.5 kWh of energy per kg of plates, while the welding contribution is negligible.

Finally the assembly is done using 81 plates and a case of 40 kg produced from polyamide.

Figure 7.2 shows each step of the process, including which partner has the task to perform it.

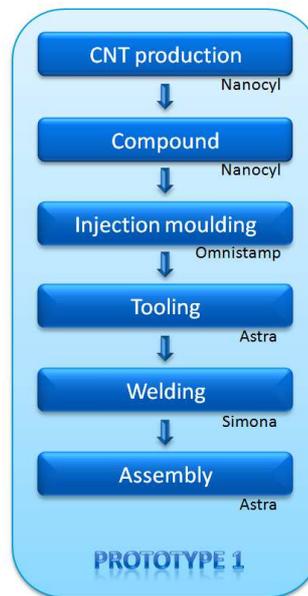


Figure 7.2: Flow model of Prototype 1

7.3.3. Prototype 2

The Prototype 2 is a nanofilled-polymer-based heat exchanger produced through a compression moulding process with a power of 16 kW and a volume of 0.007 m³.

The CNT tubes are produced by Nanocyl and used to form the master in a percentage of 5% together with 32% of PVDF and 63% of graphite.

The master is diluted (0.2 kWh/kg of electricity) and used to produce the plates of the heat exchanger through compression moulding. For each plate (725 g) the indirect contribution of machines can be summarised in 23.965 g of steel, 0.503 g of copper, 0.503 g of HDPE and 7.63 mL of oil; moreover 507.5 Wh of electricity is required.

The tooling operation requires 0.5 kWh of energy per kg of plates, while the welding contribution is negligible.

Finally the assembly is done using 21 plates and a case of 40 kg produced from PVDF.

Figure 7.3 shows each step of the process, including which partner has the task to perform it.

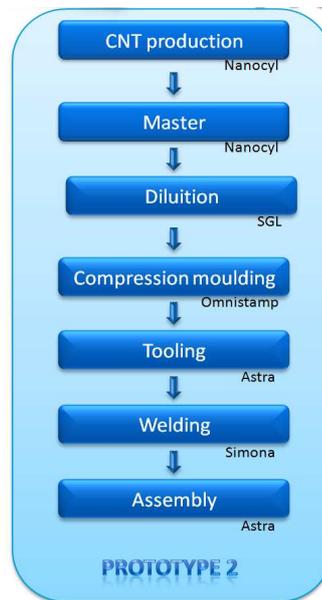


Figure 7.3: Flow model of Prototype 2

7.3.4. Prototype 3

The Prototype 3 is a nanofilled-polymer-based heat exchanger produced through a compression moulding process with a power of 95 kW and a volume of 0.03 m³.

The CNT tubes are produced by Nanocyl and used to form the master in a percentage of 5% together with 32% of PVDF and 63% of graphite.

The master is diluted (0.2 kWh/kg of electricity) and used to produce the plates of the heat exchanger through compression moulding. For each plate (725 g) the indirect contribution of machines can be summarised in 23.965 g of steel, 0.503 g of copper, 0.503 g of HDPE and 7.63 mL of oil; moreover 507.5 Wh of electricity is required.

The tooling operation requires 0.5 kWh of energy per kg of plates, while the welding contribution is negligible.

Finally the assembly is done using 127 plates and a case of 60 kg produced from PVDF.

Figure 7.4 shows each step of the process, including which partner has the task to perform it.

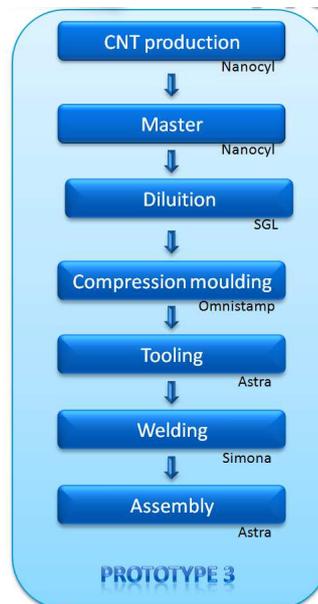


Figure 7.4: Flow model of Prototype 3

7.3.5. Prototype 4

The Prototype 4 is a nanofilled-polymer-based heat exchanger produced through a tube extrusion process with a power of 2.6 kW and a volume of 0.01 m³.

The CNT tubes are produced by Nanocyl and used to form the master in a percentage of 5% together with 32% of PVDF and 63% of graphite.

The master is diluted (0.2 kWh/kg of electricity) and extruded to produce the tubes of the heat exchanger: 0.6 kWh/kg of electricity is required. Indirect contribution of machines are neglectible.

The tooling operation requires 0.5 kWh of energy per kg of plates.

Finally the assembly is done using 1 kg of tubes and a case of 17.6 kg produced from PET.

Figure 7.5 shows each step of the process, including which partner has the task to perform it.



Figure 7.5: Flow model of Prototype 4

7.4. Life Cycle Impact Assessment

This section presents the impacts of the different heat exchangers considered. Each paragraph starts with a table showing the energy and environmental loads. Then each impact is analyzed in detail in a quantized flow sheet of the process: the arrows thickness is proportional to the impact flow that represents. Each box is quantified with a percent valued.

7.4.1. Astra Reference

Table 7.2: Results of the Life Cycle Assessment of the reference heat exchanger

Global Energy Requirement (GER)	MJ eq	62
Global Warming (GWP)	kg CO ₂ eq	3.96
Ozone Layer Depletion (ODP)	kg CFC-11 eq	2.85E-07
Photochemical Oxidation (POCP)	kg C ₂ H ₄ eq	0.00283
Acidification (AP)	kg SO ₂ eq	0.0168
Eutrophication (EP)	kg PO ₄ ³⁻ eq	0.00816
Carcinogenics	kg benzene eq	0.0745
Non carcinogenics	kg toluene eq	658

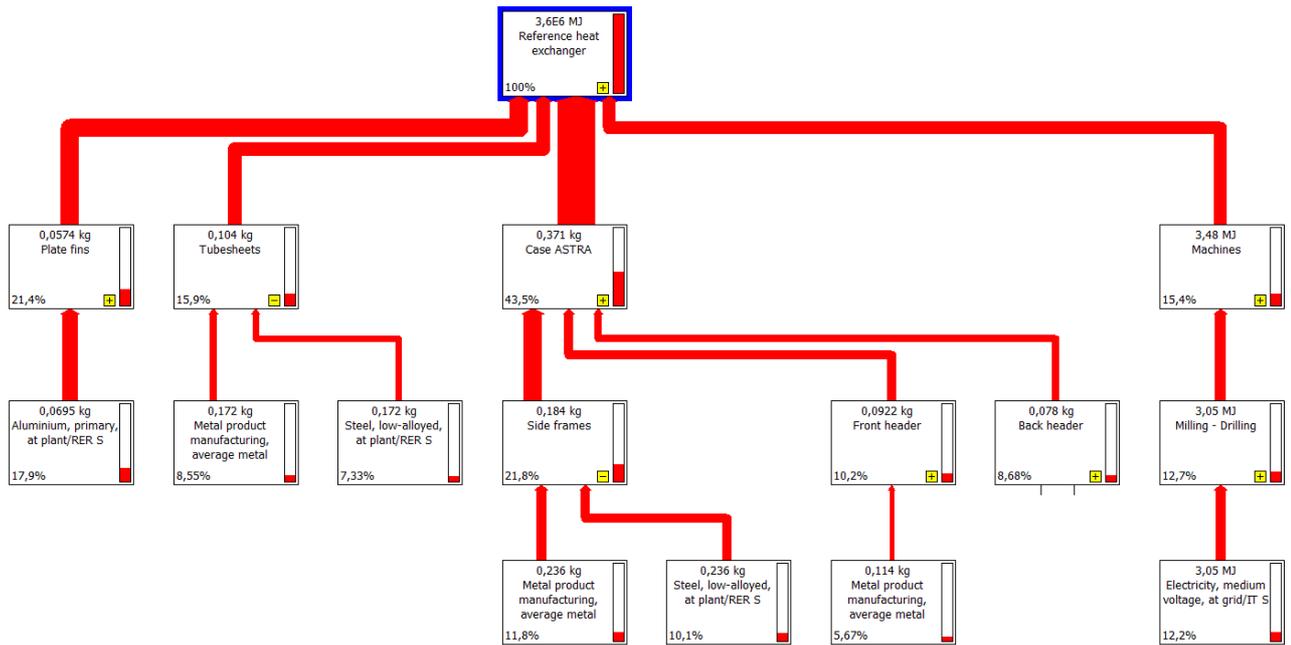


Figure 7.6: Flow sheet with GER results expressed in percentage (cut-off 5%).

Figure 7.6 shows that the greater contribution to the Global Energy Requirement is the case production (43.5%). A noticeable contribution is due to machinery (15.4%), sometimes neglected in LCAs.

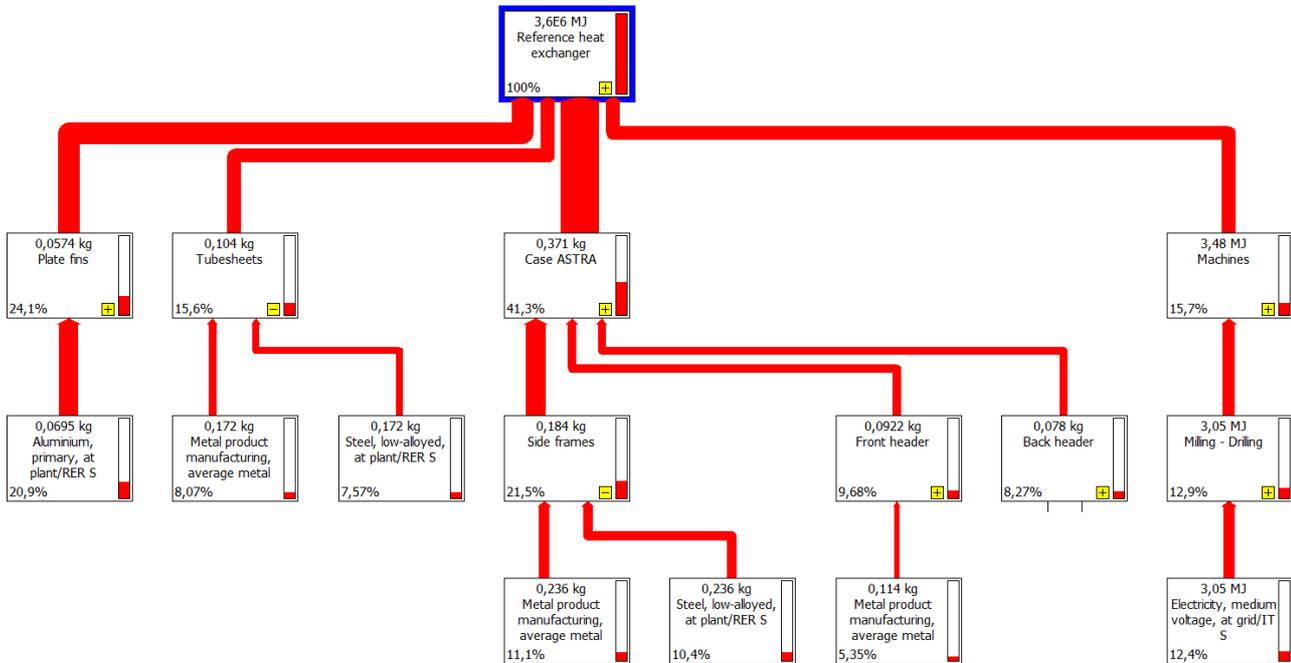


Figure 7.7: Flow sheet with GWP results expressed in percentage (cut-off 5%)

Figure 7.7 shows that the greater contribution to the Global Warming is the case production (41.3%). Contribution in percentage are quite similar to those of the GER case.

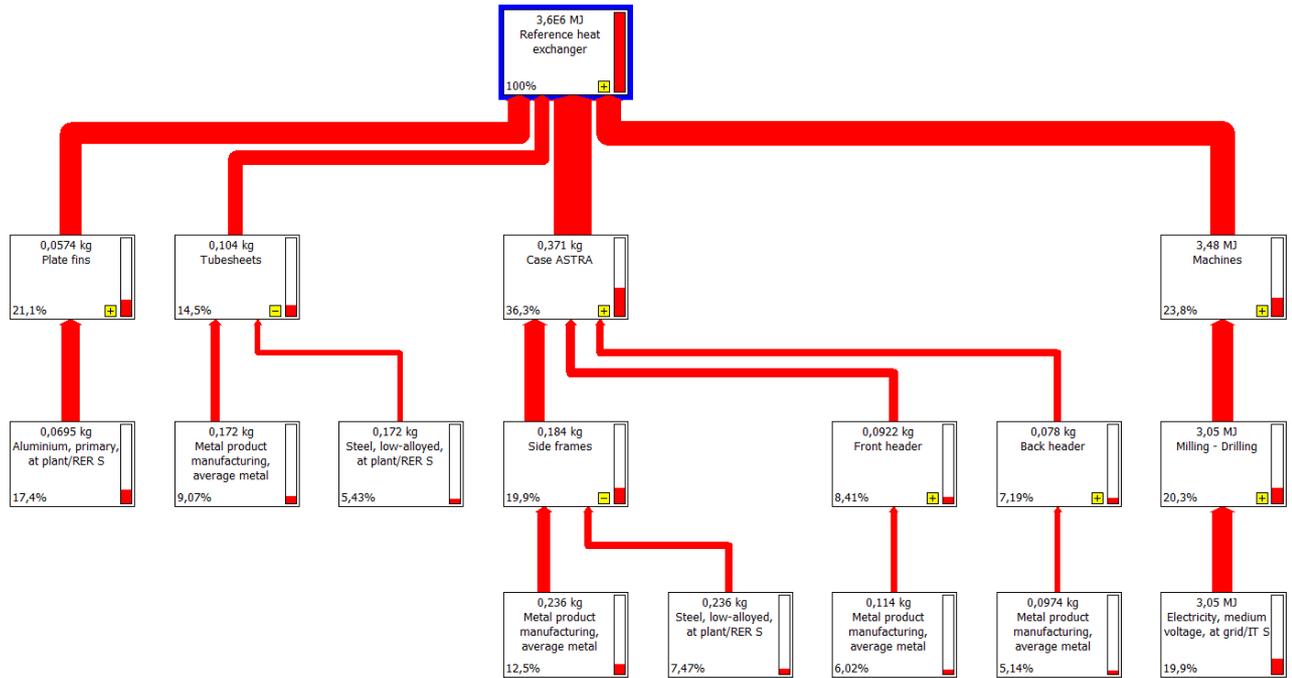


Figure 7.8: Flow sheet with ODP results expressed in percentage (cut-off 5%)

Figure 7.8 shows that the greater contribution to the Ozone Depletion is the case production (36.3%). The machinery contribution is a bit higher than in previous cases: 23.8%.

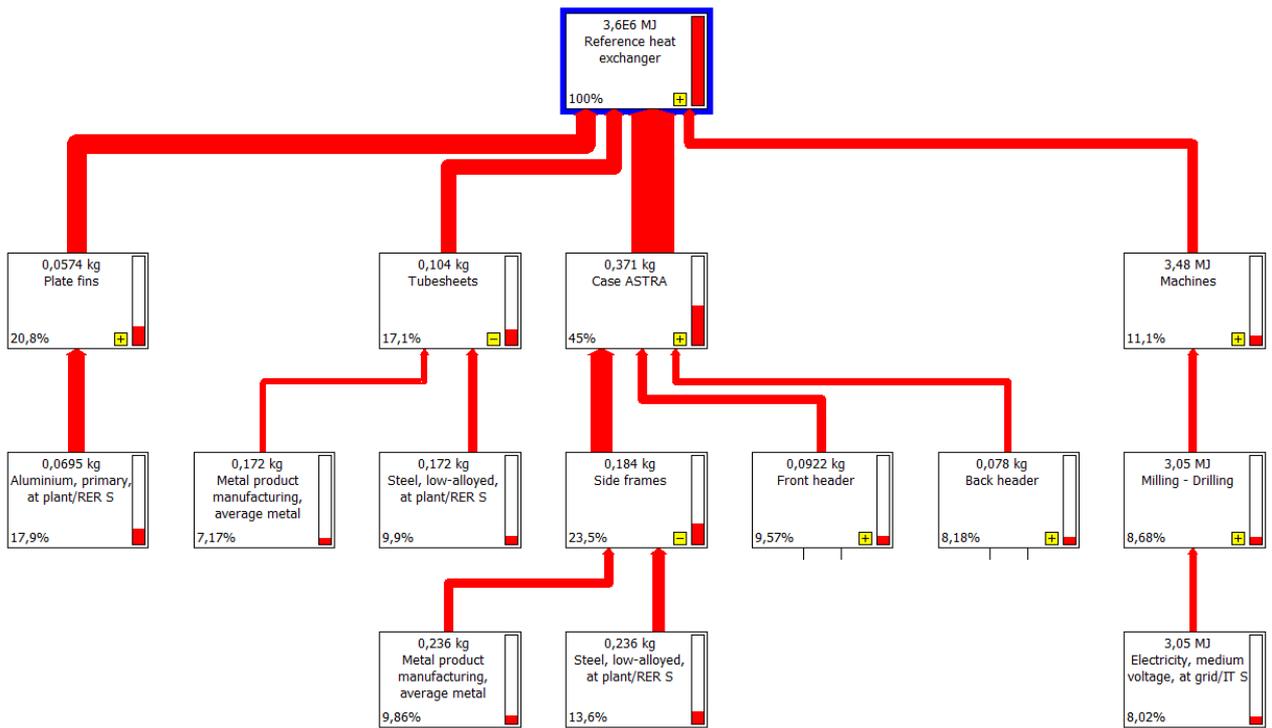


Figure 7.9: Flow sheet with POCP results expressed in percentage (cut-off 5%)

Figure 7.9 shows that the greater contribution to the POCP is the case production (45%). The machinery contribution is lower than in previous cases: 11.1%.

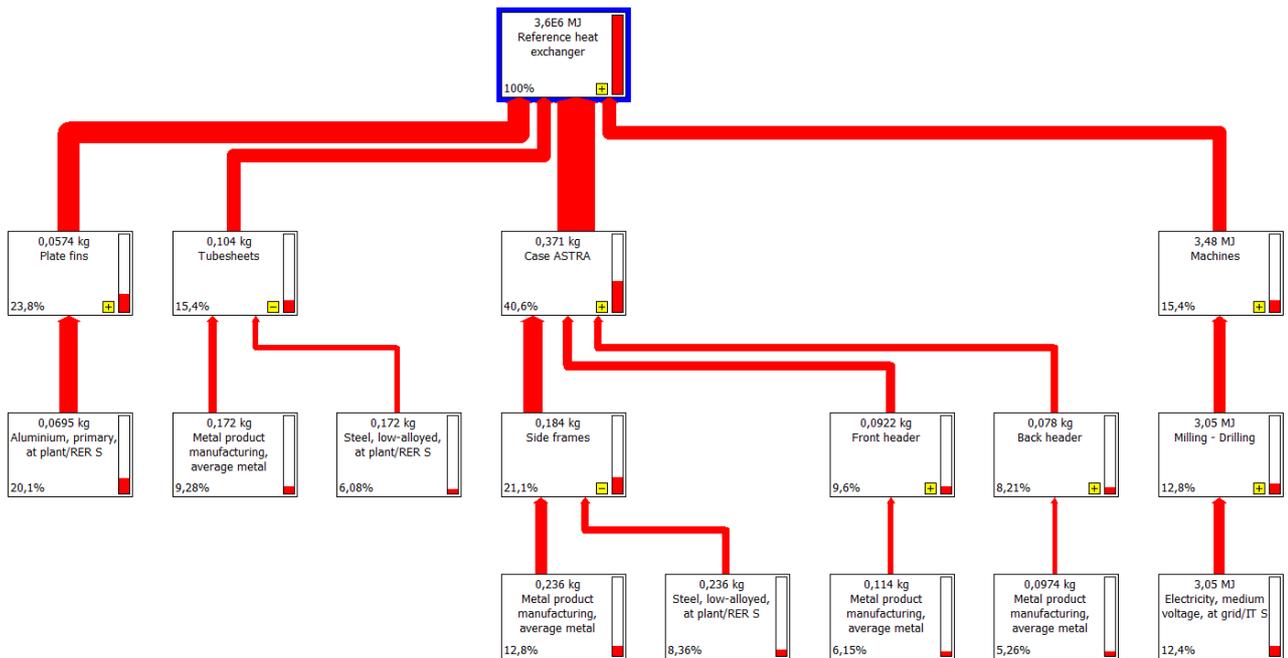


Figure 7.10: Flow sheet with AP results expressed in percentage (cut-off 5%)

Figure 7.10 shows that the greater contribution to the Acidification is the case production (40.6%), following the trend of the other impacts.

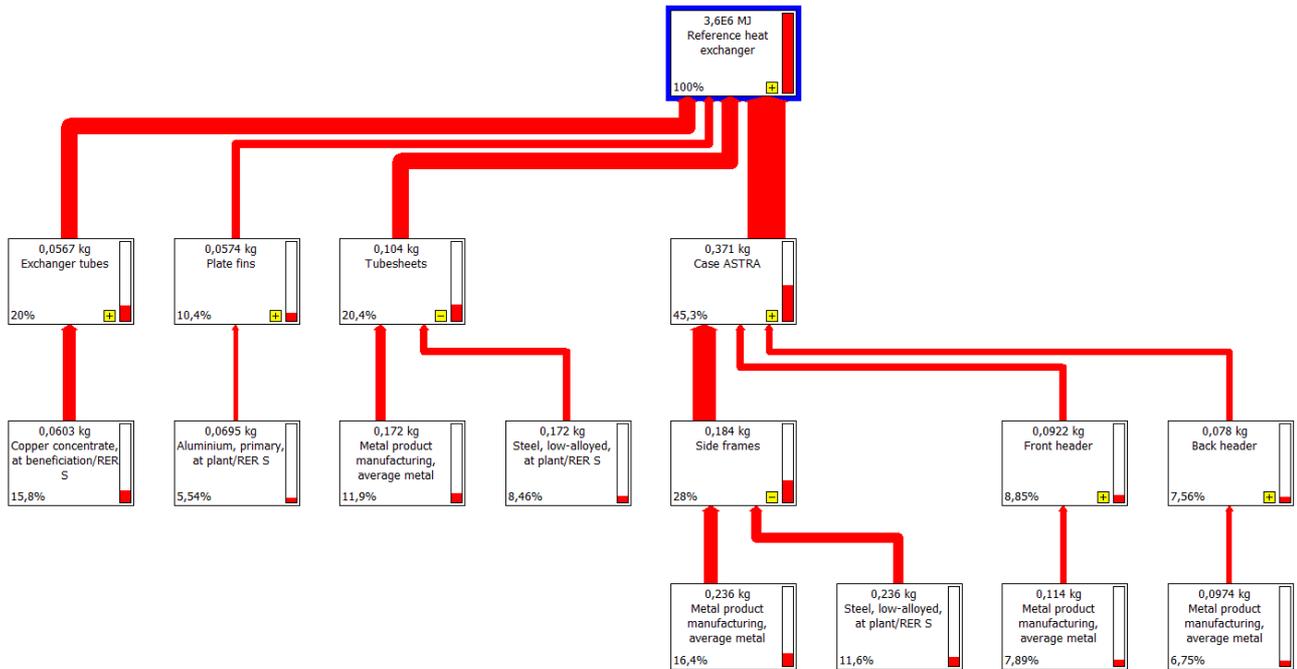


Figure 7.11: Flow sheet with EP results expressed in percentage (cut-off 5%)

Figure 7.11 shows that the greater contribution to the Eutrophication is the case production (45.3%). The machinery contribution is neglectable.

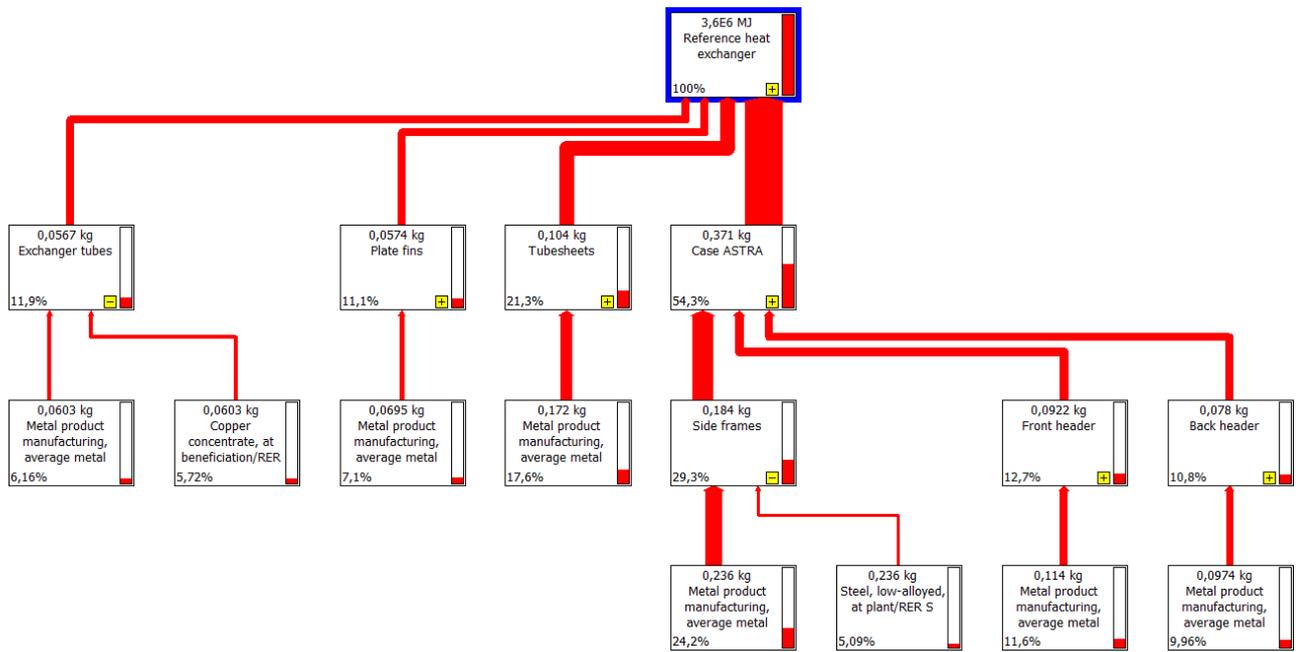


Figure 7.12: Flow sheet with Carcinogenics results expressed in % (cut-off 5%)

Figure 7.12 shows that the greater contribution to the Carcinogenics is the case production (54.3%). The machinery contribution is neglectable.

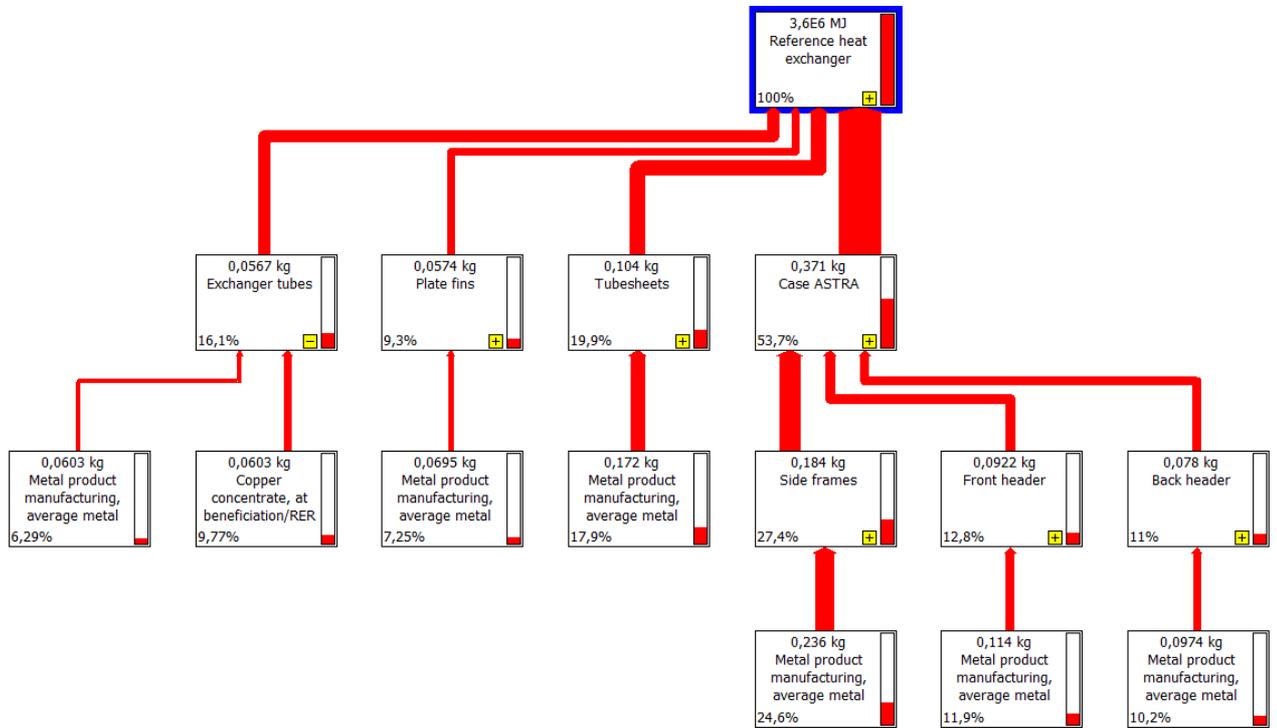


Figure 7.13: Flow sheet with Non Carcinogenics results expressed in % (cut-off 5%)

Figure 7.13 shows that the greater contribution to the Non Carcinogenics is the case production (53.7%). The machinery contribution is once again neglectable.

