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ENVIRONMENTAL ASSESSMENT OF INDUSTRIAL CHEMICAL AND PRIMARY SECTOR PROCESSES FROM A LIFE CYCLE PERSPECTIVE

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Esame finale anno 2021

Candidate presentation

During the three-year PhD program, Mirco Volanti has aimed his research project on the environmental assessment and optimisation of industrial processes through the application of the Life Cycle Assessment (LCA) methodology.

The focus has been on industrial chemical processes, with particular emphasis on the use of renewable resources. During the first year, the attention was put on the environmental assessment of alternative routes from renewable sources for the production of terephthalic acid, the major precursor of polyethylene terephthalate (PET). Two dedicated biomass pathways and one waste biomass pathway were compared with the traditional synthesis pathway from crude oil and the analysis showed that in order to obtain a true environmental benefit it is necessary to use waste. Biomass cultivation involves a high consumption of energy and resources related to the cultivation phase: use of fertilizers, occupation and land use. On the contrary, using waste is neither necessary to use other raw materials nor to spend, in environmental terms, for their disposal. This translates into greater sustainability of the whole process, even if compared to the traditional one. During this project, a collaboration with Budapest University of Technology and Economics began, leading to two publications in scientific journals, one on the terephthalic acid project and another on the use of microalgae to close the CO_2 cycle in energy production.

The second year of the PhD program was characterised by the development of a biogas upgrading project. Born in collaboration with the Catalysis group of the University of Bologna, the aim of this work was to evaluate the impacts of an innovative biogas reforming process for the production of syngas. The process, called Steam/Dry Reforming, was compared with the current syngas production technology (Autothermal reforming) through four scenarios to simulate the use of natural gas or biogas. The LCA results indicated that the new technology can provide savings in CO_2 emissions, which provides an important boost to its development.

Between the second and third year, Mirco Volanti spent six months for a research period at The University of Manchester, under the supervision of Dr. Rosa Cuéllar-Franca. During this period his research work was centred on a project concerning the prediction of the environmental impact of ionic liquids. The idea was to provide a predictive methodology, based on molecular structure, for the environmental impact of ionic liquids, in order to offer a further tool in the R&D stage of new ionic liquids. To do so, the group contribution method has been adopted and the first obtained results have been promising. The proposed methodology seems to be able to give the desired answers, but for a greater reliability and certainty of the results it is necessary to continue its development by expanding the set of ionic liquids.

During the various studies on the processes of industrial chemistry, the candidate has faced several times the environmental problems related to the production of raw materials and from this he has been able to open a line of research also in the field of primary production. In this sector, three further projects were developed, one related to the environmental assessment of some organic practices in vineyard cultivation, one on the use of a new parameter to compare different crop rotations and one on the environmental impact of meals served in school canteens. Although not directly related to the chemical industry, these projects are important from the point of view of interconnection between the different spheres of industrial production and have demonstrated the candidate's good ability to broaden the field of interest and application of the LCA methodology.

During the triennium, Mirco Volanti distinguished himself by contributing to the publication of three articles in peer-reviewed scientific journals:

- Volanti M., Cespi D., Passarini F., Neri E., Cavani F., Mizsey P., Fózer D., *Terephthalic acid from renewable sources: Early-stage sustainability analysis of a bio-PET precursor*, Green Chemistry, 2019, 21, 885–896;
- Fózer D., Volanti M., Passarini F., Varbanov P.S., Klemeš J.J., Mizsey P., *Bioenergy with carbon emissions capture and utilisation towards GHG neutrality: Power-to-Gas storage via hydrothermal gasification*, Applied Energy, 2020, 280, 115923;
- Volanti M., Savarino F. O., Passarini F., Vassura I., Grosso S. A., *Environmental analysis of crop rotations through the application of the Cereal Unit approach*, Ecological Indicators, 2021, 121, 107199.

In this period, he has also co-authored 11 contributions (oral or poster) to national and international congresses, attended the National School in Environmental and Cultural Heritage Chemistry (2018), the Chemometric School: Multivariate Analysis (2019) and the Sinchem Winter School (2020). Overall, the activity developed by the PhD student was of excellent quality.

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Abbreviations

AD	Anaerobic Digestion
AES	At Early Stage
ATR	Autothermal Reforming
BG	Biogas
BTX	Benzene, Toluene and Xylenes
CCU	Carbon Capture and Utilisation
CED	Cumulative Energy Demand
CF	Carbon Footprint
CU	Cereal Unit
DALYs	Disability Adjusted Life Years
DMF	2,5-dimethylfuran
DR	Dry Reforming
EPA	Environmental Protection Agency
FAETP	Freshwater Aquatic Ecotoxicity Potential
FE	Freshwater Eutrophication
FPMF	Fine Particulate Matter Formation
FRS	Fossil Resource Scarcity
FU	Functional Unit
GC	Green Chemistry
GDP	Gross Domestic Product

GE	Green Engineering
GHGs	Green House Gases
GW	Global Warming
GWP	Global Warming Potential
HH	Human Health
HMF	5-hydroxymethylfurfural
HT	Human Toxicity
HTP	Human Toxicity Potential
IL	Ionic Liquid
IPCC	Intergovernmental Panel on Climate Change
ISO	International Standards Organization
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCSA	Life Cycle Sustainability Analysis
LU	Land Use
MDGs	Millennium Development Goals
MAETP	Marine Aquatic Ecotoxicity Potential
ME	Marine Eutrophication
MSW	Municipal Solid Waste
NG	Natural Gas
PET	Polyethylene Terephthalate
Pt	Points
PTA	Purified Terephthalic Acid
PVSA	Pressure Vacuum Swing Adsorption
PX	Para-Xylene
QSAR	Quantitative Structure-Activity Relationships
SDGs	Sustainable Development Goals
SETAC	Society of Environmental Toxicology and Chemistry

S/DR	Steam/Dry Reforming
SR	Steam Reforming
TA	Terrestrial Acidification
TETP	Terrestrial Ecotoxicity Potential
UN	United Nations
UNCED	United Nations Conference on Environment and Development
WC	Water Consumption
WCED	World Commission on Environment and Development
WGS	Water Gas Shift
WHSV	Weight Hourly Space Velocity
YLD	Years Life lives as Disabled
YLL	Years of Life Lost

Abstract

During the PhD program in chemistry, curriculum in environmental chemistry, at the University of Bologna, the environmental sustainability of some industrial processes was studied through the application of the LCA methodology. The efforts were focused on the study of processes under development, in order to assess their environmental impacts to guide their transfer on an industrial scale. Processes that could meet the principles of Green Chemistry have been selected and their environmental benefits have been evaluated through a holistic approach. The use of renewable sources was assessed through the study of terephthalic acid production from biomass and upgrading of biogas to syngas, in both cases the alternative pathways were compared with the traditional synthesis route from fossil resources. The first project has shown that the production of terephthalic acid from biomass becomes environmentally favourable only when waste (and therefore non-impact) biomass is used, otherwise the cultivation processes compromise the benefits. A new technology for biogas upgrading was evaluated and found to have the potential to reduce anthropogenic impact on the environment, due to the CO_2 capture it can provide. Furthermore, with a view to preventing impacts, the basis for the development of a new methodology for the prediction of the environmental impact of ionic liquids has been laid. It has

already shown good qualities in identifying impact trends, but further research on it is needed to obtain a more reliable and usable model. In the context of sustainable development that will not only be sector-specific, the environmental performance of some processes linked to the primary production sector has also been evaluated. The impacts of some organic farming practices in the wine production field were analysed, the use of the Cereal Unit parameter was proposed as a functional unit for the comparison of the environmental performance of different crop rotations, and the carbon footprint of school canteen meals was calculated.

The results of the analyses confirm that sustainability in the industrial production sector (chemical but not only) should be assessed from a life cycle perspective, in order to consider all the flows involved during the different phases. In particular, it is necessary that environmental assessments adopt a cradle-to-gate approach, to avoid shifting (in space and/or time) the environmental burden from one phase to another. Only a deep knowledge of these issues is able to guide political, business and social choices towards the challenge of sustainable development.

1. Introduction

1.1. The concept of sustainability

Today the term *sustainability* is not a new concept, but it already has a long tradition that has its roots in the early 1970s. The first study published in this field dates back to 1972, with the publication of a report entitled "The Limits to Growth"[1], in which, for the first time, the consequences that increasing industrialisation would have on the population and on resource consumption were studied. Driven also by the oil crisis of the following year, a more conscious model of economic growth began to take shape, in which environmental resources began to be seen not as an infinite source but as something to be preserved for the future. This was the prelude to the concept of sustainable development, whose most popular and well-known definition is given in 1987 by the Bruntland Report "Our Common Future" published by the World Commission on Environment and Development (WCED)[2]: "development that satisfies the needs of the present without compromising the ability of the future to meet their own needs". According to the definition, we must consider future impacts when making our decisions about the present. The possibility of ensuring the satisfaction of essential needs implies, therefore, the realization of an economic development that has as its main purpose the respect of the environment[3]. The next step was the gathering at the United Nations Conference on Environment and Development (UNCED) in 1992 in Rio de Janeiro, which resulted in the Agenda 21, "a global partnership able to address the problems of the present and prepare the International Community for the challenges of the upcoming century"[4].

Three fundamental pillars for sustainable development are commonly recognised: environment, economy and society. The first discussions on the subject saw the three dimensions with different weights (Mickey Mouse sustainability models[5]), but the one considered most appropriate for the concept of sustainable development is the one given in 1995 by Clift[6] (Figure 1.1).

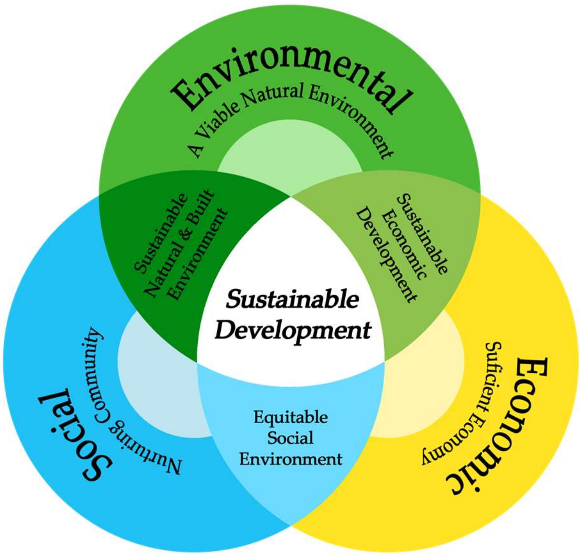

Figure 1.1 – The three pillars of sustainability.

This representation gives equal importance to all three spheres and sustainable development can only be achieved when the desired harmony between environmental, social and economic goals is achieved. These three factors should not be considered as independent of each other, but strictly interrelated by a multiplicity of connections. Sustainable development must therefore be understood as a continuous process in which different aspects are included within each dimension:

- Economic sustainability: meant as the capacity of the system to generate income and work;
- Environmental sustainability: defined as the ability to preserve over time the three functions of the environment: the function of resource supplier, the function of waste receiver and the function of direct source of utility;

- Social sustainability: represents the ability to guarantee conditions of human well-being (safety, health, education, democracy, justice) equally distributed by class and gender.

Therefore, sustainable development requires progress (or at least consideration) of all the involved parts, so as not to favour one at the expense of the others.

Over time, the concept of sustainable development has evolved, but the three pillars have always remained so. What has changed is how to achieve sustainability. A goal-setting approach is adopted to better channel funds and direct policies towards ambitious sustainability targets rather than in general terms. Around the turning of the century a set of 8 targets to be achieved by 2015 are launched. These are the Millennium Development Goals (MDGs), targets mainly related to social issues. The initiative was not as successful as hoped, so in 2012 (at the Rio+20 Summit) United Nations (UN) agreed on a different type of approach that would rebalance the weighting of sustainability concerns. Agenda 2030 was born, and in particular 17 Sustainable Development Goals (SDGs) were defined, illustrated in Figure 1.2.

Figure 1.2 – Sustainable Development Goals of UN.

The SDGs do not entirely summarise the Agenda but are "the pressure points that have the capability to affect the well-being of the entire planet and the people who live on it"[7]. They are the blueprint for a better and more sustainable future for all, address global challenges we face and are all strongly interlinked so as not to leave anyone behind. They aim to:

#1. End poverty in all its forms everywhere
#2. End hunger, achieve food security and improved nutrition and promote sustainable agriculture
#3. Ensure healthy lives and promote well-being for all at all ages;
#4. Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all;
#5. Achieve gender equality and empower all women and girls;
#6. Ensure availability and sustainable management of water and sanitation for all;
#7. Ensure access to affordable, reliable, sustainable and modern energy for all;
#8. Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all;
#9. Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation;
#10. Reduce inequality within and among countries;
#11. Make cities and human settlements inclusive, safe, resilient and sustainable;
#12. Ensure sustainable consumption and production patterns;
#13. Take urgent action to combat climate change and its impacts;
#14. Conserve and sustainably use the oceans, seas and marine resources for sustainable development;

#15. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss;

#16. Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels;

#17. Strengthen the means of implementation and revitalize the Global Partnership for Sustainable Development.

In a nutshell, SDGs aim to renew the image and efficacy of the term sustainability. In recent years, the concept has been flanked - or even overshadowed - by other terms, such as climate change, global warming, resilience and transition. Of course, these assume different meanings and purposes, but they are all part of a single objective, the achievement of sustainable development.

All these topics and the achievements of the last 50 years become particularly important now, in a historical period of severe recession due to the coronavirus pandemic, in which the concept of sustainability risks to lose its appeal in the face of the need to return to previous production levels. But isn't now the right time to change and subvert the production system that so much damage and crisis has created to the balance of our planet? Isn't this a great opportunity to establish a development that is truly sustainable and leaves no one behind?

1.2. Sustainability in the industrial chemical sector

The world of chemistry has always been one of the most pioneering sectors of the entire industry, just think of the economic boom in the second half of the 20th century, largely due to the new materials that the chemical industry has been able to offer. The chemical industry was one of the first to enter the world of sustainability when environmental awareness began to take hold. It has always had to face the fact that it is one of the heaviest industries for the ecosystem.

The chemical and petrochemical sector is by far the largest industrial user of energy, with about 14% of total worldwide demand, and the largest consumer of both oil and gas[8]. It is responsible for 7% of global greenhouse gas (GHG) emissions, third behind iron and steel and cement gas[8]. Demand for primary chemicals (ammonia and methanol) and plastics (mainly derived from high-value chemicals) has grown strongly in recent years, and will continue to do so. Therefore, it is clear that the industrial chemical sector needs a more sustainable approach to reduce the intensity of its emissions.

Among the various approaches to achieve this goal, *green chemistry* (GC) and *green engineering* (GE) are the main examples that have introduced a new production consciousness. They are commonly considered "disciplines aimed at studying chemical reactions and engineering systems with higher efficiency and safety, and able to reduce the intrinsic hazardousness of processes and the amount of waste produced[9].

1.2.1. Green Chemistry and Green Engineering principles

With the Pollution Prevention Act[10] of 1990, the US Environmental Protection Agency (EPA) has shifted the focus towards the prevention of environmental impacts rather than their management. The entire environmental strategy, which up to that point worked to reduce and neutralize pollutants before their release into the environment, is now oriented towards the development of production processes that prevent their formation.

With the aim of offering a standardised platform of guidelines for the application of this strategy to the world of industrial chemistry, in 1991 Paul T. Anastas coined the term *green chemistry*[11] and developed it into 12 principles[12], illustrated in Figure 1.3.

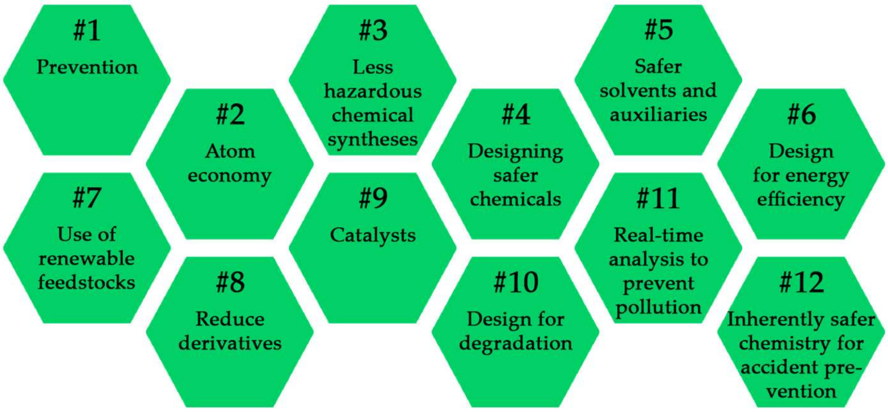

Figure 1.3 – Green Chemistry principles.

Each principle identifies and solves a specific environmental or health issue of chemical production. Particular attention is given to the use of materials and energy, to be optimised both from the point of view of efficiency and origin (preferably from renewable sources), and to the prevention of waste production, considered the ideal form of waste management.

In parallel to the GC, a similar GE concept was developed, in which the green philosophy is applied to engineering solutions that represent one of the foundations of the industry. EPA defines GE as "the design, commercialization, and use of processes and products in a way that reduces pollution, promotes sustainability, and minimizes risk to human health and the environment without sacrificing economic viability and efficiency"[13]. In 2003 Anastas and Zimmerman[14] compiled a list of the twelve principles of GE, illustrated in Figure 1.4.

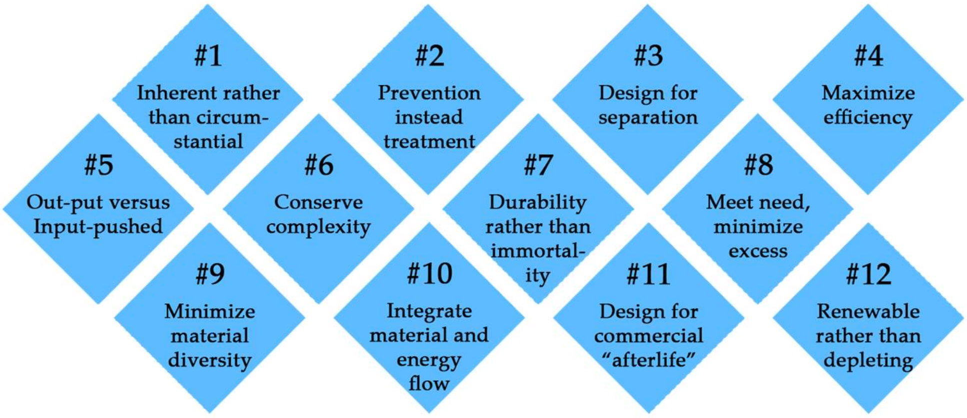

Figure 1.4 – Green Engineering principles.

Both disciplines are closely linked to the concept of sustainable development and in order to obtain truly *green* products and processes it is essential that at every level choices consider the three spheres of environment, society and economy, with the aim of maintaining a balance between them. Therefore, it is necessary that the entire life cycle of the system under study is considered, in order to have a picture as complete and representative of reality as possible.

1.2.2. Tools to evaluate sustainability in the chemical sector

Once the target had been set, it was necessary to build the tools with which to assess the sustainability of chemical processes. One of the key points of the GC is to avoid the production of waste, recognised as a hotspot of the environmental performance of processes. In order to quickly and easily evaluate the environmental load associated with them Sheldon introduced E-factor[15,16], the ratio between the amount of waste and the mass of obtained product:

$$\text{E–factor} = \frac{\text{mass of total waste}}{\text{mass of product}} \qquad \text{eq. 1.1}$$

The E-factor is easy to apply at an industrial level, as a production plant can measure how much raw material goes in and how much product and waste comes out. The closer the value of this parameter is to zero, the greater the environmental benefits. Table 1.1 shows some examples of E-factor application in the chemical industry.

Table 1.1 – E-factors across the chemical industry[17].

Industry segment	Annual production (t)	E-factor	Waste produced (t)
Oil refining	$10^6 – 10^8$	< 0.1	$10^5 – 10^7$
Bulk chemicals	$10^4 – 10^6$	< 1 – 5	$10^4 – 5 \cdot 10^6$
Fine chemicals	$10^2 – 10^4$	5 – 50	$5 \cdot 10^2 – 5 \cdot 10^5$
Pharmaceuticals	$10 – 10^2$	25 – 100	$2.5 \cdot 10^2 – 10^5$

As can be seen, the E-factor values show an inverse proportionality to the complexity of chemical processes. The distillation of crude oil in the petrochemical industry is a process that takes place in a few steps and this is reflected in less waste. The profit margin in this sector demands that waste is minimised and that uses are found for products that would normally be discarded as waste. On the other hand, in the pharmaceutical industry, syntheses require many steps, thus also producing more waste. This sector, focused on the production of quality molecules, has a high profit margin and this makes waste recycling less important. However, it should be noted that although the percentage of waste and the E-factor are high, the pharmaceutical industry produces much less waste than any other sector.

More generally, the E-factor is part of a set of *green metrics*[18] by which the aspects of a chemical process related to GC principles are measured. These parameters are used to measure the efficiency and environmental performance of chemical processes and make the benefits of green processes more tangible and perceptible. The aim is to help understanding and communicating the use of green technologies in industry to facilitate their inclusion. In addition to the E-factor, these metrics include: Atom economy, Percentage yield, Reaction mass efficiency and Effective mass efficiency.

The great advantage of these metrics lies in their simplicity, since they can be calculated from a few available data, while the limit is that they are essentially all based only on the masses of materials. They do not distinguish between more or less harmful waste and are not able to provide any information about the effects of released substances on the environment. A process that produces less waste may seem more sustainable than the alternatives, but it may actually be less green if it produces more damage to the environment.

To overcome these problems it is necessary to include all these aspects in environmental assessments and use a standardised tool. Standardisation makes it possible to have greater appeal and to replicate - according to the same rules - environmental assessments to different sectors, thus promoting their diffusion. In this context, one of the most reliable and suitable tools to address the issue of sustainability in the chemical field is the *Life Cycle Assessment* (LCA) methodology, whose principles and applications will be described in detail below.

1.3. Motivation and structure of the work

Nowadays it is clear that sustainable development and its achievements is the only possible answer to the global ecological crisis we are living through, characterised by social, economic and environmental gaps. With this motivation, SDGs are changing the way our society is facing this crisis, we have set 17 specific goals to achieve over the next ten years and we have understood that we are all, at the same time, witnesses and actors of the change we want. We have learned that problems, whether environmental, social or economic, do not remain limited to individual areas, but affect the whole world and cannot be ignored. The chemical industry and the primary production sector play a key role in our society and are at the heart of many of these objectives (SDG number #2, #7, #9, #11, #13, #14 and #15). It is commonly known that achieving sustainability in these two sectors would be the necessary driver for the necessary change.

On the basis of these considerations and analysis, and starting from a common concern and need for commitment, I decided to focus my PhD program on these environmental issues. My three years of research at the Department of Industrial Chemistry "Toso Montanari" of the University of Bologna, under the supervision of Prof. Fabrizio Passarini, were aimed at the environmental analysis of the life cycle of chemical processes and primary production systems. Through the application of the LCA methodology, different production systems were compared, with the aim of identifying the solution that could guarantee a lower environmental load. Therefore, LCA has been used as an analytical tool for environmental investigation, able to provide results to support decision-making in the development of greener processes. The holistic approach that the methodology offers makes it possible to assess the sustainability of processes along the entire production chain and to identify any strengths and weaknesses.

This approach was been applied to case studies of the industrial chemical industry, in which processes using fossil fuels and alternatives from renewable sources have been compared. During the analysis of the projects, issues related to the production of raw materials emerged, which reflect the challenges of primary sector production. This gave me the opportunity to open a new line of research, focused on the evaluation of primary production systems. Just as the SDGs are strongly interconnected, the two research themes I investigated are also complementary for a proper sustainable development.

In this thesis all the projects I developed during the PhD program are collected, organised as follows to provide a complete overview of the work done:

- Chapter 1: introduction to the concept of sustainability with a particular focus on the industrial chemicals sector;
- Chapter 2: in-depth description of the Life Cycle Assessment methodology;
- Chapter 3: application of the LCA methodology to the chemical industrial sector;
- Chapter 4: study of sustainability in the primary production sectors;
- Chapter 5: main conclusions of the studies.

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2. Methodology

2.1. Introduction to LCA methodology

As stated, environmental awareness began to make its way into our society in the second half of the last century. Although the concept of sustainable development was born as a direct response to the problem of the depletion of fossil resources, more time took for the birth of *Life Cycle Thinking*. The idea of considering the problem (either environmental or economic) in its complexity was completely innovative and broke the usual rules. Until then, in fact, the practice was to consider the processes individually, without evaluating the context in which they were inserted. In this way it was not possible to understand if the proposed improvements were really effective or only apparent when placed in a global vision. For instance, from an environmental point of view, a single industrial operation can become more efficient simply by transferring the resulting pollution into space and time.

The first example with which this approach entered the discussion of industrial production is in an internal report of the RAND Corporation of 1959[1], in which the concept of the life-cycle cost of weapons was mentioned. Therefore, it was born as a tool for the evaluation of budget management and to see its introduction on environmental issues it is necessary to wait ten years. In 1969 a study conducted for the Coca Cola Company[2] is the first case of an LCA as we understand it today. Its aim was to identify the best material for beverage containers (glass, plastic, alluminium or steel) to use both from the point of view of environmental consequences and the end-of-life (returnable or disposable) use strategy. The quality of the study was such that the company decided to replace glass bottles with plastic ones and then steel cans with alluminium ones.

Unfortunately, this and other similar evaluations did not give the necessary boost to the methodology because they remained unpublished until the early 1980s.

The driving force behind the development of the LCA has been the efforts of SETAC (Society of Environmental Toxicology and Chemistry) and ISO (International Organization for Standardization) to establish the basis for a universal structuring of the methodology. The 1990s[2] were the period in which LCA standardisation was perfected, while the new millennium saw the elaboration phase. In this way Life Cycle Thinking has become the key to addressing environmental sustainability issues and has been incorporated into decision-making strategies as a fundamental support tool. As a result, several opportunities for the application of the LCA have arisen, whose versatility and adaptability has allowed it to be used in different fields. The S-LCA (Social-LCA) and the LCC (Life Cycle Costing) are examples of this, whose aims are to analyse the positive and negative social impacts of a product[3] and to assess the costs of a product[4] from a life cycle perspective.

The LCA methodology is in continuous evolution and in 2006 a project commissioned by the EU[5] defined what will be the guidelines for the future. The methodology will be called LCSA (Life Cycle Sustainability Analysis) and will integrate those related to three pillars of sustainable development, namely LCA, S-LCA and LCC. By definition it is "the evaluation of all environmental, social and economic negative impacts and benefits in decision-making processes towards more sustainable products throughout their life cycle"[6] and can be summarised as follows:

$$\text{LCSA} = \text{LCA} + \text{S–LCA} + \text{LCC} \qquad \text{eq. 2.1}$$

This does not mean that it is a sum of the individual results, but that they are read in combination with those of the other methodologies. In particular, the focus will be shifted from products to processes, with the inclusion of physical, economic and behavioural relations in addition to technological ones.

2.2. Structure of the LCA

One of the strengths of the LCA methodology, as mentioned, is the standardisation that makes it applicable to different sectors, allowing the entire production system to be rethought from a sustainability perspective. Since 1996, ISO has published a series of standards that have defined its scheme and application, summarised in what is known as "the 14040 series"[7-10]. They include:

- ISO 1040:2006: principles and framework;
- ISO 1044:2018: requirements and guidelines;
- ISO 14047:2012: illustrative examples on how to apply ISO 14044 to impact assessment situations;
- ISO 14049:2012: illustrative examples on how to apply ISO 14044 to goal and scope definition and inventory analysis.

According to ISO 14040, the LCA methodology consists of four phases: (*1*) goal and scope definition, (*2*) inventory analysis, (*3*) impact assessment and (*4*) interpretation. As can be seen from Figure 2.1, representation of the general framework of an LCA, the phases are all interconnected and in particular the interpretation is placed transversely to the others since it must be looked at all levels of the study. The detailed description of each step will be given in the following paragraphs.

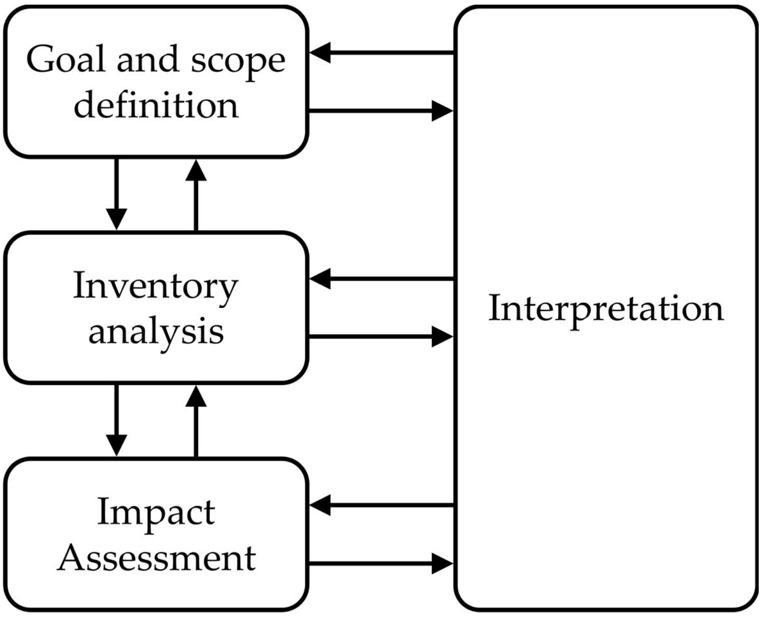

Figure 2.1 – Framework of the LCA.

2.2.1. Goal and scope definition

The first phase of the LCA study is probably the most crucial of the whole methodology because the choices made during this step will influence the whole analysis. The goals and scope of the study must be defined "clearly and must be consistent with the intended application"[7]. In order to do so, it is necessary to specify the reason why the entire life cycle of a product will be evaluated and the audience for which the study is intended (green marketing, research and development, eco-design, etc.). The definition of these parameters starts from the definition of *system boundaries* and *Functional Unit* (FU).

The system boundaries (which can be geographical, technological, temporal, etc.) define what is part of the study and what is excluded and serve to better identify the object of the analysis. Commonly there are two expressions that indicate the extension of system boundaries: cradle-to-grave or cradle-to-gate. In the first case the study considers all the life cycle of a product or process, from the extraction of raw materials to the use phase and up to the end of life, while the second expression sets the system boundaries to the industrial gate, i.e. to the obtaining of the good or process. However, further system boundaries can be identified depending on the type of study and its scope.

The FU is the reference with which impacts are calculated and different scenarios are compared, it "quantifies an identified function of the system under study, and provides the reference to which system inputs and outputs are related"[7]. Key characteristic of the FU is that it must represent the function of the system or product, which is not necessarily a physical characteristic such as mass or volume.

This phase, like all the others, should not be considered as fixed and not modifiable, but rather should be adjusted and revised according to the interpretation of the results of the other steps, to ensure that the LCA is always updated and improved. This is the deeper meaning of the double arrows in Figure 2.1.

2.2.2. Life Cycle Inventory

The second stage of the methodology is dedicated to data collection and the construction of the system models. It is called Life Cycle Inventory (LCI) and is the most time-consuming and energy-intensive step of the whole methodology because all the mass and energy balances of the processes have to be researched and reconstructed. In this phase the data (input/output flows of resources, energy, products, co-products, waste, emissions, etc.) are not interpreted, but the model that best represents the system studied is drafted and defined.