7.4.2. Prototype 1

Table 7.3: Results of the Life Cycle Assessment of the Prototype 1

Global Energy Requirement (GER)	MJ eq	19.9
Global Warming (GWP)	kg CO2 eq	1.13
Ozone Layer Depletion (ODP)	kg CFC-11 eq	1.94E-08
Photochemical Oxidation (POCP)	kg C2H4 eq	0.00042
Acidification (AP)	kg SO2 eq	0.00384
Eutrophication (EP)	kg PO43- eq	0.0011
Carcinogenics	kg benzene eq	0.000253
Non carcinogenics	kg toluene eq	1.69

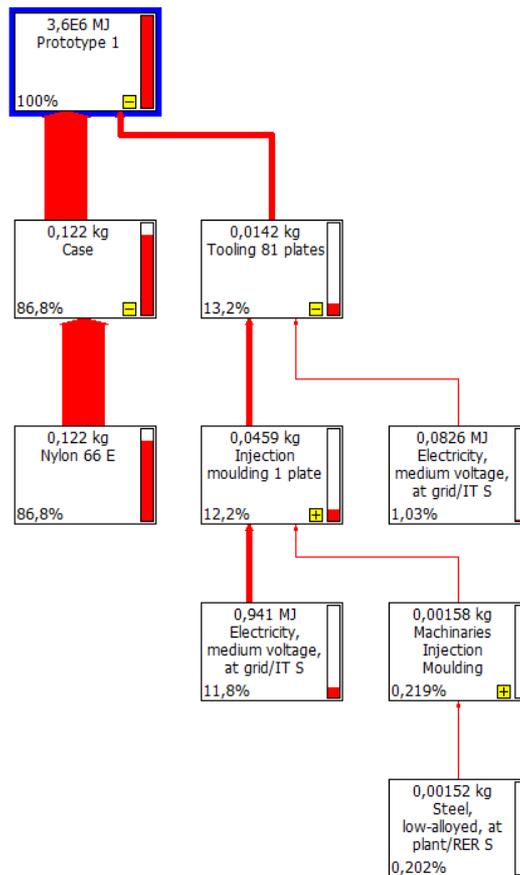


Figure 7.14: Flow sheet with GER results expressed in percentage (cut-off 0.2%)

Figure 7.14 shows that the greater contribution in GER for prototype 1 is represented by the case (86.8%), as the Astra reference heat exchanger.

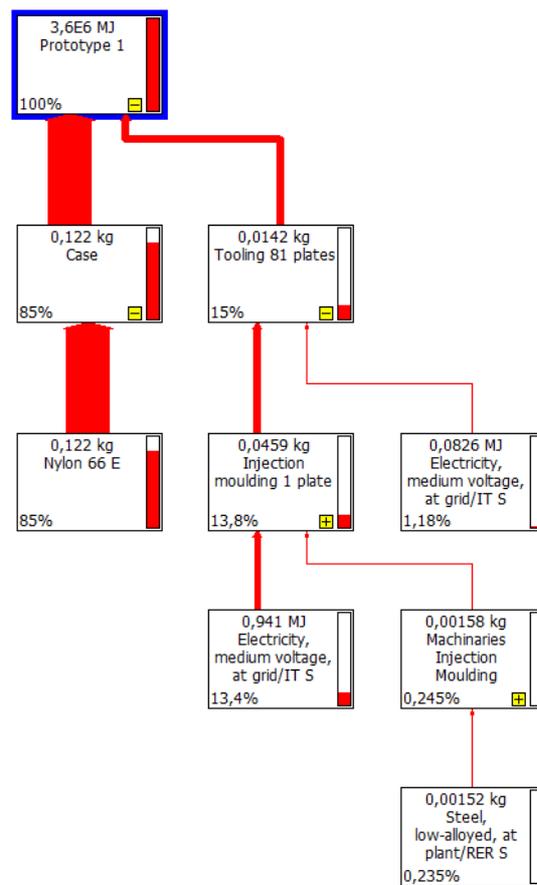


Figure 7.15: Flow sheet with GWP results expressed in percentage (cut-off 0.2%)

Figure 7.15 shows that the greater contribution in GWP for prototype 1 is represented by the case (85%), as the Astra reference heat exchanger.

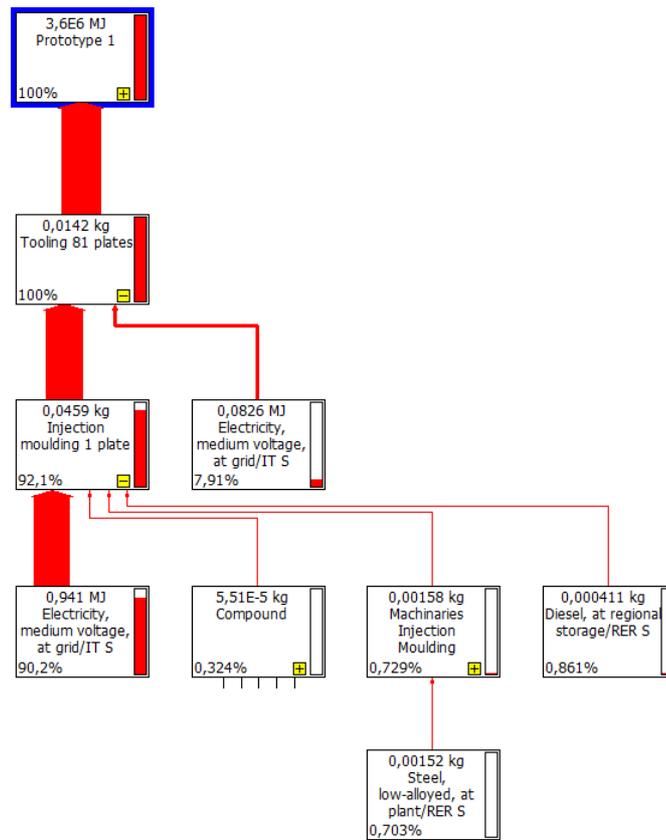


Figure 7.16: Flow sheet with ODP results expressed in percentage (cut-off 0.3%)

Figure 7.16 shows that the greater contribution in ODP for prototype 1 is represented by the electricity needed by injection moulding (90.2%), so the case contribution is neglectable for ODP.

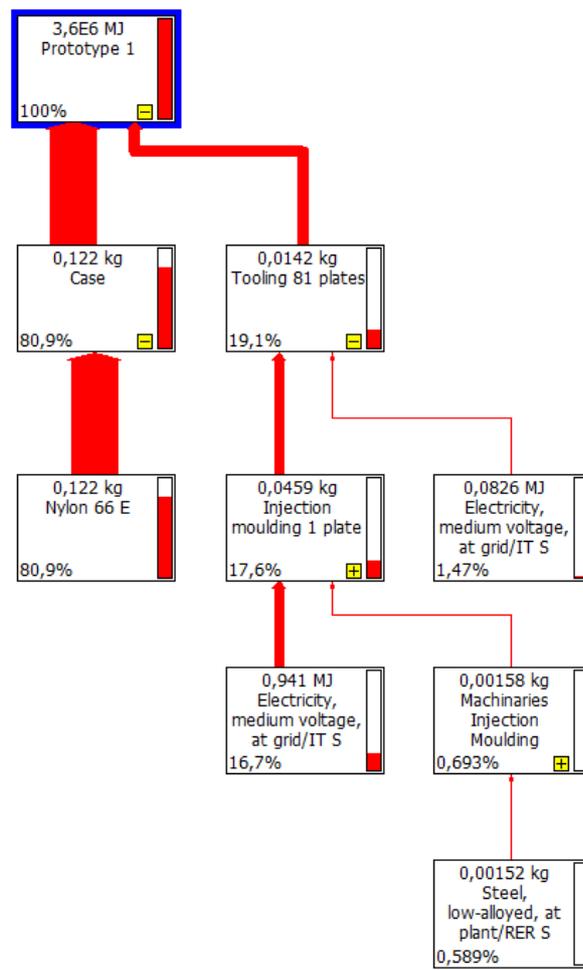


Figure 7.17: Flow sheet with POCP results expressed in percentage (cut-off 0.2%)

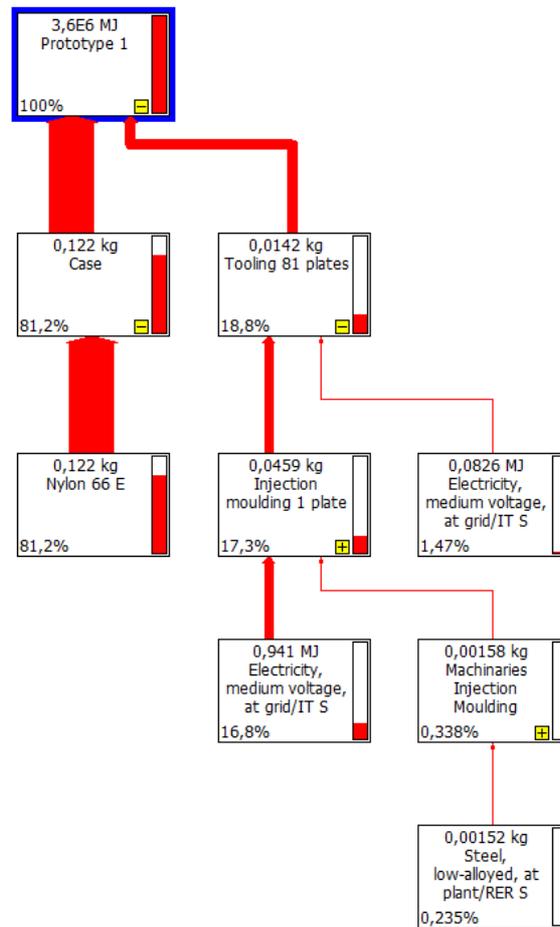


Figure 7.18: Flow sheet with AP results expressed in percentage (cut-off 0.2%)

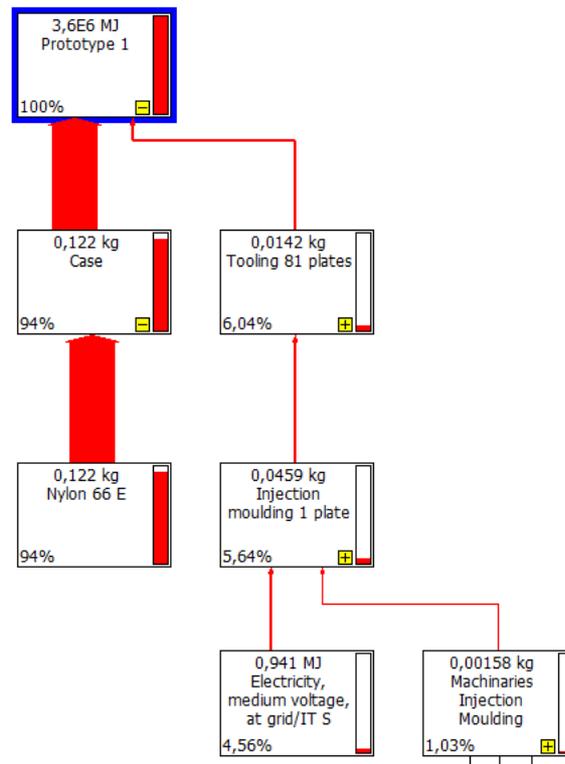


Figure 7.19: Flow sheet with EP results expressed in percentage (cut-off 0.2%)

Figures 7.17, 7.18 and 7.19 show that the case is the greater contribution for prototype 1 in POCP (80.9%), AP (81.2%) and EP (94%).

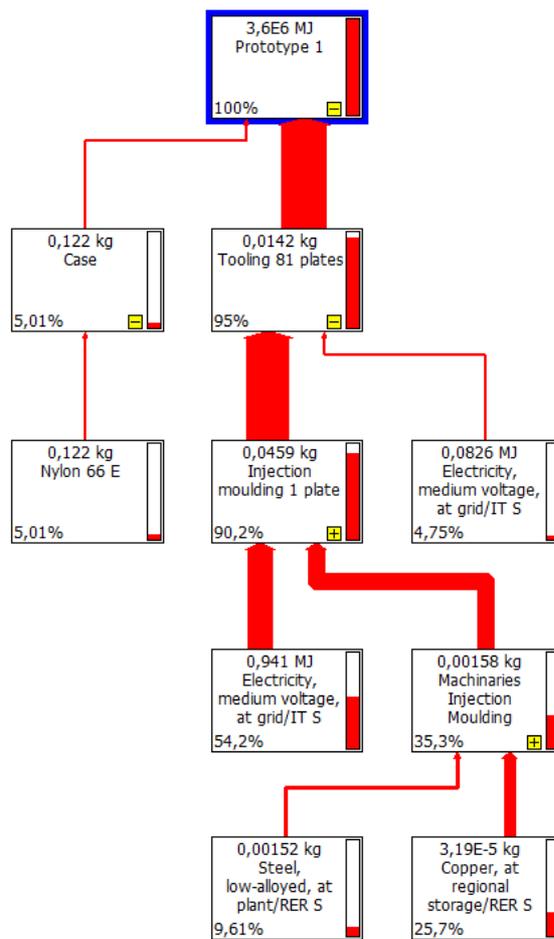


Figure 7.20: Flow sheet with Carcinogenics results expressed in percentage (cut-off 0.7%)

Figure 7.20 shows that the greater contribution in Carcinogenics for prototype 1 is represented by injection moulding (90.2%): the 54.2% is due to the electricity, while the 35.3% is due to machinaries. The case contribution for Carcinogenics is neglectable.

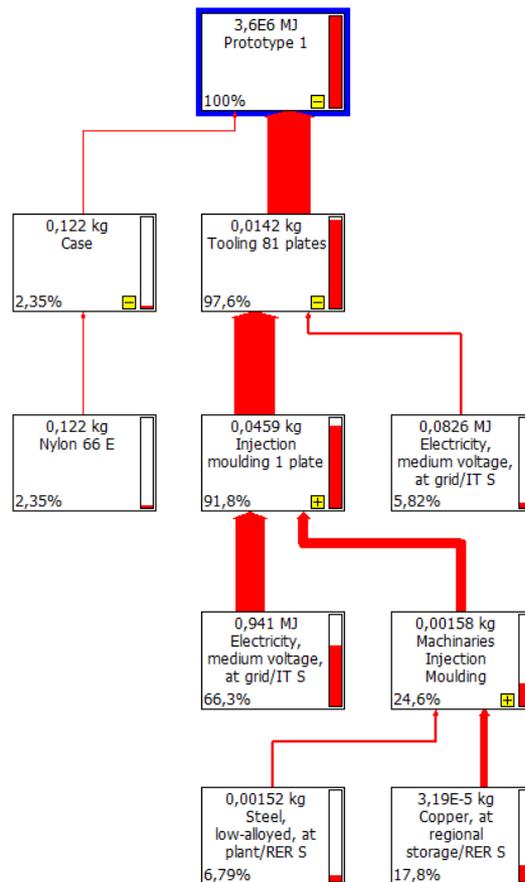


Figure 7.21: Flow sheet with Non Carcinogenics results expressed in % (cut-off 0.7%)

Figure 7.21 shows that the greater contribution in Non Carcinogenics for prototype 1 is represented by injection moulding (91.8%): the 66.3% is due to the electricity, while the 24.6% is due to machinaries. The case contribution for Non Carcinogenics is neglectable.

7.4.3. Prototype 2

Table 7.4: Results of the Life Cycle Assessment of Prototype 2

Global Energy Requirement (GER)	MJ eq	9.74
Global Warming (GWP)	kg CO2 eq	0.493
Ozone Layer Depletion (ODP)	kg CFC-11 eq	1.46E-08
Photochemical Oxidation (POCP)	kg C2H4 eq	0.000496
Acidification (AP)	kg SO2 eq	0.00224
Eutrophication (EP)	kg PO43- eq	0.000154
Carcinogenics	kg benzene eq	0.000461
Non carcinogenics	kg toluene eq	3.06

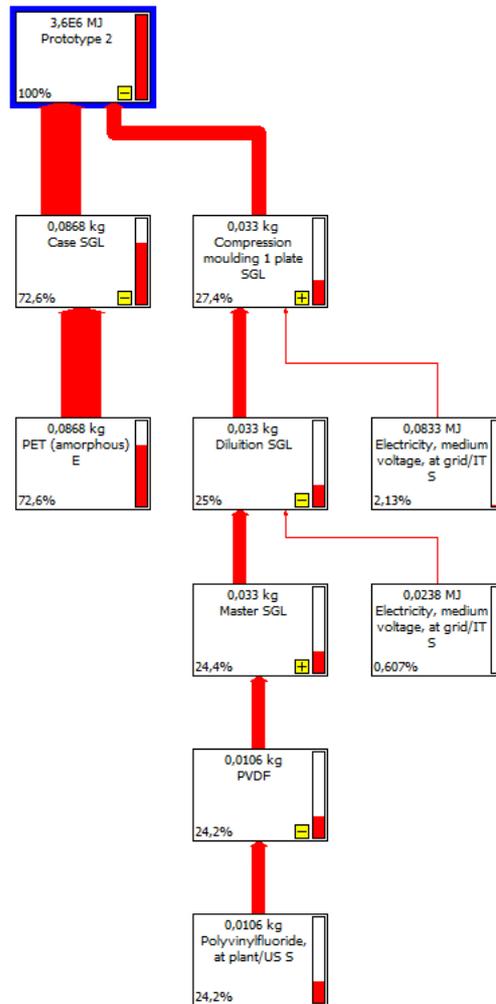


Figure 7.22: Flow sheet with GER results expressed in percentage (cut-off 0.5%)

Figure 7.22 shows that the greater contribution in GER for prototype 2 is represented by the case (72.6%), as the Astra reference heat exchanger and the prototype 1.

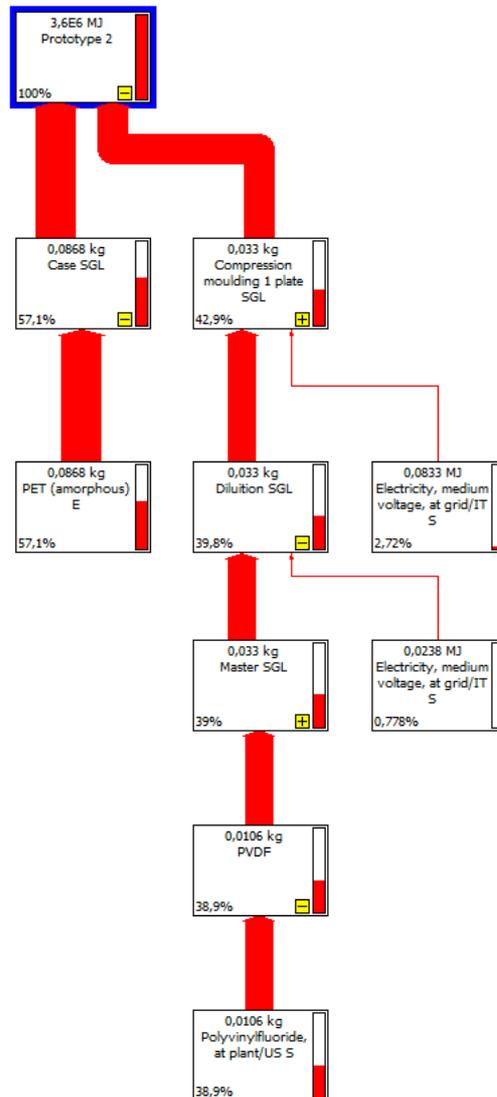


Figure 7.23: Flow sheet with GWP results expressed in percentage (cut-off 0.5%)

Figure 7.23 shows that the greater contribution in GWP for prototype 2 is represented by the case (57.1%) and by the PVDF production (38.9%).

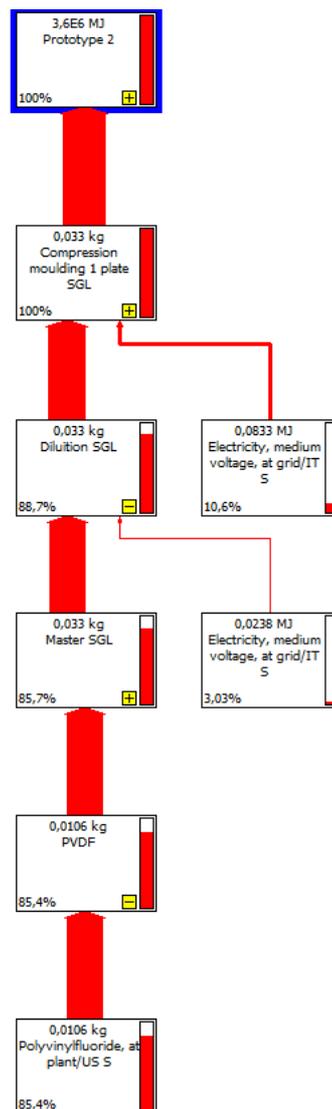


Figure 7.24: Flow sheet with ODP results expressed in percentage (cut-off 0.7%)

Figure 7.24 shows that the greater contribution in ODP for prototype 2 is represented by the PVDF production (85.4%), while the case contribution is neglectable.

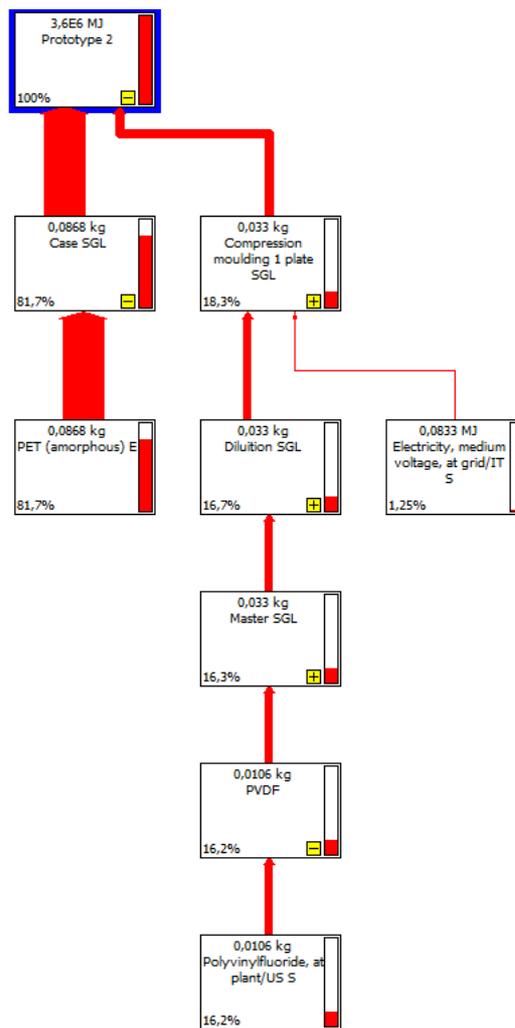


Figure 7.25: Flow sheet with POCP results expressed in percentage (cut-off 0.7%)

Figure 7.25 shows that the greater contribution in POCP for prototype 2 is represented by the case (81.7%).

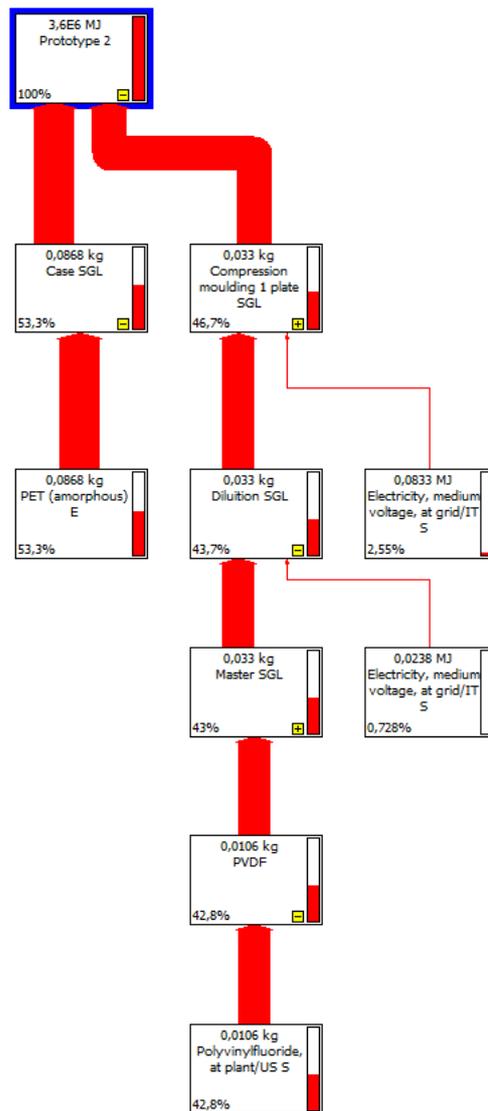


Figure 7.26: Flow sheet with AP results expressed in percentage (cut-off 0.7%)

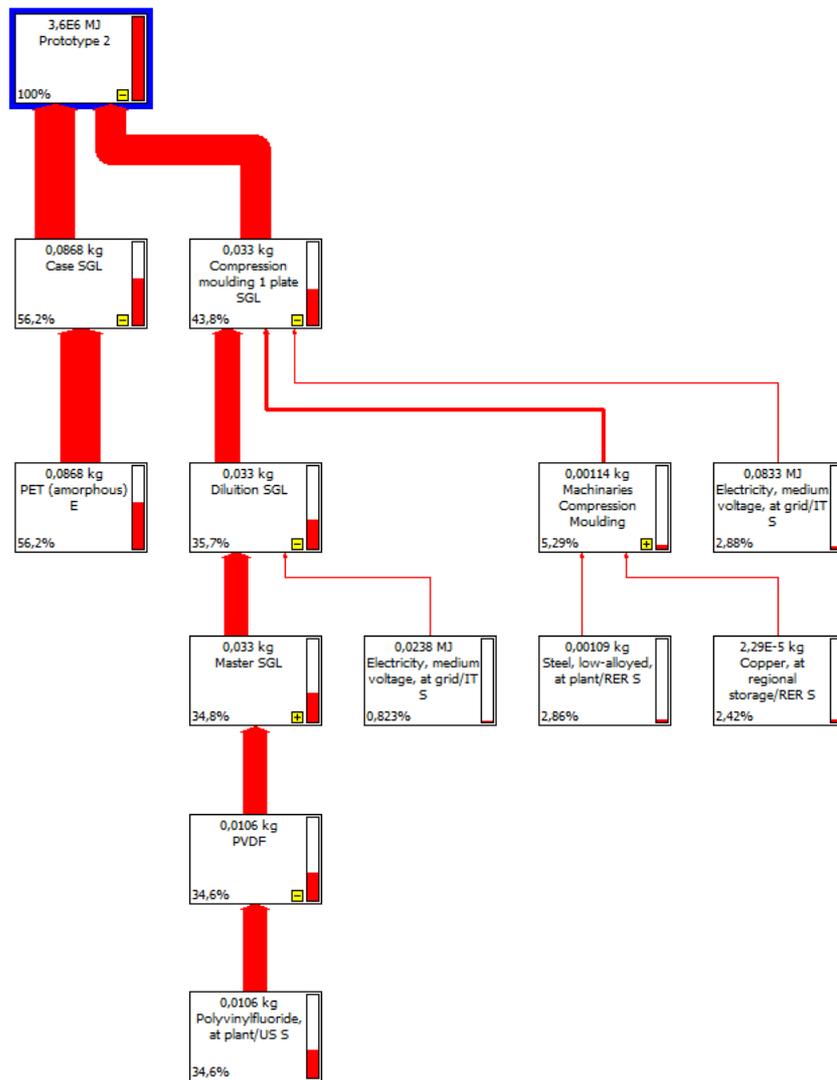


Figure 7.27: Flow sheet with EP results expressed in percentage (cut-off 0.7%)

Figures 7.26 and 7.27 show that the greater contributions for prototype 2 are represented by the case and by the PVDF production for both AP (53.3% and 42.8% respectively) and EP (56.2% and 34.6% respectively).