Therefore, it is clear that the quality of the data collected and used is at the basis of the building of realistic and reliable models. They are the bricks with which the models are made, so the more accurate they are, the more realistically the simulation will represent reality. There are two categories of data:

- Primary data: information obtained from direct measurements and data provided by the plant under study. They are the most reliable and accurate data as they are collected on site;
- Secondary data: these are the data extrapolated from the literature or from databases and are usually of lower quality than the primary data. The only case in which this type of data is preferable is for sectoral considerations (e.g. emissions produced by a truck used for transport).

Obviously, it is advisable, if available, to use primary information to obtain a high-quality study.

During the model building it is often useful to divide the structure into two macro-parts: foreground system and background system. They, represented in Figure 2.2, have the task of identifying the processes directly involved in the production of the FU (foreground) and those for the production of materials and energy that are upstream (background). Generally, primary data are used for the foreground system, while for the background system secondary data, generalised for industrial processes, are used.

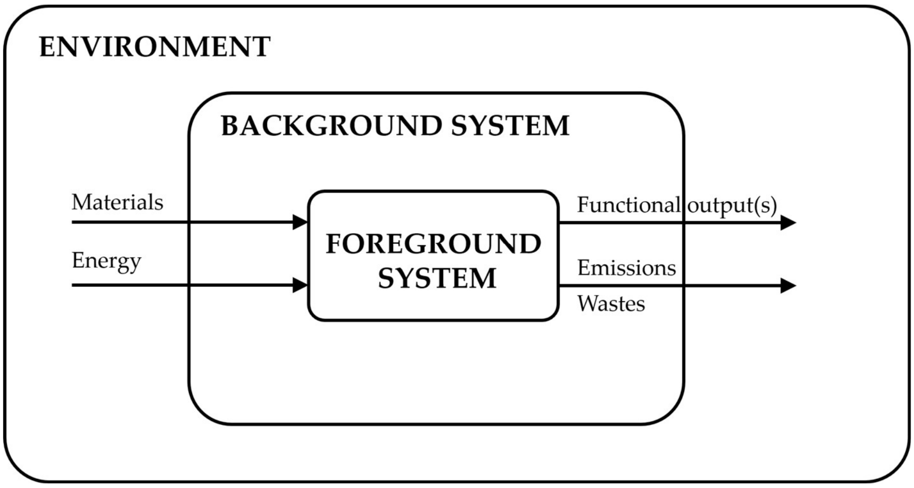

Figure 2.2 – Foreground and background systems[11].

In practice, few industrial processes produce a single output element, often the main product is in fact accompanied by other co-products and by-products. In these cases the ISO 14044 standard suggests to widen the system boundaries, but if this is not possible it is necessary to assign to each input/output its own environmental load. This operation takes the name of allocation and is carried out through a proportional and weighted distribution of responsibilities for energy and resource consumption among the various flows. Usually the parameters that are chosen to carry out this distribution of weights are of a physical type (mass, volume and energy), but sometimes it may be more appropriate to identify other relations, such as the economic value of the products.

Also the LCI is an iterative phase, as the data are collected and the system is better known, new data requirements or limitations can be identified. Sometimes problems may arise, requiring revision of the objective or scope of the study.

2.2.3. Impact assessment

The information collected in the LCI phase forms the basis for the environmental assessments to which the third phase is dedicated, often called Life Cycle Impact Assessment (LCIA). This is the phase in which there is the transition from objective data of the balances to the estimation of their environmental impacts, due to emissions and resource consumption. Impact is defined, according to ISO 14040, as any change caused by a given environmental aspect, i.e. any element that can interact with the environment[7].

In order to achieve the most standardised assessments possible, four steps have been identified to translate inputs and outputs into impacts:

- Classification: is the organization of inventory data into impact categories. The same emission can be assigned to several categories and the same substance can contribute to several distinct impact events. Two approaches can be followed at this stage: refer to the impacts caused by the substances (*midpoint oriented*) or consider the damage they have caused (*endpoint oriented*). For example, in the case of CO_2 emissions, the direct increase in its concentration in the atmosphere is part of the midpoint approaches, while the resulting damage to human health is an endpoint evaluation. The choice of categories to be used is closely related to the purpose of the study and the chosen method of analysis;
- Characterisation: is the step in which the contribution of the flows is quantitatively determined. The impact is calculated by multiplying the characterization factor of the substances, different for each category, with the quantity of the flow. In this way impact indicators are obtained that can be used for both midpoint and endpoint approaches;
- Normalisation: results are normalised to find out how much each category affects the overall environmental load. In practice this operation is carried out by dividing the value of the indicators by normalisation factors. As a consequence, it is possible to identify the order of importance of environmental problems and decide which impact categories need action or which should be excluded from subsequent assessments;
- Weighing: is the operation by which a specific weight is assigned to each category, in order to be able to add up all the contributions and obtain an aggregate score for the whole system. Social, political and economic considerations come into play to establish the weight to be assigned to each category.

Normalisation and weighing are optional steps as they are an additional manipulation of the LCI data, while the others are mandatory to obtain environmental impact results.

The LCIA process is conducted using different methods of analysis, depending on the objective of the study. Those used for the projects included in this thesis are:

- ReCiPe: is an impact assessment method developed in 2008 by the collaboration between RIVM (Rijksinstituut voor Volksgezonheid en Milieu), CML (Centrum Voor Milieukunde), and the Radboud Universiteit Nijmegen on behalf of the Dutch Ministry of Infrastructure and the Environment[12]. It integrates the midpoint approach of the CML method[13] with the endpoint approach of Eco-indicator99[14], so both impacts and damages can be assessed. In the latest update of the method (ReCiPe 2016[15]) there are eighteen midpoint impact categories and three endpoint damage categories, listed in Figure 2.3 together with the environmental mechanisms that link the levels.

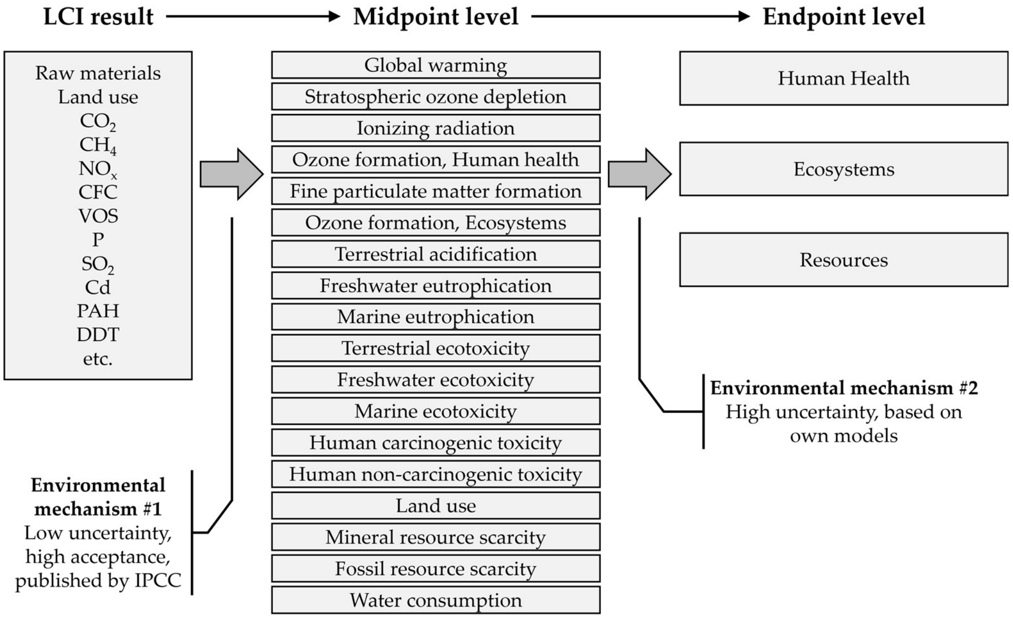

Figure 2.3 – Links between LCI parameters, midpoint and endpoint categories of the ReCiPe method[15].

As shown in the figure, the transition from midpoint to endpoint results is the most delicate. The ReCiPe method has three different damage categories (Human health, Ecosystems and Resources), each with its own unit of measurement. The Human health category uses the Disability-Adjusted Life Years (DALYs), i.e. the sum of the years of life lost due to the disease (YLL) and the years life lives as disabled (YLD, obtained from the product between a severity factor and duration):

$$\mathrm{DALY} = \mathrm{YLL} + \mathrm{YLD} \qquad \text{eq. 2.2}$$

The quality of the ecosystem is based on the diversity of species that populate it, so the damage that impacts cause to it is assessed by the number of disappeared species per year (species·yr). This is done using the Potential Disappear Fraction (PDF) of species multiplied by their density in all x compartments (terrestrial, marine water and freshwater):

$$\mathrm{CF} = \sum\nolimits_{\mathrm{x}} \mathrm{PDF}_{\mathrm{x}} \cdot \mathrm{SD}_{\mathrm{x}} \qquad \text{eq. 2.3}$$

Finally, the Marginal Cost Increase (MCI) is used for resources, which is the increase in the cost of a resource (ΔCost) due to its extraction (ΔYeld), it is calculated in US$:

$$\mathrm{MCI} = \frac{\Delta\, Cost_r}{\Delta\, Yeld_r} \qquad \text{eq. 2.4}$$

- CED: acronym for Cumulative Energy Demand, is a characterization method used to assess energy demand[16]. In particular, it evaluates the direct and indirect need for energy due to the use of materials and resources, expressing the results in energy terms (e.g. MJ). It is a method that easily identifies the most energy-intensive phases of the processes, but cannot be used as the only environmental assessment parameter because it does not consider the impacts of operations such as extraction, emissions, etc.

The CED uses a midpoint approach and considers the energy requirements of six categories of resources, divided between renewable (biomass, wind-solar-geothermal and water) and non-renewable (fossil, nuclear and biomass).The latest version (CED v. 1.11) is dated 2018;

- IPCC: is a single issue analysis method that evaluates the Global Warming Potential (GWP) associated with GHGs (such as CO, NO_x, CH_4, N_2O, hydrofluorocarbons, chlorofluorocarbons, etc.). Released by the Intergovernmental Panel on Climate Change (IPCC) in 2001, it is a parameter that evaluates the impact of the gases by expressing the results in kg of CO_2 equivalent. To do so, it considers the contribution to the greenhouse effect of substances compared to that of CO_2, which by definition has a value of 1[16]. The updated version of the method is IPCC 2013 (v. 1.0)[17].

Once the LCIA phase is completed, an environmental profile of the system under examination is obtained, useful to understand where to intervene to minimise impacts or to compare different production processes.

2.2.4. Interpretation

The interpretation should not be considered as the last phase of the LCA methodology because, as shown in Figure 2.1, it is transversal to the others. Changes and suggestions must be applied to all steps of the study, from design to calculation, in order to improve the total environmental impact. Therefore, it is essential that this phase is iterative and evaluates the entire system, the results must be interpreted at the end of each level. This characteristic is at the heart of the LCA methodology, whose objective is continuous improvement.

The interpretation of the life cycle must present the results in an easily understandable, complete and consistent way, in accordance with the definition of the chosen goal and scope ISO[7]. The conclusions must consider the limitations and assumptions made and identify those changes that would maximise the environmental efficiency of the system under review, whatever it may be. Contribution analyses are an excellent tool in this sense, because they make it possible to identify which processes contribute most to the final result.

In order to validate and test the results of the analysis, ISO 14040 suggests to perform an uncertainty analysis by applying statistical methods for the evaluation of uncertainties[18], such as the Monte Carlo method. All data are inherently characterised by an uncertainty range, so it is necessary to keep this in mind when presenting the results. The Monte Carlo statistical method allows us to do this by repeating environmental simulations for a statistically high number of times (usually 10000), each time by varying the data within its own range of certainty randomly[2]. The extent of these ranges depends on the quality of the data and is calculated using the peer-reviewed procedure developed by Weidema and Wesnæs[19]. From each simulation, different results are obtained (because the input data changes) which, once put together, determine the distribution of uncertainties.

A further test that can be done to verify the robustness of the models created during the LCI is the sensitivity analysis. It consists of changing some assumptions and/or hypotheses and recalculating the results to better understand their weight.

2.3. Software and database

The works presented in this thesis have been realized using the SimaPro software (v. 9.1), developed by PRé Consultants and one of the most widespread in the world[20]. It, in accordance with the requirements of the ISO standards, allows the creation of models thanks to the included databases and the evaluation of impacts with different methods of analysis. Furthermore, it is possible to perform uncertainty analyses using the Monte Carlo method, as well as to evaluate the contributions of the various processes through tree or network visualisations. Its structure allows studies to be carried out both on products, with the possibility of distinguishing between the various phases of the life cycle, and on processes, which can be divided into categories such as materials, energy, transport, waste treatment, etc.

The most complete database of LCA studies is Ecoinvent[21]. Available since 2003 thanks to the collaboration between several Swiss institutions, it has a large number of predefined processes covering all production sectors (energy, materials, chemicals, agriculture) and not only (transport, pollutant treatment). Its latest version, v. 3.6 released in 2019, is used as a reference database for the building of the models here presented.

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3. Life Cycle Assessment in the chemical sector

3.1. Background

Although the application of the LCA methodology is historically linked to the study of products, in recent decades it has also become widespread in field of industrial process, in particular among plastics and automotive manufacturers[1]. Generally, for studies on products, an approach from cradle-to-gate is used, while when the focus is on the process it is preferable to use the from cradle-to-gate option. This is because considering the end of life of the processes is a quite complicated operation that risks to add too many uncertainties to the results of environmental analyses. This versatility of the methodology, as well as its flexibility in application to different fields, has promoted its diffusion and today the LCA is considered an essential tool for environmental assessments at industrial level[2].

Therefore, there are many examples of application of this methodology to the world of the chemical industry, which, as seen in the first chapter, is one of the most critical sectors from an environmental point of view. Being a very wide production sector, it is not rare to find LCA applications in all its branches, from traditional production systems[3-6] to alternative processes from renewable sources[7-9], from oil refining[10,11] to pharmaceutical chemistry[12]. Obviously the function of LCAs as a decision support tool is particularly suitable for the objectives of GC and in this field it has always found great space[13-15]. In fact, the use of renewable resources is not enough to identify a process as *green*, since the environmental issue must be studied in its completeness[16].

This chapter will present in detail the research projects, carried out during the PhD program, that address this topic. In particular, three works have been published or are being evaluated by international environmental chemical journals: *i*) terephthalic acid from renewable sources (published in Green Chemistry journal), *ii*) impact assessment of a new reforming reaction of clean biogas (under review in ACS Energy & Fuels journal) and *iii*) environmental characterization of ionic liquids (in collaboration with The University of Manchester and in preparation for submission to Green Chemistry journal).

3.2. Terephthalic acid from renewable sources

The discipline of GC is currently the driving force for innovations in industries involved in the field of chemistry, such as refinery, building blocks, speciality chemicals, pharmaceuticals, nanomaterials and energy (e.g., green fuels or H_2 storage). In particular, when we talk about bio-based industry, the focus is on the 7th principle that suggests the use of renewable feedstock rather than depleting feedstock. The bio-based chemical industry is rapidly growing, reaching considerable values in the past few decades. A report commissioned by the USDA BioPreferred® Program[17] in 2016 showed that this sector has contributed to the growth of both GDP (gross domestic product) and employment producing 393 billion US$ and 4.22 million jobs, respectively, according to the 2014 data. A similar trend was identified in Europe, where a total of €3.7 billion was invested in bio-based innovations over the period 2014–2020: €975 million of EU funds[18] and €2.7 billion of private investments[19]. In addition, recent projections concerning the production trends for bio-based polymers have predicted an increase up to 17 million tons at the end of 2020: +233% compared to the 2013 value[20].

An interesting example is represented by polyethylene terephthalate (PET), a leading commodity worldwide with an annual volume of 50–60 Mt[21]. PET is mainly used to produce plastic bottles for water and soda with an impressive market: it has been estimated that 488 billion PET bottles were produced worldwide in 2016[22]. Therefore, the use of biomass to produce PET could have sensible benefits on both community (creating new jobs by the revamping plants) and environment. A recent estimation reported in the literature[23] has revealed that "if just 20% of the carbon content in the 37.5 million metric tons of PET used in making bottles worldwide were to be replaced by bio-carbon, this would absorb 17.2 million metric tons of CO_2 from the environment. That would be equivalent to about 40 million barrels of oil savings".

PET is produced by the polymerization of two monomers: purified terephthalic acid (PTA) and mono-ethylene glycol. The reaction is a polycondensation of the monomers with water as the by-product. Thus, in order to obtain 100% bio- PET both precursors should be obtained from renewable sources. Nowadays, only the mono-ethylene glycol fraction is already available on a large scale from biomass[24-28] (i.e., 30% total bio-content); the remaining 70% (approximately PTA) is still produced from fossil sources. The reason is that para-xylene (PX), the main precursor of PTA, is traditionally obtained in large quantities cheaply from the catalytic reforming of crude oil (BTX – benzene, toluene and xylenes). PX global production is estimated to be around 35 million tons per year[29], and its conversion into PTA is performed by a partial oxidation process, developed by Amoco®, using air as an oxidizing agent[30]. Nowadays, the Amoco® process represents the leading technology to produce PTA with a global production of 57 million tons (2014 data) and an annual increase of 6%[31]. The main reasons are: *i*) the large raw material availability and *ii*) the high process efficiency (98% conversion and 95% selectivity)[30]. Several intermediates are formed during the reaction. Among these, the 4-carboxybenzaldehyde (4-CBA) concentration should be reduced below 25 ppm in order to obtain a high grade of purity and prevent chain interruption during PTA polymerization to PET[30].

However, due to the high environmental costs of PX separation (high GHGs emission) and the importance given by GC to the use of renewable resources, several alternatives to produce PTA from biomass have gained significant attention, both at the pilot and laboratory scales.

In this work, three alternative pathways to produce bio-PTA were selected. Each route considers various feedstocks, such as isobutanol, 5-hydroxymethylfurfural (HMF) plus ethylene and limonene. In the first two routes, PX is converted into PTA using the Amoco® process, while the third alternative, currently developed at the laboratory scale, converts limonene into PTA. The conventional synthesis pathway from crude oil, used as a benchmark, has been added to the comparison. Figure 3.1 presents all the routes considered.

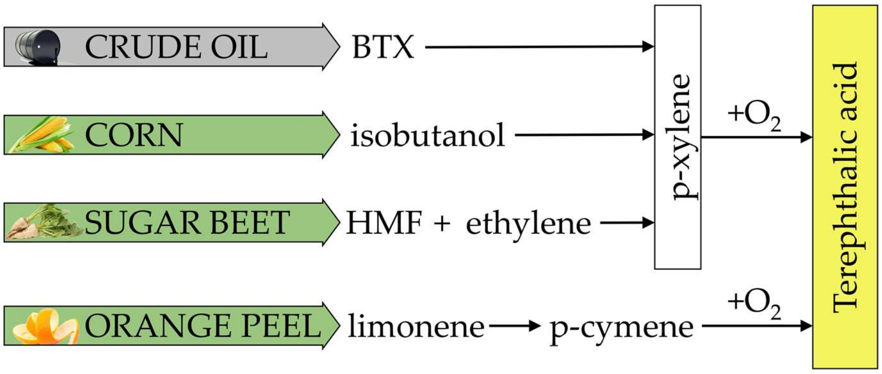


Figure 3.1 – Schematic representation of the different routes of PTA production. Reproduced from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

Aim of this research work is to perform an assessment of the environmental sustainability of different bio-routes to PTA in order to disclose the benefits and drawbacks of each of them and suggest a valuable alternative to the fossil pathway.

From now on, the three synthesis routes from renewable sources, i.e. from maize, sugar beet and orange peel, are renamed Scenario A, Scenario B and Scenario C respectively, while the traditional one is called Scenario D. The three bio-routes involve different chemical reactions and intermediates, all of which are illustrated in Figure 3.2.

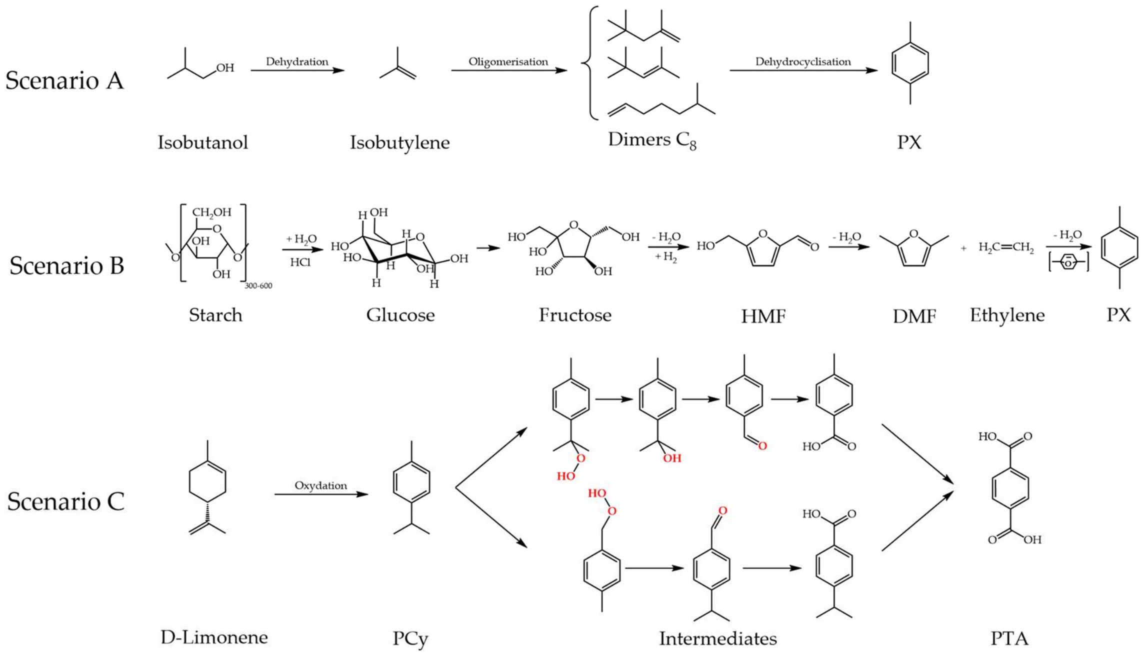


Figure 3.2 – Reaction scheme of the three bio-synthesis pathways of PTA.

A description of these three routes is reported below.

- Scenario A. This process, developed by Gevo Inc., is already operational at an industrial scale in the biorefinery of Silsbee (Texas, USA). The plant treats about 20–35 thousand liters of isobutanol per month, converting it into isooctene and PX. Built in 2011 to produce renewable fuel for the US Army, the production of PX started in 2013[33]. According to the patent[34], the process consists of three phases (Figure 3.2). Firstly, the inlet isobutanol is sent to a dehydration reactor to be converted into isobutylene with yields higher than 95%, in the presence of the BASF-AL3996 catalyst. The isobutylene is then fed to the oligomerisation reactor, where the molecules are "coupled" forming C_{12} trimers (undesired) and C_8 dimers as 2,4,4-trimethylpentene and 2,5-dimethylene, respectively. The output mixture is then sent to a distiller to separate the two species of oligomers. The remaining C_8 compounds are sent to the dehydrocyclisation reactor. Here, in the presence of a chromium oxide catalyst (BASF D-1145E), the cyclization into PX is carried out with 75% selectivity and an overall yield of 18.7 wt%. Fuel gas is also produced as a by-product;

- Scenario B. Another interesting solution to produce PX is the Diels–Alder reaction between HMF and ethylene[35], both derived from biomass. According to the literature[36], HMF can be synthesized starting from the lignocellulosic fraction of biomass, and the core of the entire process is a biphasic reactor in which starch is converted into HMF using water and THF (for the organic phase). Currently, it is developed only at the lab-scale[37], but Ava Biochem BSL AG has demonstrated that it can be upgraded on a pilot plant[38]. As shown in Figure 3.2 this transformation involves three steps: *i*) the saccharification of starch into glucose in the presence of HCl, *ii*) the isomerization of glucose into fructose through the use of Sn-Beta zeolite, and finally *iii*) the dehydration of fructose into HMF[37]. To achieve the production of PX, this process is thus integrated with the conversion of HMF into 2,5-dimethylfuran (DMF) and its further reaction with ethylene[35]. The stream of HMF is evaporated and sent to a fluidized bed reactor with hydrogen, where HMF is converted into DMF using a copper–ruthenium–carbon (Cu–Ru/C) catalyst[36]. The last step is the Diels–Alder reaction between DMF and ethylene that gives an oxygenated intermediate of the product, which can be easily dehydrated and forms PX. Then, several distillations are required to purify the product. The overall yield is 36 wt% with respect to glucose and 99.5 wt% of pure PX is then obtained[39];
- Scenario C. In recent work, an innovative pathway to produce PTA directly from para-cymene (PCY) has been proposed[40,41]. In this case, the

reaction implies the oxidation of PCY, a natural aromatic compound that can be synthesized from terpenes, eucalyptol or limonene with low technological costs[42-44]. Given that all of these precursors are easily extracted from biomass, PCY can be considered as an economical and reliable renewable resource of PTA. The literature[44] describes the possibility of extracting limonene from orange peels and using it as an intermediate to obtain PCY by dehydrogenation. The process begins with the milling of the orange peels followed by the separation of limonene from residual solids (such as pectin, which is a valuable by-product of the process) and its concentration in a decanter. The steam is then processed at 165 °C using a mesoporous silica-alumina support, obtaining a total conversion of limonene to PCY with 100% selectivity. Starting from PCY, it is then possible to produce bio-PTA using O_2 (oxidant) in the presence of a heterogeneous Mn–Fe oxide catalyst[40]. The reaction was conducted without a solvent to minimize waste generation and increase process sustainability (GC principles). The mechanism (confirmed by kinetic studies[40]) occurs through a series of multiple, parallel and consecutive reactions in which both the methyl and isopropyl groups are oxidized (Figure 3.2). PTA is the end product of these consecutive oxidations. The best results are achieved by following these operating conditions: 140 °C, 20 bar of O_2 and 24 h reaction time. In this case, a quantitative PCY conversion is achieved, obtaining 38% selectivity of PTA.

3.2.1. Methodology

Although some LCA studies on PTA are reported in the literature[3,45], to our knowledge none of them have focused on the assessment of the three bio-based pathways identified in this work. In particular, in this manuscript, an innovative route from orange peel is also considered, which has never been studied through LCA. Given that this research assesses some processes that are not fully developed at the industrial scale, the analysis approach can be considered as an early stage (AES) evaluation. This way of analysis consists of a preliminary assessment of the potential impacts of a process or a product before it is transferred to an industrial scale. The application of this approach in the chemical sector was the object of recent peer-reviewed studies[46-50] and in the last few years there has been a sensible increase in publications using it[51]. Although a system analysed on a laboratory scale might generate different impacts on an industrial scale, the need to provide decision makers with AES evaluations to accelerate innovation paths cannot be separated from an overall assessment of the associated impacts and benefits.

All scenarios were modelled and compared on the basis of the production of 1 ton of PTA (FU of the work). System boundaries of the study include all the stages involved in the production, from raw material extraction up to the synthesis of PTA. Transportation, use phase and disposal phase are voluntarily excluded (since they are assumed to be identical for each pathway). This kind of approach is defined as a cradle-to-gate analysis and is presented in detail in Figure 3.3.

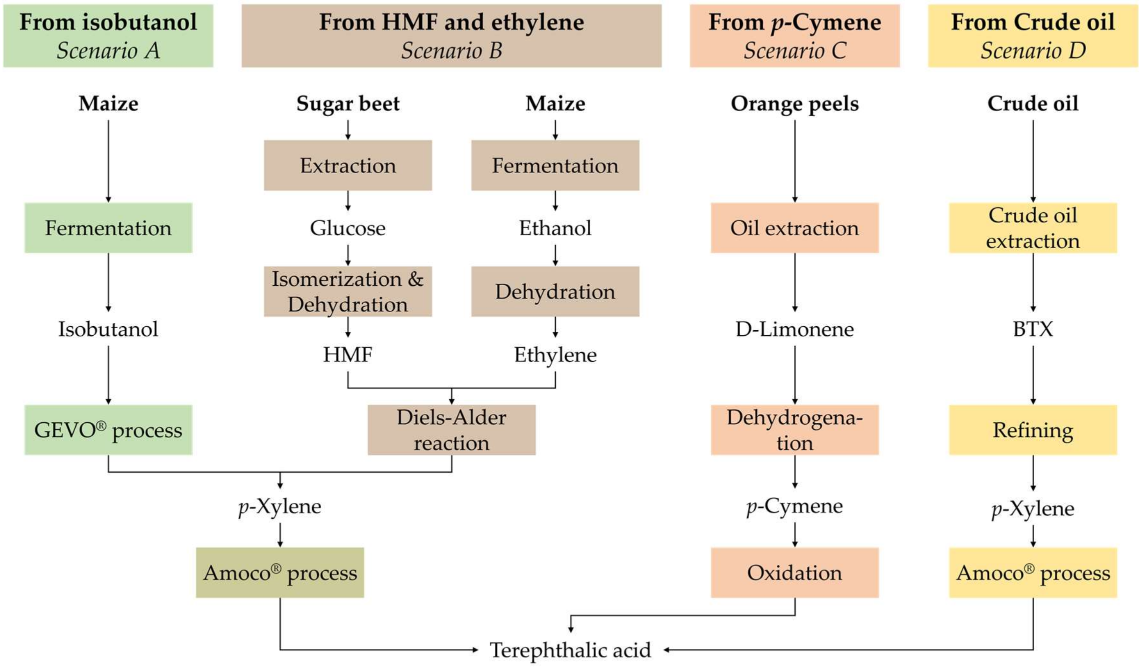


Figure 3.3 – System boundaries of the LCA study for all analysed scenarios. Adapted from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

Mass balances were performed for each route, by filling some data gap using the international peer-review literature. Among those considered, not all the processes are fully developed at the industrial scale. Therefore, to make the LCA models more reliable, it was necessary to estimate the energy consumptions of such routes. The simulation was carried out using ChemCad (v.6.4), which makes it possible to evaluate through software simulation all the requirements in terms of mass, energy and auxiliaries. This allows the comparison between existing technologies, alternative solutions and new processes under development (one of the main objectives of the AES evaluations). A full description of the LCI for each route is reported in the Annex A (Tables A1–A4). Given that all the by-products and unconverted reagents are exclusively organic molecules (mostly aromatics), we have assumed that they could have a considerable market value. Therefore, a mass allocation was performed for each route.

As shown in Figure 3.3, there are three types of biomasses used to obtain bio-PTA and the model must include all the background stages involved in their cultivation: the use of water, fertilizers and other chemical additives, the occupation of arable land and its impoverishment, the use of agricultural machinery during the sowing and harvesting procedures, etc. The assumptions made for the simulation of the models are:

- *"Sweet corn {GLO}| market for sweet corn | Cut-off, U"*[52] was chosen as the reference process for the corn. As reported in the literature, isobutanol can be produced through glucose fermentation by using modified yeasts[53,54]. In order to simulate this process, the fermentation of glucose to ethanol was used as a basis for the estimation of the mass and energy flows. The same choice was carried out by Akanuma et al.[45], by considering an approximate yield of 25 wt%;
- The impacts related to the cultivation phases of sugar beets and the sugar extraction processes for the production of HMF were simulated with the process in the Ecoinvent 3 database *"Sugar, from sugar beet {RoW}| beet sugar production | Cut-off, U"*[52]. On the other hand, no default processes are included for the simulation of the bio-ethylene chain. We filled this data gap by creating the bio-pathway starting from the dehydration of ethanol to ethylene. The data reported by Chen et al.[55] were used to complete balances by selecting database process for ethanol production from maize to include the impacts of the cultivation phase. The Diels–Alder reaction between HMF and ethylene was constructed following the data published by Lin et al.[39];
- Scenario A and Scenario B lead to the formation of PX (Figure 3.3) and to its oxidation into PTA. This last stage is called the Amoco® process and it has been chosen since it is the most consolidated worldwide. Energy and mass balances were completed using data from a detailed study conducted by researchers from Pennsylvania University, in which a feed mixture

containing PX, acetic acid (solvent), catalyst system and oxygen is used to achieve more than 95 mol% PTA[56];

- According to the national statistics, in Italy, 1.6 million tons of oranges were processed in 2017[57], about 50–60% of which was turned into waste, mainly peels[58]. This means that only in Italy there is a potentiality of around 600 000 tons of orange peels per year. These peels are derived from industrial activities and, thus, they represent industrial waste. Currently, the only fate that can give economic value to orange peels is animal food, but in any case, it is quantified <0.8% compared to fresh fruit[59]. This implies that an economic allocation would not give significant results. Considering, however, that the objective is to intercept the peels that are not currently valued, the only relevant alternative scenario is composting. Therefore, our model excludes all the duty requirements concerning their production but includes their avoided disposal by simulating the whole process through the data already published in the literature[60]. The processing of orange peels starts with extraction of limonene, and to achieve PCY production, it is dehydrogenated in the presence of a mesoporous silica–alumina support. The balances of this process are based on a techno-economic analysis provided by Dàvila et al[44]. The final oxidation of PCY into PTA was modelled according to the data reported in the literature[40]. Mass balances were completed taking the best experimental results, while the energy requirements are not reported since this pathway is still at the lab-scale. Therefore, the data gap was filled using ChemCad, which allows the estimation of the electric power and the heating/cooling needs to operate the plant;
- The process "*Purified terephthalic acid {RER}| production | Cut-off, U*"[52] was assumed as a reliable model for PTA traditional production from fossil

fuels. Due to its importance in the chemical industry, this process is well known, and no modification was necessary.

3.2.2. Results and discussion

The potential impacts of the scenarios have been evaluated using CED[61] and ReCiPe[62]. The combination of these two methods allows us to consider a wider range of impact and to obtain an exhaustive estimation of the environmental burdens[51].

As previously stated, CED does not consider the potential negative effect on ecosystems, but it gives an indication of the intensity of the resources. Therefore, it was adopted to estimate the resource consumption distribution among the four routes considered. Table 3.1 shows the main results in terms of fossil and biomass resources.

Table 3.1 – Assessment of resource consumption (in GJ eq.) for each scenario. Reproduced from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

Process	Total	Fossil	Biomass
Scenario A	122.83	77.43	45.40
Scenario B	94.63	66.54	28.09
Scenario C	23.13	22.38	0.75
Scenario D	53.18	52.58	0.60

Results highlight that the greatest consumption is still non-renewable: the contribution of fossils still has the lion's share of credit by achieving high contribution in all the processes. In the case of crude oil synthesis (scenario D), around 98% of the overall consumption is still petroleum based, due to its use as a raw material. On the other hand, in the case of bio-based processes, the fossil requirements are mainly due to the primary energy utilization in the production of heat, electricity and vehicles (transportation and harvesting procedures). Table

3.1 shows that Scenario A has the greatest need for resources (materials and energy) by reaching a cumulative value of 123 GJ eq. Nonetheless, the evaluation of the renewability grade[63] (Figure 3.4) reveals that the isobutanol route reaches a higher value (37%) compared to the other bio-based pathways, i.e. the use of fossil fuels is offset by more than 1/3 of the renewable resources.

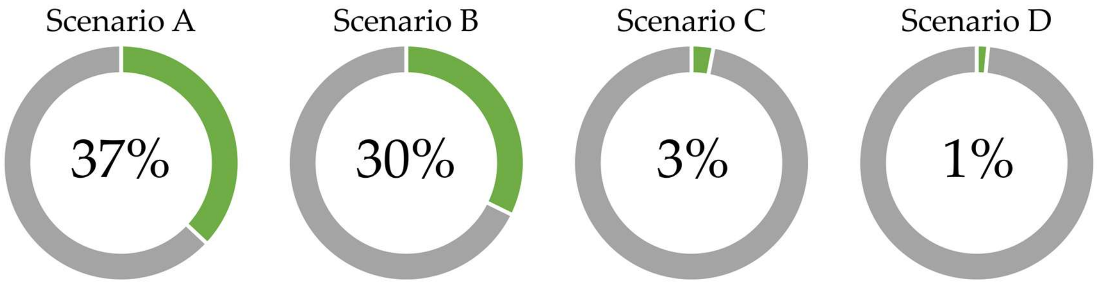


Figure 3.4 – Renewability grade calculated as a percentage of renewable resources (in green) on the total (in grey) of each route (CED method). Adapted from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

In the case of scenario B, the results in terms of the renewability grade are comparable to those of scenario A, although slightly lower (despite the fact that the total amount of resources consumed is less than isobutanol). On the other hand, scenario C has a renewability grade around 3%. This score seems not competitive at first sight. However, the possibility of using food waste (orange peels) as starting raw materials rather than dedicated renewable sources (e.g. corn) minimizes all the extensive costs due to cultivation and harvesting procedures, resulting in a consumption of the whole resources around 1/15 when compared with the results from isobutanol.

In order to estimate the results from LCI into potential burdens, the ReCiPe analysis method was adopted at both midpoint and endpoint levels. The results at the midpoint level are presented in Table 3.2.

Table 3.2 – Comparison between PTA production scenarios in terms of ReCiPe 2016 Midpoint H/A – Characterization analysis. Adapted from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

Impact category	Unit	Scenario A	Scenario B	Scenario C	Scenario D
Global Warming	kg CO_2 eq./ton	5841.8	5011.4	47.1	1915.9
Fine Particulate Matter Formation	kg $PM_{2.5}$ eq./ton	9.4	5.9	1.7	2.0
Human Toxicity	kg 1,4-DCB/ton	2530.9	1265.4	-4561.3	1045.4
Water Consumption	m^3/ton	438.1	193.2	211.2	26.9
Terrestrial Acidification	kg SO_2 eq./ton	43.4	22.1	5.1	5.4
Land Use	$m^2 \cdot a$/ton	1964.3	1040.0	32.0	28.0
Fossil Resource Scarcity	kg oil eq./ton	1694.9	1455.0	489.6	1149.6

Scenario A presents the highest value for all considered categories; only Scenario B shows comparable impacts. Analysing the Human Toxicity (HT) category, Scenario C presents a negative value and, therefore, it produces some benefits to the environment due to the avoided disposal of the organic fraction (used here as the starting raw material) through composting. The Land Use (LU) category presents the highest values for Scenarios A and B: both require dedicated crops. The same trend was detected for Water Consumption (WC) and Terrestrial Acidification (TA) categories. Scenario D (the benchmark process for PTA production) presents relevant values in the category of Fossil Resource Scarcity (FRS) since it uses crude oil as the starting material.

In order to better understand the reasons for these trends, a detailed contribution analysis (shown in Table A5 in Annex A) was carried out with the aim to point out the most onerous phases of each process:

- In the case of Scenario A, isobutanol production represents the stage with greatest impacts. It covers from 56% up to 100% of the total burden for each category. This means that the production of isobutanol from maize grain involves a high use of energy (in particular steam) and utilities for cultivation (fertilisers, drying and irrigation). The remaining is due to the energy requirements of GEVO® and Amoco® processes;

- Scenario B presents a more variable distribution of burdens. The production of reactants from biomass is the major contributor (> 50%) to the impact directly related to crop cultivation, such as Fine Particulate Matter Formation (FPMF), WC, TA and LU. In contrast, in the Global Warming (GW), HT and FRS categories their contribution comprises between 20-30% because the steam consumption and the hydrogen requirements of the subsequent reactions are most impacting. As highlighted earlier, the Amoco® process produces relevant repercussions in terms of kg CO_2 eq. and kg oil eq;
- Since no flows were considered for the production of raw materials (orange peels), the impact of Scenario C lies only on the processing stages. The utilities of the oxidation step to PTA are lower than those of the PCy production and generate a smaller impact on all considered categories, with the exception of GW and HT. In the case of GW, the benefit due to the avoided composting of orange peels is covered by the impact generated during oxidation. The balance is slightly positive and, as shown in Table 3.2, leads to the assignment of 47 kg of CO_2 to scenario C, a value much lower than other scenarios. For the category HT, the avoided impact prevails and the entire production process shows an advantage for human receptors;
- In Scenario D PX production and its oxidation to PTA equally share the impact categories on which they engrave. The first process stage has greater responsibilities on GW, WC and FRS categories; the PTA production on FPMF, HT and LU. In this case, the main contributors come

from the PX production chain and, for the oxidation stage, from the required utilities (heating energy and electricity).

A transversal analysis of the contributions shows that heat requirement and production of industrial steam play a key role in the GW and FRS categories due to the natural gas burned for their production. For the FPMF category crops supply chains and electricity generation are the main responsibilities. The production and usage of chemicals (both fertilisers in crops and reaction auxiliaries) have a strong influence on HT category, while WC, TA and LU categories are strictly dependent on crops, which account for more than 65% of these impacts.

In order to understand which scenario has the lower/higher cumulative burden, midpoint results were translated into potential damage, normalised and weighed to obtain a Single Score. This procedure is possible by the use of specific factors to convert impact category units into points (Pt). The results are presented in Figure 3.5 and listed in Table A6 in Annex A.

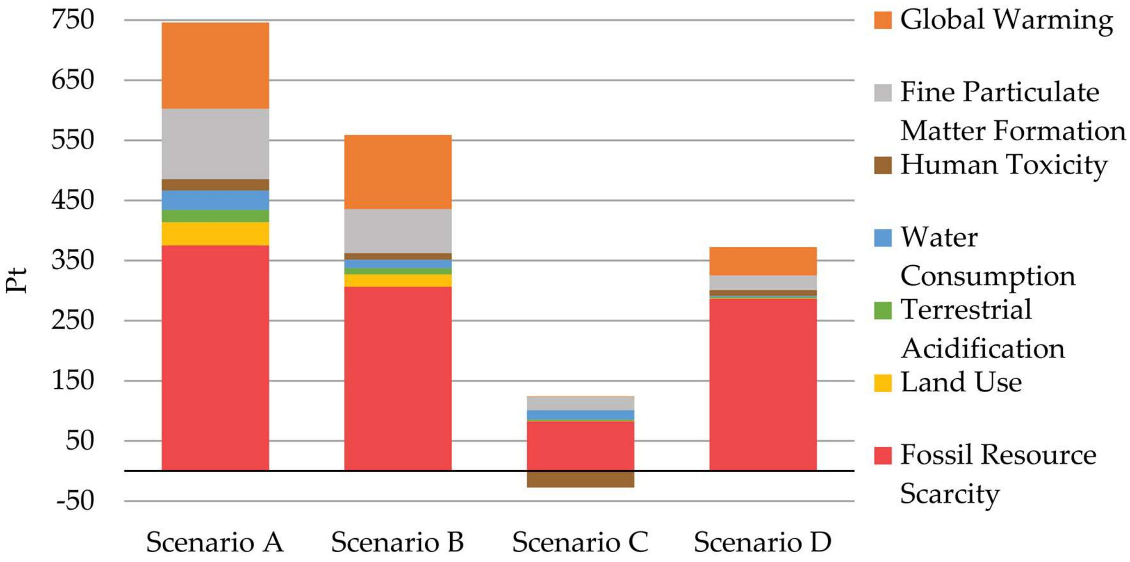


Figure 3.5 – Comparison between PTA production scenarios in terms of ReCiPe H/A – Single Score. Adapted from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

The route from isobutanol seems the most impactful among those considered (achieving 746 Pt), around 33% more compared to the second one (Scenario B, 559 Pt). These results confirm those of the CED method. On the other hand, the traditional pathway from crude oil (372 Pt) and the innovative route from p-cymene (97 Pt) seem more competitive. Given that Scenario A has been assessed as the one with the worst results for the environment, it is important to investigate which is the highest contribution phase. Figure 3.6 shows a Sankey-based chart which depicts network visualization. The red lines indicate negative effects (in terms of emissions and consumption), while the green ones indicate potential benefits due to avoided impacts. The greater the thickness, the higher the contribution to the final score.

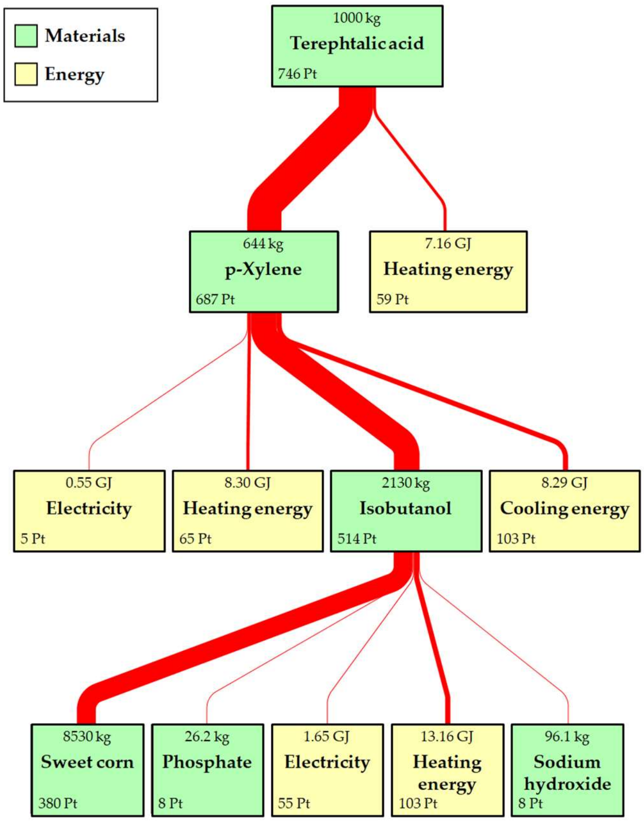


Figure 3.6 – Contribution analysis for Scenario A (ReCiPe H/A – Single Score). Reproduced from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

The production of isobutanol seems to be mainly responsible for the whole score, accounting for 69% of the cumulative score as a consequence of the great impact associated with the cultivation of sweet corn (380 Pt) and the heating energy used for its processing (103 Pt). As depicted, the sum of all the energy flows (electricity and heating and cooling energies) impacts the transformation of isobutanol into PX by only 25% (173 Pt); in contrast, the material is the major contributor (514 Pt, 75%). The Amoco® process contributes only 8% (59 Pt) to the cumulative score. This low incidence can be explained by the fact that this step occurs with a reagent conversion >98%, a selectivity >95% mol, and process characteristics higher than those of the previous steps.

The Single Scores of Scenarios B and Scenario C are the closest to those of the traditional route (Scenario D). In the case of Scenario B, it differs from the fossil-based route by only 33%. This outcome demonstrates that it could be possible to obtain PTA from renewable sources in a competitive way compared to the current technology. The network contribution analysis of Scenario B (Figure A1a in Annex A) shows that the impact of the route is principally due to the need for steam for the Diels–Alder reaction (297 Pt, 53% of the total), while the cultivation of raw materials only affects the whole score by 20% (110 Pt). Comparing these data with those of Scenario A, it emerges that different process efficiencies in terms of biomass conversion into chemicals (0.117 for Scenario A and 0.199 for Scenario B) may lead to significant changes in terms of the cumulative impact.

Scenario C is the only one with a cumulative score lower than the traditional fossil-based route (Figure 3.5). The importance of avoiding the composting of orange peels already emerged and from its network analysis (Figure A1b in Annex A) it can be quantified in the saving of 33.1 kg of diesel and 3.52 GJ of electrical energy. The contribution to the final score of the oxidation of PCy is similar to that achieved in the case of PX (Amoco® process), respectively, 53 Pt and 59 Pt. This provides further motivation to continue the development of this pathway by investing R&D resources to complete the scale-up.

The results of the analysis reveal that the routes that involve dedicated crops (Scenarios A and B) could actually produce a greater impact than the fossil one. In contrast, the use of waste biomass (as in the case of Scenario C) could produce some benefits. Therefore, in order to study and discuss this aspect, a further simulation was carried out by assuming that 50% of the starting biomass used for Scenarios A and B comes from waste. The results, calculated as Single Scores and compared with those previously obtained, are shown in Figure 3.7.

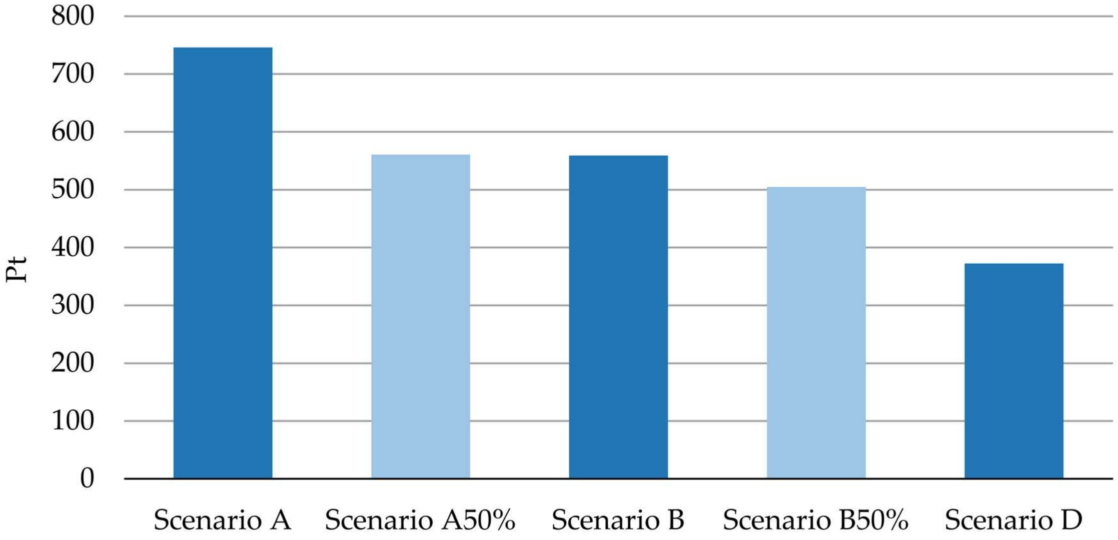


Figure 3.7 – Comparison of standard Scenarios A and B with those with 50% waste biomass (ReCiPe H/A – Single Score). Reproduced from Volanti et al. 2019[32] by permission of The Royal Society of Chemistry.

As shown, the environmental savings are higher in the case of Scenario A, which achieves a reduction around −25%, whereas Scenario B would have a decrease of −10%. Significant differences are achievable in terms of WC (from −39% up to −45%), TA (from −28% up to −45%) and LU (≈ −49%) categories. This is a further confirmation that these categories are highly dependent on crops. Therefore, even if it is difficult to use waste biomass, this solution could represent a good practice to achieve greener products. The amount of organic waste that still ends up in landfills today is too high and represents a significant loss of resources. In Italy, for example, it is estimated that about 5.5 million tonnes of organic waste per year are not recovered, but only stabilised before being disposed of in landfills[64]. Intercepting, enhancing and giving new life to these wastes is one of the focal points of our work. Orange Fiber S.r.l. could be cited as a virtuous example of this policy and demonstrates that valuable raw materials can be obtained from citrus waste. From them, a high-quality and completely new material for the fashion industry is produced[65].

Finally, it is important to note that Scenario C is only developed on a laboratory scale right now. This aspect, as already highlighted in literature[66,67], presumably overestimates the use of materials and energies because at industrial level all flows and processes are optimized in a more efficient way. This strategy avoids the underestimation of environmental impacts, which could otherwise lead to unrepresentative conclusions.

3.2.3. Conclusions

The aim of the study was to conduct an AES assessment of the sustainability of industrial production of PTA. In order to do this, the LCA methodology was selected as a recognized tool capable of assessing the environmental loads of processes, considering a cradle-to-gate perspective. Three alternative bio-based pathways were evaluated and compared with the traditional route from crude oil: Scenario A (from sweet corn), Scenario B (from sugar beet and maize grain) and Scenario C (from orange peels). The production of PTA from renewable sources would be not only an industrial success but also a social success since it is mainly used in the production of PET, one of the main components of beverage containers worldwide. The different synthesis routes were investigated with the aim of evaluating which of them had a lower environmental burden from the point of view of sustainable development. The results show that Scenario B is the closest in environmental terms to the current fossil technology, while Scenario A has more impactful crops. On the other hand, the greenest process is the Scenario C, which uses waste as a renewable source. The main result that emerges from this LCA analysis is that, among those considered, only the processes that use wastes can guarantee a lower environmental impact. As evidenced, the cultivation of dedicated biomass plays a key role in the impacts of the processes and could be reduced through the use of waste streams. The results underline the importance of considering all the stages involved in the synthesis of a chemical, in particular, during the R&D stage. LCA analysis has this feature; it allows us to understand where and how to modify substantially the process under investigation in order to reduce its impact. Analysis of the scenarios has shown that crops have a great impact, even when compared to the use of fossil fuels, and that waste is a very valuable resource from which to draw and which can allow us to achieve sustainable development. It has been demonstrated that the valorization of wastes has a double advantage. The first is that no other raw material needs to be used (wastes are available, while the biomass needs cultivation that must be dedicated to them). The second is that it is not necessary to spend, in environmental terms, to dispose of the waste itself.

Therefore, in conclusion, it can be argued that LCAs are indispensable key tools for industrial sectors such as chemistry, where there is an increasing shift towards the concepts of GC and sustainable development.

The work resulted in a publication in the journal of Green Chemistry[32], whose texts, figures and tables were reproduced with the permission of the Royal Society of Chemistry.

3.3. Impact assessment of a new reforming reaction of clean biogas

Reinventing the energy and chemical market to overcome the intensive use of fossil fuels through the efficient exploitation of renewable sources is an essential step to reduce the anthropogenic impact on the environment. In this context, a better exploitation of biogas (BG) can deal with the increasing amount of organic wastes produced by modern societies and the reduction of GHG emissions, providing a way to overtake two of the main modern life challenges and to integrate rural communities and industries into the transformation of the energy sector[68]. Delocalized small plants can in fact produce BG by the anaerobic digestion (AD) of biomasses and wastes, landfill gas recovery systems and wastewater treatment plant[69-71]. The composition of BG depends on the type of feedstock processed and on the production pathway but, after its purification (to remove H_2S, NH_3, H_2O and Siloxanes), it is composed only by CH_4 (45% up to 75%) and CO_2[72]. This way, biomethane is obtained and it can be transported and use in the same way as natural gas (NG), as it is indistinguishable from it[73]. On the other hand, biomethane production valorises only half of the resource. A different but appealing application of clean BG lies in its use to produce synthesis gas, a mixture of H_2 and CO, through the valorisation of the CO_2 content[74-76]. Syngas can be produced by different reforming technologies that nowadays are facilities to convert NG in centralized and high production plants[77]. The Autothermal Reforming (ATR) is a combined combustion and catalytic process that has been used to produce hydrogen and CO-rich syngas from NG for decades[77,78]. The reaction takes place in an adiabatic reactor that consists of a burner, a combustion chamber, and a fixed-bed catalyst, contained in a refractory lined pressure shell. A mixture of methane, oxygen and steam (S) is partially converted in a pressurized combustion chamber. A CO-rich syngas can be produced as feedstock for methanol synthesis, most conveniently synthetized using syngas with low steam content ($S/CH_4 \approx 0.6$), as demonstrated at pilot and industrial scales. The temperature of the process is around 1100-1300 °C near the catalyst bed, reaching 2500 °C in the flame core. This zone can be characterised by a single reaction of CH_4 to CO and H_2O with an O_2/CH_4 ratio of the chosen stoichiometry, while in the catalytic zone the final conversion through heterogeneous reaction of hydrocarbons takes place (eq. 3.1 and 3.2) to produce syngas with different H_2/CO ratios, depending on the operating conditions[77].

Steam Reforming (SR): $CH_4 + H_2O \leftrightharpoons CO + 3\,H_2$ eq. 3.1

Water Gas Shift (WGS): $CO + H_2O \leftrightharpoons CO_2 + H_2$ eq. 3.2

This technology is also used by H. Topsøe A/S in the two-step reforming of NG or in a stand-alone reactor to subsequently produce methanol[79]. The Steam Reforming of methane is the most common and cost-effective method for syngas production. The reaction is highly endothermic, and it is typically carried out at 20-40 bar and at 800-1000°C using a Ni-based catalyst placed in multiple fixed-bed tubular reactors contained in a heated furnace. A steam generator produces high temperature steam that is sent to the reformer, after being mixed with the carbonaceous gas stream. The heat required for the reaction is provided through burning of part of the NG fed[80,81]. This combustion produces an exhaust stream that can be thermally valorised through different heat exchangers placed before the reforming reactor. As demonstrated in literature[82], clean BG can be effectively converted to syngas in a combined reforming process that couples the SR (eq. 3.1) and the Dry Reforming (DR) reaction (eq. 3.3) in one reactor.

Dry Reforming (DR): $CH_4 + CO_2 \leftrightharpoons 2\,CO + 2\,H_2$ eq. 3.3

The DR reaction converts the CO_2 to a CO-rich syngas but has many limitations related to the high endothermicity and high carbon formation rate that limits the catalyst durability and the safety of the plant[75,82,83]. From the carbon formation curves calculated at the thermodynamic equilibrium (Figure A2 in Annex A) it can be seen that, working in DR conditions, the carbon formation is favoured in all range of reaction temperature, becoming low only at T > 1000°C (5 bar). When steam is added to the inlet stream to perform the combined Steam/Dry Reforming (S/DR) reaction, coke formation decreases and becomes negligible when $S/CH_4 > 2$ for every condition considered. This combined process produces a syngas with a H_2/CO ratio that varies as a function of the quantity of steam fed. The quantity of water drives the global reaction favouring one reaction over the other and consequently increasing the CO_2 conversion when the quantity of steam is low (and the DR favoured) as shown in Figure 3.8.

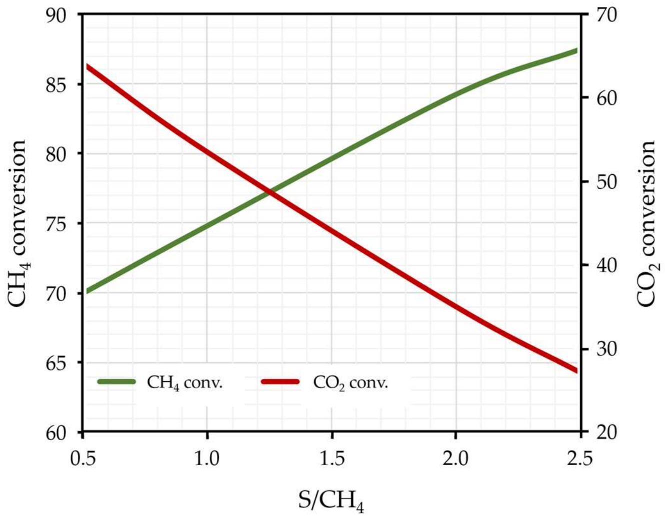


Figure 3.8 – Conversion of CH_4 and CO_2 at the thermodynamic equilibrium as a function of the steam content (S/CH_4) in the inlet stream. The values were calculated at 900 °C and 30 bar.

The reaction is conducted using a Ni/Rh-based catalyst obtained by the co-precipitation of an hydrotalcite-type precursor followed by calcination (900 °C for 6 h)[82]. The feasibility of the S/DR reaction was tested using a semi-pilot plant, feeding an equimolar mixture of CH_4 and CO_2 with S/CH_4 equal to 2. The tests were carried out at a pressure of 0.5 MPa and a reaction temperature of 900 °C maintaining a constant Weight Hourly Space Velocity of 50,000 mL/(h·g_{cat}).

Before reaction, the in-situ reduction of the catalyst was carried out feeding a continuous flow of H_2/N_2 (1/10 v/v) at 0.5 MPa increasing the catalyst temperature from 300 °C to 900 °C (10 °C/min) and holding this temperature for 1h. The composition of the outlet stream was analysed by an online gas chromatograph equipped with a CarboPLOT (carrier gas H_2, for the detection of CO, CO_2 and CH_4) and a HP-Molesieve (carrier gas N_2, to quantify H_2) columns and two thermal conductivity detectors. The calculations of the thermodynamic equilibrium at different operating pressure and temperature were performed using the CEAgui software distributed by NASA[84].

Therefore, in the present work the use of the combined S/DR technology to obtain syngas from clean BG is proposed. To demonstrate the feasibility of the process, the scale-up from lab-scale data through simulation was carried out and its environmental performances are evaluated. The process was simulated using Aspen HYSYS v. 7.3 and the thermodynamic model is based on a Peng-Robinson equation of state to describe the behaviour of the gaseous streams and possible vapour-liquid equilibria (Figure 3.8)

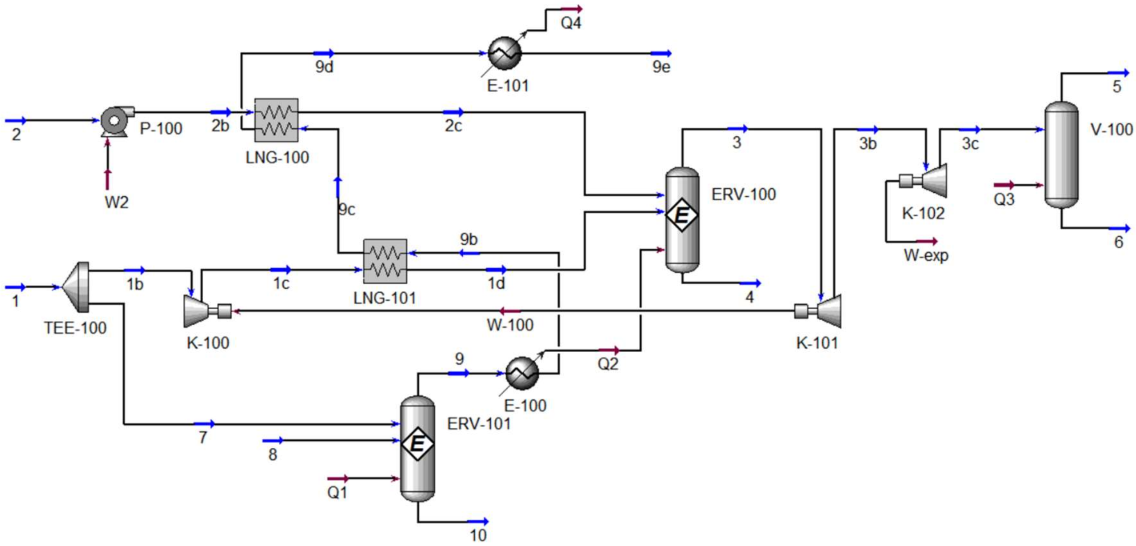


Figure 3.9 – Process flow diagram for the S/DR of biogas using a fraction of the biogas itself as heating medium.

The feed considered is a clean BG (stream 1, at ambient temperature and pressure) composed by an equimolar mixture of CH_4 and CO_2. It is split in two streams: the first one (1b) is compressed to 30 bar (K-100) and then heated to 750°C before being collected to the S/DR reactor (stream 1d), while the other (7) is sent to the adiabatic equilibrium reactor (ERV-101) for the combustion. The off gases coming from the combustion (9) are then used to heat the S/DR reactor (ERV-100) to 950 °C (with a thermal flux Q2) and then sent to a series of two steps energy recovery processes (LNG-101 and LNG-100). Liquid water (2, at ambient temperature and pressure) is compressed to 30 bar using a pump (P-100) and then heated to 950 °C using the second step of the energy recovery process of 9c. Finally, streams 1d and 2c are collected to a S/DR unit (ERV-100) where the reactions from equations 3.1 and 3.3 take place (experimental equilibrium data were used to calculate the conversion at the reactor outlet). The exiting stream (3) is then sent to a first stage expander (K-101), which is coupled with the compressor K-100 for a full recovery of mechanical energy, and then to a second stage expander K-102 (which decrease the stream pressure to the ambient pressure). Finally, the resulting stream is collected to a separating-cooling unit (V-100) to separate water (6) from the gaseous stream (5).