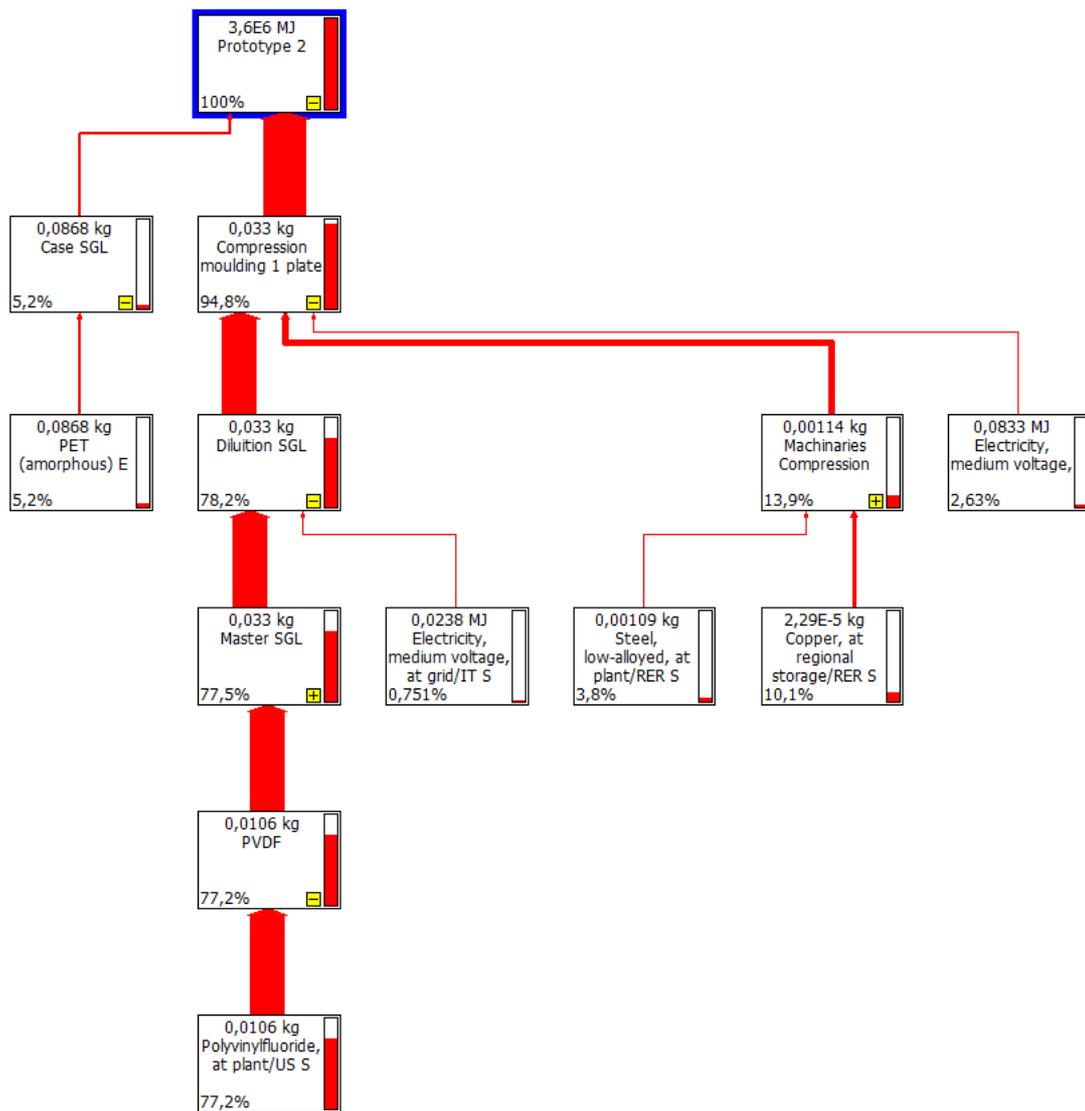


Figure 7.28: Flow sheet with Carcinogenics results expressed in percentage (cut-off 0.7%)

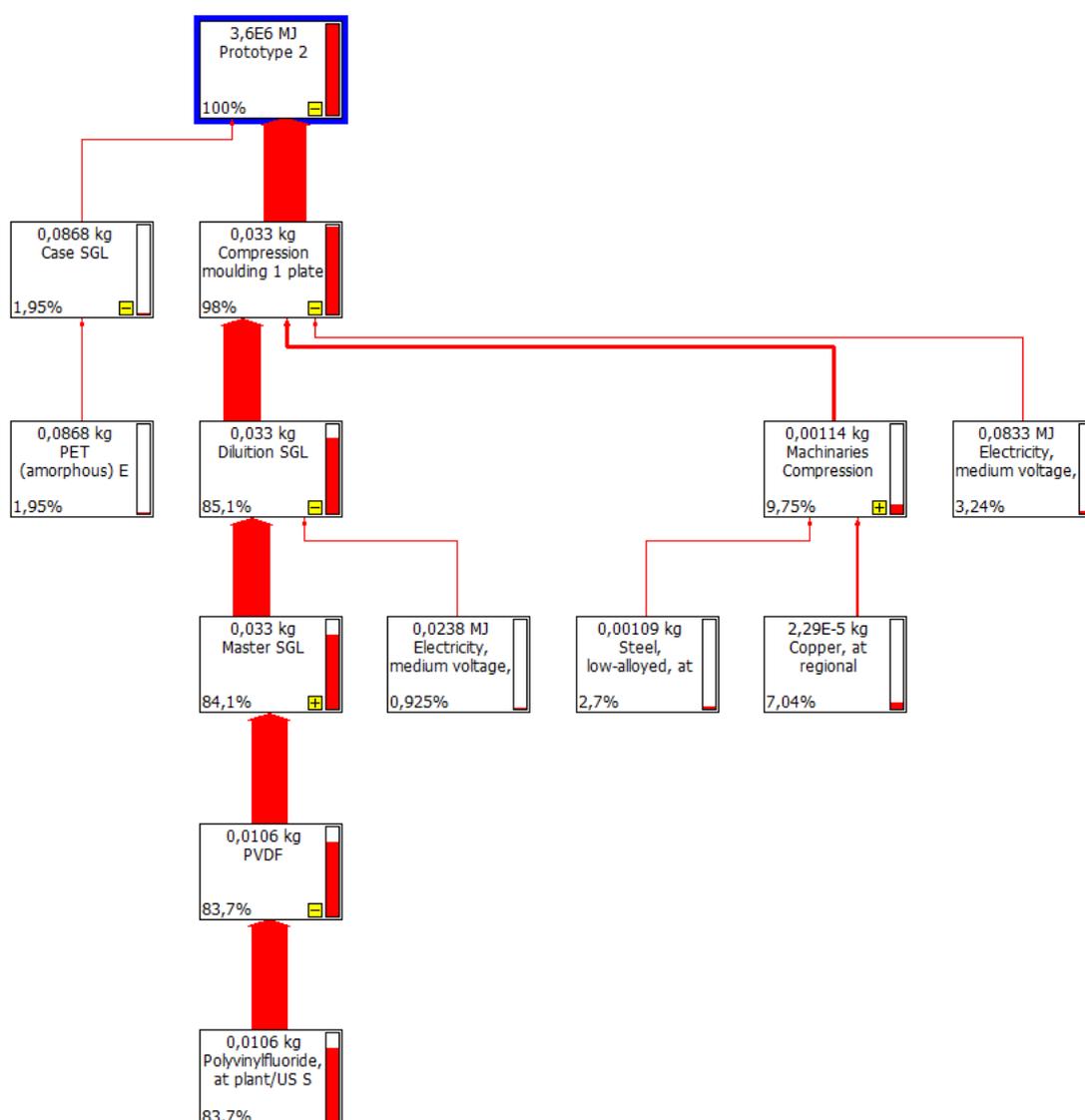


Figure 7.29: Flow sheet with Non Carcinogenics results expressed in percentage (cut-off 0.7%)

Figures 7.28 and 7.29 show that the greater contribution for prototype 2 is represented by the PVDF production for both Carcinogenics (77.2%) and Non Carcinogenics (83.72%).

7.4.4. Prototype 3

Table 7.5: Results of the Life Cycle Assessment of Prototype 3

Global Energy Requirement (GER)	MJ eq	46.6
Global Warming (GWP)	kg CO2 eq	3.74
Ozone Layer Depletion (ODP)	kg CFC-11 eq	2.51E-07
Photochemical Oxidation (POCP)	kg C2H4 eq	0.00158
Acidification (AP)	kg SO2 eq	0.0186
Eutrophication (EP)	kg PO43- eq	0.00109
Carcinogenics	kg benzene eq	0.00716
Non carcinogenics	kg toluene eq	50.6

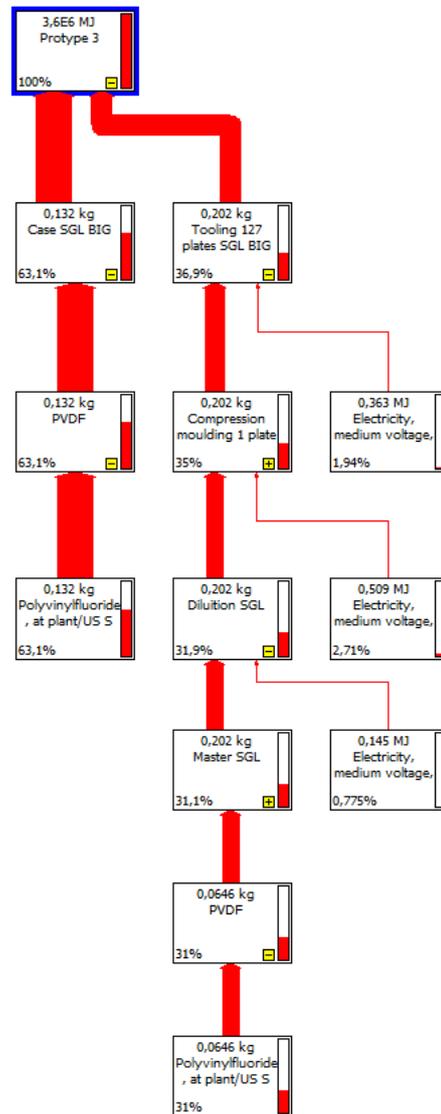


Figure 7.30: Flow sheet with GER results expressed in percentage (cut-off 0.7%)

Figure 7.30 shows that the greater contributions in GER for prototype 3 are represented by the case (63.1%) and by the PVDF production (31%).

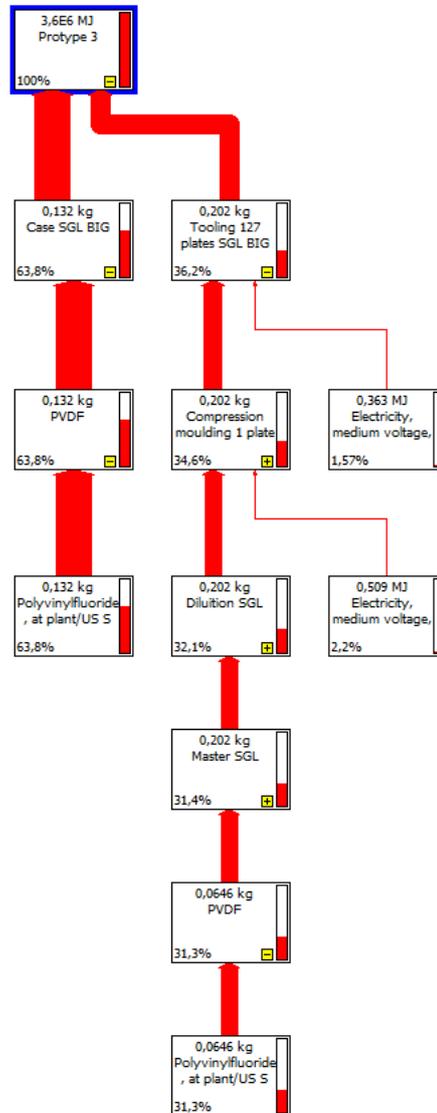


Figure 7.31: Flow sheet with GWP results expressed in percentage (cut-off 0.7%)

Figure 7.31 shows that the greater contributions in GWP for prototype 3 are represented by the case (63.8%) and by the PVDF production (31.3%).

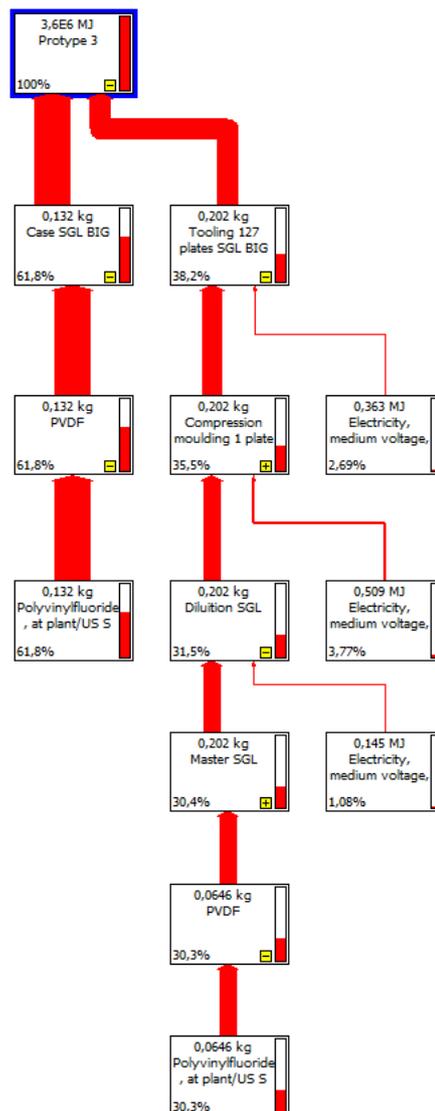


Figure 7.32: Flow sheet with ODP results expressed in percentage (cut-off 0.7%)

Figure 7.32 shows that the greater contributions in ODP for prototype 3 are represented by the case (61.8%) and by the PVDF production (30.3%).

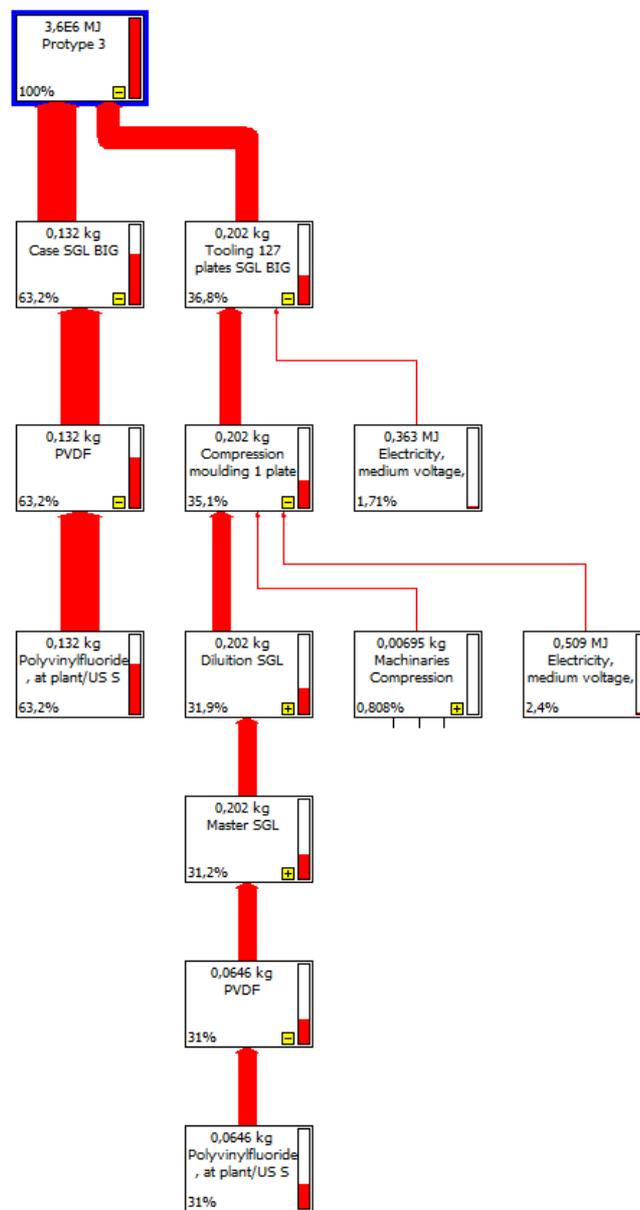


Figure 7.33: Flow sheet with POCP results expressed in percentage (cut-off 0.7%)

Figure 7.33 shows that the greater contributions in POCP for prototype 3 are represented by the case (63.2%) and by the PVDF production (31%).

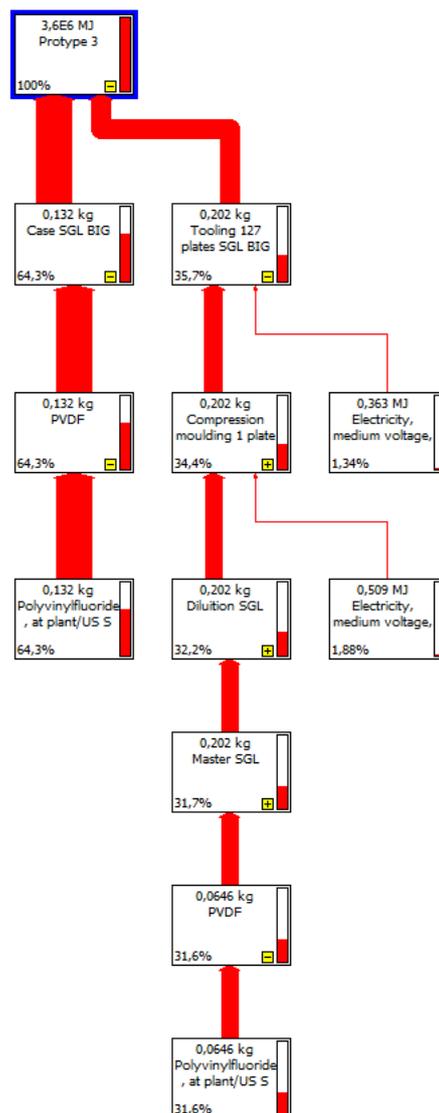


Figure 7.34: Flow sheet with AP results expressed in percentage (cut-off 0.7%)

Figure 7.34 shows that the greater contributions in AP for prototype 3 are represented by the case (64.3%) and by the PVDF production (31.6%).

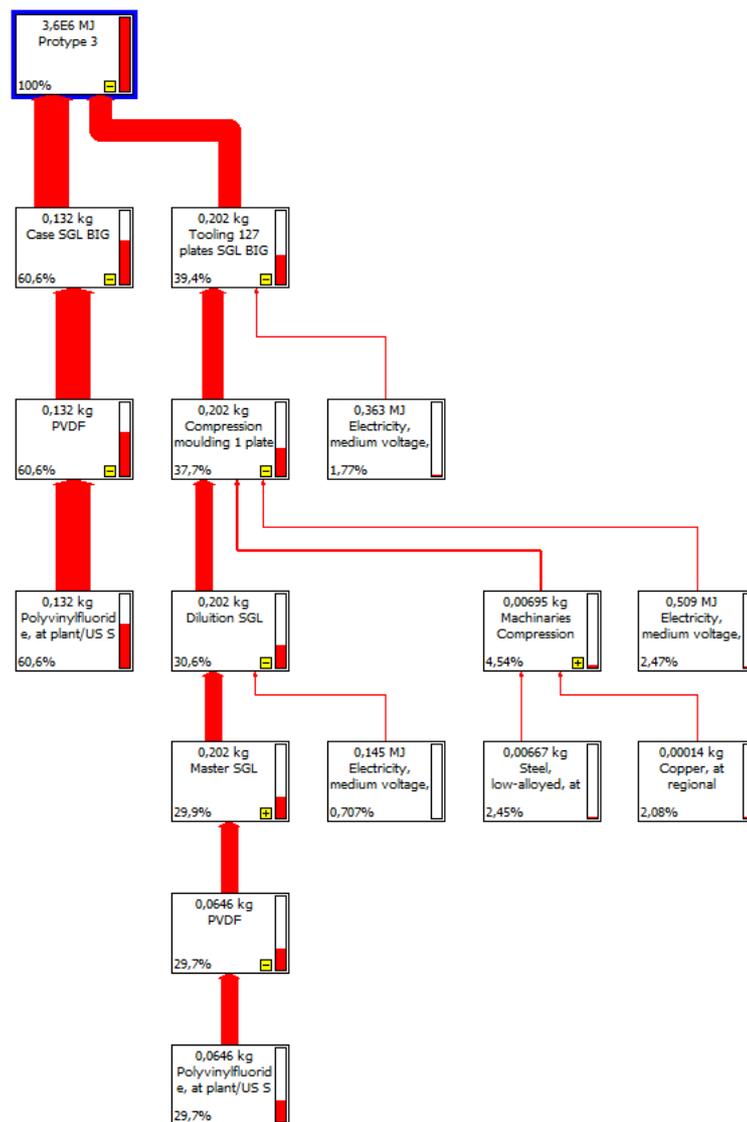


Figure 7.35: Flow sheet with EP results expressed in percentage (cut-off 0.7%)

Figure 7.35 shows that the greater contributions in EP for prototype 3 are represented by the case (60.6%) and by the PVDF production (29.7%).

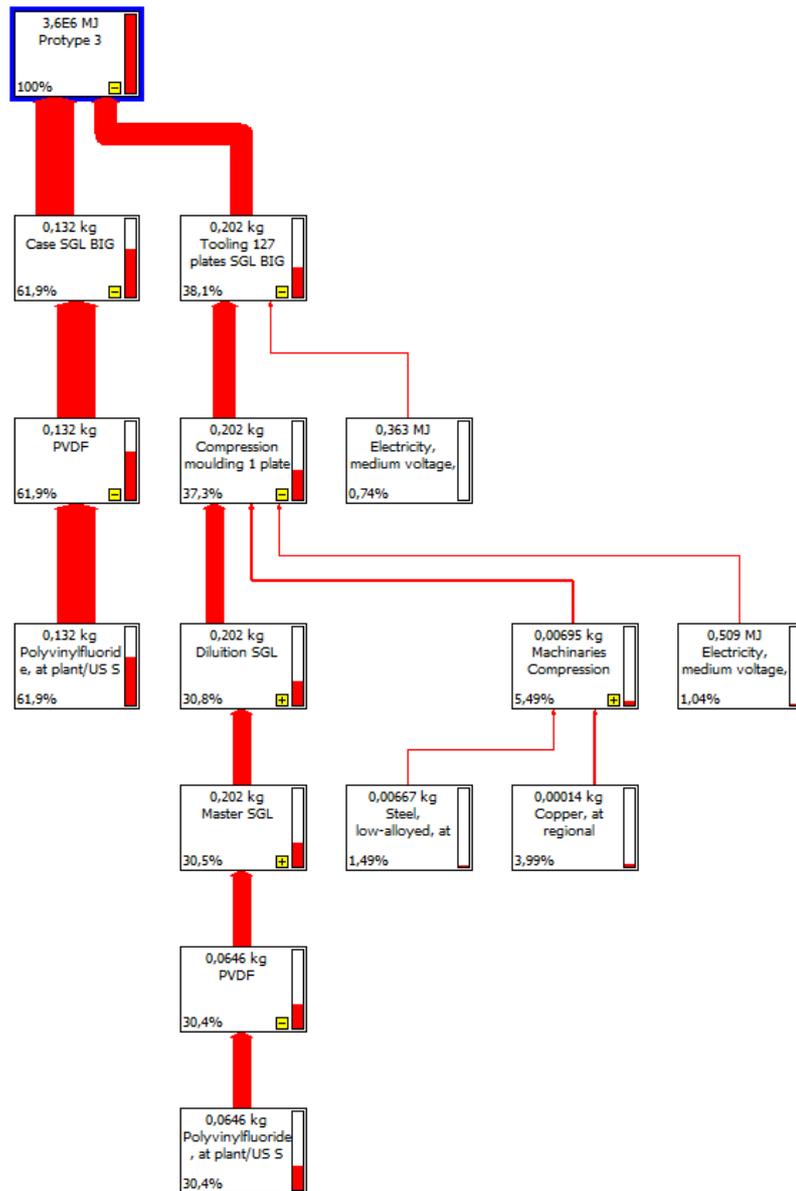


Figure 7.36: Flow sheet with Carcinogenics results expressed in percentage (cut-off 0.7%)

Figure 7.36 shows that the greater contributions in Carcinogenics for prototype 3 are represented by the case (61.9%) and by the PVDF production (30.4%).

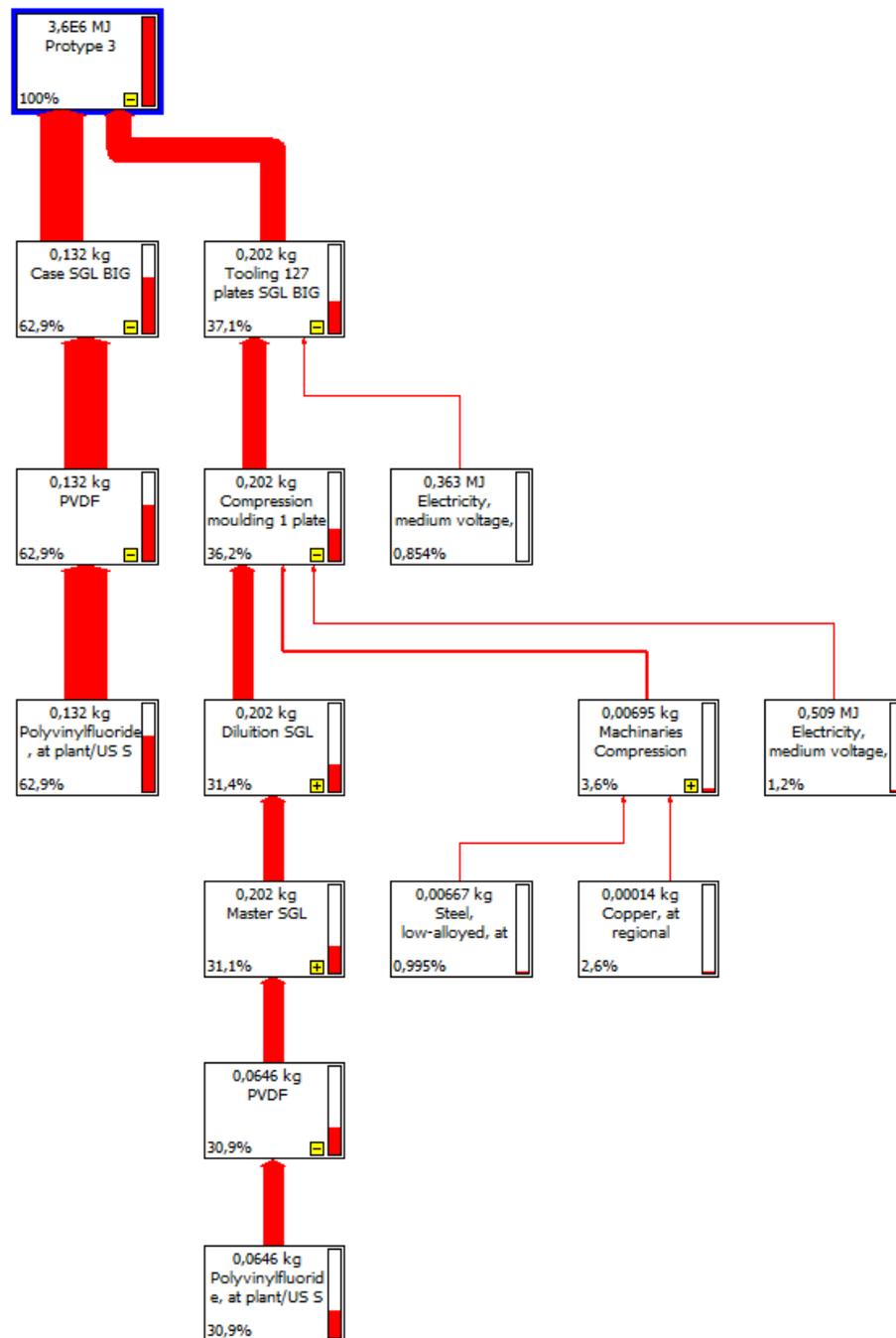


Figure 7.37: Flow sheet with Non Carcinogenics results expressed in percentage (cut-off 0.7%)

Figure 7.37 shows that the greater contributions in Non Carcinogenics for prototype 3 are represented by the case (62.9%) and by the PVDF production (30.9%).

7.4.5. Prototype 4

Table 7.6: Results of the Life Cycle Assessment of Prototype 4

Global Energy Requirement (GER)	MJ eq	41.6
Global Warming (GWP)	kg CO2 eq	1.77
Ozone Layer Depletion (ODP)	kg CFC-11 eq	2.03E-08
Photochemical Oxidation (POCP)	kg C2H4 eq	0.0023
Acidification (AP)	kg SO2 eq	0.00762
Eutrophication (EP)	kg PO43- eq	0.00054
Carcinogenics	kg benzene eq	0.000499
Non carcinogenics	kg toluene eq	3.06

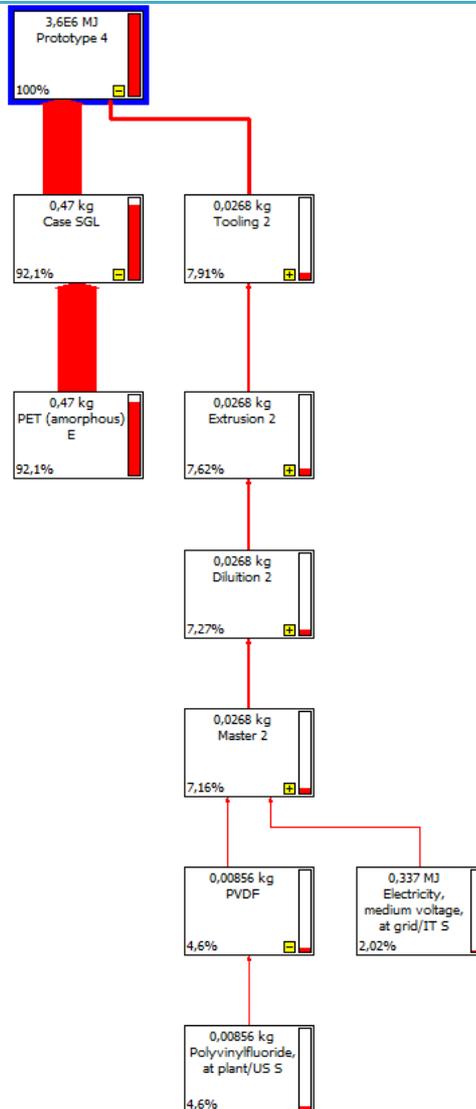


Figure 7.38: Flow sheet with GER results expressed in percentage

Figure 7.38 shows that the greater contribution in GER for prototype 4 is represented by the case (92.1%).

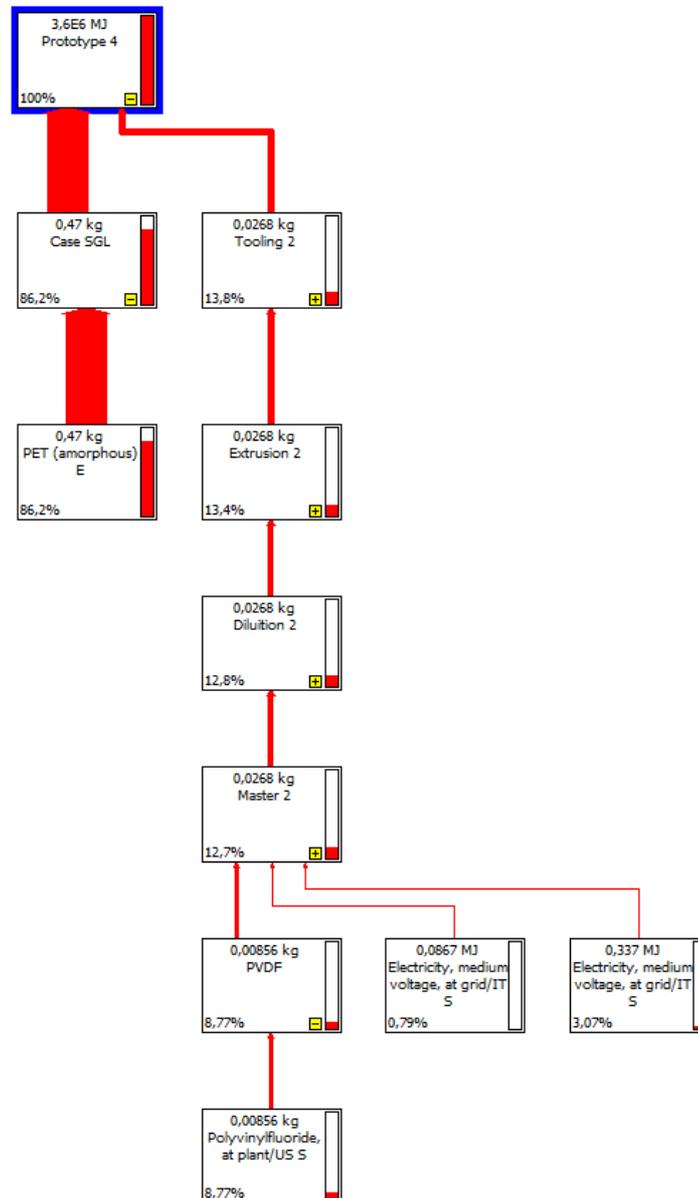


Figure 7.39: Flow sheet with GWP results expressed in percentage

Figure 7.39 shows that the greater contribution in GWP for prototype 4 is represented by the case (86.2%).

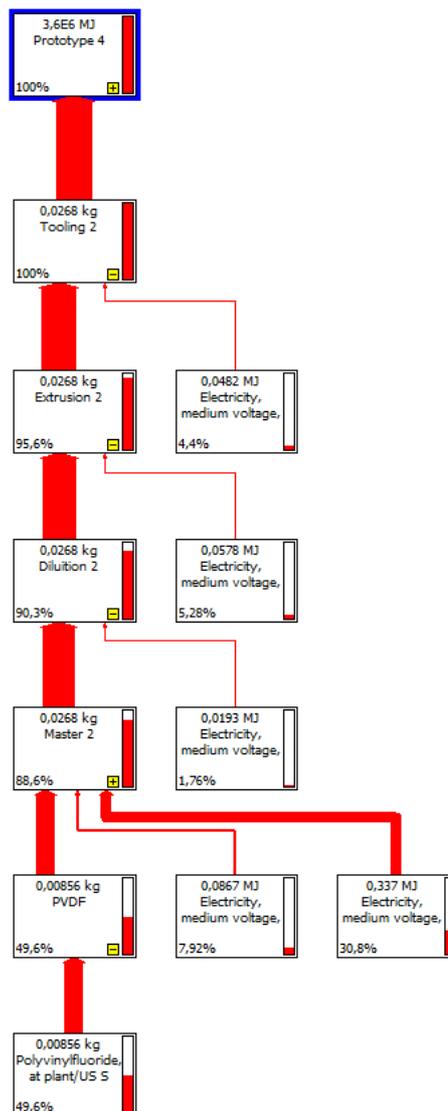


Figure 7.40: Flow sheet with ODP results expressed in percentage

Figure 7.40 shows that the greater contributions in ODP for prototype 4 are represented by the PVDF production (49.6%) and by the electricity needed for master production (30.8%).

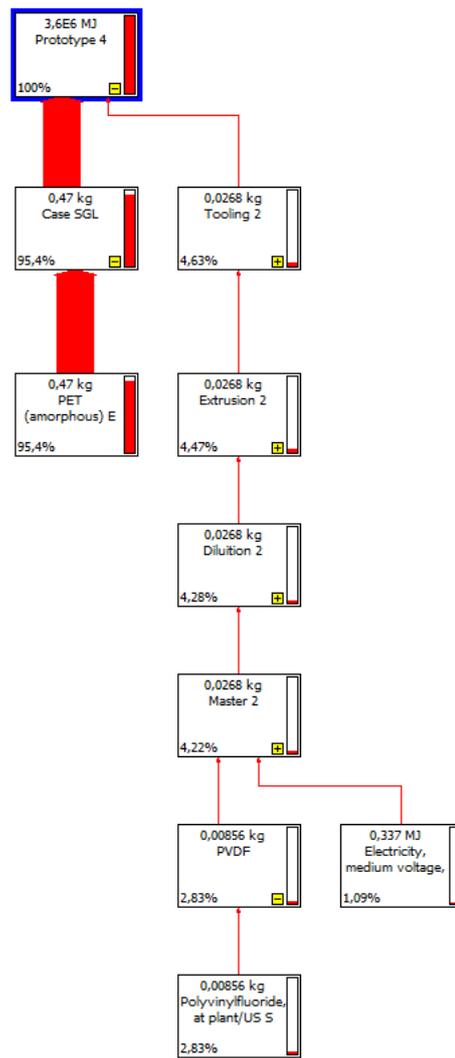


Figure 7.41: Flow sheet with POCP results expressed in percentage

Figure 7.41 shows that the greater contribution in POCP for prototype 4 is represented by the case (95.4%).

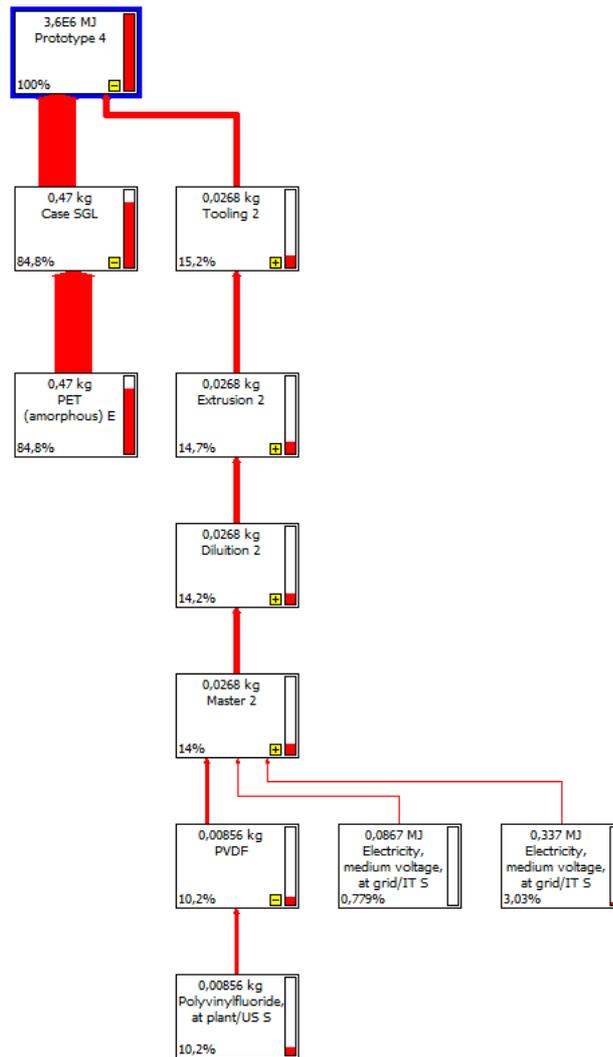


Figure 7.42: Flow sheet with AP results expressed in percentage

Figure 7.42 shows that the greater contribution in AP for prototype 4 is represented by the case (84.8%).

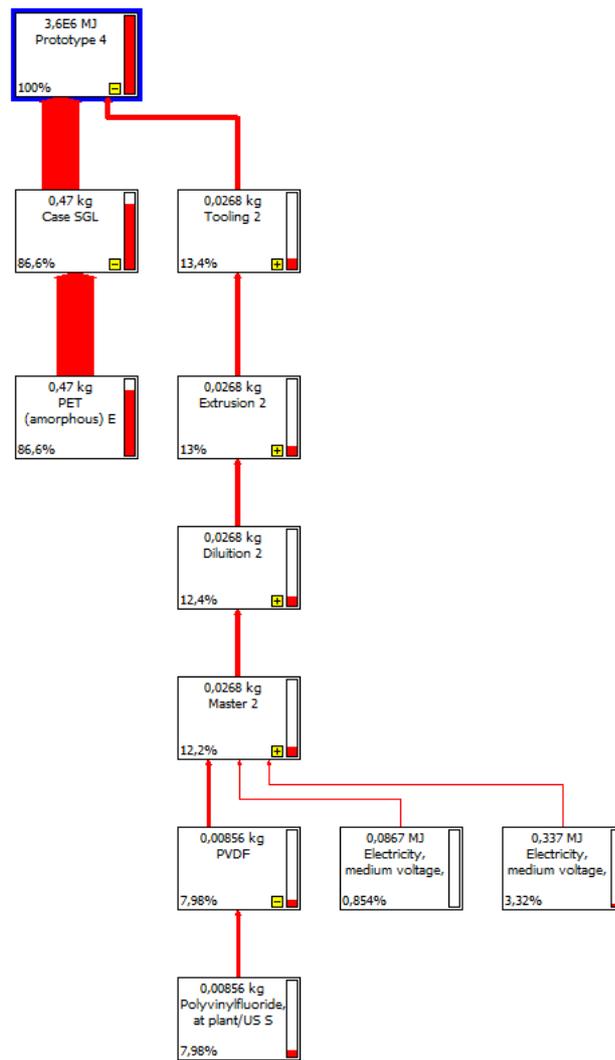


Figure 7.43: Flow sheet with EP results expressed in percentage

Figure 7.43 shows that the greater contribution in EP for prototype 4 is represented by the case (86.6%).

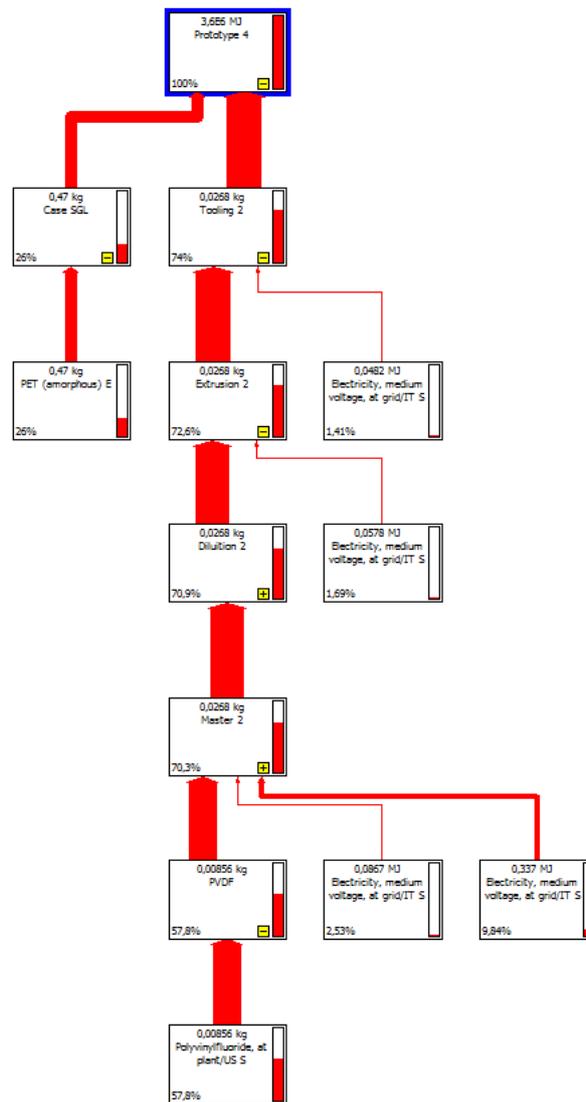


Figure 7.44: Flow sheet with Carcinogenics results expressed in percentage

Figure 7.44 shows that the greater contribution in Carcinogenics for prototype 4 is represented by the PVDF production (57.8%).

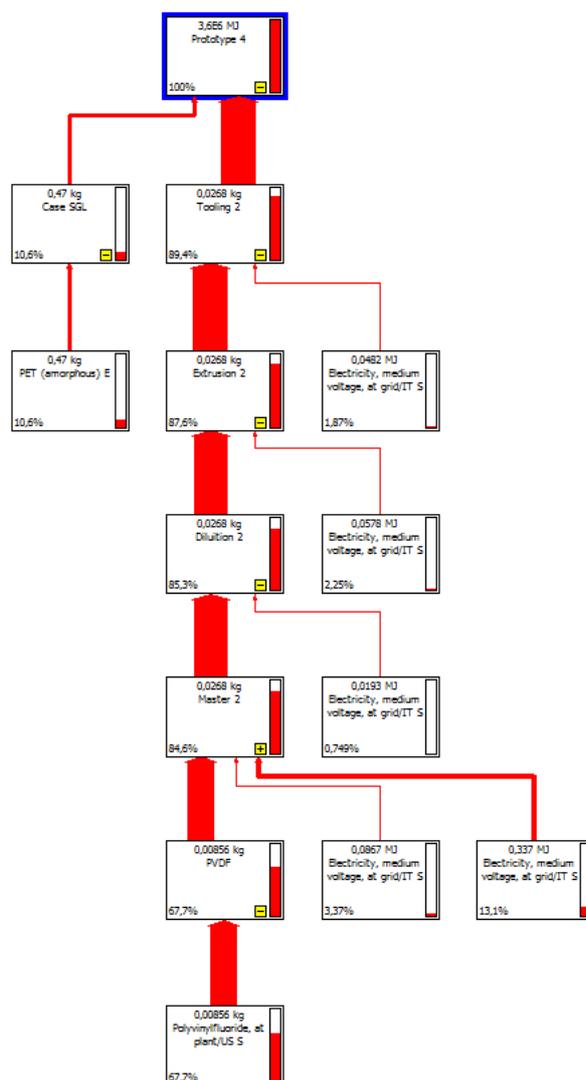


Figure 7.45: Flow sheet with Non Carcinogenics results expressed in percentage

Figure 7.45 shows that the greater contribution in Non Carcinogenics for prototype 4 is represented by the PVDF production (67.7%).

7.5. Results comparison

This paragraph aims to make a comparison among all the results that have been presented previously. Table 7.7 is a summary of all impact value results. Table 7.8 shows the same results of Table 7.7 but referred to the reference case, so values

are percentage. All the values are lower than 1, this means that the prototypes have better results than the classical heat exchanger.

Table 7.7: Results comparison

		Reference	P 1	P 2	P 3	P 4
Global Energy Requirement (GER)	MJ eq	62	19.9	9.74	46.6	41.6
Global Warming (GWP)	kg CO ₂ eq	3.96	1.13	0.493	3.74	1.77
Ozone Layer Depletion (ODP)	kg CFC-11 eq	2.85E-07	1.94E-08	1.46E-08	2.51E-07	2.03E-08
Photochemical Oxidation (POCP)	kg C ₂ H ₄ eq	0.00283	0.00042	0.000496	0.00158	0.0023
Acidification (AP)	kg SO ₂ eq	0.0168	0.00384	0.00224	0.0186	0.00762
Eutrophication (EP)	kg PO ₄ ³⁻ eq	0.00816	0.0011	0.000154	0.00109	0.00054
Carcinogenics	kg benzene eq	0.0745	0.000253	0.000461	0.00716	0.000499
Non carcinogenics	kg toluene eq	658	1.69	3.06	50.6	3.06

Table 7.8: Results comparison considering Reference values as 1

	Reference	P 1	P 2	P 3	P 4
Global Energy Requirement (GER)	1	0.32	0.16	0.75	0.67
Global Warming (GWP)	1	0.29	0.12	0.94	0.45
Ozone Layer Depletion (ODP)	1	0.07	0.05	0.88	0.07
Photochemical Oxidation (POCP)	1	0.15	0.18	0.56	0.81
Acidification (AP)	1	0.23	0.13	1.11	0.45
Eutrophication (EP)	1	0.13	0.02	0.13	0.07
Carcinogenics	1	0.00	0.01	0.10	0.01
Non carcinogenics	1	0.00	0.00	0.08	0.00

Table 7.8 points out that all the Prototypes values are lower than 1 (except Acidification of Prototype 3): this means that the prototypes have better results than the classical heat exchanger used as reference.

Another method has been used to show results with aggregated indicators: the Ecoindicator method (Figure 7.46). In general the results of the comparison support the results of the characterization carried out in the previous paragraphs.

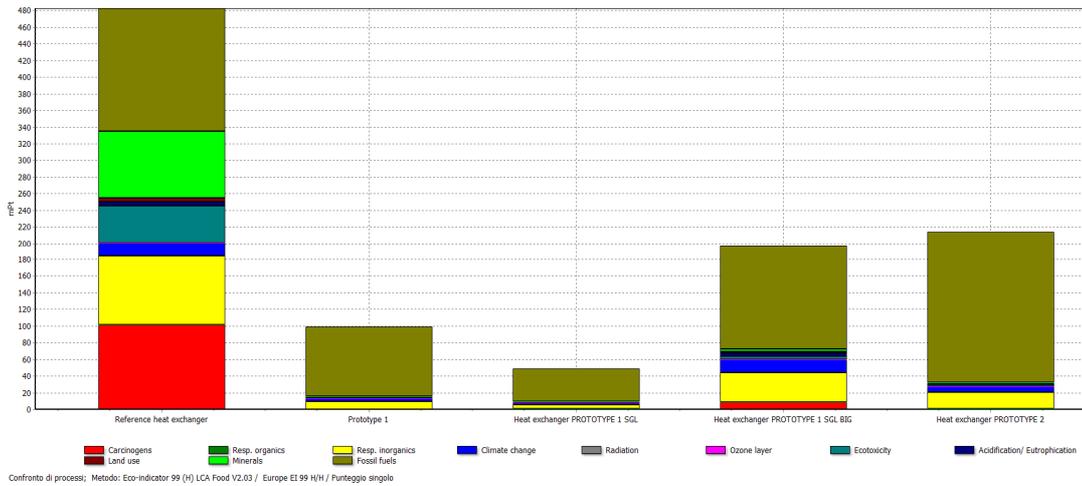


Figure 7.46: End point impacts of heat exchangers (Eco-indicator 99)

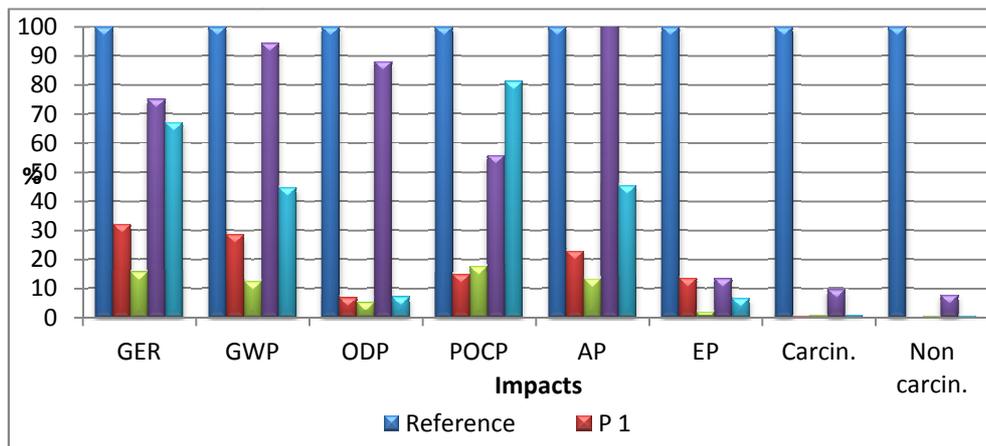


Figure 7.47: LCA results

Finally Figure 7.47 shows all the results in percentage values. Higher impacts are reached with the traditional heat exchanger (reference): this means that all the prototypes guarantee an upgrade in environmental sustainability. Among the

prototypes, the first and the second ones (P1 and P2) ensure the lowest environmental burdens: these are the best options advanced by the Thermonano project from an energy and environmental perspective.

7.6. Conclusion

The project shown in this chapter permits to practically apply the theory concepts explained in the first part of the thesis. A Life Cycle Assessment concerning four new prototypes of nanofilled-polymer-based heat exchangers and a traditional heat exchanger produced by Astra Refrigeranti S.p.A. has been developed and modelled. The new prototypes appear to be a good chance to improve a well know technology, as heat exchangers are, using the newest scientific innovation as nano-structured materials. Results demonstrate that Prototype 1 and Prototype 2 have the best performances considering sustainability (see Figures 7.46 and 7.47).

7.7. References

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- Han Z, Fina A (2011) Thermal Conductivity of Carbon Nanotubes and their Polymer Nanocomposites: A Review. Prog. Polym. Sci, 36: 914-944 DOI: 10.1016/j.progpolymsci.2010.11.004
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Chapter 8

Artificial Leaf

In this chapter a Life Cycle Assessment concerning an Artificial Leaf device has been developed and modelled. The objective is to practically apply the sensitivity approach theoretically discussed in Chapter 5 and the EROI and EPT tools described in Chapter 3 from a theoretical perspective. The goal of the study is to investigate some technological improvements for reaching sustainability.

8.1. Introduction

The present chapter has the aim to describe an LCA project performed on an Artificial Leaf. The project is part of a main project developed for the European Union, called Solhydromics.

A main topic in researches for a sustainable energy generation is the artificial photosynthesis: simulating natural processes is the purpose of many scientists from years, together with the optimization of them for energy device applications (Bensaid et al., 2012). Leaves and algae can split water into oxygen and hydrogen (in the form of reducing equivalents) at ambient conditions exploiting sun light. In photosynthesis, the reducing equivalents derived from H₂O splitting are used to reduce CO₂ giving rise to the various organic compounds of living organisms including those which provide fuel (biomass, sugars, vegetable oils as well as being the origin of the fossil fuels). However, in certain types of photosynthetic organisms

and under some conditions a specific enzyme, hydrogenase, can by-pass the CO₂ fixation process and can lead to non-negligible H₂ formation. The main goal of Solhydromics is the development of an artificial device capable of splitting water to produce hydrogen at ambient temperature composed of:

- an anode exposed to sunlight carrying Photosystem II or a PSII-like chemical mimic. Initially, PSII from microalgae known as cyanobacteria will be isolated with high water splitting activity, and immobilised for attachment to the electrically conducting membrane. In this way the generation of electrons and protons from water at the anodic surface will use the natural light harvesting system, charge separation machinery and water oxidation site of PSII. In the longer term synthetic metal-clusters will be explored which can bring about light-driven directional charge separation, thus mimicking the natural photosynthetic reaction centre, and use the oxidising potential of the “hole” to split water on a specifically tailored electrochemically active catalyst
- a cathode will carry a hydrogenase or an artificial hydrogenase catalyst in order to recombine protons and electrons into molecular hydrogen. Here again, the initial studies will involve immobilizing the natural enzymes, including those with low sensitivity to oxygen. Also, as for the water splitting site on the anodic side of the membrane, the longer term goal will be to synthesis a catalytic site which mimics hydrogenase activity in order to produce hydrogen gas.
- a membrane enabling transport of both electrons and protons via e.g. carbon nanotubes or TiO₂ connecting the two electrodes and ion-exchange resins like e.g. Nafion or SPEEK, respectively.

The overall objectives of using Life Cycle Assessment in the Solhydromics project are to evaluate environmental impacts related to the Artificial Leaf device production, to found out the hot spots of the production process and to delineate some technological improvements in order to gain the sustainability.