With the aim to fully understand the catalyst behaviour in real operating conditions, the catalytic data were first extrapolated using the semi-pilot plant. A catalytic test at 900 °C, 0.5 MPa and with a WHSV of 50,000 mL/(h*g) was carried out. The results in terms of CH_4, CO_2 conversion and the value of the H_2/CO ratio of the outlet stream are showed in Fig 3.10.

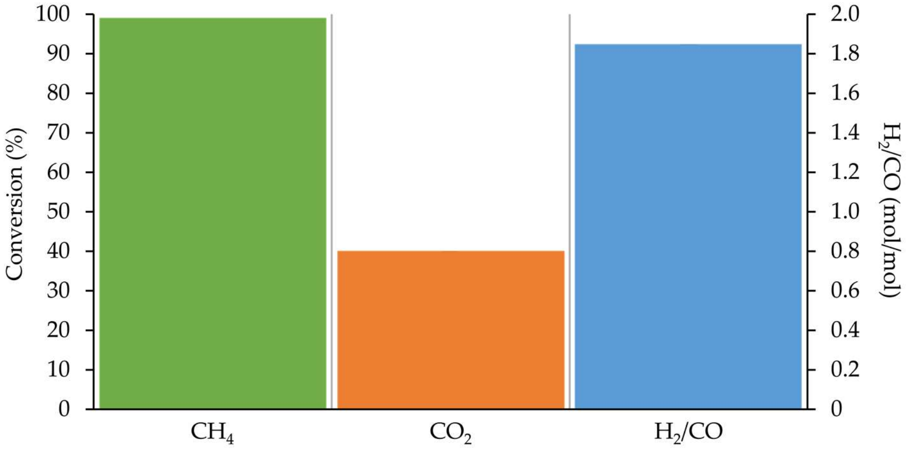


Figure 3.10 – CH_4, CO_2 conversion and H_2/CO ratio observed at 900 °C, 0.5 MPa, $S/CH_4 = 2$, using the Ni-Rh/MgAlO catalyst.

In these conditions the biogas conversion rate reached the thermodynamic equilibrium. The combined reforming converted almost the totality of CH_4, and a notable fraction of the CO_2 fed (≈ 40% v/v), producing a syngas with a H_2/CO molar ratio of 1.85. The lab-scale data demonstrate the feasibility of the combined reforming and the possibility to valorise a CO_2-rich biogas in the presence of steam. Therefore, a simulation considering an industrial scale operating condition was carried out using the CEAgui software[84]. The conditions were modulating considering an operative pressure of 3.0 MPa and a temperature of 950 °C, adjusting the S/CH_4 value to obtain an outlet stream with a similar unconverted CO_2 content (Table 3.3). By increasing the S/CH_4 value to 2.5, it is possible to obtain a syngas with a H_2/CO ratio of 1.95 suitable for methanol synthesis, without drastically decrease the biogas conversion rate (CH_4 conv. = 94%, CO_2 conv. = 33%; calculated at the thermodynamic equilibrium).

Table 3.3 – Composition of the outlet stream of the S/DR of clean biogas. Condition 1. T = 900 °C, P = 0.5 MPa, S/CH_4 = 2.0 mol/mol; Condition 2. T = 950 °C, P = 3.0 MPa, S/CH_4 = 2.5 mol/mol.

Condition	**CH_4 (%)**	**CO_2 (%)**	**CO (%)**	**H_2 (%)**	**H_2O (%)**
1	0.001	0.100	0.233	0.430	0.236
2	0.010	0.104	0.200	0.389	0.297

3.3.1. Methodology

To evaluate the advantages of this BG-to-syngas technology, the current ATR technology for the production of syngas was also included in the study. A total of four scenarios were constructed, two of the ATR process where the feed is NG (Scenario A) or BG (Scenario B) and two of the S/DR process where the feed is BG but the heat requirement can be met by the combustion of NG (Scenario C) or BG (Scenario D). The latter is the one described in Figure 3.8, while for the other scenarios similar simulations were conducted, shown in Figure A3 in Annex A for space reasons.

Since the S/DR process is not yet developed on an industrial scale, this work is part of the AES evaluations, whose characteristics have already emerged in the PTA case study. The production of 1 Nm^3 of syngas, with the specification of the $H_2/CO = 1.95$ and a grade of purity higher than 92%, was chosen as FU. This ensure an unambiguous and standardised comparison between the scenarios, and the obtained syngas is suitable for downstream applications such as Fischer-Tropsch or methanol synthesis. If the output dry gases do not reach this purity (defined by the sum of the molar fractions of H_2 and CO), they undergo a Pressure Vacuum Swing Adsorption (PVSA)[85] to remove the unconverted CO_2 and meet the required target specification.

The system boundaries of this LCA extend from the production (or extraction) of the raw materials to the obtaining of the product (syngas), following the cradle-to-gate approach. Figure 3.11 depicts the four scenarios and the system boundaries considered, showing all the necessary processes for each pathway to obtain the same FU.

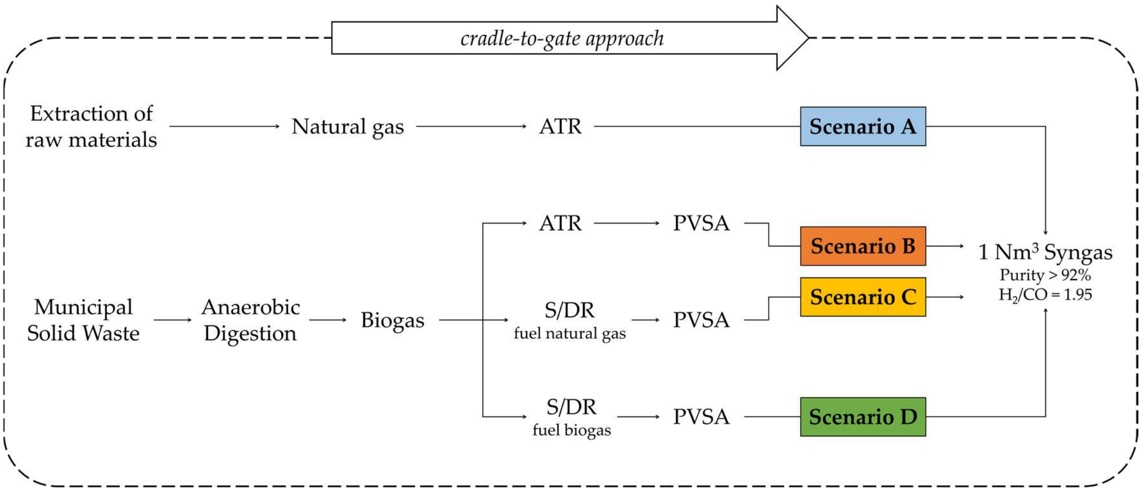


Figure 3.11 – System boundaries and FU of the study on the biogas reforming.

The production of BG was simulated with primary data from literature[60], in which it is obtained from the AD of the organic fraction of municipal solid waste. Organic waste was considered impact free, while all subsequent steps (including its processing and purification) are within the system boundaries. The impacts related to the extraction and use of NG were simulated with the database process *"Natural gas, high pressure {GLO}| market group for | Cut-off, U"*[52]. In all scenarios the demand for electricity is satisfied by the grid, while thermal consumption is covered by the different gas sources. After the reactors, the models assume that excess heat and electricity are recovered with a conversion efficiency of 50% and 31% respectively[86]. With a zero-waste perspective and with the possibility of combining BG upgrading plants with AD systems or with plants for the utilisation of the syngas, these energy recoveries were considered as avoided impacts. Since it is not necessary to produce the same amount of thermal energy and electricity, directly or indirectly, from fossil fuels, this turns out to be an advantage for the environment. The full LCI of the four scenarios is reported in Table 3.4.

Table 3.4 – LCI of the considered scenarios for the biogas reforming.

		Unit	Scenario A	Scenario B	Scenario C	Scenario D
Input	Natural gas	Nm^3/h	3.4E-01	-	2.5E-01	-
	Biogas	Nm^3/h	-	7.0E-01	4.9E-01	4.9E-01
	Biogas (fuel)	Nm^3/h	-	-	-	6.0E-01
	Water	kg/h	3.4E-02	7.0E-01	5.0E-01	5.0E-01
	Oxygen	kg/h	2.8E-01	3.3E-01	-	-
	Air	kg/h	-	-	3.1E+00	3.7E+00
	P-100 (electricity)	kJ/h	1.1E-01	2.2E+00	1.9E+00	1.9E+00
	Q-100 (electricity)	kJ/h	2.3E+02	4.7E+02	-	-
	Q-101 (electricity)	kJ/h	1.5E+02	1.7E+02	-	-
	PVSA (electricity)	kJ/h	-	5.7E+02	2.5E+02	2.5E+02
Output	Syngas	Nm^3/h	1.0E+00	1.0E+00	1.0E+00	1.0E+00
	Water	m^3/h	3.7E-05	7.2E-04	3.4E-04	3.4E-04
	Carbon dioxide (balance)	kg/h	3.5E-02	6.5E-02	-	-
	Carbon dioxide (off-gas, fossil)	kg/h	-	-	5.0E-01	-
	Carbon dioxide (off-gas, biogenic)	kg/h	-	-	-	1.2E+00
	Carbon dioxide (PVSA)	kg/h	-	7.1E-01	3.1E-01	3.1E-01
Avoided	Carbon dioxide (balance)	kg/h	-	-	1.6E-01	1.6E-01
	Q-102 (electricity)	kJ/h	2.7E+02	2.4E+02	-	-
	Q-103 (heat)	kJ/h	3.9E+02	8.6E+02	-	-
	K-102 (electricity)	kJ/h	-	-	3.0E+02	3.0E+02
	Q-104 (heat)	kJ/h	-	-	2.2E+03	3.1E+03
	V-100 (heat)	kJ/h	-	-	8.9E+02	8.9E+02

3.3.2. Results and discussion

Environmental impacts of four scenarios are evaluated using ReCiPe[62] and CED[61] analysis methods.

Among the eighteen impact categories of the ReCiPe method, the most relevant (i.e. those with the Single Scores) for the understanding environmental impacts were chosen, namely GW, FPMF, HT and WC. Furthermore, they consider global impacts and do not depend on the site where they occur. The results of the analysis at midpoint level are presented in Figure 3.12.

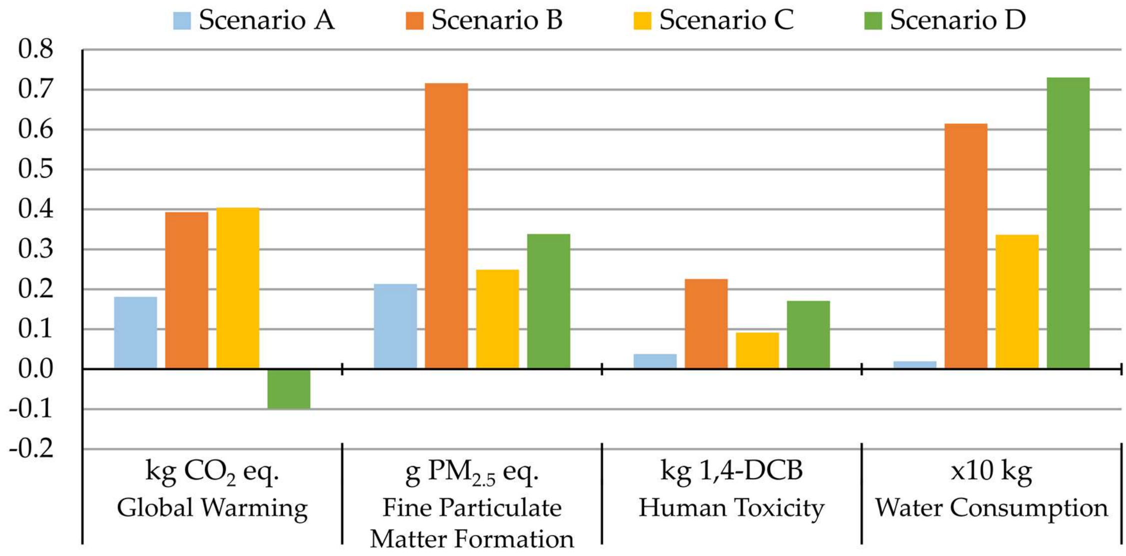


Figure 3.12 – Environmental results of syngas production scenarios (ReCiPe H/H – Midpoint).

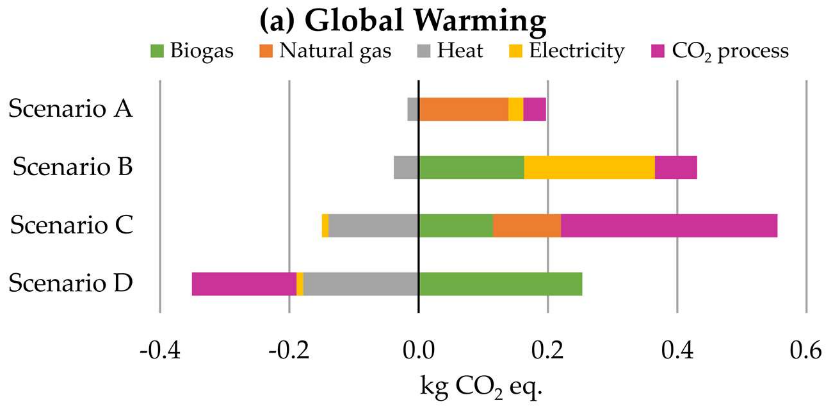
What immediately emerges is the result of Scenario D in the GW category, which shows a negative impact of -0.10 kg CO_2 eq. It means that when the heat demand in S/DR process is covered by the use of BG, the whole scenario has less CO_2 in the output than it was in input. This is possible thanks to the exploitation of the CO_2 present in the feed, which from an undesired product (as in the case of BG combustion) becomes a useful resource for obtaining syngas. This aspect is one of the strengths of the S/DR process and is particularly highlighted by Scenario D because the off-gases for the reactor heating system come from a biogenic resource (BG) and their environmental impact is zero. Scenario C, despite using the same process technology as Scenario D, has an impact on GW category estimated at 0.40 kg CO_2 eq. because the benefit of the process is cancelled by the emissions of the heating system. In this scenario, in fact, heating energy is obtained from the combustion of NG and its emissions are considered to be environmentally impacting because they derive from a fossil resource. ATR processes show quite different impacts on GW depending on whether the feed is NG (Scenario A) or BG (Scenario B). In particular, Scenario A has an impact in this category that is about half of that of Scenario B, 0.18 kg CO_2 eq. and 0.39 kg CO_2 eq. respectively. Since ATR technology is autothermal (i.e. it does not require external heating) there are no other GHG emissions than the output residues, so the reasons for this difference in impact should be investigated through a contribution analysis.

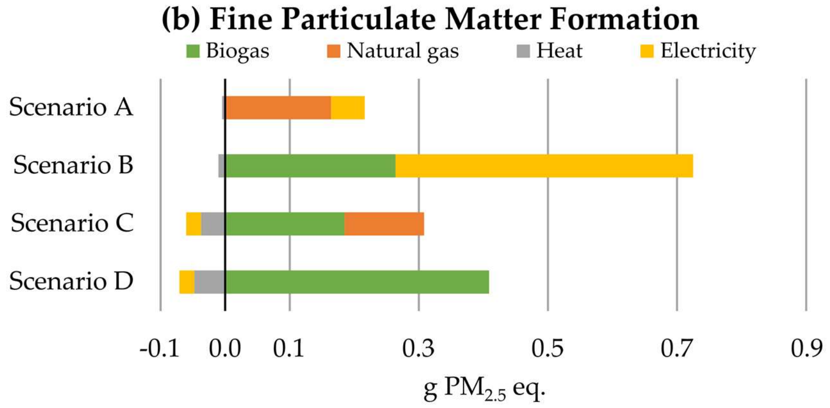
In the FPMF category, Scenario B is assigned an impact of 0.72 g $PM_{2.5}$ eq., much greater than the others which are between 0.21 and 0.34 g $PM_{2.5}$ eq. There is more difference between the two scenarios of the ATR process than between those of the S/DR process, indicating that the current technology is more sensitive to the impacts of this category when switching from NG to BG. On the other hand, the impacts of Scenario C and Scenario D mean that BG production implies a higher particulate formation than NG, since the simulation of combustion off-gas does not include this type of emission.

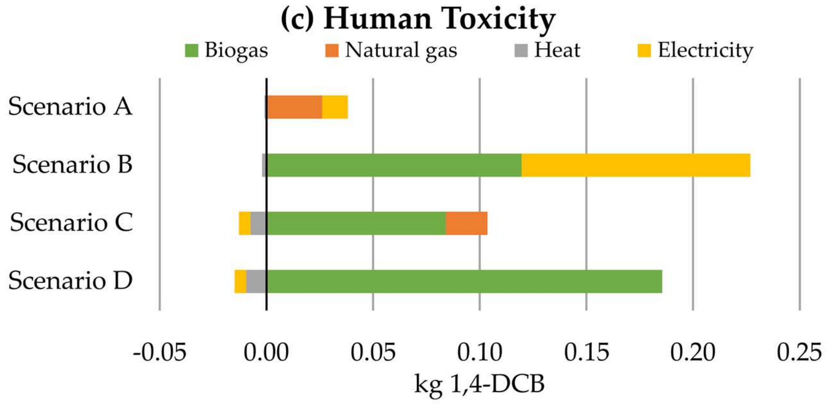
In the HT and WC categories, processes using BG show the highest impacts, suggesting that the cause of these results could be the BG itself. This is particularly evident in the WC category, where Scenario A has an impact of one order of magnitude less than the others (0.2 kg). The S/DR process uses a higher S/CH_4 ratio than the ATR process, but this does not affect the impacts of the category because Scenario B has a comparable water consumption (6.1 kg) to Scenarios C and D. The latter two scenarios seem to confirm the BG hypothesis, because when it is used in double quantities (Scenario D), the impact on water consumption also doubles (3.4 vs 7.3 kg). The same trend can also be identified in the HT category, where Scenario A has half the impact of Scenario C (0.04 vs

0.09 kg 1.4-DCB) and Scenarios B and D are the ones with the highest impacts as they use the most BG (see LCI in Table 3.4).

For a more detailed analysis of the impacts and to fully understand who is responsible for them, a contribution analysis was carried out and the results are shown in Figure 3.13.







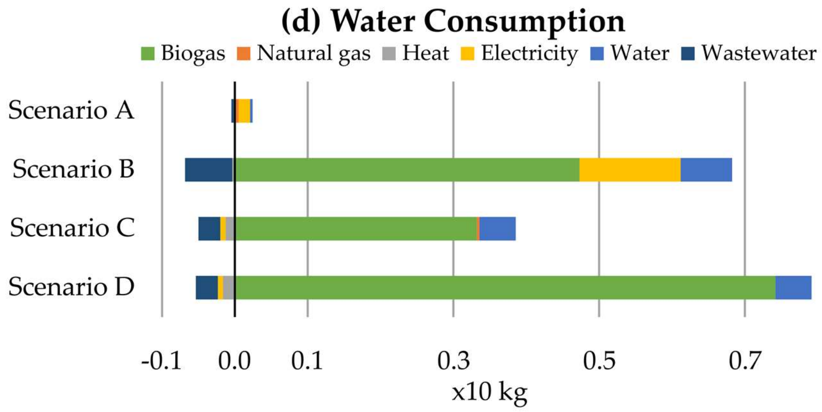


Figure 3.13 – (a) GW, (b) FPMF, (c) HT and (d) WC contribution analysis of the scenarios (ReCiPe H/H – Midpoint).

The contributions on the GW category (Figure 3.13a) confirm the findings of the previous analysis, the S/DR process exploits the CO_2 of the feed, effectively removing it from the environment. This is highlighted in Scenario D where the "CO_2 process" bar depends only on the difference between input and output and is negative. As mentioned above, Scenario C also considers the off-gases of NG combustion in the CO_2 balance and this shifts the bar to positive values. BG, however, is not free from impacts on the GW category but, on the contrary, it has an environmental burden due to the AD process of organic waste. With the same volume, its impact is lower than that of NG (0.23 vs. 0.41 kg CO_2 eq./Nm^3), but since the amount of BG is greater the two contributions are almost equal.

Scenario B, in all categories, has a large impact due to electricity that compromises its environmental performance. The reasons behind this great need for electricity lies in the composition of the ATR reactor output. When the feed is BG, in fact, the impurities of CO_2 in the output remain large and in order to obtain the same quality of syngas (purity >92%) a large use of electricity is required for the PVSA process. For comparison, in Scenario A the CO_2 molar fraction in the output flow is 0.02 (PVSA purification is not required), in Scenarios C and D it is 0.14, while in Scenario B it is 0.28. This has the greatest effect in the FPMF (Figure 3.13b) and HT (Figure 3.13c) categories, where the contribution of electricity is

64% and 48% of Scenario B respectively. Without this contribution, the results of Scenario B would be closer to those of Scenario A, which use the same type of process.

The previously formulated hypothesis on the role of BG in the HT and WC (Figure 3.13d) categories is confirmed by the contribution analysis. In both impact categories, BG takes the lion's share when used and is the main (if not the only one) responsible for the impacts. The environmental burdens that BG has (0.17 kg 1.4-DCB/m^3 and 0.68 kg_{water}/m^3) are much higher than those of NG (0.08 kg 1.4-DCB/m^3 and 0.02 kg_{water}/m^3) and derive from its production chain, whose environmental efficiency is not studied in this work.

The latest analysis carried out with the ReCiPe method is the endpoint assessment of the damage caused by the scenarios. The results are reported in Table 3.5.

Table 3.5 – Results of endpoint analysis of syngas production processes (ReCiPe method).

Damage category	Unit	Scenario A	Scenario B	Scenario C	Scenario D
Human Health	DALY	3.2E-07	9.2E-07	5.8E-07	2.1E-07
Ecosystems	species·yr	6.9E-10	1.9E-09	1.5E-09	3.7E-10
Resources	US$	1.1E-01	1.4E-02	7.4E-02	-9.0E-03

The analysis shows that the scenarios using the ATR process are those with the highest damage, in particular Scenario B in the Human Health and Ecosystems categories and Scenario A in the Resources category. An impact category can affect more than one damage category, such as GW, which influences both Human Health and Ecosystems. These two damage categories show similar trends in results, Scenario B has the highest value followed by Scenario C, while Scenario A and Scenario D have lower values. This reflects, in general, what emerged from the analysis of the impacts on GW, FPMF and HT categories. Scenario B and Scenario C showed significant positive values in all three impact categories, while Scenario D has the negative impact in category GW which lowers the damage on Human Health and Ecosystems. On the other hand, the endpoint results of Table 3.5 show an aspect of the processes not yet discussed, resource consumption. Scenario A and Scenario C clearly show that when NG is used, the damage caused to the Resources category is significantly affected. Scenario D shows avoided damage to Resources due to the low contribution of BG in this category and to the heat recovery that can be carried out after the S/DR reactor, while Scenario B is still positive due to the high amount of electricity required.

In order to deepen the issue of resources, the scenarios were also analysed using the CED method. As stated above, the CED method does not consider the negative effect (impacts or damages) of processes on the environment but provides an indicator of the intensity of resource use. Results, listed in Table 3.6, are expressed in energy terms, and divided between non-renewable and renewable resources.

Table 3.6 – Assessment of resource consumption for each scenario (CED method).

Process	Unit	Total	Non renewable	Renewable
Scenario A	MJ eq.	14.69	14.64	0.04
Scenario B	MJ eq.	5.97	5.31	0.67
Scenario C	MJ eq.	10.92	10.65	0.27
Scenario D	MJ eq.	2.28	1.68	0.59

The highest consumption is related to non-renewable resources, even for scenarios using only BG (Scenario B and D). This is mainly due to the electricity needs that are met by the grid and that currently involves the exploitation of fossil resources. In Scenario A and Scenario C, NG used in processes is a direct source of fossil resource consumption, covering almost the entire demand of the scenarios (>99%) and responsible for the significantly higher values. The results indicate that Scenario A has the greatest need for resources while Scenario D is assigned the lowest, in the middle Scenario C and B in the same order as they appeared in the damage analysis in the Resources category of the ReCiPe method.

A further information extracted from the results on resource consumption is the renewability grade[63] of the scenarios (Figure 3.14).

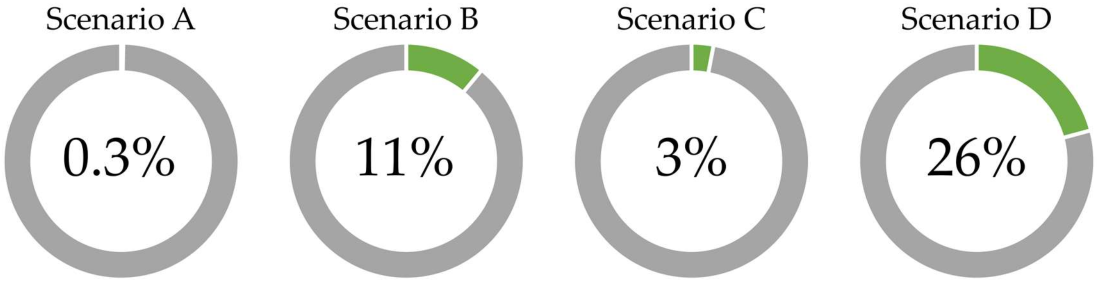


Figure 3.14 – Renewability grade calculated as a percentage of renewable resources (in green) on the total (in grey) of each route (CED method).

It evaluates the percentage of renewable resource out of the total and shows that Scenario D reaches the highest value (26%). The use of fossil resources is therefore balanced by more than 1/4 of the renewable resources and this could be used to claim the technology readiness level of the process. The other process with a similar index is Scenario B (11%) and this indicates that the way to achieve the most renewable processes possible is to replace NG in favour of BG. Scenario A and Scenario C have the worst renewability rates (3% and 0.3% respectively) and if we add to this the fact that these are also the scenarios where the demand for resources is the highest, the picture is certainly not favourable from an environmental point of view.

3.3.3. Conclusions

This work was designed to evaluate the environmental performance of a new BG upgrading process that combines the well-known reactions of steam and dry reforming to obtain syngas (S/DR process). To do this, the LCA methodology was applied and the current syngas production system (ATR process) was included in the study as a benchmark. The S/DR process uses BG as raw material and the heat requirement can be covered by NG (Scenario C) or by BG itself (Scenario D), therefore also the ATR process has been evaluated with both NG (Scenario A) and BG (Scenario B) feeds. The consideration of all these scenarios allows to conduct the evaluation with a from-cradle-to-gate perspective and the double feeding of the ATR process assures consistency and uniformity of the analysis.

The analysis showed that BG-to-syngas technology using reforming processes has the potential to reduce the anthropogenic impact on the environment. According to the ReCiPe method, the S/DR process has proven to be comparable with the already existing and widespread solutions, showing similar impacts. Furthermore, if the S/DR process is conducted using BG also as a heat source, then the CO_2 balance turns negative, ensuring that the whole process has excellent potential as a Carbon Capture and Utilization (CCU) technology providing the lowest damage in all categories and it can even guarantee avoided damage to the Resource category. On the other hand, switching the inlet feed of the current ATR technology from NG to BG is not environmentally convenient, as the impacts are more than doubled in each category. The reasons for this behaviour derive from the production chain of BG, whose contribution is accentuated in the HT and WC categories, and from the purification step of the produced syngas, which is too contaminated by input CO_2 when the BG is used. The latter issue is not particularly relevant for the S/DR process because its main characteristic is to exploit the CO_2 of the feedstock as a resource rather than treating it as waste and therefore the quantity to be removed downstream is much lower. Finally, the analysis of resource consumption with the CED method has highlighted the weight that the use of NG has in this category and that the use of BG makes it possible to increase the renewability grade of the scenarios.

To conclude, this AES evaluation shows that the S/DR process is a promising technology for the production of syngas because it can rely on CO_2 sequestration. Its development should therefore be encouraged and pursued, and the same should be done for BG production which has shown some environmental weakness. Its improvement would make it possible to further reduce the environmental burden of the entire process, which is essential for achieving sustainable development.

The results of this project led to the production of an article, currently being reviewed by the Energy & Fuels journal, edited by the American Chemical Society (ACS).

3.4. Environmental characterization of ionic liquids

The world of chemistry has always been at the forefront of continuous R&D of new materials, processes and solutions, as it was one of the first sectors to question its environmental responsibilities. The combination of these two spheres is at the heart of the definition of sustainable development and today there is no question of innovation unless the environmental aspect is also included. Kunnari et al.[87] observe that "LCA cannot be avoided in the development of new products", so the need to have tools for environmental impact assessment is increasingly evident. Only with decision support tools it is possible to guide choices and the development of new solutions towards ever greener versions. This includes AES assessments, aimed at avoiding the waste of energy, time and money for the development of technologies and/or materials with unsatisfactory environmental performance.

Ionic liquids (IL) are certainly part of the innovations in the field of chemistry. The term identifies organic chemical compounds consisting of ions and having a melting point below 100 °C, so that they present in a liquid state at low temperatures or even at room temperature[88]. These compounds, which appeared in the middle of the last century and were synthesised in stable forms at the beginning of the 1990s[89], immediately attracted the attention of research for their properties and applications. In particular, their low volatility and low flammability[90] have brought to the fore ILs as possible green solvents, to be used as a substitute for common organic solvents, which are often the cause of environmental problems (e.g. halogenated solvents such as chloroform, carbon tetrachloride, etc.). Other applications of ILs can be as catalysts in industrial chemical processes[91], for cellulose dissolution[92], in electrochemical devices[93], in carbon dioxide capture[94,95] and in many other sectors[96-99]. Another key feature that makes ILs attractive is the possibility to modulate their properties through changes in composition and chemical structure. From a structural point of view these compounds are extremely varied and it is estimated that, in principle, they can exist in at least 10^{10} variants (tens of billions), to which must be added all the possible mixtures that can be formed[100].

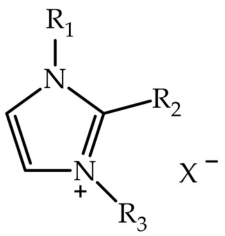
Although the literature is full of case studies on the properties and applications of ILs, the same cannot be said about the knowledge of their environmental impacts. Some LCA assessments have been conducted on them, but the focus is more on the environmental analysis of their applications[101-106] than on the impacts related to the production of them. Due to the complex synthesis steps and the difficulty in finding information, carrying out an LCA study on ILs takes time and resources, and a new assessment would be needed for each variant. Given the wide range of possible ILs, it is clear that having predictive methods to estimate environmental impacts would be a great advantage. The environmental information would be more accessible, the time savings would be substantial and the impact assessment would be part of the early stages of R&D of new molecules, rather than a retrospective analysis.

The use of predictive methods in the study of ILs is present in the literature, especially for the prediction of physical properties through the use of the quantitative structure-activity relationships model (QSAR)[107-112]. With regard to environmental aspects, some attempts have been made to predict ILs results, in particular with regard to the evaluation of the toxicity of molecules. The recent review by Abramenko et al.[113] summarizes several of these studies and illustrates the state of progress in the use of the QSAR model for the prediction of ILs toxicity. However, the results of QSAR models only consider the intrinsic properties (such as toxicity) of the molecules but do not consider the other phases of the ILs life cycle. This becomes of particular importance when it comes to environmental impacts and can be solved, as already fully described in the previous sections, through the application of the LCA methodology.

For this reason, this study was designed to set the basis for the construction of a predictive model of the environmental impact of ILs from a life cycle perspective. To do this, the group contribution method was applied[114]. It is already used for the estimation of chemical properties[115-117] and is based on the principle that the vast majority of organic compounds are made up of the same functional groups, so that some properties of the molecules can be estimated from the regressive contributions of the functional groups that compose them. These properties also include environmental impacts, as demonstrated by Tula et al[118]. Therefore, in this study, the environmental impacts of ILs are related to the contributions of their synthesis steps in order to use this information to predict the environmental impacts of new ILs (of the same family) in a similar way to the group contribution approach used to estimate the physical properties of molecules. The aim is to assist in the selection and design of more environmentally sustainable ILs in a practical and timely manner.

The first step is the selection of a representative sample of ILs from the same head group or family. In this study, the imidazolium head group was selected to illustrate the methodology as this is the most widely studied family of ILs and more likely to find the necessary inventory data for the environmental characterisation step. A sample of eight different ILs were selected and are listed in Table 3.7. These ILs were selected as they represent the different chain variations commonly reported in literature[119], i.e. alkyl, aromatic, multiple side chain and chain length variations. The chloride anion remained as a constant in all samples as the resulting ILs can be considered precursors for more complex ILs and to keep an initial focus on the head group formation reactions. The contributions from the anion exchange step were also considered using the tetrafluoroborate ($[BF_4]^-$) and the hexafluorophosphate ($[PF_6]^-$) anions due to their common use and data availability on LCA databases.

Table 3.7 – Selected sample of ILs from the imidazolium head group.

Molecular structure	**R_1**	**R_2**	**R_3**	**X^- [a]**	**Name of IL**	**Abbreviate**
	Methyl	-	-	Cl^-	1-methyil imidazolium chloride	[Hmim]Cl
	Ethyl	-	Methyl	Cl^-	1-ethyl-3-methyil imidazolium chloride	[C$_2$mim]Cl
	Butyl	-	Methyl	Cl^-	1-butyl-3-methyil imidazolium chloride	[C$_4$mim]Cl
	Hexyl	-	Methyl	Cl^-	1-hexyl-3-methyil imidazolium chloride	[C$_6$mim]Cl
	Decyl	-	Methyl	Cl^-	1-decyl-3-methyil imidazolium chloride	[C$_{10}$mim]Cl
	Allyl	-	Methyl	Cl^-	1-allyl-3-methyil imidazolium chloride	[Amim]Cl

Benzyl	-	Methyl	Cl^-	1-benzyl-3-methyil imidazolium chloride	$[PhC_2mim]Cl$
Butyl	Methyl	Methyl	Cl^-	1-butyl-2,3-dimethyil imidazolium chloride	$[C_4dmim]Cl$

[a] Anions $[BF_4]^-$ and $[PF_6]^-$ were also considered in this study.

The next step in the methodology is the selection of the synthesis pathway of the ILs under study, e.g. most prevalent commercial process, and the identification of the main synthesis steps in order to generate the necessary data for the regression analysis. The preparation of imidazolium-based ILs can be broken down into four main steps[120] as shown in Figure 3.15, consisting of the imidazole ring formation, methylation, alkylation, and anion exchange step to obtain the desired anion configuration. These steps are described in detail below.

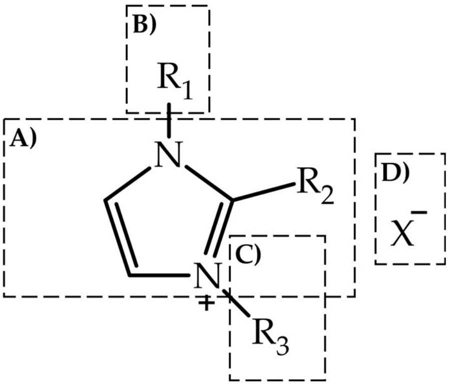
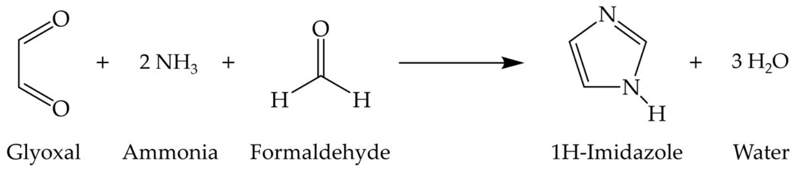


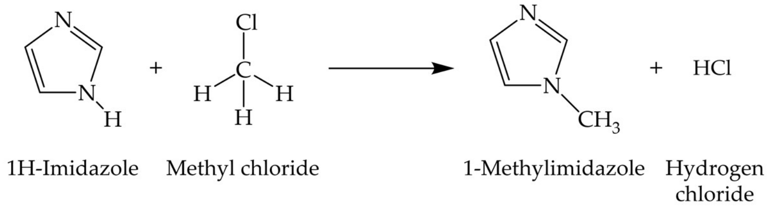
Figure 3.15 – Generic synthesis steps in the production of imidazolium-based ILs, where A) ring formation, B) methylation, C) alkylation and D) anion exchange.

The ring formation step is the starting point for all imidazolium-based ILs, where glyoxal reacts with formaldehyde (or acetaldehyde in the case of $[C_4dmim]^+$ to obtain the methyl in the second position of the ring), and ammonia to form the imidazole ring as shown in eq. 3.4, via the Debus-Radziszewski synthesis method[121]. This reaction is usually carried out in the presence of water at temperatures between 50 °C and 100 °C, with an imidazole yield of up to 85% and purity over 99%[121].



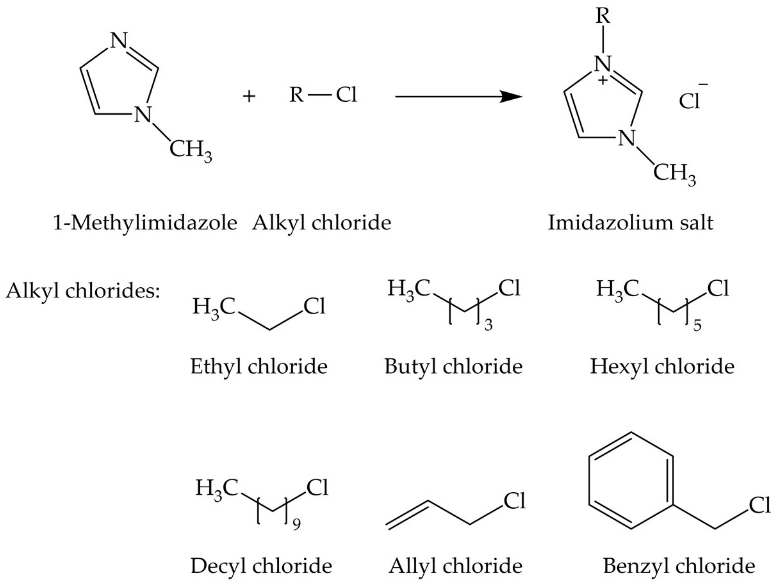
eq. 3.4

The imidazole ring reacts with methyl chloride to produce 1-methylimidazole in a methylation step as shown in eq 3.5, which is a common step for all the ILs listed in Table 3.7. The reaction is carried out at 100 °C in an aqueous solution with yields of 78%[122].



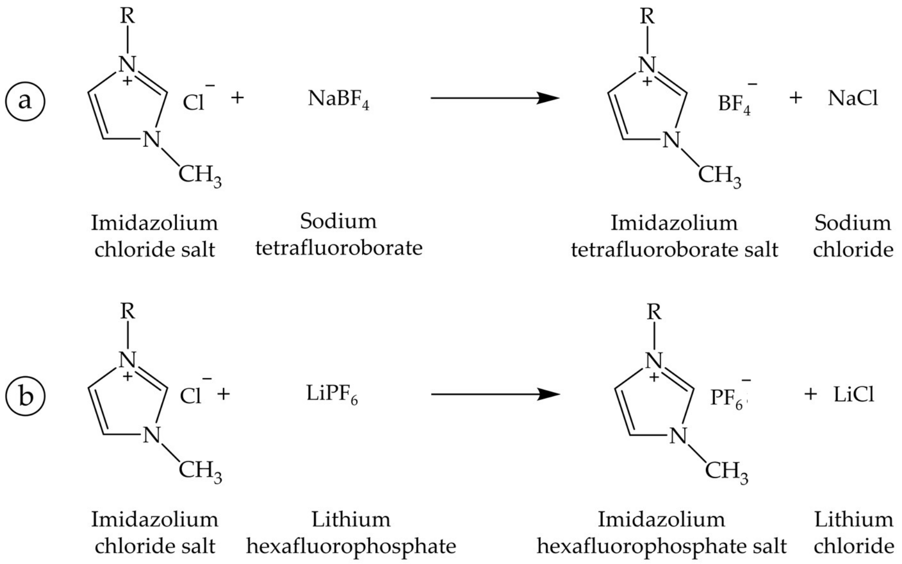
eq. 3.5

Finally, the IL is formed in the alkylation step illustrated in eq 3.6, where a second or third substituent, depending on the IL, is introduced to the imidazolium ring using an alkyl chloride. The alkyl chloride is used in stoichiometric excess to ensure the formation of the two counterions, the imidazolium cation and the chloride anion. The use of different alkyl chlorides will result in the IL variations listed in Table 3.7. For example, the use of ethyl chloride and benzyl chloride will produce [C$_2$mim]Cl and [PhC$_2$mim]Cl, respectively. In this study, ethyl chloride, butyl chloride, hexyl chloride, decyl chloride, allyl chloride and benzyl chloride were used to produce the ILs in the selected sample. It is possible to obtain yields of 99% when the alkylation reaction takes place at temperature of around 170 °C[123].



eq. 3.6

The properties of ILs can be “tuned” by changing the anion via anion exchange reactions[124]. In this study, tetrafluoroborate and hexafluorophosphate anions were considered to produce variations of the imidazolium-based ILs included in the selected sample. In this step, the imidazolium chloride IL reacts with sodium tetrafluoroborate ($NaBF_4$) or lithium hexafluorophosphate ($LiPF_6$) to produce the corresponding IL variation as shown in eq. 3.7. This step was included in order to provide a more representative pathway of the synthesis of ILs, which are commonly derived from basic IL precursors. The anion exchange reaction is typically carried out at room temperature, i.e. 25 °C, with yields of 91%[124].



eq. 3.7

3.4.1. Methodology

The goal of this study is to estimate the environmental impacts of the eight imidazolium-based ILs under study and the contributions from their different synthesis steps. This is to identify possible correlations between molecular structures and environmental impacts of ILs. The system boundaries considered in this work are from cradle-to-gate, as only the material and energy flows associated with the production of the ILs are of concern here, and the fate, i.e. application, disposal, of the ILs falls outside the scope of this study. The impacts related to the chemicals plant infrastructure and transportation of raw materials were excluded as the contributions from these life cycle stages tend to be negligible in the production of chemicals[125]. The adopted FU was "per mole of product", which was considered a more appropriate FU for the purposes of this study. For example, a FU of "per kg of product" would prevent us from estimating the cumulative contributions of each synthesis step in the formation of the IL at a molecular level, and disadvantage those ILs with lower molecular weights, e.g. more raw materials and energy resources would be required to produce one kg of IL resulting in a higher environmental burden.

The LCI of the eight ILs studied here are presented in Tables 3.8 – 3.10. The materials quantity data were obtained from stoichiometric calculations based on the synthesis steps described above. A generic life cycle tree for the production of imidazolium-based ILs is given in Figure 3.16, where the common precursors used in the synthesis of all ILs can be identified.

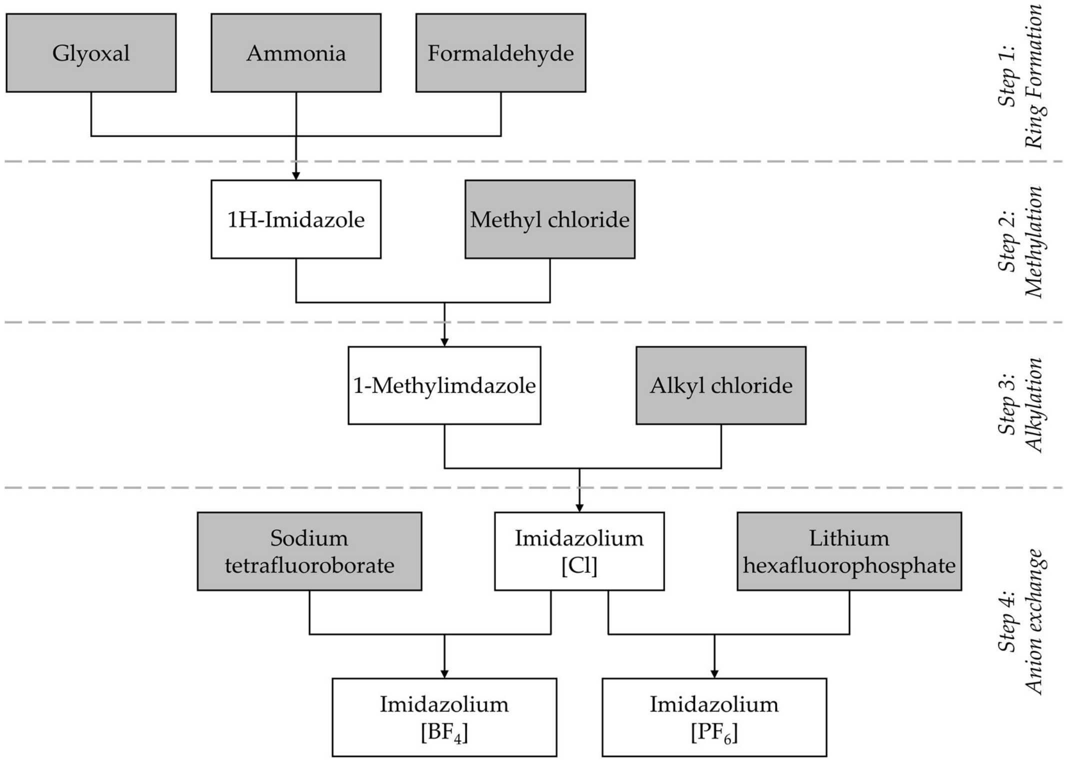


Figure 3.16 – Generic life cycle tree for the production of imidazolium-based ILs selected in this study.

The energy consumption estimations followed the methodology proposed by Cuéllar-Franca et al.[126], where the heat of formation of the reagents and products were used to calculate the theoretical energy consumption of the corresponding reactions and scaled-up using industrial empirical factors reported in literature[127]. For example, the necessary heat in endothermic reactions was assumed to be supplied from natural gas and the theoretical energy requirements was multiplied by a factor of 4.2. In the case of electricity consumption for cooling down exothermic reactions, a factor of 3.2 was applied to the theoretical estimations. These estimations only include the direct consumption of reactors, thus excluding contributions from other unit operations such as separations and pumping. However, this approach is considered to be appropriate for the purposes of this study as previous LCA studies of ILs[128] have indicated that in most cases the large number of precursors, i.e. raw materials, are the main contributors to their environmental impacts. The co-products were credited to the system, e.g. hydrochloric acid, sodium chloride and lithium chloride, and the organic waste was assumed to be treated in a wastewater treatment plant. All the background data for the raw materials, energy systems and waste management processes were sourced from the Ecoinvent database[52]. Only butyl chloride, hexyl chloride and decyl chloride have been simulated with a proxy, as there are no processes related to them in the LCA databases.

The environmental impacts were estimated with the CML-IA impact assessment method[129]. The carbon footprint and toxicity effects of ILs are often questioned when proposed as greener alternatives to conventional organic solvents, and therefore of paramount importance when designing new ILs. For this reason, this study focused on GWP and the toxicity impact categories human toxicity potential (HTP), freshwater aquatic ecotoxicity potential (FAETP), marine aquatic ecotoxicity potential (MAETP) and terrestrial ecotoxicity potential (TETP), which are the only results presented and analysed here. However, the other environmental impact results for all ILs studied here can be found in Tables A7 – A9 in Annex A.

Table 3.8 – Raw materials, co-products and waste inventory for the production of imidazolium chloride ILs.

Synthesis step	**Reactants**	**Co-products and waste**	**[Hmim] Cl**	**[C$_2$mim] Cl**	**[C$_4$mim] Cl**	**[C$_6$mim] Cl**	**[C$_{10}$mim] Cl**	**[Amim] Cl**	**[PhC$_2$mim] Cl**	**[C$_4$dmim] Cl**
			Quantity (g/mol IL)							
Ring formation	Glyoxal		96	97	97	97	97	97	97	97
	Ammonia		56	57	57	57	57	57	57	57
	Formaldehyde		50	50	50	50	50	50	50	-
	Acetaldehyde		-	-	-	-	-	-	-	74
		Water	76	77	77	77	77	77	77	77
		Organic waste	30	31	31	31	31	31	31	34
Methylation	1H-imidazole		96	97	97	97	97	97	97	-
	2-methylimidazole		-	-	-	-	-	-	-	117
	Methyl chloride		71	72	72	72	72	72	72	72
		Hydrogen chloride	40	40	40	40	40	40	40	40
		Organic waste	37	37	37	37	37	37	37	42
Alkylation	1-Methylimidazole		-	91	91	91	91	91	91	-
	1,2-Dimethylimidazole		-	-	-	-	-	-	-	107
	Ethyl chloride		-	93	-	-	-	-	-	-
	Butyl chloride		-	-	134	-	-	-	-	134
	Hexyl chloride		-	-	-	174	-	-	-	-
	Decyl chloride		-	-	-	-	255	-	-	-
	Allyl chloride		-	-	-	-	-	110	-	-
	Benzyl chloride		-	-	-	-	-	-	183	-
		Organic waste	-	23	33	42	62	27	44	33

Table 3.9 – Raw materials, co-products and waste inventory for the production of imidazolium (a) tetrafluoroborate and (b) hexafluorophosphate ILs.

Synthesis step	**Reactants**	**Co-products and waste**	**[Hmim] Cl**	**[C_2mim] Cl**	**[C_4mim] Cl**	**[C_6mim] Cl**	**[C_{10}mim] Cl**	**[Amim] Cl**	**[PhC_2mim] Cl**	**[C_4dmim] Cl**
			Quantity (g/mol IL)							
Anion exchange $[BF_4]^-$	Imidazolium chloride		90	161	192	223	284	174	229	207
	Sodium tetrafluoroborate		121	121	121	121	121	121	121	121
		Sodium chloride	58	58	58	58	58	58	58	58
		Organic waste	19	25	28	31	36	27	32	30
Anion exchange $[PF_6]^-$	Imidazolium chloride		90	161	192	223	284	174	229	207
	Lithium hexafluorophosphate		167	167	167	167	167	167	167	167
		Lithium chloride	42	42	42	42	42	42	42	42
		Organic waste	23	30	32	35	41	31	36	34

Table 3.10 – Energy consumption data for the production of imidazolium-based ILs.

Synthesis step	**Type of energy**	**[Hmim] Cl**	**[C_2mim] Cl**	**[C_4mim] Cl**	**[C_6mim] Cl**	**[C_{10}mim] Cl**	**[Amim] Cl**	**[PhC_2mim] Cl**	**[C_4dmim] Cl**
		Quantity (MJ/mol IL)							
Ring formation	Cooling	1.71	1.73	1.73	1.73	1.73	1.73	1.73	1.60
Methylation	Heating	-	-	-	-	-	-	-	0.03
	Cooling	0.16	0.16	0.16	0.16	0.16	0.16	0.16	-
Alkylation	Heating	-	1.95	2.15	2.09	2.38	1.33	1.42	2.15
Anion exchange $[BF_4]^-$	Heating	6.13	6.13	6.13	6.13	6.13	6.13	6.13	6.13
Anion exchange $[PF_6]^-$	Heating	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00

3.4.2. Results and discussion

The results of all imidazolium chloride ILs were analysed first in order to focus on the contributions from the cationic part of the molecule, followed by the results for the imidazolium tetrafluoroborates and the imidazolium hexafluorophosphates to look at the anion contributions. First the GWP results are presented, while HTP, FAETP, MAETP and TETP results are presented later.

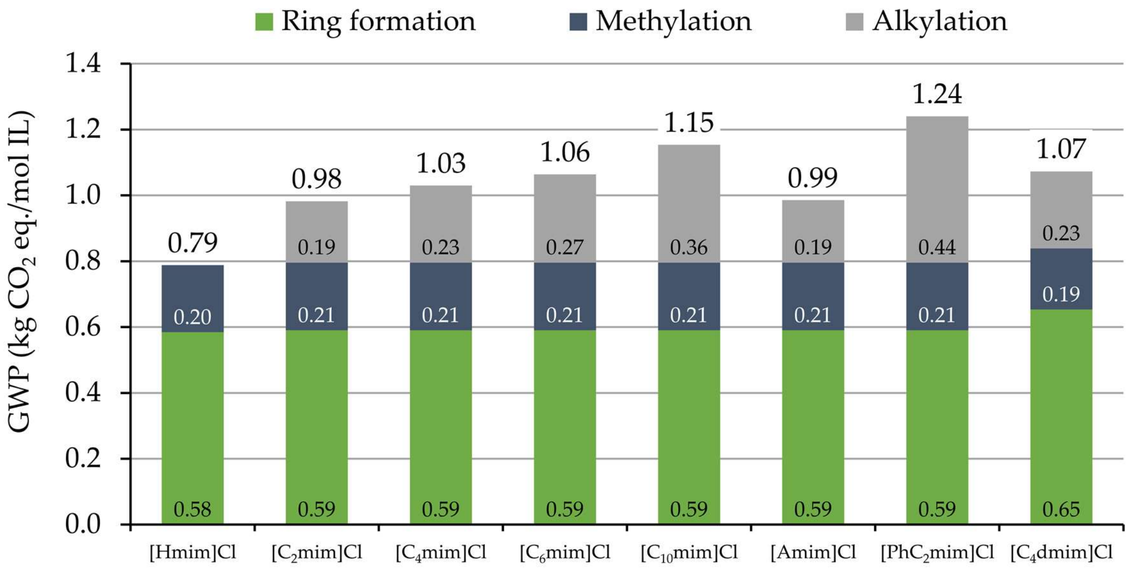


Figure 3.17 – GWP of imidazolium chloride ILs, showing synthesis steps contributions.

The GWP results of all the imidazolium chloride ILs are presented in Figure 3.17. As it can be observed, the estimated total GWP for these ILs ranges from 0.79 kg CO_2 eq./mol to 1.24 kg CO_2 eq./mol. The formation of the imidazole ring is responsible for the majority of the impact, contributing between 47% and 74% of the total GWP mainly due to the use of glyoxal. In the particular case of [Hmim]Cl, the ring formation step contributes the highest (74%) because this IL only has one substituent and therefore requires two synthesis steps. This is also the reason why it has the lowest GWP (0.79 kg CO_2 eq./mol), i.e. requires less reagents overall.

Figure 3.17 also shows that the GWP of the ring formation step for IL [C_4dmim]Cl is 10% higher compared to the other ILs. This is because of the use of acetaldehyde instead of formaldehyde, which is needed to obtain the three alkyl substituents.

The GWP of the methylation step is estimated around 0.20 kg of CO_2 eq./mol for all imidazolium chloride ILs under study, as this step is the same for all, i.e. all precursors react with methyl chloride to produce 1-methylimidazole or 1,2-dimethyilimidazole in the case of [C_4dmim]Cl. Consequently, the slight variations between these values are due to yield differences and corresponding energy requirements. This step contributes between 17% and 26% of the total GWP impact, and the use of methyl chloride is responsible for the significant contributions from this synthesis step.

With the exception of [Hmim]Cl, the alkylation step is the second hotspot for all ILs and contributes with 19% to 36% of the total GWP results. It can be inferred that the magnitude of the environmental impacts of the imidazolium chloride ILs studied here, will depend on the alkylation step as each IL will require a specific alkyl halide, which in turn will have different environmental burdens depending on their production, e.g. presence of aromatics, length of alkyl chain. For example, [C_{10}mim]Cl and [PhC_2mim]Cl have the highest GWP reported at 1.15 kg CO_2 eq./mol and 1.24 kg CO_2 eq./mol, respectively, mainly because of the use of decyl chloride (0.25 kg CO_2 eq./mol) and benzyl chloride (0.40 kg CO_2 eq./mol) in their alkylation step. [C_2mim]Cl, on the other hand, has a total GWP of 0.98 kg CO_2 eq./mol as it used ethyl chloride (0.09 kg CO_2 eq./mol). Therefore, the side chain variations obtained during the alkylation step can potentially be considered the most influential step in the overall GWP of imidazolium-based ILs.

The effect that the number of substituents on the imidazole ring has on the GWP of imidazole-based ILs was also studied using 1-butyl-3-methyilimidazolium chloride ([C_4mim]Cl) and 1-butyl-2,3-dimethyilimidazolium chloride ([C_4dmim]Cl) as an example, as they have two and three substituents, respectively. In addition, both ILs use the same alkyl halide (butyl chloride) in the alkylation step. The GWP results for these ILs are estimated at 1.03 kg CO_2 eq./mol and 1.07 kg CO_2 eq./mol. Although the use of formaldehyde and acetaldehyde in the ring formation step is the main cause for the difference in their GWP impacts, the number of substituents plays a negligible effect in the overall GWP of these two ILs as there is a difference of 3%. It was also observed that the presence of a double bond in any of the side chains does not seem to influence the GWP of the ILs. For example, the GWP of 1-allyl-3-methyilimidazolium chloride ([Amim]Cl), which contains a three carbon unsaturated substituent, is estimated at 0.99 kg CO_2 eq./mol. This value sits between the GWP results for [C_2mim]Cl at 0.98 kg CO_2 eq./mol and [C_4mim]Cl estimated at 1.03 kg CO_2 eq./mol, which have a two and four carbon saturated substituents, respectively.

The contributions from the anion exchange step are shown in Figure 3.18 for both the tetrafluoroborate ($[BF_4]^-$) and hexafluorophosphate ($[PF_6]^-$) anions. The imidazolium chloride ILs are the precursors for the preparation of the corresponding imidazolium tetrafluoroborate and imidazolium hexafluorophosphate ILs shown in Figure 3.18. According to these results, the GWP of the resulting ILs is 2 and 4 times higher when substituting the chloride anion with $[BF_4]^-$ and $[PF_6]^-$ anions, respectively. This is because an equimolar amount of salt (with respect to the imidazolium chloride precursor) is required in the anion exchange step, and these particular anions are derived from salts with considerably high carbon footprints. For example, the GWP of sodium tetrafluoroborate and lithium hexafluorophosphate salts are reported at 10.3 kg CO_2 eq./kg and 19.3 kg CO_2 eq./kg, respectively[52]. The contributions from this step will largely depend on the environmental burdens of the salts or other chemicals used to obtained the desired anions. Therefore, given the great influence this step has over the total GWP impact of imidazole ILs, special consideration should be given to the selection and sourcing of the anion. The use of LCA databases can help when considering the latter.

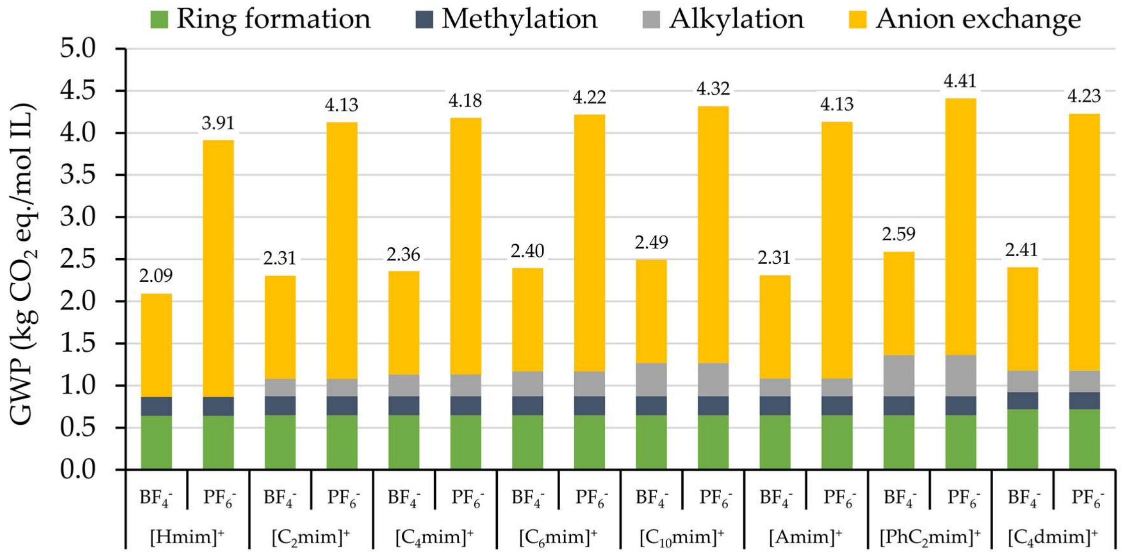
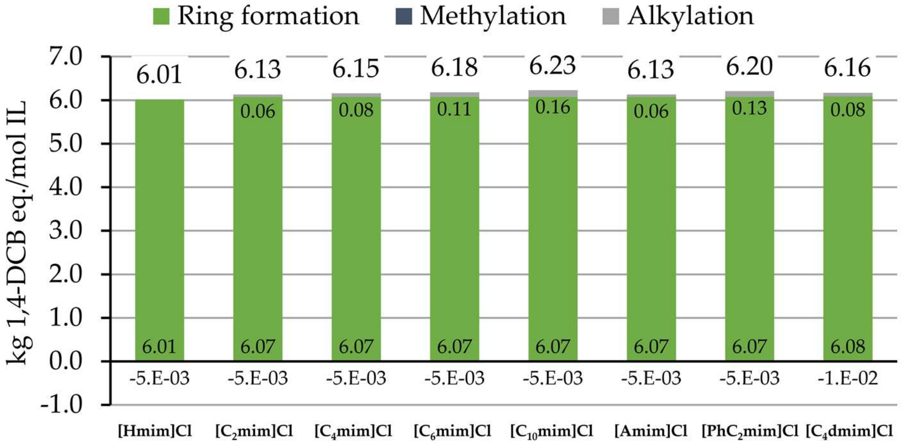


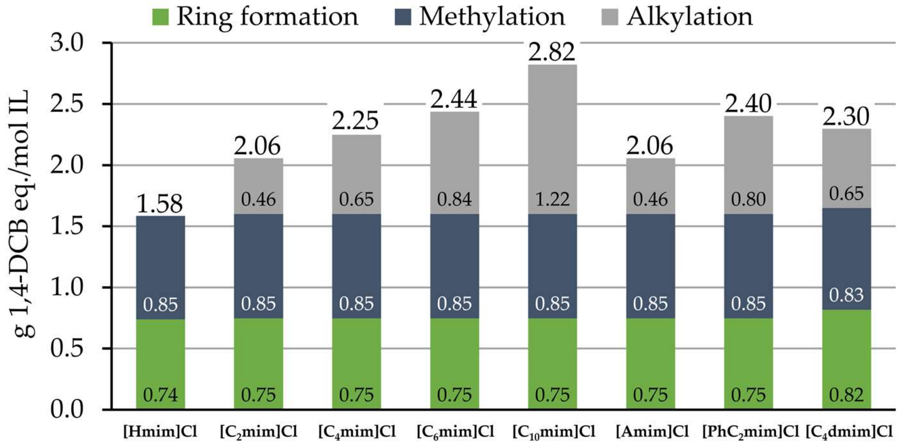
Figure 3.18 – GWP of imidazolium tetrafluoroborate and imidazolium hexafluorophosphate ILs, showing synthesis steps contributions including the anion exchange.