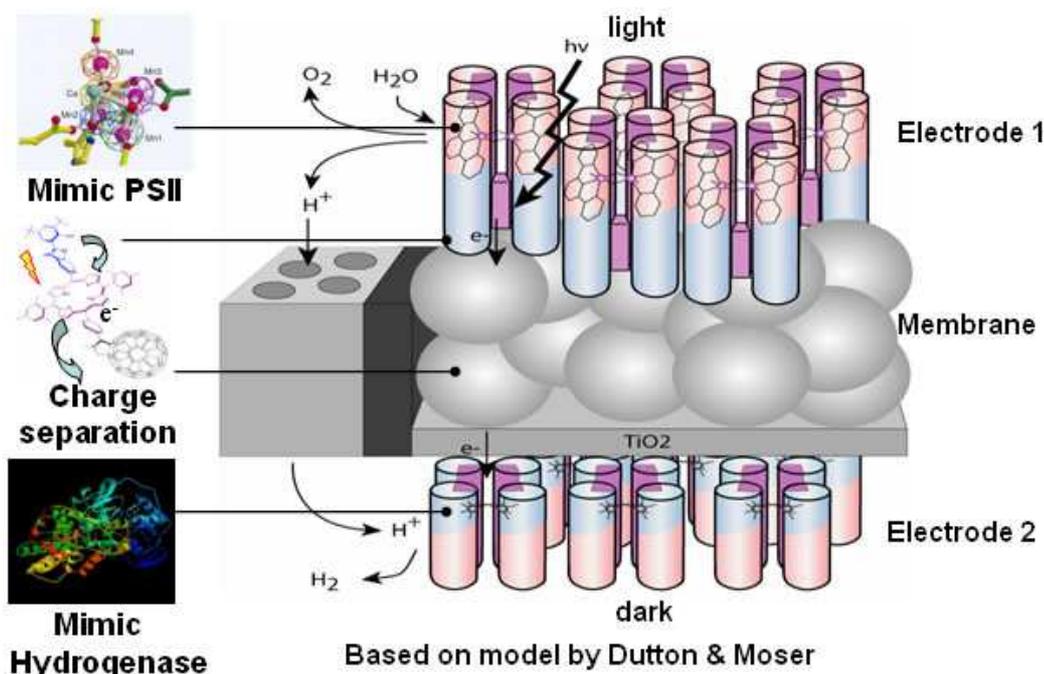


Figure 8.1: Scheme of the SOLHYDROMICS device concept, based on the original idea by Dutton & Moser (personal communication to J. Barber) (available online at: <http://www.solhydromics.com/index.php?/eng>)

The LCA is performed considering standard indicators such as Global Warming Potential, Acidification, Eutrophication, Human Toxicity, and Energy Resources. The sustainability evaluation is performed applying a sensitivity analysis and moreover using two environmental tools: EROI and EPT.

8.2. Goal and scope definition

The goal of the present LCA is to define the environmental burdens associated to the production of an Artificial Leaf device. A sensitivity analysis is required in order to identify the hot spots of the process and to find out the best direction in which focus the research. Artificial Leaf is nowadays in an infancy stage of development: it is important to use tools that permits to direct the project in the more efficient and more sustainable path.

8.2.1. Software and database

The software SimaPro 7.2 (Pré, 2010) was used in order to perform the present study. Primary data are collected from Solhydromics' partners, while secondary data are derived from databases, particularly Ecoinvent (2007).

8.2.2. Functional Unit

Functional unit is the reference unit, to which environmental indicators are associated. In this study two functional unite are used: 1 cm² of Artificial Leaf device and 1 mol of hydrogen produced. The first one refers to the device, while the second one to the product obtained using the device: both the functional units permits to obtain important results for sustainability evaluation. The best choice is not to choose one of them, but to use them both integrating results: in this way there is a broader perspective to examine the system and improve it.

8.2.3. System Boundaries

The definition of system boundaries of the study is one of the most important steps of a LCA. This report provides the eco-profile of the base, starting from the extraction raw materials, until the Artificial Leaf device is ready to be used.

8.3. LCA Inventory

Life Cycle Inventory (LCI) analysis involves creating an inventory of flows from and to nature for a product system. Inventory flows include inputs of water, energy, and raw materials and releases to air, land, and water. To develop the inventory, a flow model of the technical system is constructed using data on inputs and outputs. The input and output data needed for the construction of the model are collected for all activities within the system boundary.

Next paragraphs present in detail the flow model and the inputs of the Artificial Leaf device.

Three main parts of the Artificial Leaf device processes are considered in the evaluation of the impacts:

- **Anode** production, intending the materials and all the necessary operation to produce it
- **Cathode** production, intending the materials and all the necessary operation to produce it
- **Artificial Leaf**, the assembly of the anode and the cathode and the membrane between them.

8.3.1. Anode production

A brief description of the anode preparation is here reported. A glass surface with a density of 50 mg/cm^2 is treated with a specific solution in order to make a FTO thin layer adherent on surface. The solution is prepared using: tin (IV) chloride, ammonium fluoride and methanol in a quantity of respectively 7 mg/cm^2 , 0.1 mg/cm^2 and 20 mg/cm^2 . During this operation $2,040 \text{ J/cm}^2$ of electricity (medium voltage) has been used. The production of FTO needs 9 mg/cm^2 of tin 2-ethylhexanoate and 90 mg/cm^2 of ethanol. The next step requires a laser treatment in order to make geometrical holes, with an energy expenditure of 50 Wh/cm^2 as electricity (medium voltage).

Then the FTO/glass assembly must be dipped in Piranha solution in order to make an APTES thin layer: the Piranha solution creates OH groups on the FTO surface, APTES reacts with the OH groups and links to the FTO surface through oxygen bridges. The Piranha solution is constituted by sulphuric acid (75% w/w) and hydrogen peroxide (25% w/w) and it is used in a quantity of 1 mL/cm^2 . The APTES is a 3-aminopropyltriethoxysilane, and it is used in a quantity of $3 \text{ }\mu\text{L/cm}^2$.

The amino groups remain free on the surface and are useful to attach the MOF layer, specifically 2 mg/cm^2 . The MOF is produced using cobalt nitrate (4.2 g/gMOF), 2 methyl imidazole (1 g/gMOF) and dimethylformamide (432 mL/gMOF). An energy expenditure of 12.8 kWh as heat is required for producing 1 g of MOF.

8.3.2. Cathode production

The cathode is constituted by a carbon cloth with a thickness of 0.28 mm doped with platinum (0.5 mg/cm²).

8.3.3. Artificial Leaf device

The Artificial Leaf device is completed putting together the anode and the cathode with a layer of nafion in the middle, the thickness of nafion is 177.8 μm.

8.4. Life Cycle Impact Assessment

This section presents an overview of the environmental impacts of the Artificial Leaf device. Each impact is analyzed in detail, showing its contribute along the flow-sheet of the process considering as Functional Unit 1 cm² of device. Two tree diagrams are presented: the first one shows the impact values expressed in the specific unit, while the second one shows results in percentage and the arrows thickness is proportional to the impact flow that represents. In this way it is easy to find out the hot spots and consequently to know how improving the process. A cut-off of 1% is exploited: this means that the boxes with a contribution lower than 1% are not shown. This permits to have an intelligible flow sheet.

Finally Tables 8.1 and 8.2 summaries all the results using both the two Functional Units: 1 cm² in the first case and 1mol of H₂ produced in the second one.

8.4.1. Global Energy Requirement

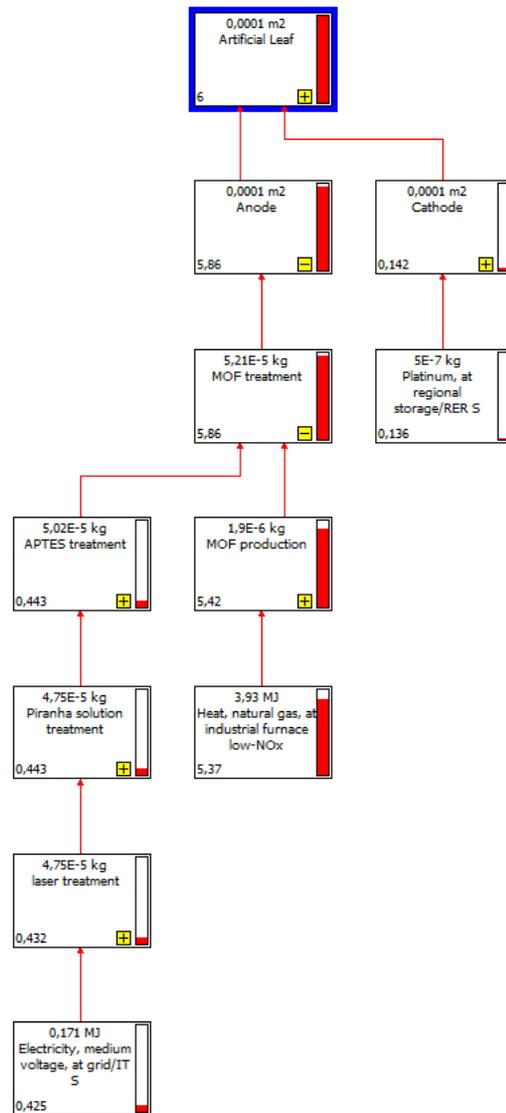


Figure 8.2: Flow sheet of the Global Energy Requirement impact (cut-off 1%)

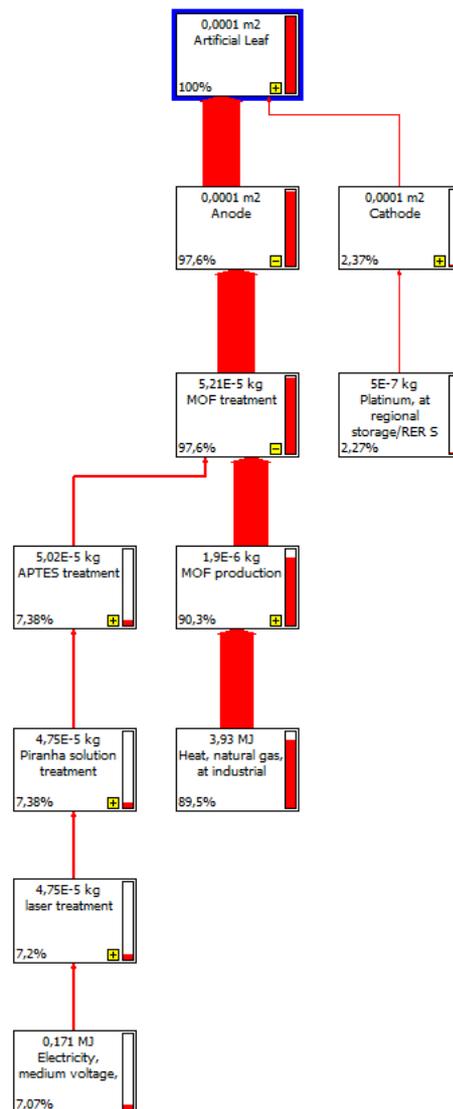


Figure 8.3: Flow sheet of the Global Energy Requirement impact in % (cut-off 1%)

Figure 8.3 shows that the highest quantities of necessary energy to prepare 1 cm² of the Artificial Leaf belongs to the anode preparation (97.6%): this value is composed by a main contribution due to the heat necessary for the MOF production (89.5%) and a lower contribution due to the electricity required by the laser for holding the glass support (7.07%).

8.4.2. Global Warming Potential

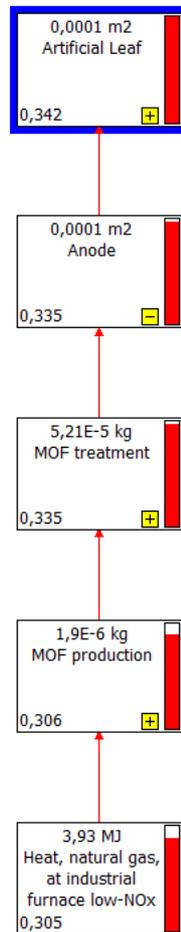


Figure 8.4: Flow sheet of the Global Warming Potential impact (cut-off 1%)

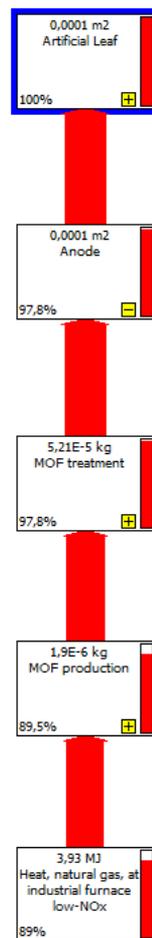


Figure 8.5: Flow sheet of the Global Warming Potential impact in % (cut-off 1%)

Figure 8.5 shows that the highest Global Warming Potential (GWP) impact to prepare 1 cm² of the Artificial Leaf belongs to the anode preparation, particularly to the heat required for MOF production (89%).

8.4.3. Ozone layer depletion

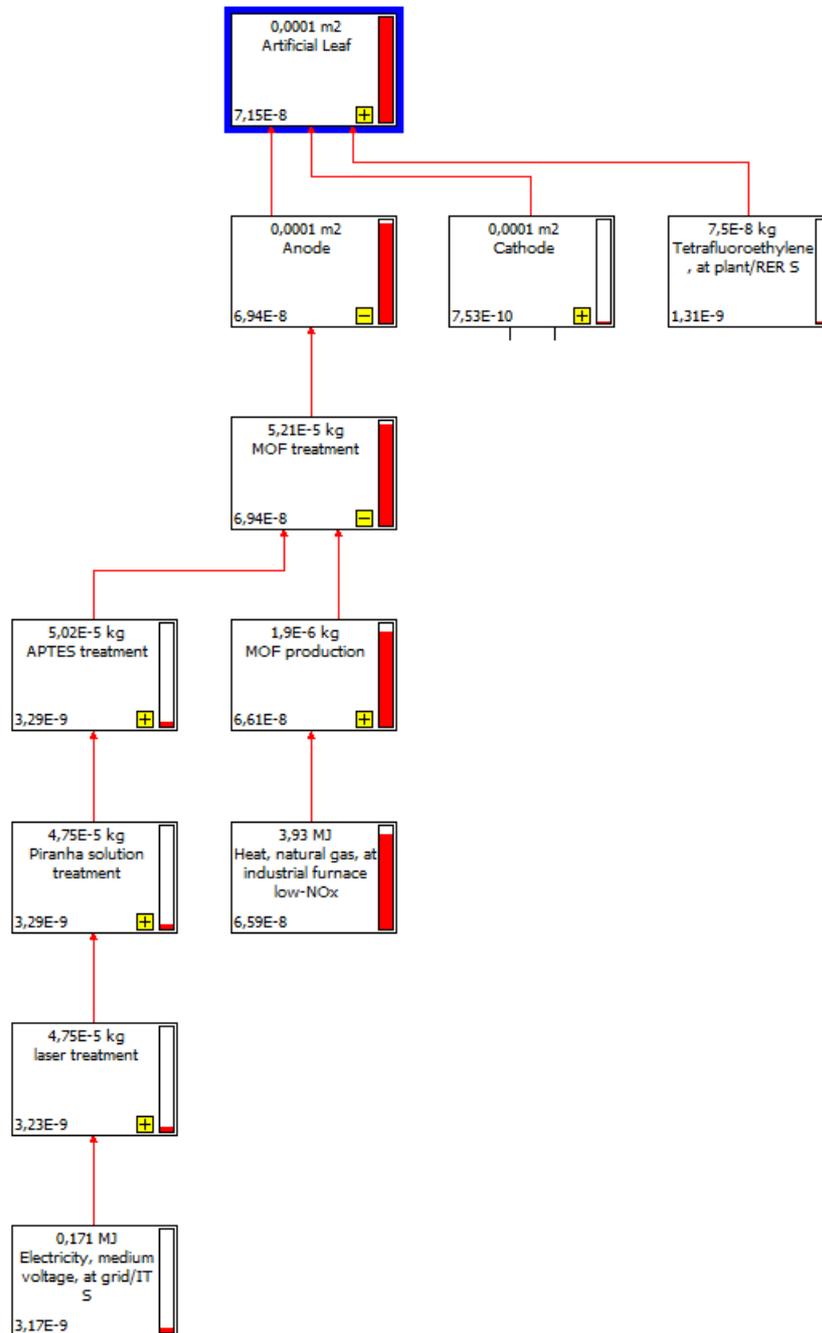


Figure 8.6: Flow sheet of the Ozone Layer Depletion impact (cut-off 1%)

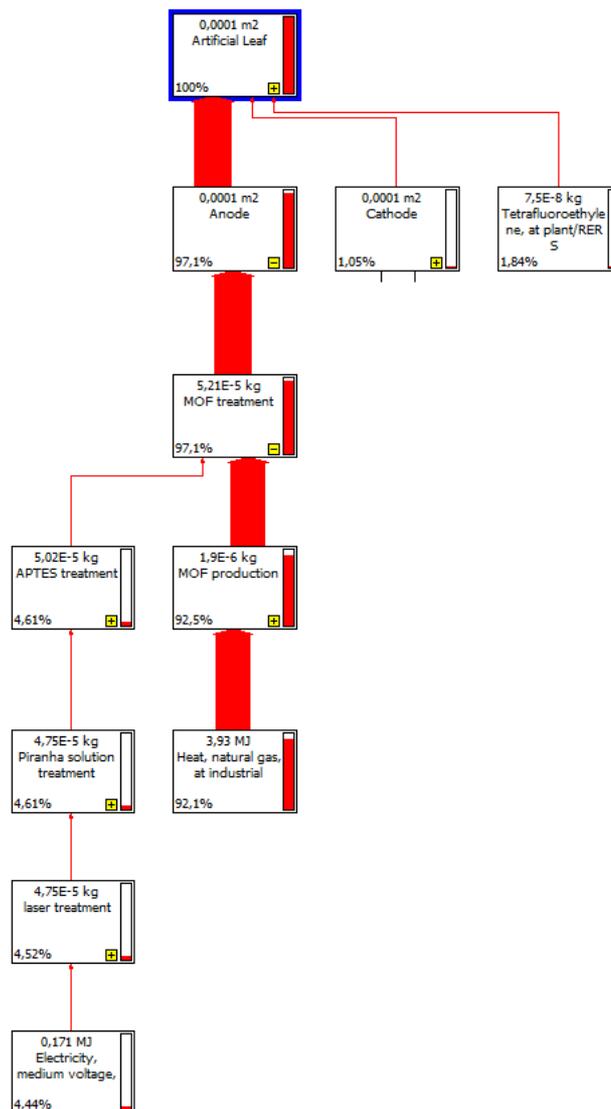


Figure 8.7: Flow sheet of the Ozone Layer Depletion impact in % (cut-off 1%)

Figure 8.7 shows that the highest Ozone Layer Depletion impact to prepare 1 cm² of the Artificial Leaf belongs to the anode preparation (97.1%): this value is composed by a main contribution due to the heat necessary for the MOF production (92.1%) and a lower contribution due to the electricity required by the laser for holding the glass support (4.44%).

8.4.4. Photochemical oxidation

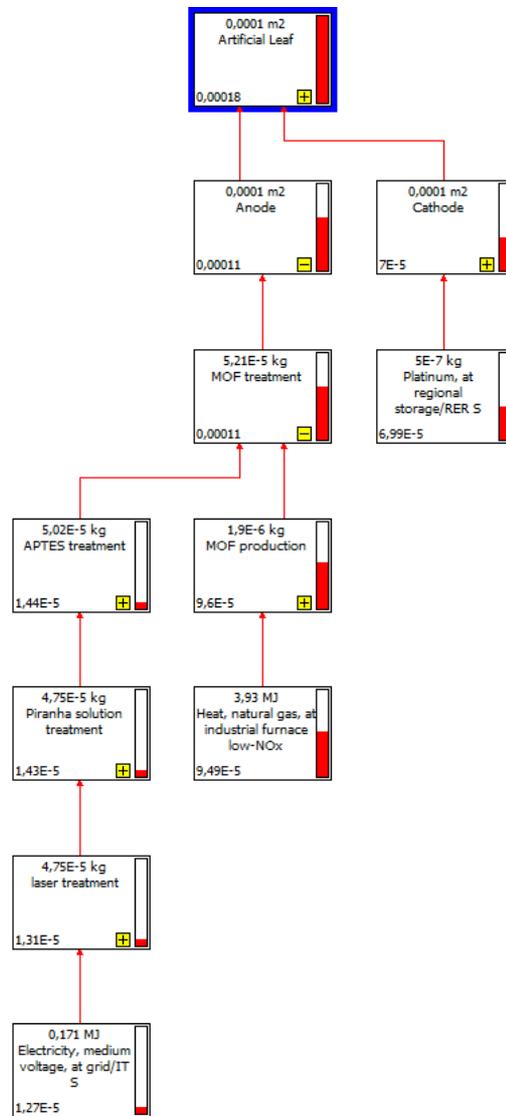


Figure 8.8: Flow sheet of the Photochemical Oxidation impact (cut-off 1%)

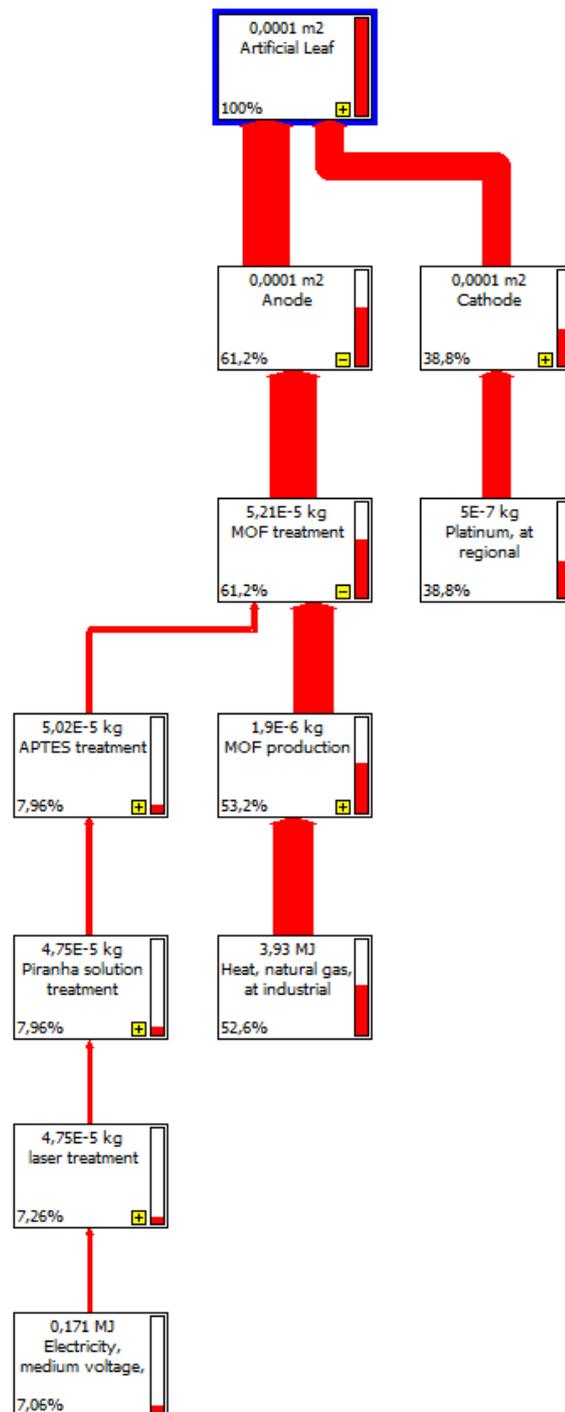


Figure 8.9: Flow sheet of the Photochemical Oxidation impact in % (cut-off 1%)

As concerns the Photochemical Oxidation impact, Figure 8.9 shows that the anode presents the higher contribution (61.2%), mostly due to the heat required for MOF production (52.6%) and to the electricity necessary for holding the glass support with

the laser (7.06%). This time the cathode presents a remarkable contribution (38.8%), totally due to the platinum.

8.4.5. Acidification Potential

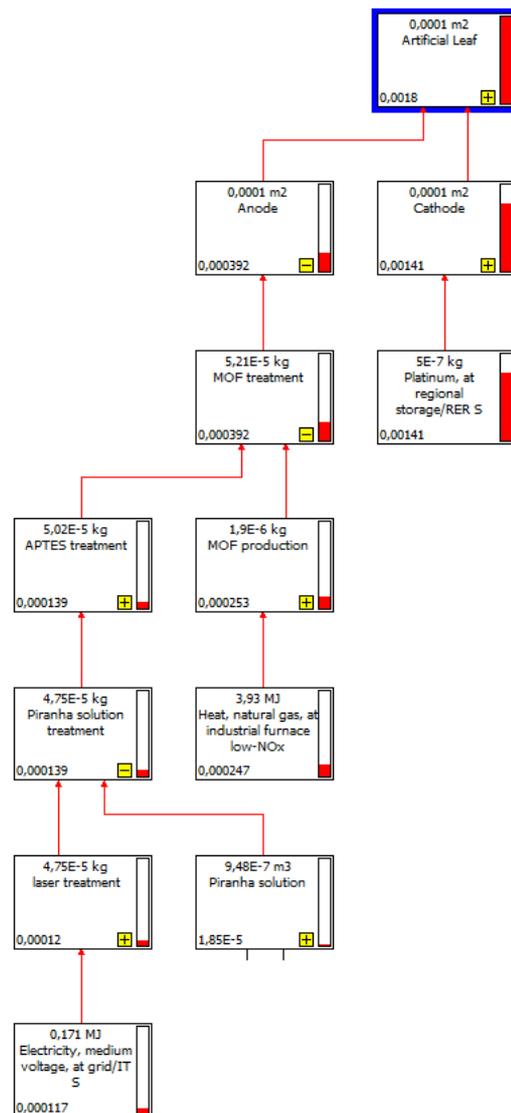


Figure 8.10: Flow sheet of the Acidification Potential impact (cut-off 1%)

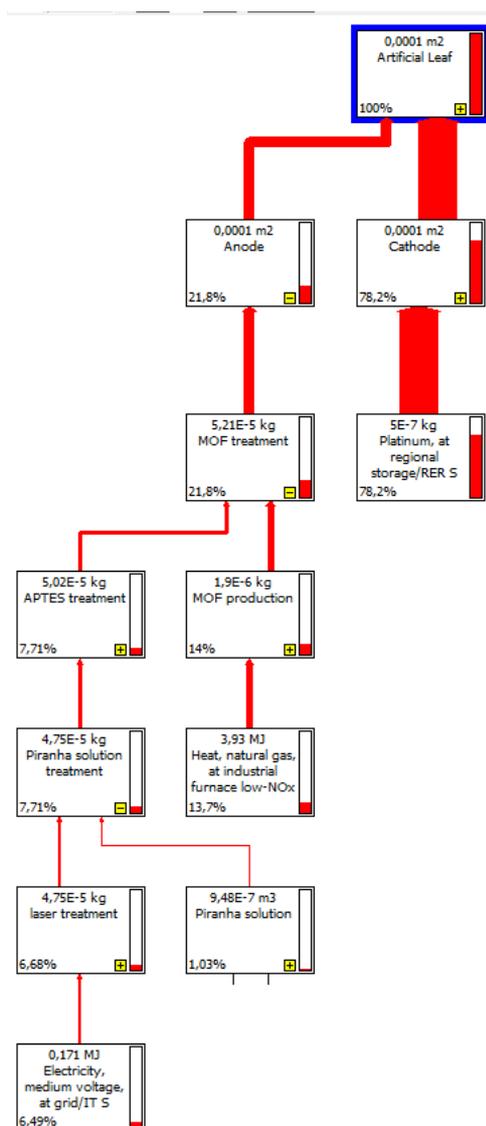


Figure 8.11: Flow sheet of the Acidification Potential impact in % (cut-off 1%)

As concerns the Acidification Potential impact, Figure 8.11 shows that the cathode presents the higher contribution (78.2%), totally due to the platinum. The contribution of the anode (21.8%) is due to the heat required for MOF production (13.7%) and to the electricity necessary for holding the glass support with the laser (6.04%).

8.4.6. Eutrophication Potential

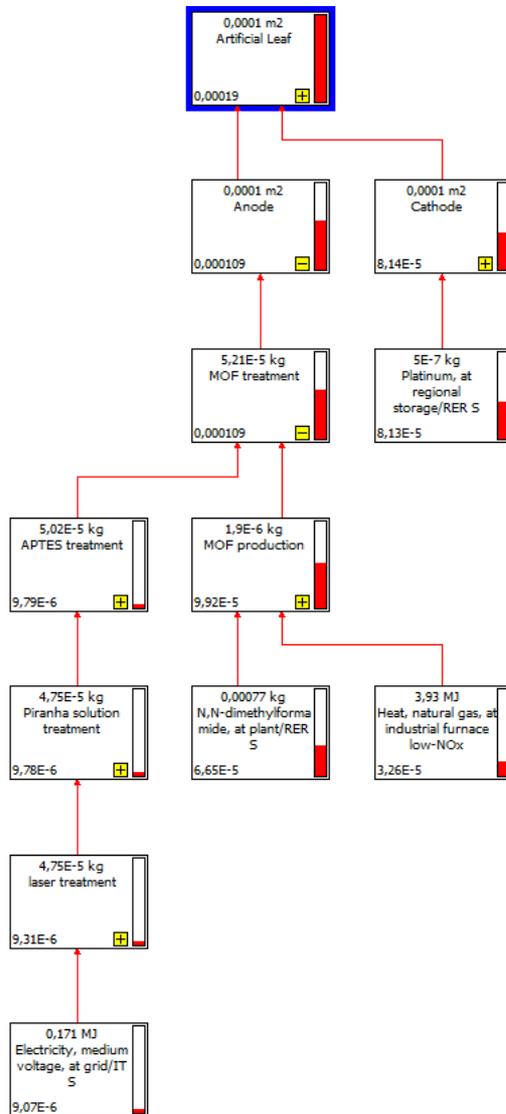


Figure 8.12: Flow sheet of the Eutrophication Potential impact (cut-off 1%)

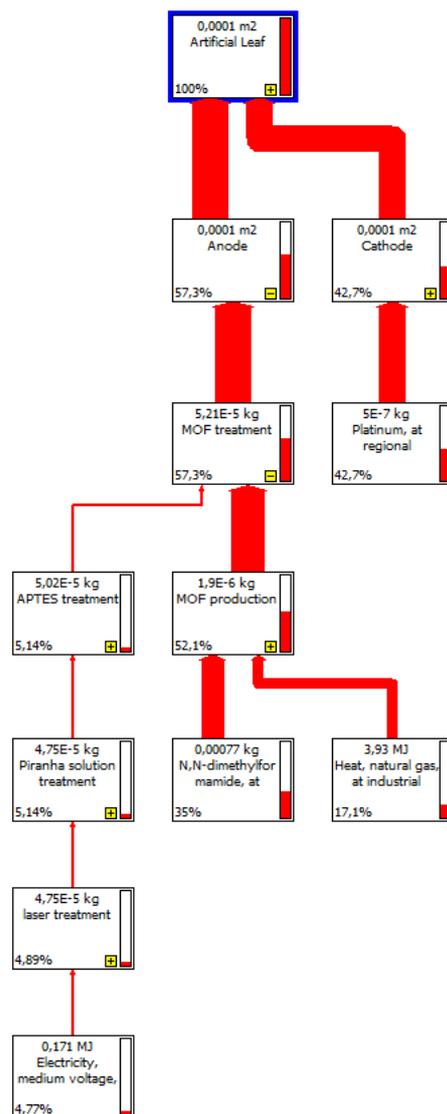


Figure 8.13: Flow sheet of the Eutrophication Potential impact in % (cut-off 1%)

The Eutrophication Potential impact is equally distributed between the anode (57.3 %) and the cathode (42.7 %). The main contributions for the anode are the heat required for MOF production (17.1%) and the raw materials used for MOF production (35%). The contribution of the cathode is totally due to the platinum.

8.4.7. Carcinogenics

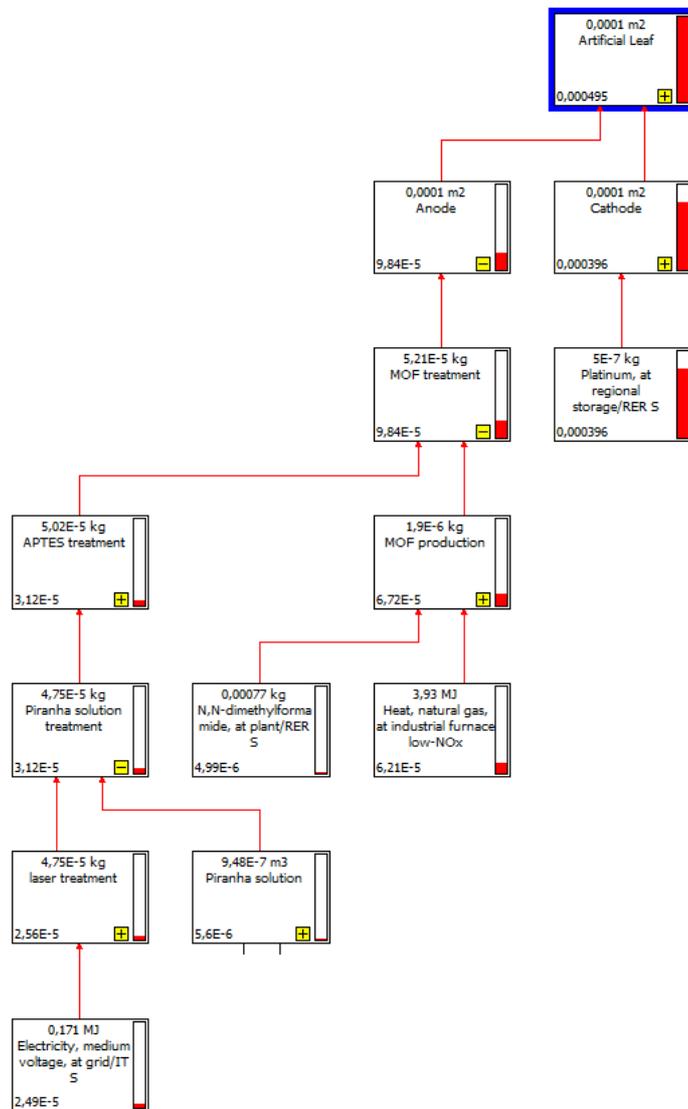


Figure 8.14: Flow sheet of the Carcinogenics impact (cut-off 1%)

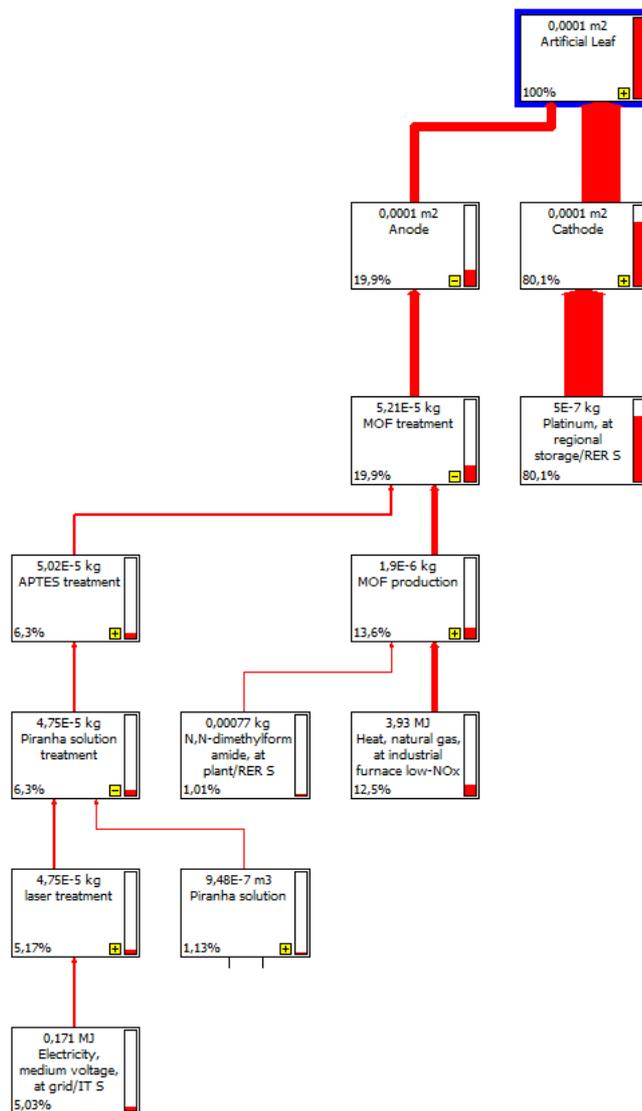


Figure 8.15: Flow sheet of the Carcinogenics impact in % (cut-off 1%)

Figure 8.15 shows that the Carcinogenics impact is mainly due to the use of platinum for cathode production (80.1%). Regarding anode (19.9%), the main contributions are the heat required for MOF production (12.5%) and the electricity for holding the glass support with the laser (5.03%).

8.4.8. Non Carcinogenics

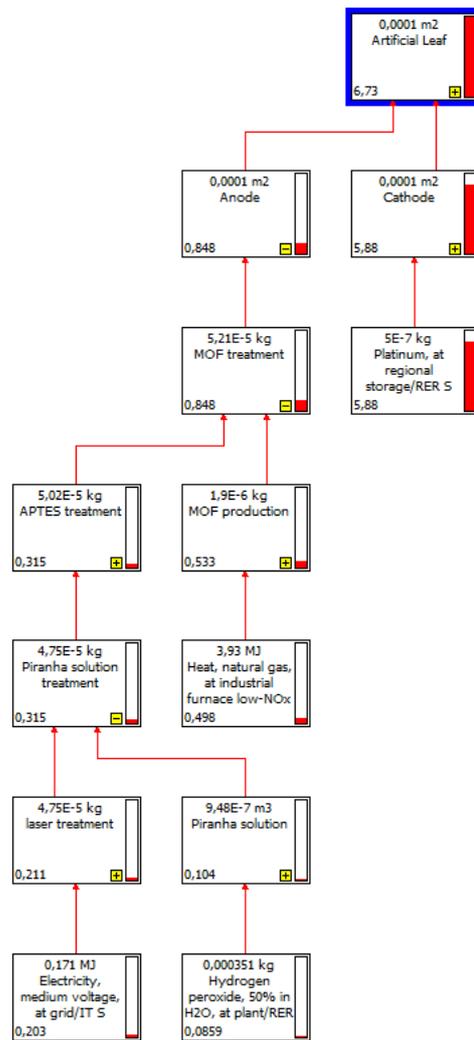


Figure 8.16: Flow sheet of the Non Carcinogenics impact (cut-off 1%)

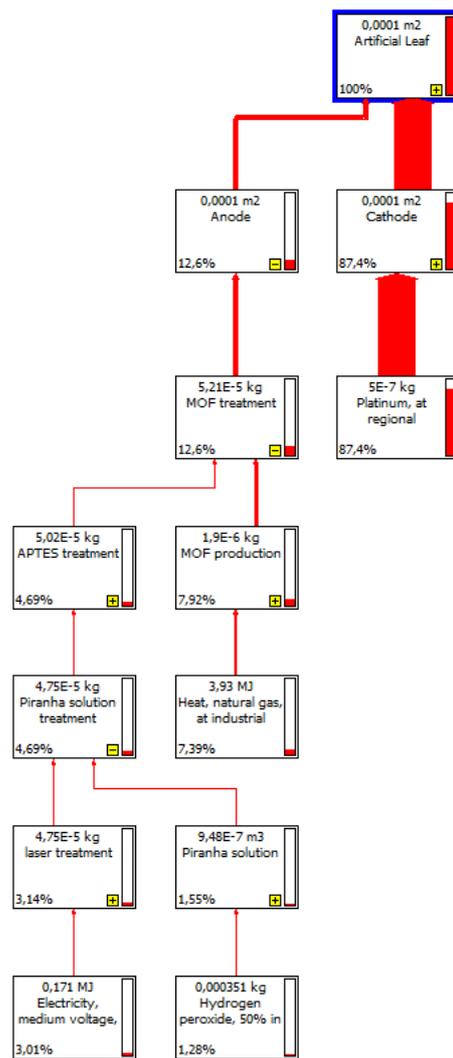


Figure 8.17: Flow sheet of the Non Carcinogenics impact in % (cut-off 1%)

Figure 8.17 shows that the Non Carcinogenics impact is mainly due to the use of platinum for cathode production (87.4%). Regarding anode (12.6%), the main contributions are the heat required for MOF production (7.39%) and the electricity for holding the glass support with the laser (3.01%).

8.4.9. Summary of the results

In Tables 8.1 and 8.2 values of the impact indicators are reported using the two Functional Unit: per unit of cm^2 of Artificial Leaf device and per unit of mol of hydrogen produced by the device.

Table 8.1: Summary of the results expressed in function of 1 cm^2 of device surface

Impact	Units	Total	Anode	Cathode
GER	MJ eq	6	5.86	0.142
GWP	Kg CO_2 eq	0.342	0.335	0.00753
ODP	Kg CFC-11 eq	7.15E-08	6.94E-08	7.53E-10
POCP	Kg C_2H_4 eq	0.0018	1.10E-04	7.00E-05
AP	Kg SO_2 eq	0.0018	3.92E-04	0.00141
EP	Kg PO_4^{3-} eq	1.19E-04	1.09E-04	8.14E-05
Carcinogenics	kg benzene eq	4.95E-04	9.84E-05	3.96E-04
Non Carcin.	kg toluene eq	6.73	0.848	5.88

Table 8.2: Summary of the results expressed in function of 1 mol of produced hydrogen

Impact	Units	Total	Anode	Cathode
GER	MJ eq	1.12E-04	1.10E-04	2.66E-06
GWP	Kg CO_2 eq	6.40E-06	6.27E-06	1.41E-07
ODP	Kg CFC-11 eq	1.34E-12	1.30E-12	1.41E-14
POCP	Kg C_2H_4 eq	3.37E-08	2.06E-09	1.31E-09
AP	Kg SO_2 eq	3.37E-08	7.34E-09	2.64E-08
EP	Kg PO_4^{3-} eq	2.23E-09	2.04E-09	1.52E-09
Carcinogenics	kg benzene eq	9.27E-09	1.84E-09	7.41E-09
Non Carcin.	kg toluene eq	1.26E-04	1.59E-05	1.10E-04

The high contribution for most of the considered impacts is due to the anode production. The hot spots for anode production are the MOF production (it requires a huge amount of energy for heating the reagents for three days in a reactor) and the laser holing of the glass support (it requires a high amount of electricity). The cathode contribution, when it is relevant, is totally due to the use of platinum.

There is a focus on the two first indicators for further sustainability assessment: Gross Energy Required (GER) and Global Warming Potential (GWP). The following section is devoted to evaluate their variation when some improvements in anode production are hypothesized. Improvements concern anode as it represents the most contribution for both the impacts. This can be regarded as the application of the LCA analysis in the selection of trajectories of research improvements in the field.

8.5. Sensitivity Analysis

This section has the aim to analyse the environmental impact of the Artificial Leaf device performing some modifications to the base case previously described. In section 8.4 the hot spots of the process are identified: MOF production and laser treatment; here other two parameters are considered for improving the process sustainability: lifetime and efficiency of the device, which affect the performance of the artificial leaf.

The sensitivity analysis is performed evaluating two impacts: GER and GWP. This choice is motivated by the fact that using too many parameters makes the comprehension of the results very hard.

The sensitivity analysis has been conducted by varying the following parameters: the time required for MOF production is reduced, the glass support is replaced with a rock wool of FTO so the laser treatment is not necessary, the efficiency of the device and its life time are increased and this increases the quantity of produced hydrogen. In the following sections the results of the evaluations are reported; in performing the sensitivity analysis only one parameter has been changed taking all

the others constant, at the end a so called “best case” has been considered as the collection of the best results of each evaluation.

8.5.1. MOF production

The MOF production requires a huge amount of energy since the reactor needs to be heated for 3 days. It is supposed to improve this step of the process reducing the heating time from 3 days (base) to 1 day (1d) and till 3 hours (3h).

Table 8.3: GER and GWP impact values expressed in function of 1 cm² of surface

Impact	Units	BASE	1 d	3 h
GER	MJ eq	6	2.54	0.892
GWP	Kg CO ₂ eq	0.342	0.146	0.0526

Table 8.4: GER and GWP impact values expressed in function of 1 mol of produced hydrogen

Impact	Units	BASE	1 d	3 h
GER	MJ eq	320513	135684	47650
GWP	Kg CO ₂ eq	18269	7799	2810

Tables 8.3 and 8.4 report the results per cm² and per mol of H₂ produced; in both cases the impact parameters dramatically decrease: this is a good path to follow for sustainability improvement.

8.5.2. Device life time

At present the Artificial Leaf device has a short lifetime: 20 minutes (base). It is supposed to extend it gradually, till 1 year (1y), 5 years (5y) and 10 years (10y). The global impact of the device on the environment stays unchanged, while the amount of produced energy grows: GER and GWP do not change considering 1 cm² as FU,

while there is a considerable improvement in sustainability considering as FU 1 mol of H₂ produced (this means lower impacts). Tables 8.5 and 8.6 report the results expressed in both Functional Units.

Table 8.5: GER and GWP impact values expressed in function of 1 cm² of surface

Impact	Units	BASE	1 y	5 y	10y
GER	MJ eq	6	6	6	6.01
GWP	Kg CO ₂ eq	0.342	0.342	0.342	0.342

Table 8.6: GER and GWP impact values expressed in function of 1 mol of produced hydrogen

Impact	Units	BASE	1 y	5 y	10y
GER	MJ eq	320513	12.196	2.439	1.222
GWP	Kg CO ₂ eq	18269	0.695	0.139	0.070

8.5.3. Laser – Rock wool

The present process involves a glass layer with geometrical holes obtained with a laser treatment that requires a huge amount of energy. It is supposed to improve the process avoiding the use of glass and obtaining directly a rock wool of FTO (rw) by little modification of the present process to produce it. This modification has a little beneficial effect as one can see either from Table 8.7 or Table 8.8, because laser contribution on global Artificial Leaf GER and GWP is around 7-8%.

Table 8.7: GER and GWP impact values expressed in function of 1 cm² of surface

Impact	Units	BASE	Rw
GER	MJ eq	6	5.87
GWP	Kg CO ₂ eq	0.342	0.331

Table 8.8: GER and GWP impact values expressed in function of 1 mol of produced hydrogen

Impact	Units	BASE	Rw
GER	MJ eq	320513	313568
GWP	Kg CO ₂ eq	18269	17682

8.5.4. Hydrogen production

The device presents now an efficiency of 4% (base). It is supposed to improve it till 8% (8%) and 10% (10%) in order to grow the amount of produced hydrogen. As for device lifetime, also in this case GER and GWP do not change considering 1 cm² as FU, while there is a considerable improvement in results considering 1 mol of produced H₂ as FU. Tables 8.9 and 8.10 report results expressed in both Functional Units.

Table 8.9: GER and GWP impact values expressed in function of 1 cm² of surface

Impact	Units	BASE	8%	10%
GER	MJ eq	6	6	6
GWP	Kg CO ₂ eq	0.342	0.342	0.342

Table 8.10: GER and GWP impact values expressed in function of 1 mol of produced H₂

Impact	Units	BASE	8%	10%
GER	MJ eq	320513	137741	107296
GWP	Kg CO ₂ eq	18269	7851	6116

8.5.5. Best case

In this paragraph, finally, the “best case” is evaluated, considering to apply all the improvements described before. The “best case” is referred to an hypothetical device constructed and assembled in a manner to present the best results obtained

by the sensitivity analysis. It could be regarded as a “reference model” of such Artificial Leaf toward the actual effort of scientific research need to move. The “best case” is constituted in the following manner: the MOF production requires 3 hours, the device has a lifetime of 10 years, the glass support is not necessary as FTO is produced as a rock wool, the efficiency of the device is 10%. Tables 8.11 and 8.12 show results expressed in both Functional Units.

Table 8.11: GER and GWP impact values expressed in function of 1 cm² of surface

Impact	Units	BASE	best case
GER	MJ eq	6	0.445
GWP	Kg CO ₂ eq	0.342	0.0235

Table 8.12: GER and GWP impact values expressed in function of 1 mol of produced H₂

Impact	Units	BASE	best case
GER	MJ eq	320513	0.030
GWP	Kg CO ₂ eq	18269	0.002

Tables 8.11 and 8.12 point out that the proposed hypothesis permit to highly improve the sustainability of the Artificial Leaf.

8.5.6. Results comparison

This paragraph aims to make a comparison among all the results that have been presented previously. Table 8.13 is a summary of all impact value results considering as Functional Unit 1 cm² of Artificial Leaf device. Table 8.14 shows the same results of Table 8.13 but referred to 1 mol of produced hydrogen by the Artificial Leaf device.

Table 8.13: Results comparison (FU=1cm²)

CASE	GER	GWP
Base	6	0.342
MOF 1d	2.54	0.146
MOF 3h	0.892	0.0526
1y	6	0.342
5y	6	0.342
10y	6.01	0.342
Rw	5.87	0.331
8%	6	0.342
10%	6	0.342
Best	6	0.445

Table 8.14: Results comparison (FU=1mol H₂)

CASE	GER	GWP
Base	320513	18269
MOF 1d	135684	7799
MOF 3h	47650	2810
1y	12.196	0.695
5y	2.439	0.139
10y	1.222	0.070
Rw	313568	17682
8%	137741	7851
10%	107296	6116
Best	0.030	0.002

8.6. EROI & EPT

The present section has the aim to show two important tools for energy sustainability evaluation of the Artificial Leaf device: EROI (*Energy Return on Investment*) and EPT (*Energy Payback Time*), described in Chapter 3. Next paragraphs show EROI and EPT values for each case analyzed in the sensitivity analysis (section 8.5).

8.6.1. MOF production

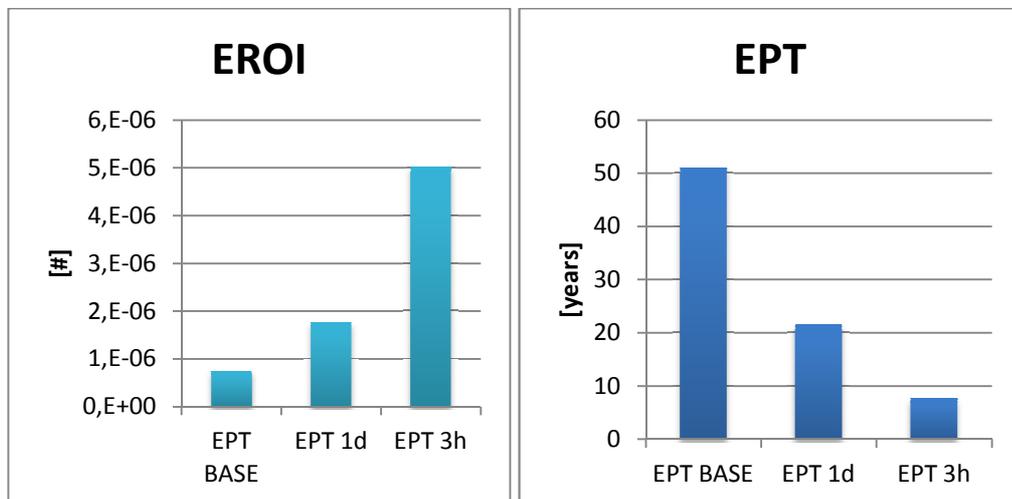


Figure 8.18: EROI values varying the time required for MOF production: 3 days (base case), 1 day (1d) and 3 hours (3h)

Figure 8.19: EPT values varying the time required for MOF production: 3 days (base case), 1 day (1d) and 3 hours (3h)

EROI values increase with the reduction of the time required for MOF production: this means that there is an improvement in process sustainability, however the process still remains unsustainable. EROI in fact still has values lower than 1. This hypothesis is not sufficient but it may represent a good path to follow together with other assumptions. EPT values decrease with the reduction of the time required for MOF production, confirming what stated before for EROI.

8.6.2. Device life time

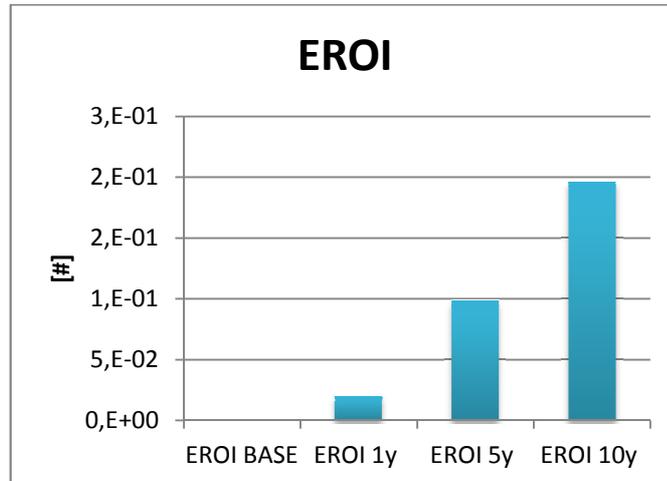


Figure 8.20: EROI values varying the lifetime of the device: 20 minutes (base), 1 year (1y), 5 years (5y) and 10 years (10y)

EROI values increase with the increase of device lifetime: this means that there is an improvement in process sustainability, however the process still remains unsustainable. EROI in fact still has values lower than 1. This hypothesis is not sufficient but it may represent a good path to follow together with other assumptions. In this case the EPT figure is not presented because there are not differences from the base case: the global impacts of the device do not change, while the produced energy grows with the lifetime growing.

8.6.3. Laser – Rock wool

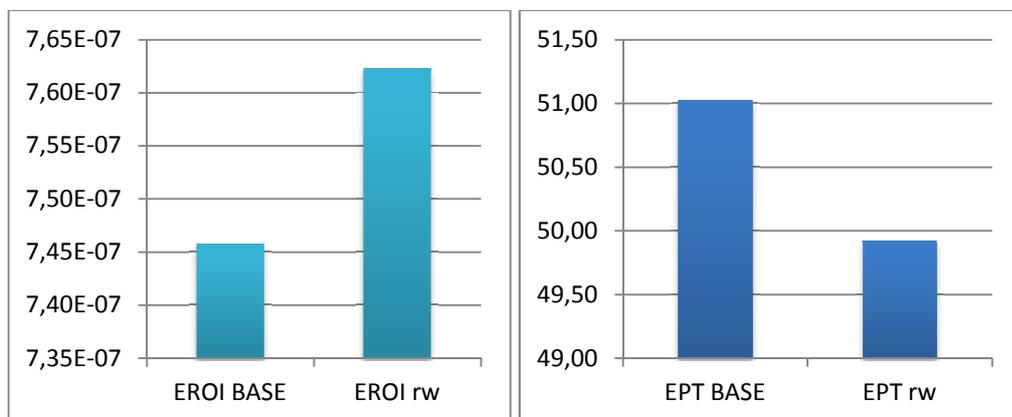


Figure 8.21: EROI values replacing the glass support with a rock wool in FTO (rw)
Figure 8.22: EPT values replacing the glass support with a rock wool in FTO (rw)

EROI value increases producing FTO as a rock wool instead of using a glass support that requires to be holed with a laser: this means that there is an improvement in process sustainability, however the process still remains unsustainable. EROI in fact still has values lower than 1. This hypothesis is not sufficient but it may represent a good path to follow together with other assumptions. EPT value increases but not much, confirming what stated before for EROI.

8.6.4. Hydrogen production

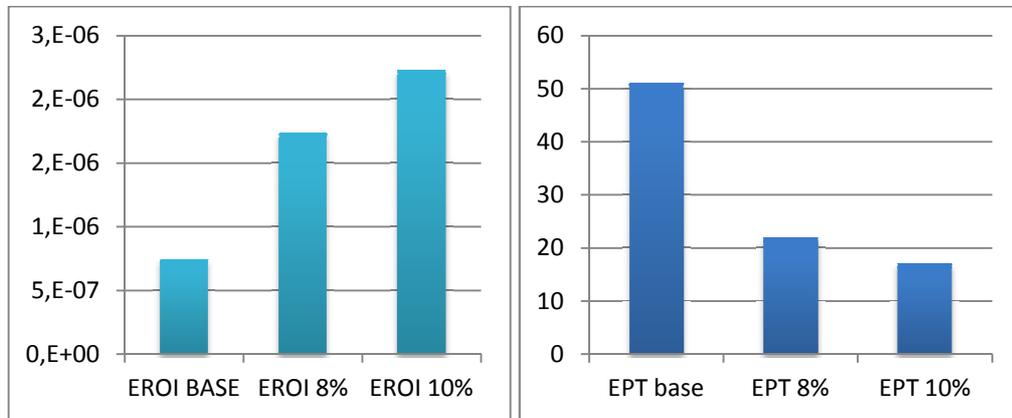


Figure 8.23: EROI values varying the device efficiency: 4% (base), 8% (8%) and 10% (10%)

Figure 8.24: EPT values varying the device efficiency: 4% (base), 8% (8%) and 10% (10%)

EROI values increase with the increase of the device efficiency: this means that there is an improvement in process sustainability, however the process still remains unsustainable. EROI in fact still has values lower than 1.

This hypothesis is not sufficient but it may represent a good path to follow together with other assumptions. EPT values decrease, confirming what stated before for EROI.