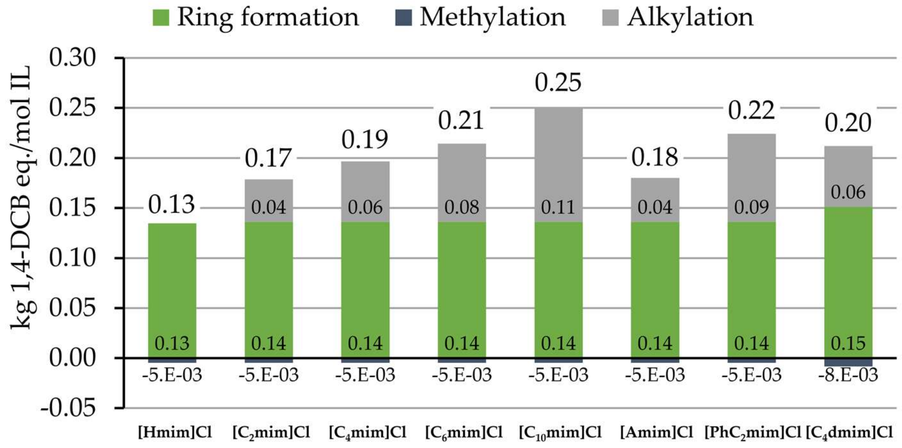
The results for the toxicity impact categories are presented in Figure 3.19, with the contributions from the anion exchange step shown in Figure 3.20. The HTP results presented in Figure 3.19a indicate that the formation of the imidazole ring is the dominating synthesis step under this category as it contributes with over 98% of the total impact. This is largely due to the production of glyoxal via the oxidation of ethylene oxide, as it releases toxic emissions of ethylene oxide to water and air, a well-known genotoxic substance[130]. Although the contributions from the alkylation step differs between ILs, the differences can be considered negligible under this impact category and the HTP results for all imidazole chloride ILs is estimated around 6 kg 1,4-DCB eq./mol.

Figure 3.19b presents the TETP results of the studied ILs, and this is calculated between 1.58 g 1,4-DCB eq./mol and 2.82 g 1,4-DCB eq./mol. As it can be observed, the contributions from the different synthesis steps are more evenly distributed compared to the rest of the impacts, with the methylation step contributing the highest between 30% and 53% of the total impact. This is followed by the ring formation with 26% and 47% of the total impacts, and the alkylation step influencing with 22% and 43% of the total TETP.

The FAETP and MAETP impact results are presented in Figure 3.19c and 3.19d and are estimated at 0.13 – 0.25 kg 1,4-DCB eq./mol and 0.38 – 0.70 t 1,4-DCB eq./mol, respectively. Very similar trends can be observed for this two impact categories, where the ring formation is the predominant step, contributing between 54% and 75% of the total impacts of the ILs. The alkylation step contributes around 24% and 45%, depending on the length of the chain. For example, ethyl chloride and decyl chloride used in the preparation of [C_2mim]Cl and [C_{10}mim]Cl have the lowest and highest contributions, respectively. The methylation step, on the other hand, causes a negligible effect under these impact categories. This is because of the co-production of hydrochloric acid, which is credited to the system and therefore showing a net-negative impact in the case of FAETP and minimal contribution for MAETP. In the case of [Hmim]Cl, the ring formation step contributes >98% of the impacts as there is no alkylation step and the contributions from the methylation step are negligible as previously explained.


(a) Human toxicity potential (HTP)


(b) Terrestrial ecotoxicity potential (TETP)


(c) Freshwater aquatic ecotoxicity potential (FAETP)

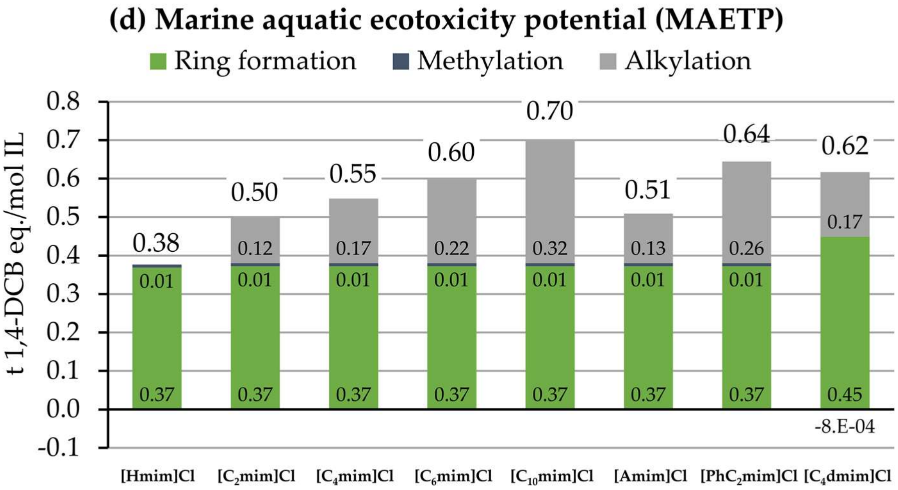
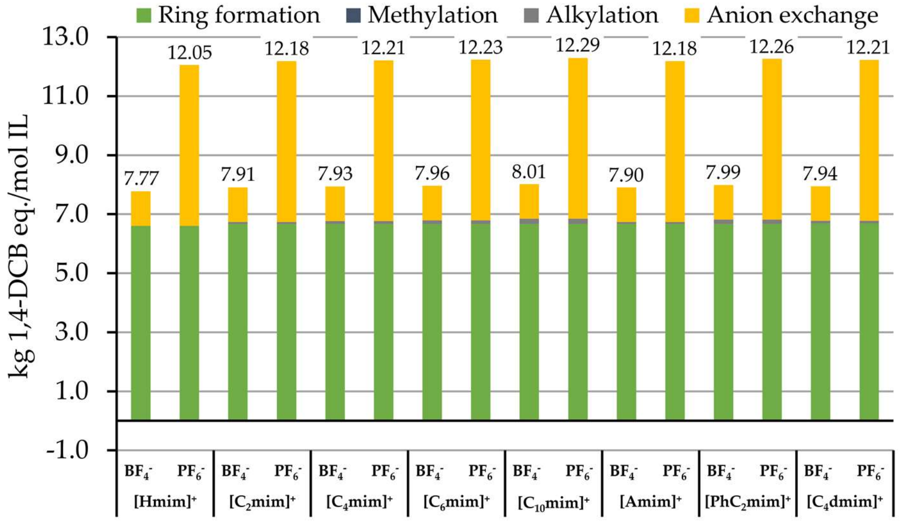


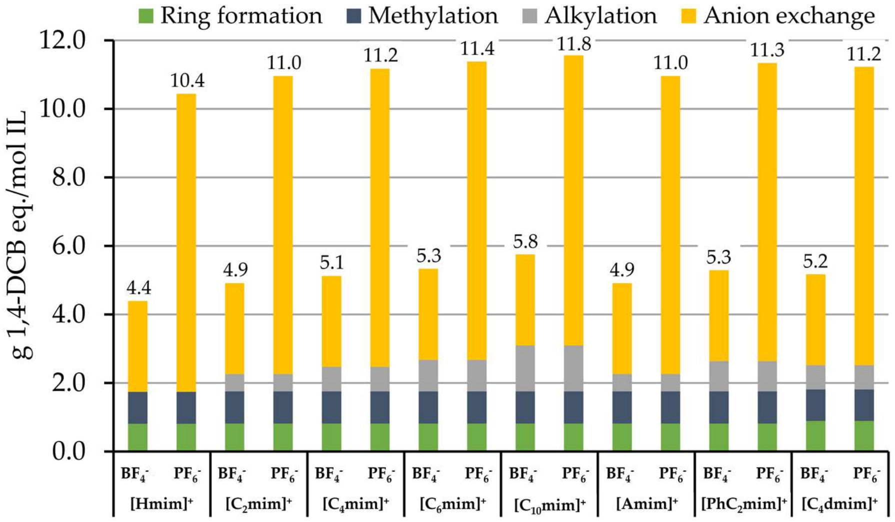
Figure 3.19 – (a) HTP, (b) TETP, (c) FAETP and (d) MAETP impact results of imidazolium chloride ILs, showing synthesis steps contributions.

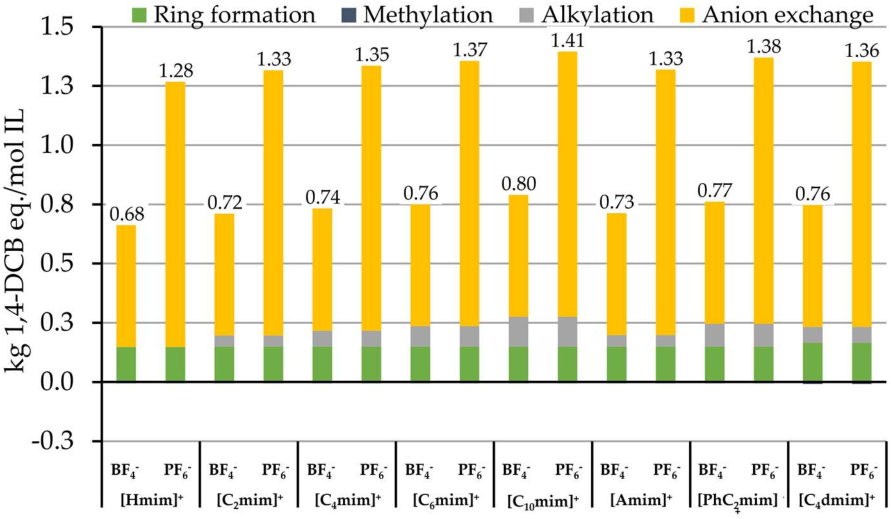
The results presented in Figure 3.19 also indicate that the use of alkylation agents with longer chains or aromatic chains will cause higher contributions to the overall toxicity of the IL. In this case, it is observed that the use of decyl chloride and benzyl chloride causes the highest contributions among all toxicity impact categories. However, it is also observed that decyl chloride has higher toxicity impacts than benzyl chloride, because its molecular weight is higher and therefore a greater amount is required for the alkylation step.

Figure 3.20 shows the toxicity results with the inclusion of the anion exchange step. As it can be observed, the use of sodium tetrafluoroborate and lithium hexafluorophosphate salts causes significant increases to the total toxicity impacts of the ILs. For example, the impact results of imidazolium tetrafluoroborate ILs for HTP, TETP, FAETP and MAETP are around 1.3, 2, 4 and 17 times higher compared to their corresponding imidazolium chloride counterpart. For the imidazolium hexafluorophosphate ILs, these are approximately 2, 5, 7 and 104 times higher.

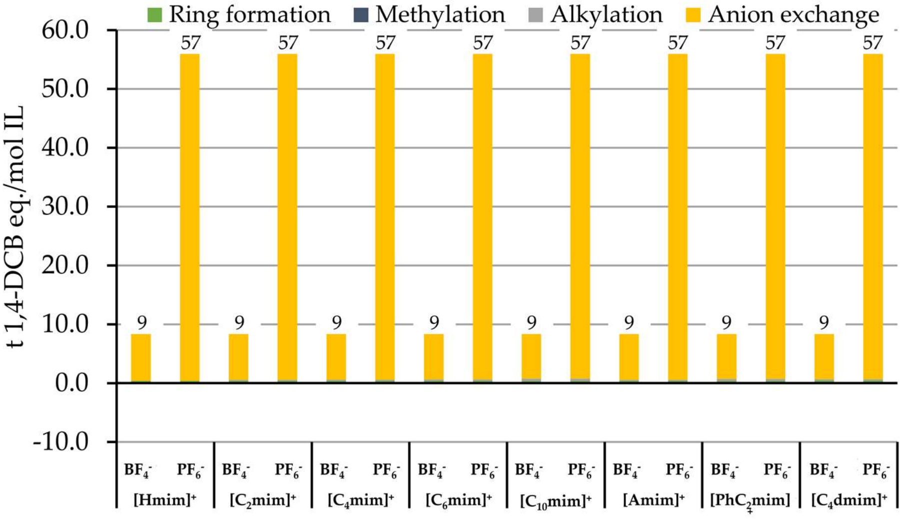
The total impact results for TETP, FAETP and MAETP are predominantly driven by the anion exchange step due to the choice of anion, whilst for HTP, the ring formation step continues to be the major contributor for all imidazolium tetrafluoroborate ILs. Similar to GWP, the $[PF_6]^-$ anion causes higher environmental impacts across all toxicity impact categories. This is due to emissions that occur in its production chain, in particular hydrogen fluoride in air, whose toxic characteristics are documented[131]. This intrinsic toxicity of lithium hexafluorophosphate is increased by the fact that this salt has a higher molecular weight and must therefore be used in greater quantities than the respective tetrafluoroborate salt.


(a) Human toxicity potential (HTP)


(b) Terrestrial ecotoxicity potential (TETP)



(c) Freshwater aquatic ecotoxicity potential (FAETP)

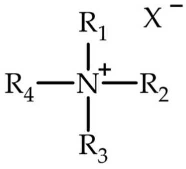


(d) Marine aquatic ecotoxicity potential (MAETP)

Figure 3.20 – (a) HTP, (b) TETP, (c) FAETP and (d) MAETP impact results of imidazolium tetrafluoroborate and imidazolium hexafluorophosphate ILs, showing synthesis steps contributions including the anion exchange.

In order to conduct a validation assessment of the results, two ammonium-based ILs, tetrabutylammonium chloride ([Bu_4N]Cl) and trihexylmethylammonium chloride ([N_{6661}]Cl), were included in the study. These are summarised in Table 3.11.

Table 3.11 – Selected sample of ILs from the ammonium head group.

Molecular structure	**R_1**	**R_2**	**R_3**	**R_4**	**X^{-} [a]**	**Name of IL**	**Abbreviate**
	Butyl	Butyl	Butyl	Butyl	Cl^-	Tetrabutyl-ammonium	$[Bu_4N]Cl$
	Hexyl	Hexyl	Hexyl	Methyl	Cl^-	Trihexylmethyl-ammonium	$[N_{6661}]Cl$

[a] Anions $[BF_4]^-$ and $[PF_6]^-$ were also considered in this study.

The synthesis pathway for the ammonium ILs can be divided in three main reaction steps. These include the tertiary amine formation, followed by the alkylation and finally the anion exchange. The same anions Cl^-, BF_4^- and PF_6^- were considered here for consistency. The first step consists of the alkylation of aqueous ammonia with an alcohol to form a tertiary amine. Butanol and hexanol were used in this case to produce $[Bu_4N]$ and $[N_{6661}]$, respectively (eq. 3.8 in Annex A). The reaction is carried out in aqueous solution at 135°C with an excess of alcohol and with a yield of 80%[132]. In the second step, the tertiary amines react with an excess of alkyl chlorides to form the quaternary ammonium salts (eq. 3.9 in Annex A). This reaction is commonly known as the Menshutkin reaction and is carried out in an aqueous solution at 100°C, with a yield of 97.5%[133]. In this step butyl chloride and methyl chloride where used to produce tetrabutylammonium chloride ($[Bu_4N]Cl$) and trihexylmethylammonium chloride ($[N_{6661}]Cl$), respectively. Lastly, the anion exchange takes place following the same steps described above[124], as the same reagents were used, e.g. sodium tetrafluoroborate or lithium hexafluorophosphate, under the reaction conditions to produce $[Bu_4N][BF_4]$, $[N_{6661}][BF_4]$, $[Bu_4N][PF_6]$ and $[N_{6661}][PF_6]$ (eq. 3.10 in Annex A). The generic life cycle tree for these ILs is shown in Figure A4 and the inventory data for the production of these ILs can be found in Table A10, both in Annex A.

As in the previous discussion of imidazolium ILs results, the GWP will be analysed first and then the toxicity impacts. However, for reasons of space, the discussion will only focus on ammonium tetrafluoroborates and ammonium hexafluorophosphates ILs.

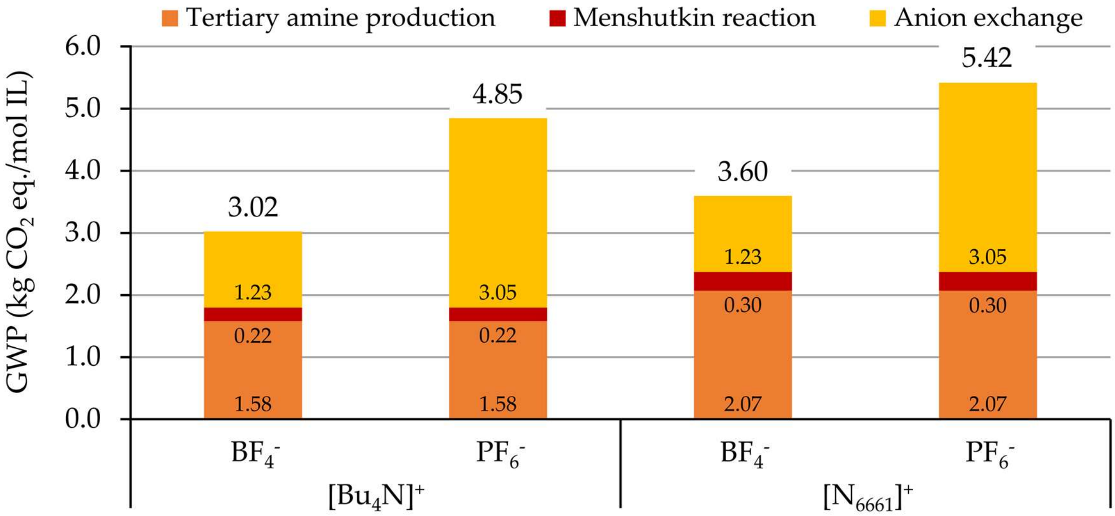


Figure 3.21 – GWP of ammonium tetrafluoroborate and ammonium hexafluorophosphate ILs, showing synthesis steps contributions.

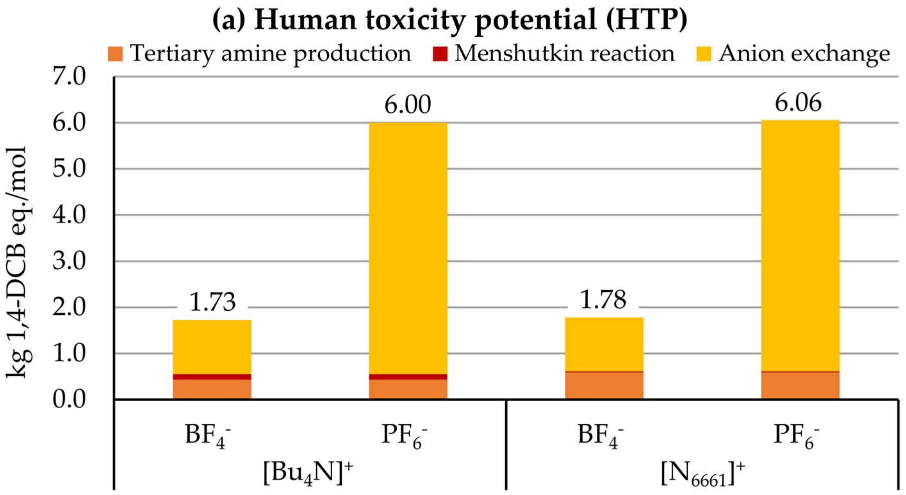
The GWP results of ammonium ILs (Figure 3.21) show that they range from 3.02 kg CO_2 eq./mol of $[Bu_4N][BF_4]$ to 5.42 kg CO_2 eq./mol of $[N_{6661}][PF_6]$. The lightest step in terms of GHG emissions is the Menshutkin reaction, which accounts for 4 – 8% of the impact of ILs, while tertiary amine production and anionic exchange share the rest of the responsibility almost equally. In particular, the production of tertiary amines is the step with the highest contribution for tetrafluoroborate ILs (52 – 58%), while anionic exchange for hexafluorophosphate ILs (56 – 63%). The GWP of the tertiary amine production is higher for trihexylamine, since hexanol is used for its synthesis instead of butanol used for tributylamine. The two alcohols are simulated with the same database process, but as the hexanol has a higher molecular weight, a greater amount of reagent is needed to achieve the same molar amine production. This, and a small difference in reaction heat, makes the production of trihexylamine 30% heavier for the environment.

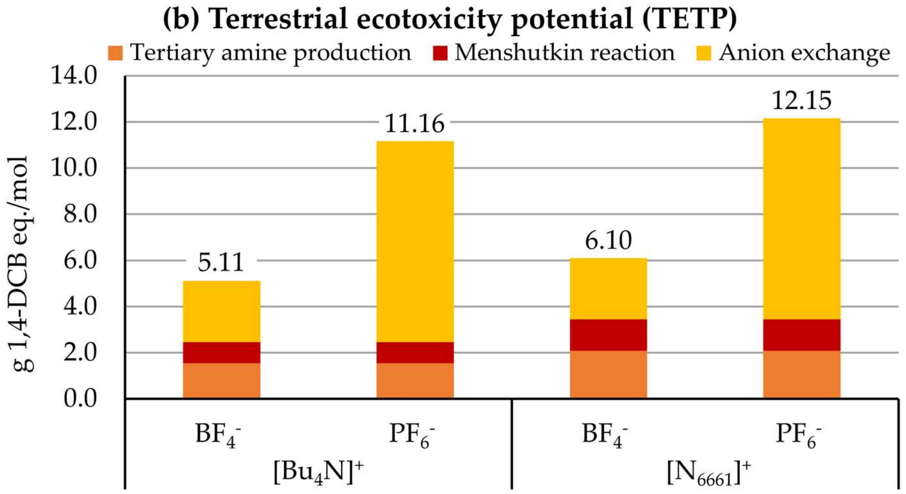
The GWP impacts of the second step, the Menshutkin reaction, are mainly caused by the alkyl chlorides used to obtain the two ILs, butyl chloride for the $[Bu_4N]^+$ and methyl chloride for the $[N_{6661}]^+$. Since methyl chloride is more impacting than butyl chloride (3.2 vs 1.0 kg CO_2 eq./kg) it results that also in this case the greater weight is the IL of trihexylmethyl, about +40% compared to the IL of tetrabutyl.

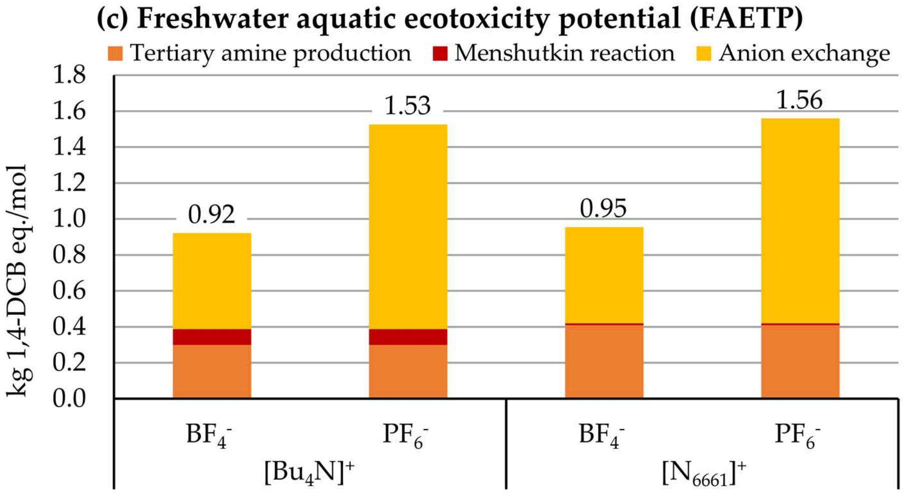
Figure 3.21 also shows that the GWP impact per mole of the anion exchange step is the same as for the imidazolium ILs, 1.23 kg CO_2 eq./mol for tetrafluoroborate and 3.05 kg CO_2 eq./mol. This is because the molar quantity of the anions is the same in both cases, in order to obtain the same FU of product, i.e. 1 mol of IL.

In this case, compared to the previous one, the IL synthesis pathways use different reagents for all reaction steps, so it is not possible to identify which step is the most influential for the GWP impacts of ammonium based ILs. However, what can be seen, is that moving from short-chain substituents (such as $[Bu_4N]^+$) to substituents with the longer chain ($[N_{6661}]^+$) the total impact of the IL increases. As stated, this is due to the higher molecular weight of this type of substituents, which results in a higher mass demand for reactions.

Figure 3.22 shows the results of the assessment for the toxicity impact categories: HTP, TETP, FAETP and MAETP. In all categories the anion exchange step is primarily responsible for the impacts and, as the shown in the previous ILs family analysis, this is due to emissions to air that occur during the production of the salts needed for the anion exchange.


(a) Human toxicity potential (HTP)
Tertiary amine production
Menshutkin reaction
Anion exchange
kg 1,4-DCB eq./mol
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.73
6.00
1.78
6.06
BF_4^-
PF_6^-
BF_4^-
PF_6^-
$[Bu_4N]^+$
$[N_{6661}]^+$


(b) Terrestrial ecotoxicity potential (TETP)
Tertiary amine production
Menshutkin reaction
Anion exchange
g 1,4-DCB eq./mol
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
5.11
11.16
6.10
12.15
BF_4^-
PF_6^-
BF_4^-
PF_6^-
$[Bu_4N]^+$
$[N_{6661}]^+$


(c) Freshwater aquatic ecotoxicity potential (FAETP)
Tertiary amine production
Menshutkin reaction
Anion exchange
kg 1,4-DCB eq./mol
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.92
1.53
0.95
1.56
BF_4^-
PF_6^-
BF_4^-
PF_6^-
$[Bu_4N]^+$
$[N_{6661}]^+$

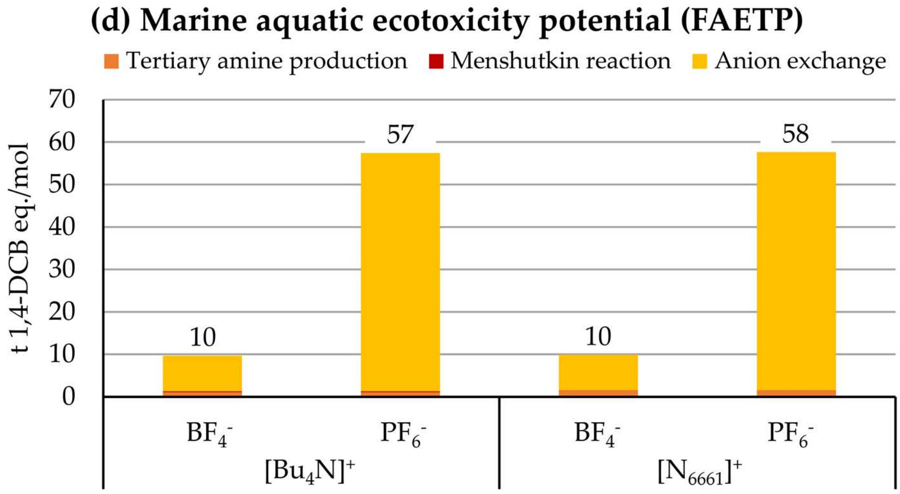


Figure 3.22 – (a) HTP, (b) TETP, (c) FAETP and (d) MAETP impact results of ammonium tetrafluoroborate and ammonium hexafluorophosphate ILs, showing synthesis steps contributions.

The category in which the weight of the anion exchange is greater is the MAETP (Figure 3.22d), where the impacts are calculated between 10 ton CO_2 eq./mol and 58 ton CO_2 eq./mol. Here the contribution of the anion exchange step varies between 85% and 98% of the total impact. The production of tertiary amine is responsible for the other part of impacts, while the reaction of Menshutkin produces a negligible impact (up to 3% of the total).

In the HTP category (Figure 3.22a) anion exchange is also dominant, covering 66% to 91% of ILs impacts. In this category the results, ranging from 1.73 kg CO_2 eq./mol to 6.06 kg CO_2 eq./mol, are also significantly influenced by tertiary amine production, whose maximum contribution to the total is 33%.

The TETP impacts (Figure 3.22b) estimated at 5.11 – 12.11 g CO_2 eq./mol are those in which the Menshutkin reaction step produces the highest impact, from 8% to 22% of the total impact of ILs. The cause of this weight lies in mercury emissions from the alkyl halide production chain. In this category, the impacts are more distributed among the synthesis formation, especially for tetrafluoroborate ILs.

The contribution of the tertiary amine production step ranges from 14% to 34% and that of anion exchange from 44% to 78%.

Finally, Figure 3.22c shows the FAETP impacts of the analysed ILs, ranging from 0.92 kg CO_2 eq./mol to 1.56 kg CO_2 eq./mol. The tertiary amine production step has its maximum weight in this category, contributing from 20% to 43% to the total impacts of ILs. However, anionic exchange remains the most impacting step (58% – 75%) and the Menshutkin reaction has contributions between 1% and 10%.

3.4.3. Conclusions

This work has been designed to identify potential environmental impact trends in ILs. The final aim is to obtain, if any, a mapping of such impacts in order to create a predictive model of environmental analysis. In this way it would be possible to predict the environmental performance of new ILs from their structure.

To do this, a family of ILs with as many different characteristics associated with the same basic structure has been selected. The purpose of this choice is to attempt to assign to each characteristic (such as the presence of double bonds, aromatic rings or simple aliphatic chains) the corresponding environmental impact. To meet this aim, the group contribution method, already used in chemistry for the prediction of the thermodynamic and rheological properties of substances, has been adopted. In this study, for the first time to our knowledge, this method is applied to the investigation of environmental impacts. For these reasons, the choice has fallen on imidazolium-based ILs, since they are already widespread and present with various structures depending on their use. In particular, eight molecules with imidazolium head group were chosen for this study, which differ in number, type and length of imidazolium ring substituents.

Moreover, three different counterions were considered (Cl^-, BF_4^- and PF_6^-), in order to also evaluate the weight and characteristics of the anionic part of the molecules. The impacts are calculated, from a life cycle perspective through the application of the LCA methodology, in the GWP category (the most widespread in environmental analysis) and in toxicity, being one of the critical points of ILs.

In general, the results, calculated on the production per mole of IL, show that the anionic exchange step (from Cl^- to BF_4^- and PF_6^-) is the most impacting on both GWP and almost all toxicity categories. This is due to the high demand for salts of the step (tetrafluoroborate and hexafluorophosphate respectively), which are needed in equimolar quantities compared to the IL precursors. On the other hand, looking at the structure of the cationic part, the analysis shows that environmental impacts depend more on the formation of the imidazole ring than on subsequent additions of substituents. Nevertheless, in the comparison between ILs, and in line with the purpose of the study, what is most interesting are the impacts of the alkylation reactions. This is where the main differences between the eight selected molecules lie. These results show that, when considering the same type of substituent, the environmental impact increases with the molecular weight of the substituent. The reason for this trend, in addition to the nature of alkyl halide, is that all molecules need the same reagent molecules to perform alkylation, so the heavier the alkyl halide, the greater the amount (in mass) needed. Consequently, the greater the substituent to be added, the greater its impact in terms of GWP and toxicity.

In order to find the first confirmation of the results, the environmental performance of two ammonium-based ILs, chosen with the same criteria as the previous ones, were also analysed. These are tetrabutylammonium and trihexylmethylammonium, which are included in the study to evaluate the weight that the length of the substituents has on the impacts of ammonium head group ILs. Overall, the results are in line with the previous ones, anionic exchange remains the weakest link in the environmental assessment and the IL with the heavier substituents is the one with the greatest environmental impacts (with the same moles production).

Therefore, the environmental results of the two families of ILs seems to go in the same direction, but to obtain a definitive map and to make more reliable considerations it is necessary to continue the research started with this project. Future developments will include the expansion of the sample/data set to include more ILs, the creation of further models for different families and the study of other anions to see if this step has a general major influence.