8.6.5. Best case

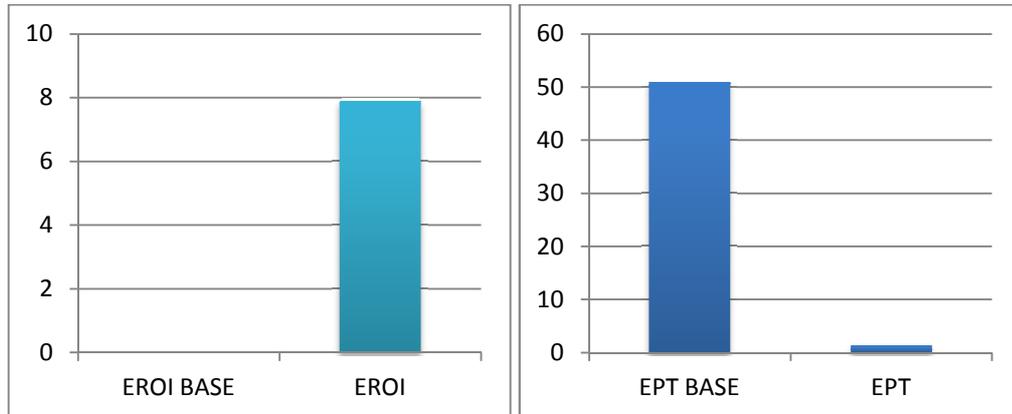


Figure 8.25: EROI values of the base case and the best case

Figure 8.26: EPT values of the base case and the best case

Figures 8.25 and 8.26 show that applying all the hypothesis together EROI increases and EPT decreases, both drastically. The best case is highly sustainable as EROI reaches a value of 8 and the EPT is lower than 2 years. The best case is not existing at the present, but it represents the direction in which the research on Artificial Leaf may focus.

8.6.6. Results comparison

Table 8.15: EROI and EPT comparison

CASE	EROI [-]	EPT [year]
Base	7.46E-07	51.03
MOF 1d	1.76E-06	21.60
MOF 3h	5.02E-06	7.59
1y	1.96E-02	51.03
5y	9.80E-02	51.03
10y	1.96E-01	51.03
rw	7.62E-07	49.92
8%	1.74E-06	21.93
10%	2.23E-06	17.08
Best	7.89	1.27

This paragraph has the aim to present all the results together in order to compare the sustainability improvement obtained by the different hypothesis. Reducing the time required for MOF production and increasing the device efficiency lead to similar results if applied singularly: EROI increases of one order of magnitude, but it remains lower than 1. Producing FTO as a rock wool instead of using a glass support, that requires to be holed with a laser, does not represent by itself a significant improvement, as EROI and EPT maintain more or less the same values. Best results are reached increasing the device lifetime, however this hypothesis is still not sufficient by itself. If all the hypothesis are applied the process is highly sustainable.

8.7. Conclusion

In this chapter a Life Cycle Assessment concerning an Artificial Leaf device has been developed and modelled. The goal of the study is to enlighten the hot spots of the process and to propose some hypothesis in order to improve its sustainability. A sensitivity approach theoretically discussed in Chapter 5 is here applied practically. Several technological improvements have permitted to define a “best case” showing a technological trajectory toward an efficient sustainable device.

EROI and EPT described in Chapter 3 from a theoretical perspective are here used for an energy sustainability analysis for comparing the device with its actual configuration (base case), with each singular improvement, and finally with all hypothesis considered (best case).

These improvements are, in order of relevance:

- increasing the device lifetime till 10 years
- reducing the time required for MOF production to 3 hours
- increasing the device efficiency till 10%
- producing FTO as a rock wool instead of using a glass support.

The best case can be considered as an Artificial Leaf with performances towards the actual scientific efforts could be oriented.

8.8. References

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Chapter 9

Dietary vs. Transport

In this chapter the environmental impacts of individual consumers during a normal work day is investigated, offering concrete data in order to promote pondered behaviour, in order to enhance consumers' global awareness of their responsibility towards the ecosystem. Two main topics of daily life are considered: dietary and transport. The Sustainability Environmental Index (SEI) described theoretically in Chapter 4 is here practically applied.

9.1. Introduction

The concept of sustainable development is gaining considerable importance, as the necessity of finding a synchronism between the needs of society and those of planet ecosystems is becoming more and more evident. The urgency to act in this field is constantly underlined by many associations, such as the World Wildlife Fund (WWF), which, in the Living Planet Report 2010, analysed the current trends of natural resources exploitation. This report has predicted that a "business as usual" scenario means that humanity will be using resources and land at the rate of two planets per year by 2030, and has shown how the actual model of growth, which does not consider environmental constrains, is evidently unsustainable (WWF, 2011).

According to this scenario, the possibility of developing new highly efficient and eco-friendly economy system will be not sufficient, if it is not supported by a responsible life-style that pays greater attention to the consequences of our daily actions on the environment. The opportunity of guaranteeing well-being and basic needs to future generations is closely related to the choices made today to invest in responsible policies and education. Decisions made by single citizens, particularly in developed or developing countries, offer a huge opportunity to tackle most of the problems that currently affect the environment. One of the most important and concrete opportunities, in this context, is offered by the dietary, due to the extremely high impact of the modern technologies that are used to produce food and its manufacturing (Roy et al., 2009). The dairy and meat production sectors are characterised by high environmental loads, such as greenhouse gases emissions, land and water use and the acidification of soils (Nguyen et al., 2010; Pelletier et al., 2010; Eide et al., 2003). A 2006 report by the Food and Agriculture Organization (FAO) of the United Nations, highlighted how the meat production sector, considering the whole lifecycle, appears to be the first contributor of greenhouse gases emissions, producing 18% of the total amount, while transport, instead, accounts for just 13%. Additionally, intensive farming is indirectly responsible for many other global problems such as famine, deforestation, desertification and nitrification of ground water. Many of the deforested areas of undeveloped countries have been used for the production of cereals for animal feeds, instead that for the human dietary exasperating the local malnutrition (FAO, 2006). The problem of deforestation of rain forests, due to cattle ranching, is becoming particularly critical in areas like South America (Mertens et al., 2002; Seidl et al., 2001). In 1997, the WWF asserted that 88% of the deforested territory of the Amazon Forest had been used for grazing (WWF, 1997). In addition, recent studies have predicted that meat consumption will increase again in the near future, suggesting the necessity of initiating a debate on the sustainability of dietary in modern society (Vinnari, 2008).

A second way of making responsible choices that could mitigate the impact of our society on the environment, is offered by the choice of transport. First, a series of decisions to improve the environmental benefits could be taken by public policies. Promoting the use of public transport or introducing fuel taxes could reduce the emission of pollutant gases and CO₂ (Storchmann, 2001). Second, a growing awareness of individual citizens to choose a means of transport could also reduce our impacts on the environment, such as a reduction in the Global Warming, or an improvement in the quality of the air in towns. Additionally, the decision of a critical group of citizens environmentally minded could influence the automotive market to invest more effort in eco-friendly cars (hydrogen-fuelled, electric,...). The possibility of choosing a public transport, such as a bus, instead of a private means, e.g. a car, is one way of reducing greenhouse gas emissions (Paravantis, 2007). Moreover, in a sustainable scenario, the use of fossil fuels and energy should also be taken into account, and lower fuel consumption cars should be promoted to replace older ones (Sprei et al., 2008).

With these considerations in mind, the present chapter has the aim of evaluating the environmental burdens of a typical work day, by comparing the impact of transport from home to work and the food supplied for lunch. This study proposes an analytical approach to support sustainable development by offering consumers an overview on the environmental consequences of their daily actions. The opportunity of considering our life-style, together with a stronger environmental consciousness, could concretely help to mitigate the dangerous trend that our society is actually following. The benefits that could be obtained by adopting a different life-style could be very effective, as long as it is adopted by a large critical mass and with appropriate global policies. The necessity to reflect on how society is affecting the environment and the opportunities offered to future generations, are duties that can no longer be more postponed.

Environmental impacts are estimated by means of the LCA (Life Cycle Assessment) methodology. A rigorous LCA study has the purpose of evaluating the overall impacts “from cradle to grave”, starting from the raw materials extraction until the

end of life of the investigated product, and crossing through the phase of use (ISO, 2006). Although the effectiveness of the life cycle approach is well accepted to quantify correctly the impacts and its potentiality of supporting the sustainable development is out of the question, a global consensus about the interpretation of results is not yet achieved. It is, as example, not still unanimously accepted which impact categories should receive more attention and higher priority from decision makers (Miettinen and Hamalainen, 1997). Eshun et al. (2011) criticized how almost the totality of methods that aims to quantify the environmental impacts evidence the limit to evaluate these problems only considering how they manifest themselves in the western world, instead than globally, and cannot be easily adapted to different realities like the African countries. The a priori definition of the system boundaries is crucial in order to clearly assess the analysis range of an LCA. In this chapter, meals have been hypothesised to have been provided by a canteen, thus avoiding an additional journey home during the lunch break. Different transportation means and different balanced diets, supported by data available in software libraries or in literature, have been analysed. The final goal is to evaluate the environmental impacts of individual consumers during a normal work day (but neglecting the impacts due to his work), and to offer concrete data in order to promote pondered behaviour, in order to enhance consumers' global awareness of their responsibility towards the ecosystem.

9.2. Goal and scope definition

The goal of the present study is to investigate a normal workday in order to evaluate the environmental burdens of an individual worker, focusing particularly on dietary and transport.

9.2.1. Software and database

The SimaPro 7.2.4 (Pré, 2010) software was employed to conduct the LCA analysis, and EPD 2008 (Environmental Product Declaration) (ISO 14025, 2006) and CED

v1.07 (Cumulative Energy Demand) (Frischknecht et al., 2007) methods were used to evaluate the environmental impacts.

9.2.2. Functional Unit

Functional unit is the reference unit, to which environmental indicators are associated. In this study two functional units are used: “1 meal” for dietary and “1 service of transportation per day” for transport. The functional unit is “service of transportation per day”. The whole process has to be defined, and a flow chart that considers inputs and outputs of each single step was to be prepared, in order to correctly evaluate the total mass and energy involved in the process.

The indicators that will be used in this work to quantify the environmental loads of a standard work day, are:

- GER (Global Energy Requirement)
- GWP (Global Warming Potential)
- ODP (Ozone layer depletion)
- POCP (Photochemical oxidation)
- AP (Acidification Potential)
- EP (Eutrophication Potential)

9.2.3. Menus scenarios

The menus were drawn up on the basis of indications given by the canteen at the Politecnico of Turin (Italy); the quantity and the kind of dishes proposed in order to offer balanced and complete meals (Politecnico di Torino, 2010) are reported.

The environmental load attributable to the cooking process has been estimated on the basis of the natural gas and the electrical energy consumed by a canteen kitchen. Average transport values based on the information available from Sotral EPD (Sotral, 2008) have been added to each menu.

Four different menus, proposing three different kinds of meat (beef, poultry or pork) have been proposed together with a vegetarian menu, where meat has been substituted by peas (IOM, 2008).

- Menu 1: Omnivorous menu (beef based): rice (100g), beef steak (120g), carrots (150g), bread (50g)
- Menu 2: Omnivorous menu (poultry based): rice (100g), poultry (120g), carrots (150g), bread (50g)
- Menu 3: Omnivorous menu (pork based): rice (100g), pork steak (120g), carrots (150g), bread (50g)
- Menu 4: Vegetarian menu: rice (100g), peas (120g), carrots (150g), bread (50g)

9.2.4. Transport scenarios

For the transport the following power mobility tools are considered: cars, buses, trams and bicycles. An important parameter that should be considered when evaluating the impact of transport is fuel. The type of fuel used has an important influence on performance, both as far as the energy and the environmental impacts are concerned. Two options are analysed for cars: petrol and diesel powered cars, since they are the most common choices in Europe. Buses are considered to be diesel-fuelled, while trams are considered to be powered by electricity, according to the European average for this means of transport. No fuel is considered for bicycles. The following aspects are considered for all the different types of mobility: type fuel, vehicle production and maintenance, roads (rails in the tram case) construction and maintenance. As far as the distance is concerned, three scenarios are considered: 2, 5 and 10 km from home to the work location; all the distances are considered twice to cover the journey to and from work.

The three considered distances aim to approximate a typical scenario that can be referred to inhabitants of a standard middle-high European urban area. This study considers some of the options that can be more representative to cover the distances hypothesised and avoiding the use of possible alternatives promising for the future, such as e-bikes or electric cars and middle-long distances like metro or train.

9.3. LCA Inventory

This section describes the assumptions made for the different kinds of food and transport means considered in this study.

9.3.1. Rice

The data on the environmental impacts of rice are taken from an LCA study (Blengini et al., 2009), that evaluates the whole production chain. The work is based on primary data from industries and farmers operating in the Vercelli district (Italy). The contribution of pesticides, fertilizers and transport is included, as well as the contribution of methane due to rice fermentation during the cultivation step, which is estimated to account for 10 to 13% of worldwide anthropogenic emissions (Neue, 1997).

9.3.2. Beef steak

The data on beef steak are taken from the LCA Food Database (Nielsen et al., 2008), referring to information provided by three Danish slaughterhouses in 2001-2002. The main slaughter processes are: transport of cattle to the slaughterhouses by lorries, stunning of the cattle and cutting their throats, blood tapping, removal of the intestines, skin, legs and heads, washing, cutting the meat into pieces, packaging and storing it for distribution on the market. All the production processes are considered automated and modern. Impacts concerning feed production and breeding are also considered. Non-edible by-products such as bone, blood and intestines were sold to bone meal factories and skins are used for leather production. The wastewater generated during the process was treated by a previous screening before it has diverted towards municipal wastewater plants for treatment. The system boundaries are therefore "from cradle to gate".

9.3.3. Poultry

The chicken meat data are based on Danish market information, published by the LCA Food Database (Nielsen et al., 2008). Again in this case, the boundaries of the system are "from cradle to gate". The data refer to eleven Danish slaughterhouses for the years 1997-1999. The main slaughter processes are: transport of the chickens to the slaughterhouses in plastic containers, positioning of the chickens upside down on a conveyor, stunning and cutting their throats, blood tapping, scalding in water at 60 °C, removal of their feathers, intestines, heads and legs, washing, cutting the meat into pieces, packaging and storing it for distribution on the market. The impacts of feed production and breeding are also considered. All the production processes are considered automated and modern. The wastewater generated during the process is treated before it is directed to a municipal wastewater plant for treatment. The feathers, blood, intestines, heads and feet are sold to bone meal factories.

9.3.4. Pork

The data on the pork steak are taken from the LCA Food Database and calculated on the basis of information from Danish slaughterhouses (Nielsen et al., 2008). The data refer to Danish slaughterhouses for the years 1997-1998. The main slaughter processes are: transport of the pigs to the slaughterhouses by lorries, drugging the pigs with carbon dioxide, stunning the drugged pigs in the throat, blood tapping, scalding in water at 60°C, lightly frying with a gas flame, removal of the intestines, cutting the meat into pieces, packaging and storing it for distribution on the market. All the production processes are considered automated and modern. The impacts of feed production and breeding are also considered. Manure is considered to be in part sold to biogas plants and in part returned to farmers as a fertiliser. The scraps are sold to bone meal factories. The system boundaries are therefore "from cradle to gate".

9.3.5. Peas

The data on peas are taken from the LCA Food database (Nielsen et al., 2008), referring to Danish vegetables grown outdoors. Fertilizers and transport are considered. The system boundaries are "from cradle to gate".

9.3.6. Carrots

The data on carrots are taken from the LCA Food database (Nielsen et al., 2008), referring to Danish vegetables grown outdoors. Carrots are covered with a thick layer of straw to protect the crop during the winter: the supply of fresh carrots is therefore guaranteed during most of the winter. Fertilizers and transport are considered. The system boundaries are "from cradle to gate".

9.3.7. Bread

The data concerning bread are provided by the LCA Food Database (Nielsen et al., 2008). The bread is produced by an industrial bakery, considering consumption related to the whole process (electricity, heat, etc.). The flour comes from a mill where the wheat is the input product that has to be processed. The system boundaries are "from cradle to gate".

9.3.8. Tap water

The data concerning tap water are provided by the Ecoinvent Database (Ecoinvent Centre, 2007). The system boundaries are "from cradle to gate".

9.3.9. Passenger car

The data concerning passenger cars are provided by the Ecoivent Database (Ecoinvent Centre, 2007) as the European average of the car fleet for the year 2010. The impacts due to the processes concerning the operation of the vehicles, production, maintenance and disposal of the vehicles, construction and maintenance and disposal of the roads, are included. Two different kinds of car are considered: petrol and diesel fuelled cars.

9.3.10. Bus

The data concerning buses are obtained from the Ecoinvent Database (Ecoinvent Centre, 2007). The impacts from the processes concerning the operation of the vehicles, production, maintenance and disposal of the vehicles, construction and maintenance and disposal of the roads are included and they refer to the Swiss scenario. The buses are considered diesel fuelled.

9.3.11. Tram

The data concerning trams are provided by the Ecoinvent Database (Ecoinvent Centre, 2007) and refer to the Swiss scenario. The impacts for the processes concerning the operation of the vehicles, production, maintenance and disposal of the vehicles, construction and maintenance and disposal of the rails are included.

9.3.12. Bicycle

The data concerning bicycles are estimated on the basis of the following hypothesis: the environmental loads pertaining to their use are zero, while the impacts due to the bicycle manufacturing are negligible, considering the entire life cycle of a bicycle.

9.4. Life Cycle Impact Assessment

The results of the impact assessment on menus and transport are compared. Both energy and environmental impacts are considered: Global Warming Potential (kgCO₂eq), Ozone Layer Depletion (kgCFC₋₁₁eq), Photochemical Oxidation (kgC₂H₄eq), Acidification (kgSO₂eq), Eutrophication (PO₄³⁻eq) and energy consumption (MJeq). The obtained results refer to different impact categories of energy and environmental burdens of dietary versus transport, over a standard work day.

As a general consideration, it is possible to assert that the bicycle appears to be the best transport option, due to the assumptions reported in section 9.3.12. As its

global impact over its entire life cycle is negligible, the following figures do not show the values pertaining to bicycles.

9.4.1. Global Energy Requirement

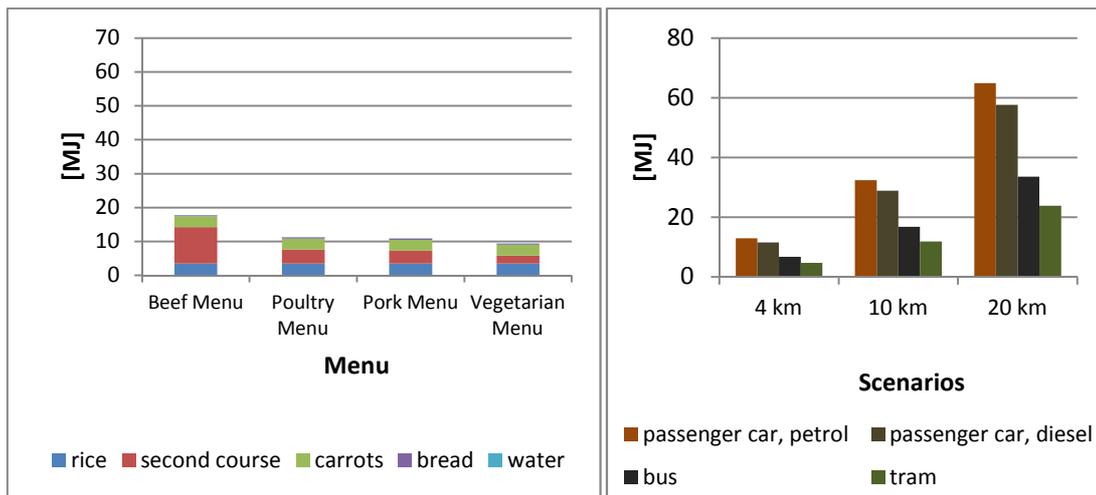


Figure 9.1: Comparison between the total energy to produce industrial food for single menus and for transport

Figure 9.1 reports the energy consumption in MJeq, associated to the different menus and to each type of transport. It should be recalled that the total number of km associated to each type of transport is doubled. On the basis of the considered hypothesis, several comments can be made. First, the choice of a public transport (bus or tram) instead of a private means is always preferable, when available, in terms of energy consumption and it can potentially save approximately 50% or more energy. Further considerations can be made concerning the two categories (public or private transport). Choosing a tram instead of a bus appears to be the best solution as far as a public transport is concerned in terms of environmental load. When the use of a car is necessary, a diesel fuel propelled engine is slightly preferable to a petrol one in terms of consumed energy. As for the menus, the choice of the beef steak is associated to an extremely high energy consumption, while the vegetarian menu, even though it represents the best choice in terms of

energy savings, does not show a considerable difference compared to the other menus (poultry or pork). The energy consumed to provide the considered menus is approximately comparable with that associated with the use of public transport for the second scenario (5 km) or the use of a car for the first scenario (2 km).

9.4.2. Global Warming Potential

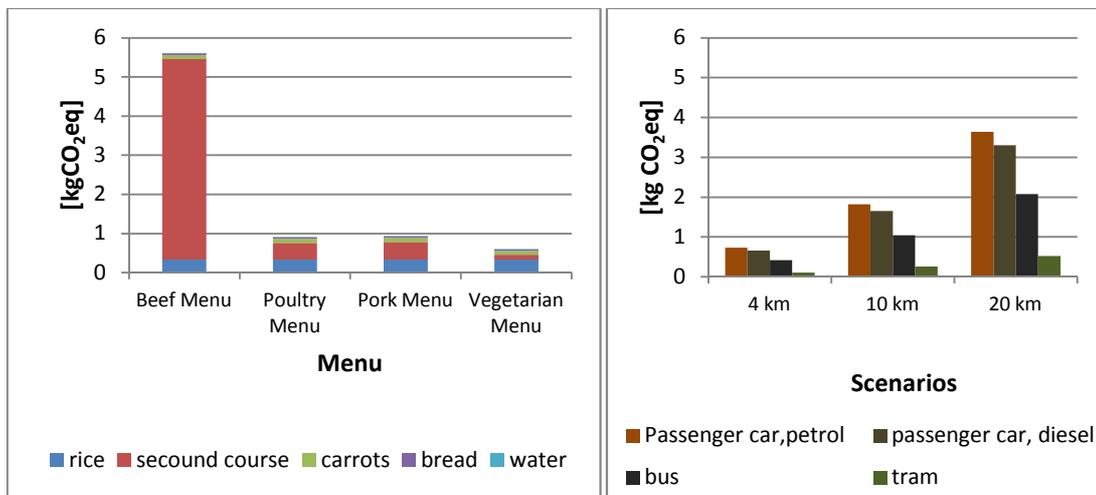


Figure 9.2: Comparison between the GWP of single menus and transport

Figure 9.2 shows the contribution to Global Warming Potential (GWP) of each menu and each transport means. The beef based menu appears to be the main contributor, with a potential emission of 5.6 kg of equivalent CO₂. A single beef steak (120 g) potentially produces a quantity of equivalent CO₂, that is almost twice as high as the one produced by the worst transport scenario (petrol fuelled car driven for 20 km). The beef steak, compared to the other second courses, shows an almost five times higher GWP. The environmental benefits, in terms of GWP, associated with the choice of a vegetarian menu are higher than the meat based menus, as far as energy consumption is concerned. As far as transport is concerned, the results again show a marked environmental benefit for public transport and indicate that trams are the best eco-friendly option.

9.4.3. Ozone layer depletion

An estimation of the ozone layer depletion (ODP) is presented in Figure 9.3. The beef based menu shows an ODP potential that is equivalent to a passenger car in scenario 3. The environmental benefit offered by trams appears higher than in the case of the previous indicators, while the vegetarian option is once again the best one as far as menus are concerned.

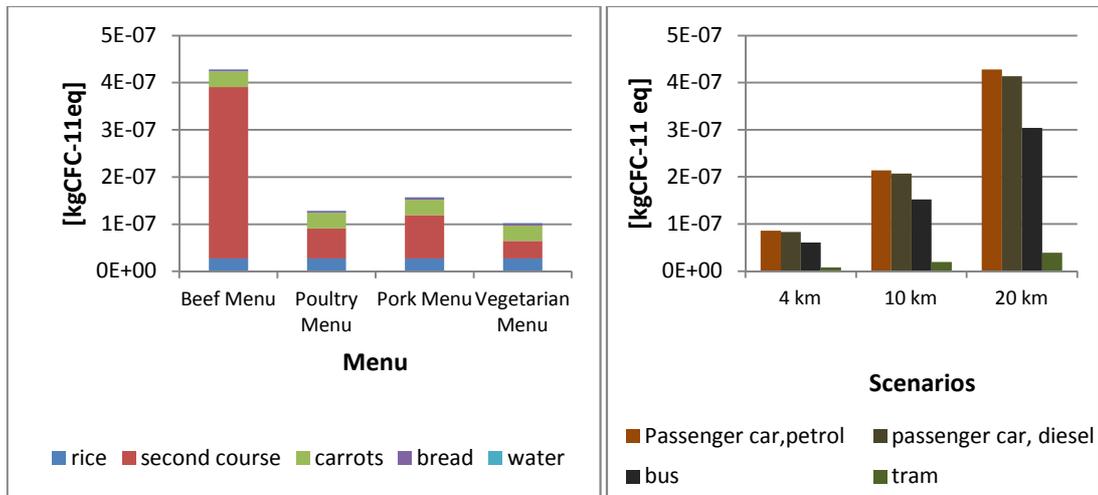


Figure 9.3: Comparison between the ODP of single menus and transport

9.4.4. Photochemical oxidation

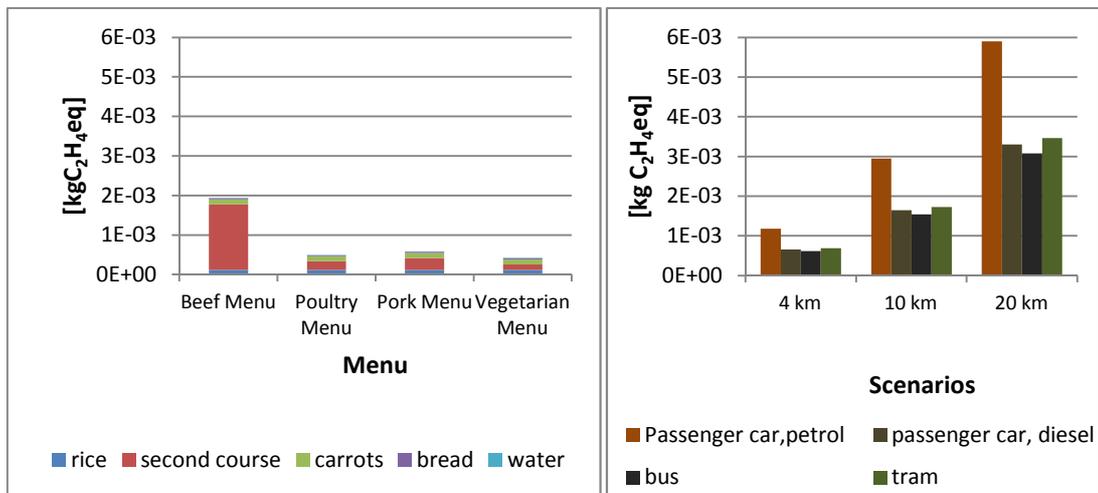


Figure 9.4: Comparison between the POCP of single menus and transport

The Photochemical oxidation potential (POCP) impact is presented in Figure 9.4. In this case, transport shows higher environmental impacts, with a peak for the petrol fuelled car. The POCP of the petrol fuelled car is, in fact, almost twice as high as that of the other options (diesel car, bus or tram) and three times higher than the beef based menu, which is once again the menu with the highest impact.

9.4.5. Acidification Potential

The Acidification Potential (AP) is presented in Figure 9.5. The AP associated with the menus, with the exception of the vegetarian menu, is considerably high. Once again the beef steak is responsible for the highest environmental load, and it shows a specific AP that is four times higher than that of transport. As far as transport is concerned, it is important to underline that, with the exception of trams, which are still decisively the best option, the other alternatives appear to have more or less the same impact as AP. The worst scenario, in this case, is represented by the buses, probably due to the lower quality of diesel used to fuel the buses mentioned in the database.

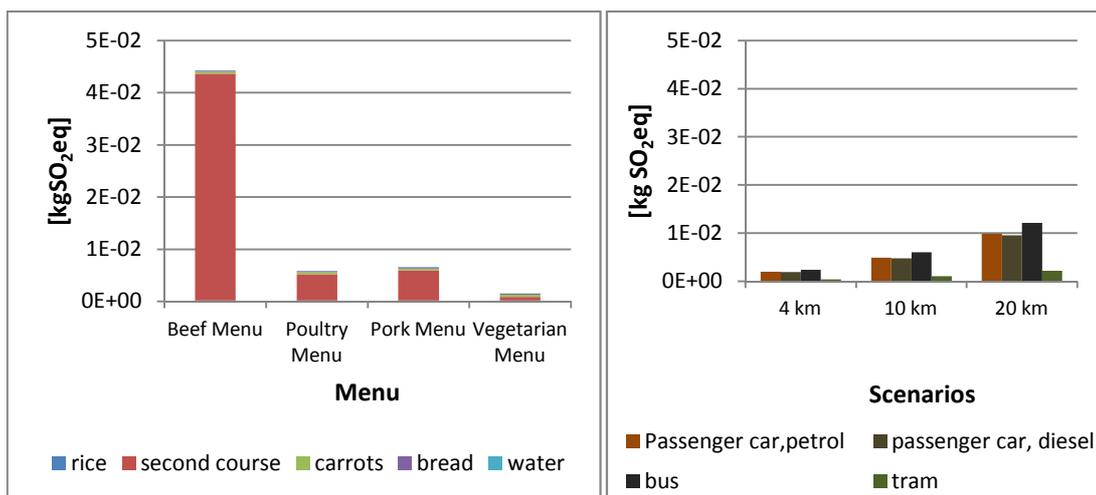


Figure 9.5: Comparison between the AP of single menus and transport

9.4.6. Eutrophication Potential²

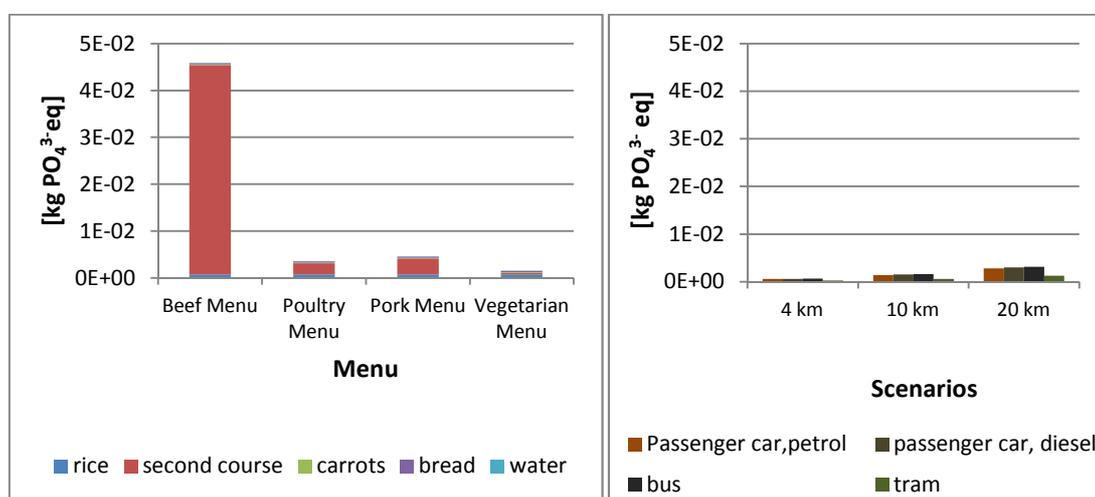


Figure 9.6: Comparison between the EP of single menus and transport

Figure 9.6 shows the eutrophication potential (EP). In this example, the difference between food and transport is remarkably high and the environmental load attributable to transport is considerably lower. The beef based menu again appears the worst option, in terms of environmental consequences, appears around two order of magnitude higher than transport. As in the case of the AP, the EP of the buses is comparable with the car options (petrol and diesel), while the EP of the trams is decisively lower.

9.4.7. Summary of the results

The values of the single impact categories, related to each single food (FU=1kg) and for the considered menus (FU=1 meal) are reported in Tables 9.1 and 9.2, respectively.

Table 9.1: Contribution of each type of food on the environment (FU=1kg)

Food (1 kg)	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
rice	17.8	2.88	1.20 E-07	5.30 E-04	8.97 E-03	7.36 E-03
beef steak	72.1	42.19	2.88 E-06	1.32 E-02	3.60 E-01	3.72 E-01
poltry	17.6	3.04	3.79 E-07	1.20 E-03	4.03 E-02	1.95 E-02
pork	14.4	3.24	6.14 E-07	1.89 E-03	4.63 E-02	2.76 E-02
peas	2.4	0.48	1.59 E-07	5.60 E-04	4.28 E-03	2.16 E-03
carrots	0.5	0.06	3.05 E-08	1.07 E-04	4.69 E-04	2.75 E-04
bread	4.8	0.77	8.72 E-08	3.53 E-04	3.85 E-03	5.59 E-03
water	6.2 E-03	3.2 E-04	1.71 E-11	1.64 E-07	1.21 E-06	8.74 E-07

Table 9.2: Contribution of each menu on the environment (FU= 1 meal)

Menu	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
Beef	17.8	5.60	4.28 E-07	1.93 E-03	4.53 E-02	4.59 E-02
Poultry	11.2	0.91	1.28 E-07	4.91 E-04	6.90 E-03	3.58 E-03
Pork	10.8	0.93	1.56 E-07	5.73 E-04	7.52 E-03	4.55 E-03
Vegetarian	9.4	0.60	1.02 E-07	4.14 E-04	2.58 E-03	1.49 E-03

The values for the considered impact indicators for the transport scenarios are reported in Table 9.3.

Table 9.3: impact indicator values for the transport scenarios

Transport	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)	
Scenario 1: 4 km	passenger car, gasoline	12.97	0.73	8.56 E-08	1.18 E-03	1.97 E-03	5.64 E-04
	passenger car, diesel	11.53	0.66	8.28 E-08	6.60 E-04	1.91 E-03	6.00 E-04
	Bus	6.71	0.42	6.08 E-08	6.16 E-04	2.43 E-03	6.32 E-04
	Tram	4.76	0.10	7.84 E-09	6.92 E-04	4.40 E-04	2.49 E-04
	Bicycle	0.00	0.00	0.00 E+00	0.00 E+00	0.00 E+00	0.00 E+00
Scenario 2: 10 km	passenger car, gasoline	32.43	1.82	2.14 E-07	2.95 E-03	4.93 E-03	1.41 E-03
	passenger car, diesel	28.83	1.65	2.07 E-07	1.65 E-03	4.77 E-03	1.50 E-03
	Bus	16.78	1.04	1.52 E-07	1.54 E-03	6.07 E-03	1.58 E-03
	Tram	11.90	0.26	1.96 E-08	1.73 E-03	1.10 E-03	6.23 E-04
	Bicycle	0.00	0.00	0.00 E+00	0.00 E+00	0.00 E+00	0.00 E+00
Scenario 3: 20 km	passenger car, gasoline	64.84	3.64	4.28 E-07	3.53E-03	9.86 E-03	2.82 E-03
	passenger car, diesel	57.66	3.30	4.14 E-07	1.79E-03	9.54 E-03	3.00 E-03
	Bus	33.56	2.08	3.04 E-07	1.65E-03	1.21 E-02	3.16 E-03
	Tram	23.80	0.52	3.92 E-08	1.63E-03	2.20 E-03	1.25 E-03
	Bicycle	0.00	0.00	0.00 E+00	0.00 E+00	0.00 E+00	0.00 E+00

The results of this study refer to different impact indicators for energetic and environmental burdens, pertaining to food and transport, for a standard work day. This study compares the environmental loads of different menus, with a variety of

protein sources from animals (beef, pork, chicken) and vegetables (peas) as well as different transport options: public (buses and trams) and private (petrol cars, diesel cars and bicycles). The highest source of impact generally comes from the beef based menu, with the exception of the consumed energy and the photochemical oxidation. A larger consumption of proteins from vegetables and the use of bicycles or public transport instead of private cars could significantly mitigate the environmental consequences on the environment. Moreover, the adoption of such a scenario does not show any apparently limitations, such as immaturity of technologies or high investment costs to penetrate the market. Sustainable policies, supported by the contribution of single consumers, could be adopted in order to concretely act in this direction and to pay more attention and respect towards our planet, and for future generations.

The possibility to reduce environmental impacts promoting more eco-friendly life styles, appears in fact as a very potent weapon for fighting against climate change and ecological damages. The main obstacle to adopt different behaviours is principally due to the necessity to break the mixture of conservatism, cultural heritage and indifference rooted in developed societies but, on the other hand, offers the advantage to have an immediate effectiveness and do not present any technological or economical drawback that can slow down their penetration in the market.

The results here presented show clearly how the possibility to prefer the use of public or ecological solutions, like tram or bicycle, as well as a wider diffusion of a vegetarian or at least beef-free dietary, can largely promote the environmental sustainability.

As a final consideration, it is important to remark how this work considers a series of environmental indicators that have been chosen by the international community as some of the most representative and critical for the evaluation of sustainability of anthropogenic life. The debate concerning which indicators should be privileged in order to perform an LCA analysis correctly and exhaustively is still an open question and many issue remain unsolved. However, this work was aimed to offer a

holistic analysis of environmental consequences, in order to encourage individual consumers to reflect on their daily actions. The possibility of promoting these kinds of studies, and integrating additional indicators, such as the loss of rain forests, the use of drinkable water in industrial processes or the use of land, still needs to be considered in order to analyse sustainable development from a global points of view.

9.5. Sustainability Environmental Index (SEI)

The stage of interpretation and implementation of results represents the final additional phase of a LCA study. The possibility to have a subsequent critical analysis of the results, possibly involving subjects with a different know-how, is a milestone for implementing and proficiently using the high number of information coming from the LCA, with the purpose to save energy and raw materials as well as to identify possible risks for the environment and human health.

This section aims to focalize its attention to this stage, and proposes an index to assess the sustainability of the different analyzed solutions for transportation and lunch, assigning to each option a score, and hence a mark as Sustainability Environmental Index (SEI). The possibility to present the environmental load with a simple index can be easy and quick understood by decision makers and single consumers. With an internationally-accepted simplification of the results of the LCA, it would be easier to identify the products which promotes or not sustainability and force institutions and companies to go through the route of sustainable development. Table 9.4 presents the environmental index proposed in Chapter 4: it offers a simple and quick interpretation, and it assesses a scale of sustainability. It has been assumed that an impact achieving 1 or 2 as SEI can be considered as a sustainability promoter, 3 represents the sufficiency while 4 or 5 are considered do not promote sustainability.

Table 9.4: Sustainability Environmental Indexes (SEI) descriptions

SEI	Description
1	Very low impact
2	Low impact
3	Medium impact
4	High impact
5	Very high impact

The following expression has been used in order to assign to each transportation means as well as each menu a global environmental index SEI which takes into account all the environmental stressors:

$$SEI = \frac{1}{n} \sum_{i=1}^n (I_i * w_i) \quad (9.1)$$

where I is the indicator (like GER, GWP and others) expressed in SEI terms as explicated in Table 9.5 , w is the weight factor, n is the total number of i indicators.

Table 9.5: Indicator values expressed in SEI terms

I_i	Description	Percentage
1	Very low impact	0% - 15%
2	Low impact	15% - 40%
3	Medium impact	40% - 60%
4	High impact	60% - 85%
5	Very high impact	85% - 100%

The indicators values expressed in SEI terms have been assigned on the basis of the percentages obtained dividing each impact value by the highest one of the same category.

In the present study w_i is considered equal to 1, this means that all the indicators concur equally to the SEI. Different w_i values could be considered: if more attention

is required for global environmental effects, for example, w_i of Global Warming Potential may be defined greater than w_i of Eutrophication, which has a local effect (see Table 1.2 in Chapter 1). If the focus of the study are the environmental burdens on regional scale, higher w_i values are given to Acidification, Eutrophication and Photochemical Smog rather than to Global Warming, Ozone Depletion and Gross Energy Requirement. However the choice at moment remains subjective.

9.5.1. Dietary

Table 9.6 reports the impact values of the menu evaluated in section 9.4 and moreover reports the evaluation of the % of the impact in order to assign the SEI at each menu. As example, in order to assign a sustainability index to the Global Energy Requirement (GER) impact of a vegetarian menu, it is necessary to divide the GER impact of the vegetarian menu by the GER impact of the beef menu (highest value of the same category): the percentage is 53% and consequently the environmental index is 3; using the same approach it is possible to assign the environmental index at each menu.

Table 9.6: Impact values and impact percentages of the proposed menus

Menu	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
Beef	17.75	5.60	4.28 E-07	1.93 E-03	4.53 E-02	4.58 E-02
Poultry	11.21	0.90	1.28 E-07	4.90 E-04	6.90 E-03	3.57 E-03
Pork	10.83	0.93	1.56 E-07	5.73 E-04	7.62 E-03	4.54 E-03
Vegetarian	9.39	0.59	1.01 E-07	4.14 E-04	2.58 E-03	1.49 E-03
% Beef	100	100	100	100	100	100
% Poultry	63	16	30	25	15	8
% Pork	61	17	37	30	17	10
% Vegetarian	53	11	24	21	6	3

Applying the equation (9.1) it is possible to assign at to menu options a value of the SEI which is able to combine all the environmental indicators. As stated before, in

the present paper a linear combination as been used, but if a higher impact value to some stressor would be considered it is sufficiently to change the w_i for the i -th stressor different than the stressor considered. In Table 9.7 environmental index of the menu option are reported considering $w_i=1$.

Table 9.7: SEI related to the impact indicators of each menu

Menu	SEI Average	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
Beef	5.0	5	5	5	5	5	5
Poultry	2.2	4	2	2	2	2	1
Pork	2.2	4	2	2	2	2	1
Vegetarian	1.5	2	1	2	2	1	1

Table 9.7 presents the sustainability indexes related to the fully-balanced menus of the canteen. It can be asserted how the beef menu can be totally rejected as promoter of sustainability, while the vegetarian menu represent the best available option for the environment with a average SEI mark of 1.5. Between these two options there are instead the alternatives presenting pork or poultry in the menus, with the same mark of 2.2 that can be still considered promoter of sustainability.

9.5.2. Transport

Table 9.8 reports the impact values of the transport means evaluated in section 9.4 and moreover reports the evaluation of the % of the impact in order to assign the SEI at each transport means. The two categories (food and transport) have been deliberately considered separately, in order to evidence the sustainable behaviours that can supply basic necessities. The total impacts of the considered menus and means of transportation are reported next.

Table 9.8: Impact values and impact percentages of the proposed transport options

Transport option	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
passenger car (petrol)	31.42	1.82	2.14 E-07	2.95 E-03	4.93 E-03	1.41 E-03
passenger car (diesel)	11.21	0.90	2.07 E-07	1.65 E-03	4.77 E-03	1.50 E-03
Bus	10.83	0.93	1.52 E-07	1.54 E-03	6.07 E-03	1.58 E-03
Tram	11.90	0.26	1.96 E-08	1.73 E-03	1.10 E-03	6.23 E-04
Bicycle	0	0	0	0	0	0
% passenger car (petrol)	100	100	100	100	81	89
% passenger car (diesel)	92	91	97	56	79	95
% bus	53	57	71	52	100	100
% tram	38	15	9	59	18	39
% bicycle	0	0	0	0	0	0

Applying the equation (9.1) it is possible to assign at to each transportation options a value of the SEI which is able to combine all the environmental indicators. As stated before, in the present paper a linear combination as been used, but if a higher impact value to some stressor would be considered it is sufficiently to change the w_i for the i -th stressor different than the stressor considered. In Table 9.9 environmental index of the transportation option are reported considering $w_i=1$.

Table 9.9: SEI related to the impact indicators of each transport option

Transport option	SEI Average	GER (MJ)	GWP (kgCO ₂ eq)	ODP (kgCFC-11eq)	PO (kgC ₂ H ₄ eq)	AP (kgSO ₂ eq)	EP (PO ₄ ³⁻ eq)
passenger car (petrol)	4.67	5	5	5	5	4	4
passenger car (diesel)	4.33	5	5	5	3	4	4
bus	3.83	3	3	4	3	5	5
tram	2.00	2	1	1	3	2	3
bicycle	1.00	1	1	1	1	1	1

Table 9.9 reports the SEI which could be considered as sustainability marks, related to the transport options considered by this study. As general consideration it is possible to assert that the private fuelled-options (petrol and diesel car) can be rejected as promoter of sustainability while the public transportation options such as bus and tram, represent a more eco-friendly alternative. In particular the tram, in European countries, can represent a preferable option in comparison to the bus in urban areas. Finally the bicycle, due to the negligible impacts of its life-cycle, is the best option and the possibility to promote the use of this solution in the town can be a very effective solution to sustain the environmental sustainability.

9.5.3. Dietary vs. Transport

Lastly in order to score the environmental impact of the combination of transportation means and menu the following linear combination equation was used:

$$SEI = \frac{1}{2} (SEI_{mi} + SEI_{ti}) \quad (9.2)$$

where the subscripts m and t are referred respectively to menu and transport option.

Table 9.10 shows the sustainable behaviours of a hypothetical worker, combining menus and means of transportation during its work day obtained applying the equation (9.2). The choice of the beef at lunch never implies a sustainable behaviour and only when supported by the use of the bicycle achieves the sufficiency. On the other side, a vegetarian worker promotes the sustainability and, in particular when used together with the bicycle, produces a very low impact. Between these two dietary options, there are the menus having on poultry and pork, that when combined with public transport or with the bicycle represents a sustainable option, while when they are associated to a private car do not constitute a virtuous behaviour.

Table 9.10: Sustainability Environmental Indexes of habits in a work day

	beef menu	poultry menu	pork menu	vegetarian menu
passenger car (petrol)	4.83	3.43	3.43	3.08
passenger car (diesel)	4.67	3.27	3.27	2.92
Bus	4.42	3.02	3.02	2.67
Tram	3.50	2.10	2.10	1.75
Bicycle	3.00	1.60	1.60	1.25

This study assesses the environmental sustainability of two basic need of the modern society, evaluating the environmental impact of different dietary and transport options during a work day. The possibility to reduce environmental impacts promoting more eco-friendly life styles, appears in fact as a very potent weapon for fighting against climate change and ecological damages. The main obstacle to adopt different behaviours is principally due to the necessity to break the mixture of conservatism, cultural heritage and indifference rooted in developed societies but, on the other hand, offers the advantage to have an immediate effectiveness and do not present any technological or economical drawback that can slow down their penetration in the market.

If the necessity to access food and transportation is a fundamental right for each citizen of modern society, a mature reflection about how we can supply them in a more responsible and social manner should represent as well a mandatory duty. The results here presented shows clearly how the possibility to prefer the use of public or ecological solutions, like tram or bicycle, as well as a wider diffusion of a vegetarian or at least beef-free dietary, can largely promote the environmental sustainability.

9.6. Conclusion

This chapter proposes an application of the Sustainability Environmental Index (SEI) theoretically described in Chapter 4. It is a simple and quick presentation of the LCA results with specific marks, which can facilitate the interpretation of the sustainability level of daily behaviours or industrial productions to common man. A scale to quantify the environmental burdens resulting from a LCA analysis is proposed, believing how the establishment of internationally-accepted parameters defined by well known and respected institution, such as International environmental agencies, or governments agreement, will facilitate the penetration of the LCA adoption within companies and productive realities as well as increase the idea of sustainable development in the public opinion.

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Conclusion

The purpose of this Thesis is the development of theoretical approaches for sustainability assessments of anthropic processes, and subsequently their application to real cases. In Chapter 1 the Life Cycle Assessment has been introduced and described in its features, as it is the leitmotiv of the entire research developed during my last three years. Adopting the LCA approach allows to compare different technologies, both traditional and innovative ones, evaluating the best performances from an energy and environmental perspective. Starting from a macro vision of a generic process, we come down to each little particular during the step of Inventory Analysis; subsequently the perspective is extended again till embracing all the system in the final step assigning a global judgment. Currently there are many technologies that are presented as sustainable at the theoretical level. However there are actually insufficient tools to verify that technologies are truly sustainable, not only at the theoretical level and considering not only the final stage of the operation, but the entire life cycle. Moreover there are insufficient tools for ranking technologies on the basis of their sustainability. While I was thinking how to select the most efficient technology, the question that I asked to myself was: "Which criteria can be used for selecting the most appropriate technology?". The present Thesis proposes instruments to answer that question: the Analogical Model, EROI (Energy Return On Investment) and EPT (Energy Payback Time), and SEI (Environmental Sustainability Index).

In Chapter 2 the Analogical Model has been presented and described from a theoretically perspective: it is useful for graphically summarize the energy flows of a

generic process, starting from the energy theoretically available till the useful energy. The Analogical Model has been developed adopting a LCA approach: each energy contribution is included, focusing particularly on Indirect Energy Consumed which is often not considered in the literature. Disregarding it is a theoretical and a practical error, because it has a great impact as quantitative value. The term *useful* has been here introduced for indicating the energy delivered into the society, making a distinction with the term *net*, that is the energy produced by the process minus the direct energy necessary to run the process itself. Useful and Net Energy differs each other for the Indirect Energy Consumed flow. Performing a Useful Energy Analysis (UEA) offers several advantages over the standard economic analysis: primarily because it assesses the change in the physical scarcity of energy resources, then because it is a measure of the potential of such a technology to work in a sustainable way, and finally because it is possible to rank alternative energy supply technologies according to their capacity to produce useful energy. All these properties are able to support the decision towards sustainable technologies. Energy Returned On Investment (EROI) and Energy Payback Time (EPT) have been presented in Chapter 3. They were primarily used in economic evaluations and subsequently they were introduced in energy estimations. In this Thesis they have been described on the basis of the Useful Energy for a sustainability assessment. EROI is the ratio between the total amount of Net Energy delivered to society by a technology during its working lifetime and the total amount of Indirect Energy Consumed in such process. It is a ratio between two energy quantities, and it is therefore dimensionless. The higher the EROI value, the higher the sustainability of the technology. If EROI is less than 1, sustainability is certainly not guaranteed as the energy gained from the process is lower than the expended energy. EPT permits to score a technology against the time parameter. It represents the time necessary to the plant to produce the energy necessary to rebuild the plant itself. The higher the EPT value, the lower the annual rate of useful energy, and hence the lower the sustainability of the technology.

Sustainability Environmental Index (SEI) has been described in Chapter 4: it aims to facilitate the interpretation of many indicators summarizing them and offering to the reader a quick and comprehensible response. The possibility to associate a mark, that synthesises the results of the LCA, can represent a simple and understandable tool to the decision makers and single consumers, influencing their decision towards the sustainability. SEI values stay in a range between 1 and 5: a process achieving 1 or 2 as SEI can be considered sustainable, 3 represents the sufficiency while if a process reaches 4 or 5 its sustainability is not guaranteed. The use of weight factors in the formula for SEI evaluation makes it a very flexible tool: sustainability may be evaluated focusing on local burdens, or adopting a global perspective, or giving the same importance to both local and local environmental aspects. It is important that the hypothesis are clearly explicated by analyst before applying the SEI. When sustainability indexes can be internationally accepted and they will be known to the large population not only the expertise of LCA analysis, the possibility to promote or reject a product or a behaviour as sustainable will be easier.

Uncertainty is a fundamental element in a LCA in order to assure a good comprehension about the quality of results and so Chapter 5 has been totally dedicated to this topic. A LCA is constituted by four phases, and each of them presents significant associated uncertainties: their quantification permits to increase the transparency of LCA data and results, however it is often disregarded. In my opinion this lack in uncertainty assessment, though it is clearly recommended by the ISO methodology, it is due to an intrinsic difficulty rather than to a negligence of the analysts. Performing a Monte Carlo analysis requires the knowledge of a range of data for a single input, and practically this occurs quite rarely. Nowadays databanks often offer data with uncertainty information: these data are however secondary data. If we want to perform a LCA with primary data, we are often divided between the desire of using real data and that of evaluating their uncertainty. Which one is the best choice: using data with uncertainty information from databanks or using data measured from the specific process

under study but without uncertainty information? I chose this second option for my studies, integrating results, when it is possible, with a sensitivity analysis.

The first section of the Thesis has been dedicated to the theoretical development of tools for sustainability evaluation of processes. These tools have been applied in the second section in four case studies.

In Chapter 6 an Anaerobic Digestion (AD) process has been explored: the Life Cycle Assessment has been practically applied, as well as the Analogical Model. The Useful Energy Analysis (UEA) has been revealed that the AD process producing hydrogen in one step is not sustainable: Net Energy is always negative. The production of hydrogen and methane in a two-steps process leads to positive values of both Net Energy and Useful Energy. Each energy flow has been evaluated in a dedicated paragraph, even those which together constitute the Indirect Energy Consumed. Moreover the sustainability of the process has been verified using EROI and EPT: sustainability is guaranteed for diameters higher than 1.5 meters. Finally a sensitivity analysis has been performed considering three cases: changing the insulating material (best results for straw instead of polystyrene), using a different substrate (best results for glucose instead of organic waste material) and performing a different pre-treatment (best results for thermal-basic pre-treatment instead of just basic one).

In Chapter 7 a LCA has been performed on nanofilled-polymer-based heat exchangers: the project is part of a main project developed for the European Union, called Thermonano. The goal is the comparison among a traditional heat exchanger and four new prototypes, which differs each other for dimension, power and production process. The new prototypes appear to be a good chance to improve a well know technology, as heat exchangers are, using the newest scientific innovation as nano-structured materials. Each heat exchanger has been deeply studied, evaluating the Global Energy Requirement (GER), the Global Warming (GWP), the Ozone Layer Depletion (ODP), the Photochemical Oxidation (POCP), the Acidification (AP), the Eutrophication (EP), the Carcinogenics and the Non Carcinogenics. Results have indicated that all the prototypes guarantee an upgrade

in environmental sustainability. Among them, the first and the second ones ensure the lowest environmental burdens: they have both a power of 16kW, and they are produced respectively through an injection and a compression moulding processes. These are the best options advanced by the Thermonano project from an energy and environmental perspective.

In Chapter 8 an Artificial Leaf has been investigated: it is an artificial device capable of splitting water to produce hydrogen at ambient temperature. It is nowadays in an infancy stage of development. Sustainability tools have been used in order to direct the project in the more efficient and more sustainable path, enlightening the hot spots of the process and proposing some technological improvements. The LCA has shown that the higher contribution for most the environmental impacts is due to the anode production: the hot spots are the MOF production (it requires a huge amount of energy for heating the reagents for three days in a reactor) and the laser holing of the glass support (it requires a high amount of electricity). The cathode contribution, when it is relevant, is totally due to the use of platinum. A sensitivity analysis has been performed focusing on two indicators: GER and GWP. This choice has been motivated by the fact that using too many parameters makes the comprehension of the results very hard. The sensitivity analysis has been conducted by varying the following parameters: the time required for MOF production has been reduced, the glass support has been replaced with a rock wool of FTO so the laser treatment is not necessary, the efficiency of the device and its life time have been increased and this has increased the quantity of produced hydrogen. Several technological improvements have permitted to define a *best case* showing a technological trajectory toward an efficient sustainable device. These improvements are, in order of relevance: increasing the device lifetime till 10 years, reducing the time required for MOF production to 3 hours, increasing the device efficiency till 10%, producing FTO as a rock wool instead of using a glass support. EROI and EPT have been evaluated for each single proposed improvement and they have shown that sustainability is reached only in the case in which all the hypothesis are applied together.

In Chapter 9 the environmental impacts of individual consumers during a normal work day have been investigated. The necessity to reflect on how society is affecting the environment and the opportunities offered to future generations, are duties that can no longer be more postponed. Two main topics of daily life have been considered: dietary and transport. This study has compared the environmental loads of different menus, with a variety of protein sources from animals (beef, pork, chicken) and vegetables (peas) as well as different transport options: public (buses and trams) and private (petrol cars, diesel cars and bicycles). Results have demonstrated that the highest source of impact generally comes from the beef based menu, with the exception of the consumed energy and the photochemical oxidation. The Sustainability Environmental Index (SEI) has been here practically applied in order to score the different analyzed solutions for transportation and menu. Results have shown that the choice of the beef menu never implies a sustainable behaviour and only when supported by the use of the bicycle achieves the sufficiency. On the other side, a vegetarian worker promotes the sustainability and, in particular when used together with the bicycle, produces a very low impact. Between these two dietary options, there are the menus having on poultry and pork, that when combined with public transport or with the bicycle represent a sustainable option, while when they are associated to a private car do not constitute a virtuous behaviour. The benefits that could be obtained by adopting a different life-style could be very effective, as long as it is adopted by a large critical mass and with appropriate global policies.