In conclusion, the results of this study confirm that the LCA methodology is also suitable and useful in the R&D phases of chemical substances. In addition, an AES approach has also been followed in this work, as the assessment of the environmental impacts of ILs based on their structure can become a useful tool for the design of new substances.

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4. Life Cycle Assessment in the primary production

4.1. Background

As emerged from the previous chapter, any environmental analysis of the life cycle of processes is closely linked to the production of raw materials and ends up involving all the previous steps. When synthesis from renewable sources are involved, the necessary biomass for the production of raw materials shows an environmental load that risks to compromise their environmental performance[1-4]. Often this burden comes from the cultivation phases if they are not optimized in terms of impacts. Considering these aspects was necessary in the study of industrial chemical processes and gave me the opportunity to deepen a topic that is at the heart of many SDGs, the environmental assessment of primary production processes.

Primary sector has a central role in the realization of a sustainable future, firstly because it is an area of significant importance for the provisioning of food and then because it is the oldest activity humans have developed that has impacted and modified the environment directly[5] and, at the same time, has been affected by environmental changes[6,7]. In the ongoing research in this field, LCA methodology is recognised as an important scientific tool to predict the environmental impacts, as evidenced by the numerous studies that have been carried out on the subject[8-12]. The incidence of agricultural analyses in LCA research papers has begun to gain more and more ground and now represents about 20% of the total (291 documents out of a total of 1444 relating to the first quarter of 2020)[13].

In this section three projects, carried out during the PhD program, related to this theme will be described. In particular, they address: *i*) environmental sustainability analysis of wineries (in collaboration with the University of

Valencia), *ii*) comparison of different crop rotations (in collaboration with the Universidad Nacional del Litoral, Santa Fe, Argentina) and *iii*) environmental impacts of meals.

4.2. Environmental sustainability analysis of wineries

The term *sustainable agriculture* refers to the agricultural sector based on understanding of ecosystem services that consider all the relationships between organisms and their environment[14]. In general, sustainable agriculture encourages integrated systems that enhance environmental quality and the natural resource base upon which agricultural economy depends and makes the most efficient use of non-renewable resources and water as well. Amongst the many practices that comprise sustainable agriculture, one of the most significant is organic agriculture[15]. It is defined as a "system aiming at producing food with minimal harm to ecosystems, animals or humans"[16], thus avoiding or minimizing the use of synthetically compounded fertilisers, pesticides, growth regulators, and relying upon crop residues, animal and green manures, and mineral-bearing rocks to maintain soil productivity[17] to a maximum extent. In addition, organic agricultural practices are internationally regulated and legally enforced by many nations, thanks to which organic food market has grown rapidly, surpassing the $100 billion mark for the first time in 2018[18].

Organic agricultural practices are applied in the production both of food and beverage, and, among the latter, wineries represent one of the most significant and promising sectors. Nowadays, almost 70% of the wine worldwide commercialized is made in Europe, being France, Italy and Spain the most significant producers[19]. The P.D.O. (Protected Designations of Origin) system is commonly used as a warranty of quality of wine[20,21], but it is not the only one.

Consumers pay attention to certain attributes of the products and have a growing appreciation for some characteristics, such as being organic[22]. However, even if organic, the production of wine, as well as all the anthropogenic activities, is not free of several environmental loads.

The aim of this study is to have an estimation of the life cycle environmental sustainability of wineries by considering different agricultural practices that normally occur. For this purpose, three different vineyards were selected as case studies. On the one hand, two of them (Scenario A and Scenario B) are located in the region of Valencia, within the Utiel-Requena P.D.O., both using organic grape growing methodologies (e.g. using manure and rainfed vines). On the other hand, the third winery (Scenario C) is a smaller vineyard, located in the Tierra de Leon P.D.O. (Castilla y Leon region), which produces grapes following the conventional (non-organic) cultivation methods with low concentration of pesticides.

Attempts to improve the environmental performance of vineyards have usually been mostly focused on energy and water efficiency[23,24] and localized issues such as pesticide reduction[25] and spread[26]. The hypothesis of this study is, therefore, that vine crops that are irrigated and those that have a greater use of pesticides or fertilisers will have a higher ecological footprint than those non-irrigated and without pesticides or fertilisers. The results of this study will guide winemakers towards more sustainable alternatives that translate into reducing the impacts their vineyards cause to the environment.

4.2.1. Methodology

The application of LCA analysis in the sector of wine/winery is not new. Several international studies have confirmed its importance as harmonized tool (stand-alone or combined with other methodologies) to evaluate sustainability within the agricultural[11,27] and winery sectors[28-31], also considering different countries, such as Spain[32,33], Italy[34-36], United States[37] or Canada[38].

In these years, some environmental indicators were identified as the most common indexes to express sustainability within the wine sector, for instance Carbon Footprint (CF)[39,40]. On the other hand, impact categories such as eco-toxicity related to the field emissions of pesticides[41], land use and land use changes[42] or water quality[43] have been less studied due to the lack of data. Here in this manuscript, more than one ecological indicator has been considered with the aim of considering a broader range of impacts.

In this study, a cradle-to-farm gate perspective was applied, including all the processes from the resource extraction (e.g. water) up to the grape production (wine production was voluntary excluded being considered non-relevant). All processes involved in the entire production chain were considered, including the production of energy, chemicals, fertilisers/pesticides, fuels, transportation and machineries application (e.g. tractors). Figure 4.1 depicts a schematic view of the considered system boundaries.

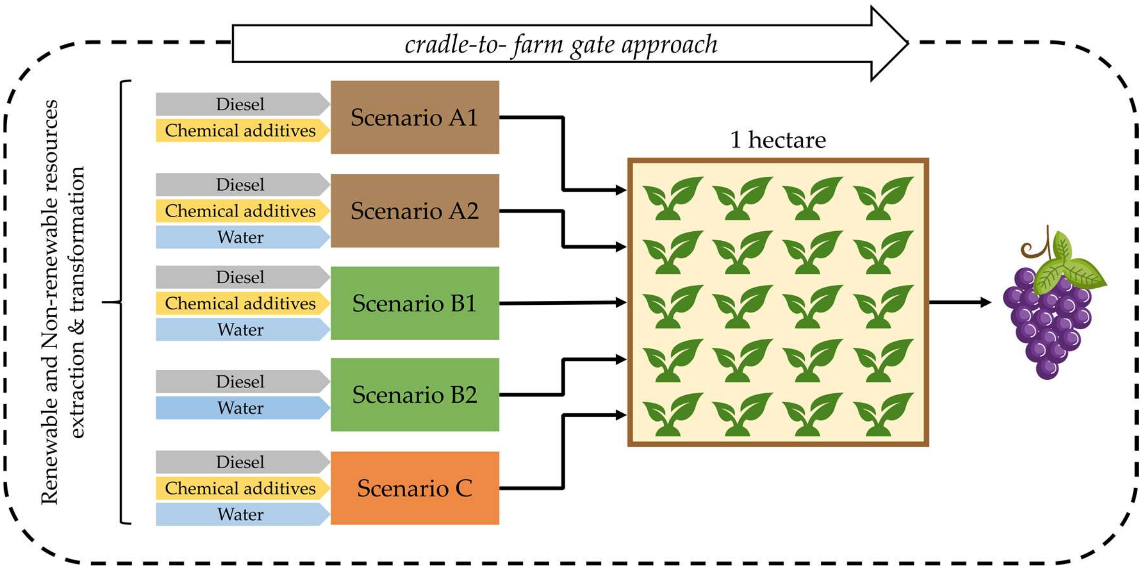


Figure 4.1 – System boundaries of the winery study: cultivation of 1 hectare to produce grapes.

In order to simulate the cultivation procedure, 1 ha of grapevine crop was selected as FU to refer all the input and output flows which characterize the system. This FU was selected to properly understand the contribution of many variables on the total impacts, deriving from different agricultural practices on the same land extension, coherently with the LCA's purpose. Only primary data directly furnished by the farmers' companies were adopted to fill up the LCI of the models. From the data provided by the three wineries, five scenarios were created to analyse the environmental burdens of the different techniques: two from vineyard A to study the impacts of rainfed or irrigated cultivation, two from vineyard B to evaluate the impact of the use of fertilisers or manure and lastly one from vineyard C where a conventional production is analysed to have a benchmark with which to contextualize the environmental results of organic wineries (Figure 4.1).

Table 4.1 summarises the inventories per hectare of the analysed scenarios.

Table 4.1 – Inventory for 1 ha extension of Scenarios.

Substance	Unit	Scenario A1	Scenario A2	Scenario B1	Scenario B2	Scenario C
Water	l	2500	30000	4.9	4.3	1750
Potassium oxide	kg	-	-	0.5	-	-
Copper oxide	kg	1.5	1.5	-	-	270.6
Sulphur	kg	81.9	81.9	55.4	35.7	1.1
Lime algae	kg	-	-	1.1	-	-
Potassium carbonate	kg	1.3	1.3	-	-	-
Glyphosate	kg	-	-	-	-	55.1
Superphosphate	kg	-	-	-	-	300
Dithiocarbamate compounds	kg	-	-	-	-	7.7E-01
Alkylbenzene sulfonate	kg	-	-	-	-	1.5E-01
Boscalid®	kg	-	-	-	-	3.9E-02
Kresoxim methyl	kg	-	-	-	-	1.8E-01
Solid manure	kg	-	-	-	20000	5000

Diesel for machinery	kg	56	56	5.9	5.9	5.6
Diesel for water extraction	kg	-	10.1	-	-	-

The main difference between the scenarios of winery A is that part of their vineyard is rainfed (Scenario A1) and the rest is irrigated (Scenario A2). Scenario A1 requires water only to dissolve and spread the pesticides, so it represents the ideal situation when no irrigation is required, because rain provides sufficient water provision. This will constitute a benchmark to estimate the environmental effects deriving from water extraction and pumping. The vineyard uses copper oxide and sulphur, as inorganic additives, and potassium carbonate (K_2CO_3), which is the main component of Armicarb® (an organic-based pesticide). Since both parts of the vine crops are grown following the same agricultural practices, all inputs are the same except for irrigation water and its extraction costs.

Two different scenarios were created to simulate the different cultivation practices applied in the winery B. In particular, while a bio-based fertiliser, extracted from marine algae (Algagreen®), was used in Scenario B1, animal manure was applied in Scenario B2. Compared to Scenario B2, B1 needs more water (to dissolve pesticides) and sulphur (main component of Cepsul® and Cepsul Oxidant® pesticides) and uses potassium oxide (Aton K® fertiliser) and lime algae (Algagreen® fertiliser). On the other hand, Scenario B2 includes the use of 20 tons of manure per hectare, whose impacts were simulated with the database process called *“Manure, solid, cattle {GLO}| market for | APOS, U”*[44]. We decided to exclude from this process the impacts of feed production because it is given to animals to obtain products (such as meat, milk, fat, etc.), while manure can be considered as waste. The result of a specific analysis on manure (reported in Table B1 in Annex B) show that feed production has a significant weight, so, although the baseline scenario is the one in which it is excluded, the discussion of the results will also consider these impacts.

The inventory of Scenario C, directly completed by the owners, includes the water used to dissolve the main chemical substances such as Grytos® (described in the model as glyphosate), Cuprocol® (copper oxide), Cabriotop® (alkylbenzene sulfonate and dithiocarbamate) and Collis® (defined by processes Boscalid® and Kresoxim-methyl). To simulate the synthesis of Boscalid® and Kresoxim-methyl, the database Ecoinvent processes "*Pyridine-compound {RER}| production | Cut-off, U*" and "*Dinitroaniline-compound {RER}| production | Cut-off, U*"[44] were respectively used, as suggested by a report of the French Environment & Energy Management Agency[45].

4.2.2. Results and discussion

The main results of the impact assessments in terms of ReCiPe midpoint level for all scenarios are shown in Table 4.2.

Table 4.2 – Impacts of all considered scenarios in terms of ReCiPe 2016 Midpoint H/A.

Impact category	**Unit**	**Scenario A1**	**Scenario A2**	**Scenario B1**	**Scenario B2**	**Scenario C**
Global Warming	kg CO_2 eq./ha	60.8	66.3	17.5	251.9	2273.7
Fine Particulate Matter Formation	kg $PM_{2.5}$ eq./ha	2.7E-01	2.9E-01	4.2E-02	2.5E-01	26.8
Human Toxicity	kg 1,4-DCB/ha	696.4	698.0	6.0	53.8	1.3E+05
Water Consumption	m^3/ha	3.1	30.7	0.1	0.7	52.3
Fossil Resource Scarcity	kg oil eq./ha	125.4	137.9	43.9	39.9	630.3

First, each vineyard is discussed separately in order to highlight the inter-scenario differences of Scenarios A and B, then a comparison between the agricultural practices of the three wineries is done.

No significant differences are detected from the two Scenarios A. This is due to the similarities in the cultivation method, which only differ in the use of water for irrigation (Scenario A2) or the lack of it (Scenario A1). The impact category in which these two parts of the vineyard A strongly differs is WC, where the total footprint achieved by the Scenario A1 is one tenth of that of Scenario A2. A contribution analysis confirms that almost all (>97%) of the impact of WC category for Scenario A2 is due to water extraction for irrigation; the rest is embodied water (e.g. energy and fuels production, chemical auxiliaries supply chain, etc.). In order to understand the contribution of the flows in the others categories, a detailed analysis was carried out. In the FRS category, diesel and sulphur are the main factors contributing 55% and 40% of the total impact respectively. The total impact of Scenario A1 (125.4 kg oil eq.) is lower than in the case of Scenario A2 (137.9 kg oil eq.), since in the latter more diesel is used to extract the water and to distribute it amongst the vines. Diesel is the main contributor also to the impact on GW category, accounting for half of the impact both in Scenario A1 and A2. This explains the lower result achieved by Scenario A1 (60.8 kg CO_2 eq.), which does not require energy for extracting and pumping water. Sulphur is responsible for one third of GW's impact because of the crude oil used within its production chain, a further confirmation that GW and FRS categories are strictly related. The impact on FPMF category is similar between the two scenarios (0.27 vs 0.29 kg PM2.5 eq.) and depends on several factors, among which copper oxide, diesel and sulphur are the main culprits. On the other hand, production chain of copper oxide is responsible for more than 97% of the HT impact. In particular, the disposal of sulfidic residues produced during metal extraction is the process that weighs most in terms of HT. In order to understand how much each impact category contributes to the environmental weight of the two scenarios of vineyard A, an endpoint level analysis was conducted (Figure 4.2).

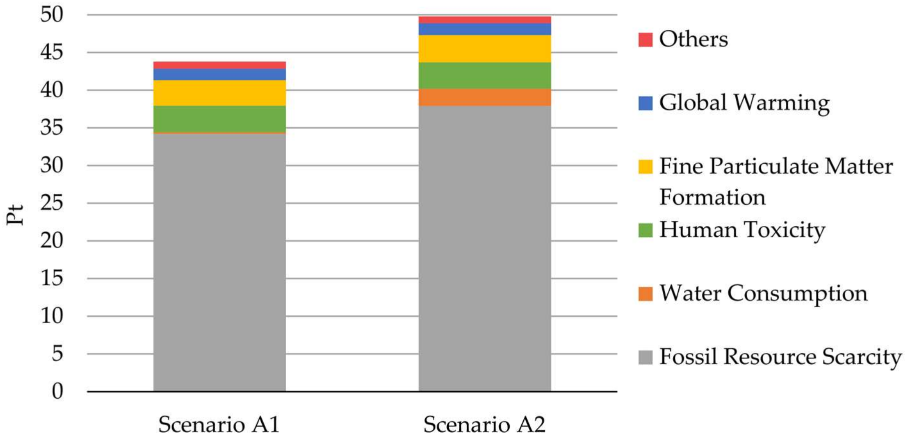


Figure 4.2 – Single Score results for winery A scenarios (ReCiPe 2016 Endpoint H/A).

Scenario A2 has a greater overall impact than Scenario A1. What is new is that the FRS category is primarily responsible for the impacts in both cases, covering over 75% of the impacts. HT and FPMF categories both contribute about 8% of the total impacts of the two scenarios, while the GW category shows less importance by accounting for only 3%. In overall terms, the endpoint analysis indicates that Scenario A1 has an impact -12% compared to Scenario A2 (43.8 Pt vs 49.8 Pt), due to savings in irrigation. This means that the environmental weight of irrigation is to be considered rather limited compared to the overall impact.

As regarding winery B, the results of Table 4.2 show that Scenario B1 has impacts between 7% and 17% compared to Scenario B2, except for the FRS category where its value is higher (if animal feed was considered in manure production, the impact of B2 would be grater). The impacts ascribed to FRS category depend mostly from the supply chain of sulphur. Since in Scenario B1 a greater quantity of sulphur is used, its demand for fossil resources is greater than that of Scenario B2, despite the fact that in the latter the animal manure contributes for 9 kg of oil eq. to the impact of the category. The use of manure has a great impact on the

GW, FPFM and HT of Scenario B2, contributing for >90% of the total impact of the categories. In Scenario B1 the lion's share is taken by sulphur production (GW and FPMF categories) and by the use of diesel for agricultural machinery (HT category). Including feed in manure production would significantly increase its weight but would not change the overall picture. An endpoint analysis has been carried out for this Scenario and the results are shown in Figure 4.3.

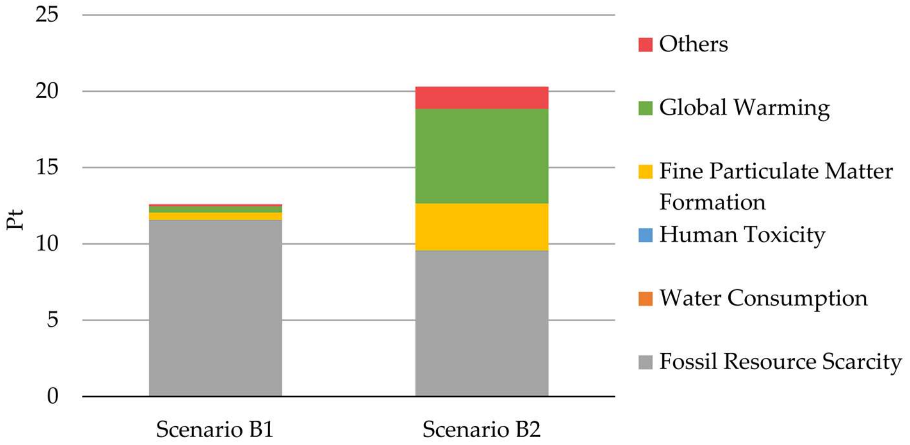


Figure 4.3 – Single Score results for winery B scenarios (ReCiPe 2016 Endpoint H/A).

Scenario B2 has a higher total impact estimated at 20.3 Pt (42.5 Pt if animal feed was included in manure production), while Scenario B1 seems to be more sustainable with a score of 12.6 Pt. The shift from the use of organic fertilisers (Scenario B1) to animal manure (Scenario B2) is therefore quantified in +7.7 Pt. The FRS category is confirmed, as in the case of Scenarios A, to be the critical one for the life cycle of the vineyard, while GW increases its weight (from 3% to 31%) when manure is used. Furthermore, the FPMF and HT categories increase their contribution from Scenario B1 to B2 but remain of secondary importance compared to FRS and GW.

Since the previous analysis shows that animal manure is a product with a high environmental burden that can significantly worsen the impacts of the vineyard, a characterization analysis was carried out on it in order to understand the reason of this characteristic (Figure 4.4).

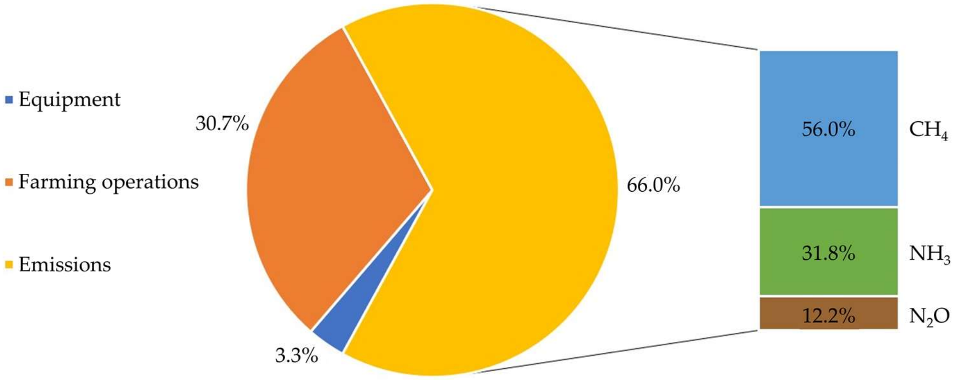


Figure 4.4 – Analysis of impacts of animal manure (ReCiPe 2016 H/A – Single Score).

As it can be observed, most of the impact lies in the emissions that occur when it is spread on the fields. Two thirds of the manure impacts can be attributed to these emissions, but also the farming operations (such as energy and auxiliary materials for lighting, storage and drying of raw materials, manure scraper, slurry agitator, cleaning, drinking water, etc.) show to be a relevant step in environmental assessment since it accounts for the 31% of the impacts. The equipment (which includes wood chips and straw used for animal litter) contribute more moderately to the manure's life cycle and covers only 3% of its impacts. A more detailed analysis of emissions (the weak link of manure) reveals that there are three types of emissions: methane (CH_4), ammonia (NH_3) and dinitrogen monoxide (N_2O), responsible for 56%, 32% and 12% of the impact respectively. If manure production also included the animal feed, its impact would increase by about three times. In this case, therefore, the feed would be responsible for two thirds of the environmental weight, while the other processes would share (in the same proportions shown in Figure 4.4) the remaining one third.

The impacts of Scenario C shown in Table 4.2 are at least one order of magnitude greater than in all other cases. The peak is observed in the HT category, while the FRS is the one where the results are closest to the other scenarios, but still 5-15 times higher. The only exception is the WC category where Scenario C has twice as much impact as Scenario A2 (irrigated cultivation). As in the other cases, the Single Score of the Scenario C have been calculated, shown in Figure 4.5 in a non-cumulative way.

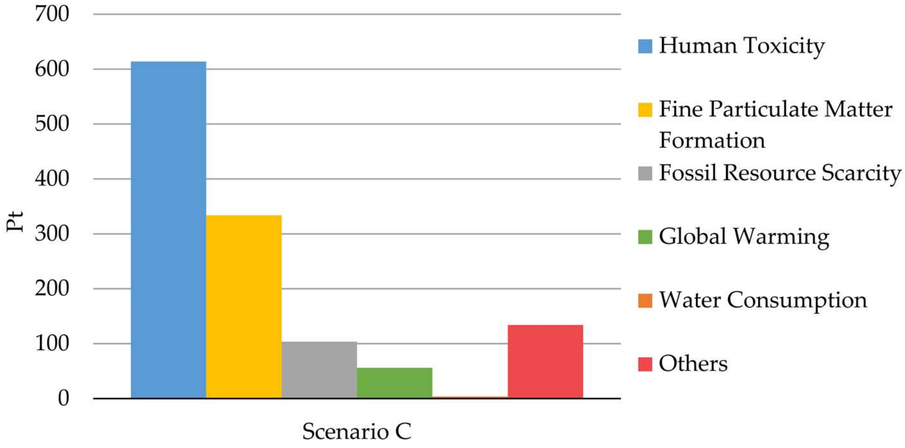


Figure 4.5 – Single Score results for Scenario C (ReCiPe 2016 Endpoint H/A).

HT category is the main contributor, with an impact of 614 Pt it covers about half of the total score (1245.1 Pt). Its high impacts derive almost completely (98%) from the copper oxide (main component of the pesticide Cuprocol®), which also is the main contributor to the other categories, with a weight ranging from 80% to 90%.

Although a comparison between different wineries is not the aim of this study, some considerations are useful to understand which agricultural practices are suggested. For example, a reduction in the use of chemical auxiliaries (especially pesticides) could contribute to reduce the impact on GW category: a CF value lower than 53% was obtained in the case of the Scenario B1, if compared to the value achieved in the case of Scenario A1. However, the values achieved in

Scenario B1 represent only 7% of the whole GWP estimated for the Scenario B2 (17.5 vs 251.9 kg CO_2 eq.), were manure was used to replace synthetic fertilisers and causes the emission problems already discussed. On the other hand, the use of animal manure entails a reduction in the FRS category because it avoids the production of chemical auxiliaries. Without considering the impact of the diesel, the amount of fossil resource needed in Scenario B2 (32.6 kg oil eq.) is 42% lower compared to Scenarios A (56.6 kg oil eq.). The use of manure not only avoids the impacts in the production of chemical auxiliaries, but also is a way of reusing a material that otherwise would be considered as a waste. This represent one of the simplest and oldest, but better, succeeded example of green and circular economy.

Figure 4.6 shows the impacts of all the scenarios, so as to have a clear and immediate overview (Single Scores are reported in Table B2 in Annex B). It is presented with a truncation of the y-axis in order to allow a better visualization of the Scenarios A and B.

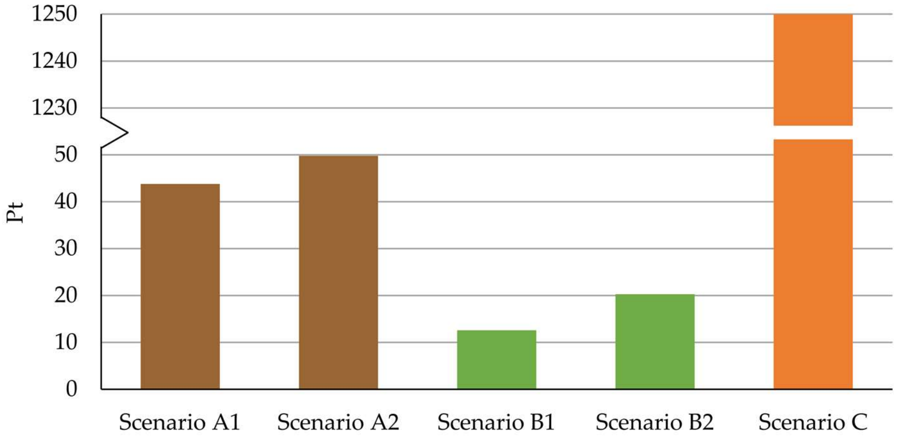


Figure 4.6 – Comparison of vineyards scenarios in terms of ReCiPe 2016 Endpoint H/A – Single Score.

The results indicate that conventional and non-organic agricultural practices (Scenario C) have a much higher environmental impact per hectare than organic vineyards (Scenarios A and B). This huge difference, as seen, lies mainly in the large amount of copper oxide used as a pesticide, which is found to be very impacting on the environment. The comparison between the two organic vineyards, on the other hand, states that winery B pursues greener agricultural practices than winery A, which are less use of sulphur and less use of agricultural machinery. Even when animal manure is used (which raises the GW of the Scenario), the impact of vineyard B remains lower than that of vineyard A, indicating a good environmental robustness of the adopted cultivation techniques. If the impacts of the animal feed were included in manure production process, Scenario B2 would still have a lower score than those of winery A (42.5 Pt vs 43.8 – 49.8 Pt).

4.2.3. Conclusions

Referring to 1 ha of vineyard, organic grapevine crops have proved to be much more sustainable and harmless to the environment and to humans than those considered conventional. In the latter, the use of chemical auxiliaries is common and results in an ecological footprint that can be between 25 and 100 times larger than organic crops. Although the study is carried out in a dry region (Valencia, Spain), and therefore the demand for pesticides is lower than in the wetter regions, it was found that the impact of these chemicals makes conventional vineyards not environmentally competitive compared to organic ones.

When the changing variable between two scenarios was the use of water (vineyard A), irrigated organic vine crops (Scenario A2) have been found to have a larger impact than those rainfed (Scenario A1), even if the difference between the two is not very large (+12.1%). When the changing variable was the use of manure as fertiliser (vineyard B), it was found that fertilised vines (Scenario B1) displayed a lower total impact than those which used manure (Scenario B2).

Although manure is considered an organic fertiliser and brings environmental benefits in some aspects, such as the avoided use of fossil resources for the synthesis of chemical fertilisers, its gas emissions cause a high impact on GW compromising the environmental performance (+38%). This gap increases when the impacts of animal feed in manure production are considered.

Although both wineries produce organic grapes, some aspects could be improved to still ensure that grape production is even more harmless to the environment. In addition to what has been said about irrigation and manure, it is good that the machinery is used in the most efficient way, since diesel has also played a significant role in the impact assessment (15 to 50% of the total). In the conventional vineyard (Scenario C), the weight of diesel is much lower, so in this case it would be better to focus on reducing the amount of pesticides.

In conclusion, the results of this study show that the choice of fertiliser (chemical auxiliaries, manure, etc.) could result in a great contribution on the CF balance. This appears to be a crucial point to address to properly review agricultural practices and should be considered in order to move towards less impacting scenarios.

4.3. Comparison of different crop rotations

One of the main difficulties that emerges from these applications of the LCA methodology to agricultural systems is the identification of the appropriate FU to be used. It, as described in chapter #2, must represent the function of the system under study and becomes a crucial step when systems that may have more than one function, such as agriculture, are analysed.

Heller et al. in their review[46] underline the importance of adopting more than one FU when applying the LCA to the agri-food sector as products have different characteristics from each other. This solution allows a study of the system from different points of view and results could consider the different roles that food plays. Other authors reached similar conclusions, combining one FU based on the price of products, with one on mass and one on nutritional values[47], or with one on mass and one on the hectare of land occupied[48]. Mass based FUs are quite common in LCA studies, especially when it comes to products[49-51], but in the case of food, function cannot be limited to its amount expressed in mass units, because it should involve nutrient intake. A FU that includes the nutritional quality of foods has been used in several studies, looking at nutritional density[52,53], resource consumption related to nutritional quality[54] or the impact of the individual product within a diet[55,56]. In particular, when evaluations consider different types of food with different roles (as in diets or crop rotations), an approach that includes a quality-corrected FU is needed[46,57].

Among the various available options, the Cereal Unit (CU) parameter was chosen as one FU for this project, because a study on crop rotations will be carried out and this parameter proved to be the most appropriate in these cases[58-60]. Therefore, the aim of this work is to discuss and encourage the use of CU as a criterion of comparison between different crops. Secondly, as a consequence of the analysis of the results on a case study, the project allows to provide suggestions (based on a life cycle approach) to farmers in order to minimise the impacts of their agricultural practices. CU, which will be better described below, is a physicochemical and biophysical parameter that considers both the characteristics of crops (amount of fibre, protein, carbohydrates, etc.) and the energy content that can be metabolised for food. Its use in LCA studies considering crop rotations was firstly suggested by Brankatschk and Finkbeiner[61] and it is considered particularly important in order to capture all the functions of the agricultural products[62]. Therefore, a comparison between two crop rotations in Argentina using CU as FU is presented. However, to respect the multi-FU indication of previous studies, the same comparison was then carried out with a revenue-based FU, to estimate the differences and discuss the information that both methods could provide.

4.3.1. Methodology

Within the system boundaries of the study the impacts of land use, operation of agricultural machinery, seeds, growth promoters and chemicals (such as fertilisers, herbicides, insecticides and fungicides) per hectare of crop are considered. Since the CU includes the fate of agricultural products (the metabolisable energy depends on the receptor), the study was conducted following a from-cradle-to-grave perspective. A full depiction of the system boundaries is shown in Figure 4.7.

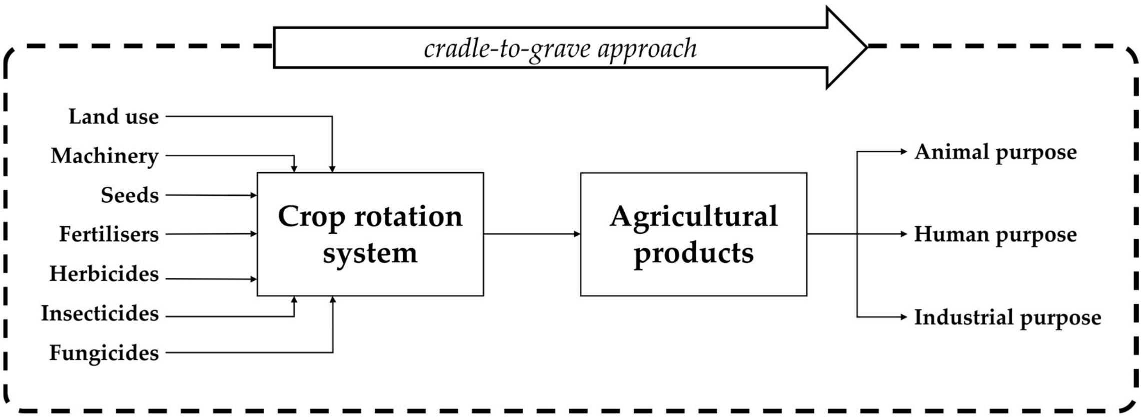


Figure 4.7 – System boundaries of the crop rotations study: inputs and outputs of rotations are calculated on a CU-based FU and a revenue-based FU. Reproduced from Volanti et al. 2021[63].

For the comparison of the crop rotations, two scenarios are modelled on the basis of the same CU production, i.e. the production of each crop multiplied by its CU, and on the revenue of the rotation. Data comes from the company "La Cautiva", located in the department of San Justo (Santa Fe, Argentina), and can be considered as primary since they are measured, gathered and calculated by the local cooperative of producers. The conventional crop rotation used in this area, for the purposes of the study, is called "Rotación San Justo" (San Justo Rotation, SJ), while the other, called "Rotación Siempre Verde" (Evergreen Rotation, EG), is an alternative one. Both rotations cover a period of six years and apply the sod-seeding method, a conservative agronomic technique of soil management that provides for no-tillage in order to maintain a physical fertility comparable to that of natural soil[64]. The SJ Rotation is a system that provides for a less intensive cultivation, in which only in the first year the soil is exploited in all seasons, from the second year the land is rested in autumn-winter and cultivated in spring-summer. On the other hand, the EG Rotation does not involve fallow periods but requires, in the autumn-winter season of the second and fourth year, the cultivation of rapeseed and ryegrass, with the intent to regenerate the properties of the soil and not to produce goods. They are labelled as “coverage” and their products are not valorised. Table 4.3 shows the two rotations, assigning each crop to the season and year in which it is planned.

Table 4.3 – Schematic representation of (a) San Justo and (b) Evergreen Rotations. (A-W: Autumn-Winter; S-S: Spring-Summer). Reproduced from Volanti et al. 2021[63].

a) SJ Rotation

Season	1st year	2nd year	3rd year	4th year	5th year	6th year
A-W	Wheat	Fallow	Fallow	Fallow	Fallow	Fallow
S-S	Soybean	Sunflower & Corn	Soybean	Soybean	Soybean	Soybean

b) EG Rotation

Season	1st year	2nd year	3rd year	4th year	5th year	6th year
A-W	Sunflower	Rapeseed (coverage)	Wheat	Ryegrass (coverage)	Rapeseed	Corn
S-S	Corn	Soybean	Corn	Soybean	Soybean	Mung Bean

In order to better understand the results, it is important to investigate in depth the used FUs. As said, the CU parameter considers the fate of the agricultural products, which can be of three types: (i) animal feed, (ii) human food and (iii) industrial use. In all cases, since Argentina is a net exporter of these products[65], not only the local consumption must be considered, but also the use made in importing countries. The international importance of Argentine market is one of the key points of this study. To our knowledge, in fact, this is the first case of application of the CU parameter in Argentina, whose importance is linked to the fact that it exports all over the world. An extensive analysis of the destination and consumption of each product was thus necessary, which is reported in detail in Table B3 in Annex B. In the same table the CU indexes were calculated in accordance with Brankatschk and Finkbeiner[66]. For use as feed, the metabolisable energy content of the products, different in each animal and weighted by the percentage of distribution, was considered. For human consumption, the methodology provides for the assignment of a level of production intensity to the crop, which is then divided by the actual production of the crop itself. The CU index for industrial purposes is calculated on the basis of gross energy content of the products. When the index is obtained in energy terms (feed and industrial purposes) it is normalised to the CU by its definition: 1 CU = 12.56 MJ (the metabolisable energy of 1 kg of barley).

The CU factor of each product was then obtained by multiplying the CU indexes of each purpose by their distribution. Finally, the CU factor of each crop is multiplied by its productivity (kg/ha) to define its Cereal Unit, the FU used for comparison. In this context, it is evident that CU is a site-specific parameter, as geographical differences, together with variations in the proportion of feed per animal, as well as food and market differences are relevant. With this in mind, and following the guidelines, the CU indexes obtained in this work are to be considered valid only for the aims of this study with reference to the Argentinian geographic area, even though the same approach could be replicated everywhere.

To carry out the comparison with a revenue-based FU, the cost per kg (in USD$) of all agricultural products were identified. The most recent average annual prices available were considered, in order to limit market fluctuations and because the two rotations can have the same product in two different periods (see the case of sunflower and corn, obtained both in spring-summer and autumn-winter). Single product prices are listed in Table B3 in Annex B. Again, prices are multiplied by the production amount to obtain the revenue that each crop generates, the FU used for this comparison. Table 4.4 summarises the CU and the revenue obtained from each crop. The two systems will be compared on the basis of the same total CU and total revenue respectively. The full LCI of the crops are given in Annex B (Table B4-B5).

Table 4.4 – The two rotations are compared on the same total CU and total revenue. Reproduced from Volanti et al. 2021[63].

SJ Rotation			EG Rotation		
Crop	**CU**	**Revenue [$]**	**Crop**	**CU**	**Revenue [$]**
Wheat	8008	404	Sunflower	2451	410
Soybean	3206	470	Corn	6847	671
Fallow	0	0	Rapeseed (coverage)	0	0
50% Sunflower	1226	205			
50% Corn	4184	410	Soybean	3946	578
Fallow	0	0	Wheat	8008	404
Soybean	3946	578	Corn	7282	714
Fallow	0	0	Ryegrass (coverage)	0	0
Soybean	3946	578	Soybean	3946	578
Fallow	0	0	Rapeseed	4199	569
Soybean	3946	578	Soybean	3946	578
Fallow	0	0	Corn	8368	821
Soybean	3946	578	Mung Bean	3996	794
TOTAL	**32407**	**3801**	**TOTAL**	**52989**	**6117**

4.3.2. Results and discussion

As Table 2 shows, the ratio between EG and SJ Rotations is 1.61 when the revenue-based FU is considered (6,117 vs 3,801 USD$), and 1.64 in the case of the CU-based FU (52,989 vs 32,407 CU). Although in this particular case the two rotations will show similar ratios in the comparison results, the use of CU as FU can guarantee a greater stability of results over time as most of the Argentinian agricultural products end up on the international market and their price is strongly influenced by its fluctuations. Figure 4.8 shows the price trend of four of the cereals involved in the study during 2019 and as can be seen the variation can be significant (from +61% to +87%).

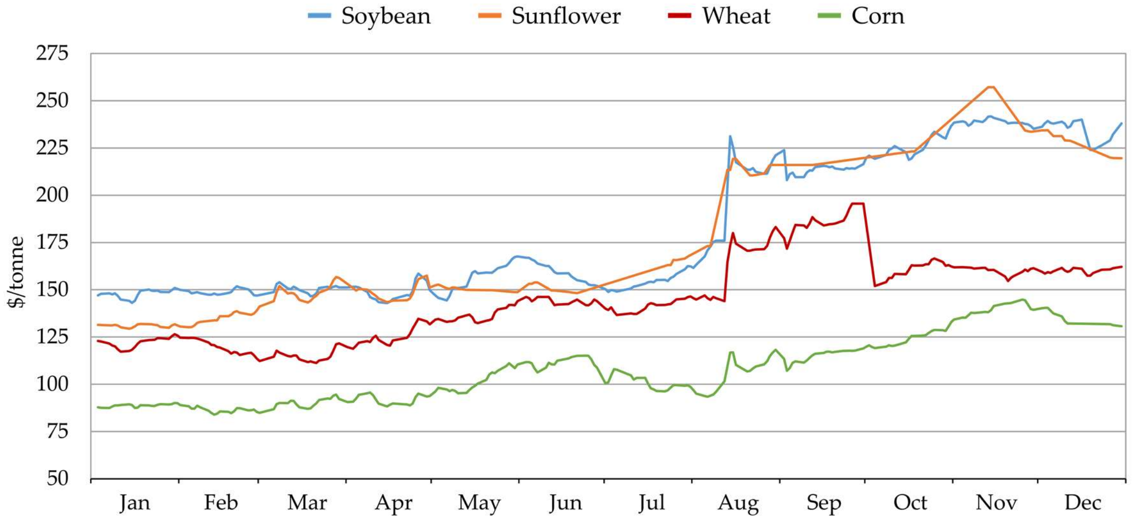


Figure 4.8 – Trend of cereal prices in 2019[67]. Reproduced from Volanti et al. 2021[63].

If a 6-year period is considered (like the time span of rotations) the variations are even greater, from 2014 to 2019 prices increased 5-8 times depending on the product[67]. On the other hand, the difficulty in using the CU parameter as FU lies in finding all the information necessary for its definition. It must include both national and international market information, especially in the case of countries where exports represent a large market share, such as Argentina.

CED results, shown in Table 4.5, indicate that the two scenarios require a similar total amount of resources: 2.5 MJ eq./CU and 21.3-21.5 MJ eq./$. The demand for fossils is higher for EG Rotation, while the biomass request in SJ Rotation. In both rotations fossil consumption is the main one, responsible for 80-89% of total energy demand. Fossil resources are needed to produce chemical additives (in particular fertilisers as urea and phosphate compounds) and for agricultural machinery, both of which are greater for EG Rotation than for SJ Rotation. However, also CU and revenue are higher in EG Rotation, so the difference in fossil resource demand between scenarios is mitigated, but still slightly higher for EG Rotation. On the other hand, biomass request is mainly due to seeds, which explains the difference of one order of magnitude with the fossil demand.

Since the seed difference between the two rotations is lower than other inputs, the FUs normalisation makes the biomass demand for EG Rotation about half that of SJ Rotation.

Table 4.5 – Resource consumption of the scenarios for both FUs (CED method). Reproduced from Volanti et al. 2021[63].

Scenario	Unit	Fossil	Biomass	TOTAL
SJ Rotation	MJ eq./CU	2.0	0.5	2.5
EG Rotation	MJ eq./CU	2.2	0.3	2.5
SJ Rotation	MJ eq./$	17.1	4.2	21.3
EG Rotation	MJ eq./$	19.2	2.3	21.5

In order to know which crop is the main responsible for the resource consumption, a contribution analysis was carried out. In SJ Rotation the wheat is the major contributor, responsible for 20% of total resource demand, while in EG Rotation the situation is more evenly distributed between maize, wheat and sunflower. Both rotations have non-productive seasons, but in different ways. In the SJ Rotation the land is left completely fallow, while in coverage periods of EG Rotation it is cultivated to restore the soil quality, but without the harvesting of agricultural products. This difference emerges in CED results: fallow periods need no resources, while coverage periods contribute for 1% to the resource demand of EG Rotation. Overall, from the point of view of CED method, the two rotations seem to be equivalent, but the resource consumption alone is not enough to describe their environmental performance.

In order to complete the analysis, ReCiPe method was applied, with a hierarchical cultural perspective, at midpoint level to quantify the environmental impacts of the rotations. Table 4.6 shows the main ReCiPe results of the two rotations for both FUs (full results are available in Table B6 in Annex B).

Table 4.6 – Impact assessment of the scenarios for both FUs (ReCiPe 2016 Midpoint H/H). Reproduced from Volanti et al. 2021[63].

Impact category	**Unit**	**SJ**	**EG**	**Unit**	**SJ**	**EG**
Global warming	kg CO_2 eq./CU	1.63E-01	1.48E-01	kg CO_2 eq./$	1.39E+00	1.28E+00
Fine particulate matter formation	kg $PM_{2.5}$ eq./CU	3.76E-04	3.70E-04	kg $PM_{2.5}$ eq./$	3.20E-03	3.21E-03
Terrestrial acidification	kg SO_2 eq./CU	8.37E-04	8.88E-04	kg SO_2 eq./$	7.14E-03	7.69E-03
Freshwater eutrophication	kg P eq./CU	4.92E-05	4.32E-05	kg P eq./$	4.20E-04	3.74E-04
Marine eutrophication	kg N eq./CU	3.89E-05	2.96E-05	kg N eq./$	3.31E-04	2.57E-04
Human toxicity	kg 1,4-DCB/CU	1.73E-01	1.79E-01	kg 1,4-DCB/$	1.47E+00	1.55E+00
Land use	$m^2 \cdot a$ eq./CU	1.92E+00	1.17E+00	$m^2 \cdot a$ eq./$	1.64E+01	1.02E+01
Water consumption	m^3/CU	4.73E-03	5.43E-03	m^3/$	4.03E-02	4.70E-02

The results show that the largest difference between the two scenarios lies in the impacts attributable to the LU category, where SJ Rotation has an impact 60% higher than EG with both FUs. Since the crops are grown on the identical land area, the difference is due to the FUs. In particular, the ratios between the LU impacts are 1.61 and 1.64 for the CU-based FU and the revenue-based FU respectively, the same ratios identified at the beginning of this section. In all other categories the impacts are closer between the two scenarios, with differences under ±15%. SJ Rotation has higher impacts in GW, Freshwater Eutrophication (FE) and Marine Eutrophication (ME) categories, EG Rotation in TA, HT and WC categories, while in the FPMF the impacts are much similar.

A contribution analysis, Figure 4.9, was carried out to identify the cause of impacts in each category.

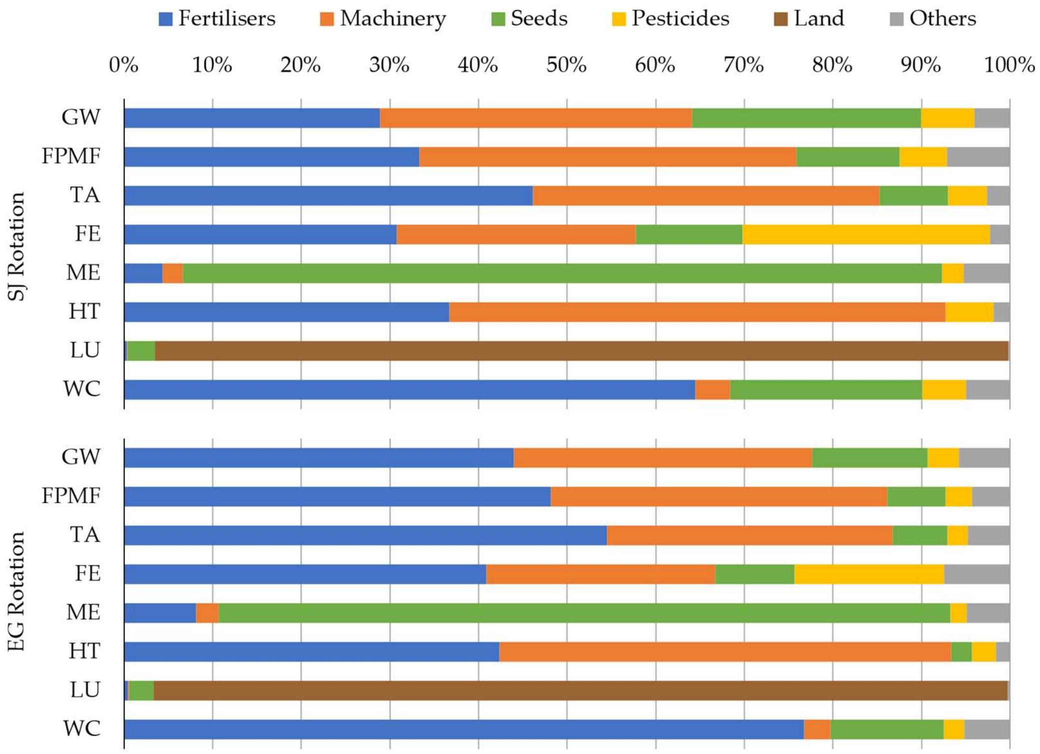


Figure 4.9 – Contribution analysis of inputs to the impact of categories (ReCiPe 2016 Midpoint H/H). Reproduced from Volanti et al. 2021[63].

In GW, FPMF and TA impact categories, fertilisers and agricultural machinery are the inputs that contribute most, ranging from 30% to 55%. Machinery impact on GW and FPMF is due to the use of fossil fuel for their movement, which directly produces GHGs and atmospheric particulate matter, the fall of these elements to the ground causes impacts on TA. As regards fertilisers (whose share is higher in EG Rotation because they are used in greater quantities) the impacts are mainly derived from the raw materials and electricity of their production chain. Seeds show more incidence in GW category than FPMF and TA, while pesticides contribute 2-5% to the impacts of the categories. In the FE category, the contribution of fertilisers and machinery remains high (30-40% for the first and around 26% for the second), but the contribution of pesticides increases, accounting for 28% and 17% in SJ and EG Rotation respectively. This is because FE impact category measures kg P eq. and glyphosate (the most important pesticide in both rotations) is a compound containing phosphorus. In the ME category the impact lies for more than 80% in the seeds, caused by the previous crops from which they were obtained. Although pesticides and fertilisers include nitrogenous compounds (the ME category estimates the kg N eq.), they do not bring particular environmental burdens to the category. HT is affected by emissions from agricultural machinery, which covers more than half of the impact category, and by fertilisers, more because of their production than their direct use. LU category, as imaginable, depends almost exclusively on the direct land occupation required by the crops and only a marginal part (about 3%) on that demanded for seed production. Rotations do not involve artificial irrigation, so WC impacts are associated only with the inputs. In this category the contribution of fertilisers is maximum, 64% and 77% in SJ and EG rotations respectively, and comes from the water needed for the production of some precursors (such as ammonia, sulphuric acid and phosphoric acid). On the other hand, seeds affect WC because the Ecoinvent database processes used for their simulation (to ensure the same background for all) include crop irrigation.

Due to their important contribution in 6 out of 8 considered categories, the impacts of fertilisers and machinery have been deepened. The analysis showed that among fertilisers, diammonium phosphate and urea share the responsibility for impacts almost equally, while the machinery that contributes most is the harvesting machine, followed by the sprayer and the sower.

Lastly, another contribution analysis was carried out, this time to identify the responsibilities of the different crops to the ReCiPe impacts.

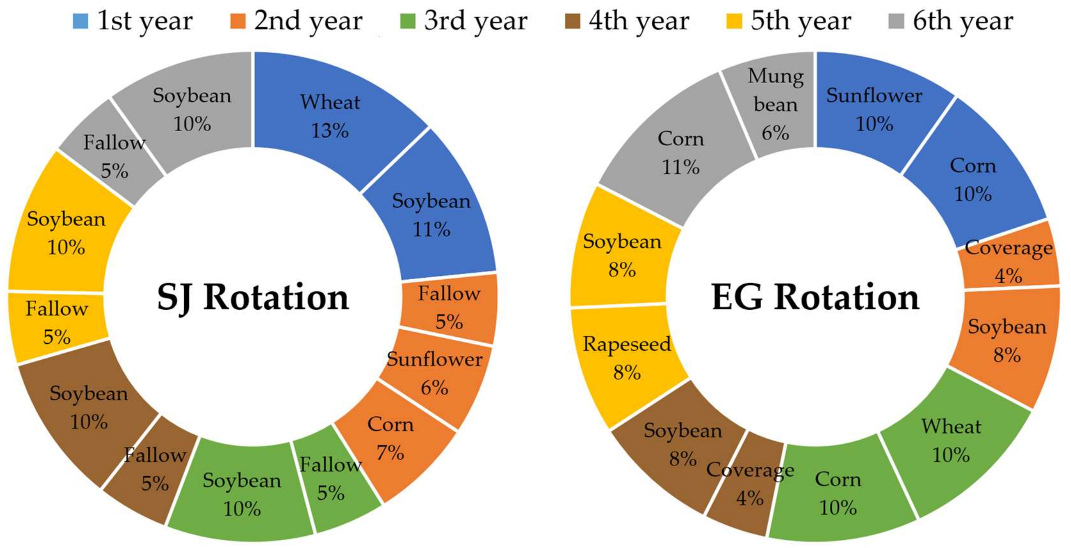


Figure 4.10 – Contribution analysis of each crop to the impact of the rotation (ReCiPe 2016 Midpoint H/H). Reproduced from Volanti et al. 2021[63].

The results (Figure 4.10) indicate that in SJ Rotation the crop with the highest share is wheat, followed by soybean planned immediately afterwards. Soybean in the first year shows a slightly higher contribution than in subsequent years because its productivity is lower and thus causes an increase in impact. Corn and sunflower crops show lower contributions because they are grown together during the second year (they are designed on 50% of the land each), but if added together they would contribute the same as wheat. The impacts of the EG Rotation, as its resource consumption in the CED method, are more distributed among its crops. However, in this case the different contribution of corn during the years is not only given by its productivity but also by different inputs of materials. Mung bean shows the lightest contribution to the environmental burden of the rotation and is slightly higher than the coverage periods. In both rotations, contributions from non-productive periods (4-5% each) provide an important information: land occupation is a significant source of impact, whether something is cultivated (EG Rotation) or left completely fallow (SJ Rotation). This confirms the complementarity of the two methods of analysis, the importance of land occupation does not emerge from the CED comparison as it only assesses the resource consumption, where the contribution of fallow periods is zero and that of coverages is very small, about 1%.

Finally, important suggestions for the achievement of the UN's Sustainable Development Goals can be drawn from the results of the analysis. First of all, the critical issues emerged on LU must lead to an increase in agricultural productivity, in order to not lose potential resources in the fight against hunger. This is particularly important in Latin America and is one of the critical points of goal #2 "zero hunger"[68]. However, the importance of soil quality (goal #15 "life on land"[68]) should not be overlooked, and agricultural practices that go in this direction, such as EG Rotation coverage periods, should be encouraged. Another key point revealed by the results is related to the emissions of agricultural machinery and fertiliser production chain. To counteract their impact, and thus meet goal #13 "climate action"[68], the use of renewable energies should be promoted, but waiting for technological upgrading (which may not depend on the farmer) the suggestion is to use them as consciously as possible. For machinery, this can be done by maximising the efficiency of its use or by replacing machinery work with manual work, unless productivity suffers too much. Furthermore, since fertilisers are essential to maintain high agricultural production, it could be considered to replace them with organic, natural or more eco-sustainable fertilisers.

4.3.3. Conclusions

In agricultural practice, the use of crop rotation is an essential strategy that improves nutrient availability, phytosanitary conditions, soil composition and helps to counter biodiversity loss. Assessing the environmental impact of an entire crop rotation is a method able to capture crop-interactions information, not possible in a single crop analysis[58]. In this study, based on primary data from the province of Santa Fe in Argentina, a new and alternative crop rotation is compared with the conventional one in the region, characterised by a high export market. The analysis was conducted through the application of the LCA methodology and two different FUs were used, both able to represent all the functions of agricultural products. Using CU production of the rotation as FU allows to summarise in a single parameter the quantity, quality and purpose of each agricultural product, key features of the crops. Alternatively, total crop rotation revenue is often used as a FU that can well approximate all these characteristics. The study showed that the use of a CU-based FU is appropriate for this type of investigation to guarantee stable results over time as it does not depend on price fluctuations of individual agricultural products such as in the case of a revenue-based FU. In addition, compared to the use of energy content, CU is also able to look at the destiny of agricultural products, adding an extra step to the life cycle assessment. In contrast, in order to reliably represent crop rotations, this parameter requires considerable effort to find information on all agricultural products.

The results indicate that from the point of view of resource consumption the alternative crop system (EG Rotation) requires more fossil resources since they are linked to the production of chemicals (pesticides and fertilisers), used more here than in the conventional system (SJ Rotation). However, when the analysis is extended to the impacts, it emerges that the key factor in the environmental assessment is the land use. As already shown in other studies[69], the importance of the impact on land use is of primary importance and in this category the SJ Rotation is assigned an impact +60% compared to the EG, with both FUs. Since in the other impact categories the differences are not so large, this aspect tips the balance of better environmental performance towards EG Rotation. The critical activities, in environmental terms, that have emerged for both rotation systems are the use of agricultural machinery and fertilisers.

In conclusion, with this project, the use of CU-based FU is encouraged when problems arising from different crop quality have to be overcome, since it could represent the most stable parameter among those which could estimate properly all the functions of the crops.

With the results of this study, an article has been published in the journal of Ecological Indicators[63] edited by Elsevier.

4.4. Environmental impacts of meals

According to the United Nation projections, world population is expected to grow by 2 billion people by 2050 reaching 9.7 billion individuals worldwide[70]. More people on this planet means higher food demand and consequently greater competition for natural resources. Food production relies on the exploitation of natural capital inputs such as water, land, energy and biodiversity, and is responsible for negative externalities as land degradation, water stress and air pollution: food production are responsible for 60% of terrestrial biodiversity[71].

The demand and consumption of food within the agri-food sector are determined by many different economic, social and environmental factors. Income, population size, prices of both food and other commodities along with cultural tradition, consumers' preferences, expectations and personal beliefs are the principal drivers of food demand responsible for shaping the consumption patterns[72]. Consumers' preferences and choices of products and services can be explained and predicted analysing the individual values, which constitute the background of behaviour at both conscious and non-conscious level[73]. Therefore, products attributes are evaluated by consumers, who express their preferences considering their personal values[74]. Consumers care about the different aspects of the products they buy and many studies have identified several values that guide individual purchasing decisions: price, health, tradition, natural content, convenience and sensory appeal[73,75-81]. Some food values even refer to the production process and not to the product itself, such as ethical concern about environmental sustainability, animal welfare and children labour. From the literature it also emerged that food values in different countries and cultures are similar, however, they differ on the relative importance which individuals attach to them. Understanding how people choose among various products with many different characteristics is crucial in order to determine the most important features of a product. This is relevant not only for companies but also for scientists and governments when it comes to work on product innovation and packaging, to develop new technologies and advertising campaigns, or even to adopt new food policies[73].

Nowadays, the topic of the environmental burden of food production and dietary choice is becoming more widespread both within the scientific community[82-85] and the general public. Studies aimed to analyse the environmental impact of food have been conducted by other authors[86-89], but they generally focused on a single product or at least few items. On the other hand, a wide variety of fresh food items were investigated by Clune et al.[90], who carried out a systematic literature review of GHG emissions; the authors employed many sources of data but not the databases of LCA software.

The purpose of this study is to analyse, from a life-cycle perspective, the environmental impact of meals provided in school canteens. Differently from individual foods, meals served in canteens have proportionate nutritional values, are prepared considering the indications of nutritionists and are part of a planned and balanced diet. These aspects are particularly important in school-age nutrition and represent an additional step in the analysis of the environmental impact of food. Together with the CF analysis of the dishes, an index has been created to relate the environmental impact of the meals with their food energy. This, by definition, is the energy released within the body when food nutrients (carbohydrates, fats and proteins) are burned and is expressed in kilojoules or kilocalories[91]. This index is useful to provide a ranking of the most impacting meals when normalized to food energy. Although the study was conducted at regional level in Italy, it can be seen from a general point of view because the guidelines for the composition of dishes in Italy are common at national level[92] and because the considered ingredients (120) are produced in different countries. The food sector is becoming increasingly global, the links among different actors of the value chain create international networks[93] and the production systems are more and more standardised[94]. In this context, economic, social and environmental externalities arising from the food sector spread among different countries[95]. For this reason, the methodology and the results of our work could be generalizable.

4.4.1. Methodology

The list of meals and the ingredients quantities for the recipes considered in this study were published by the health care system of the city of Bologna (Italy)[96] according to the national guidelines, which indicates the Levels of Nutrient and Energy Reference Assumption for the Italian population[92]. The environmental impacts of meals production are evaluated with a from-cradle-to-gate approach, i.e. considering from raw material production up to the transport of the ingredients to the meals producer (Figure 4.11). Where only partial data on the agricultural stage are available, the packaging stage and the transport of the ingredients to the meal producer are added. Concerning GHG emissions, the packaging phase has been assumed to emit 0.04 g CO_2 eq./g product, while the transport phase 0.09 g CO_2 eq./g of product[90].

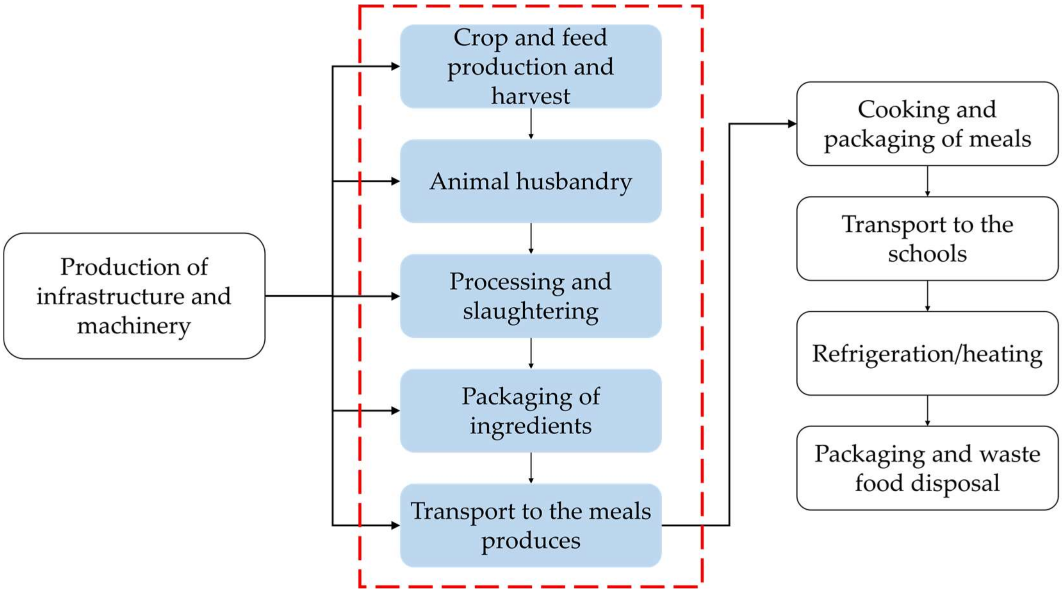


Figure 4.11 – System boundaries of the meals study: from-cradle-to-gate approach.

The FU, to which the inputs and outputs of the system are related, is one dish provided to school canteens. The dishes are clustered in three subcategories, that are 'first course', 'second course' and 'side dish', which all together represent the complete meal for each student. The canteens have two slightly different menus, one for winter and one for summer, because, as suggested by the health care system, the seasonality of fruit and vegetables should be considered as much as possible when it comes to preparing meals for children at school)[96]. The list of dishes provided to the schools is shown in Table 4.7. Both menus contain a list of dishes for 20 days, clustered in 4 weeks (from Monday to Friday), which are repeated every month. The ingredients quantities considered in the study are those for children attending the first-grade secondary school and were taken from the same health care system of Bologna.

Table 4.7 – Winter (W) and summer (S) menu of schools in the municipality of Bologna[96].

			First course	Second course	Side dish
Week 1	M	W	Pasta with tuna	Potato pie	Mixed salad
		S	Rice with tomato sauce	Chicken salad	Carrots
	T	W	Barley soup	Meat skewers	Steamed potatoes
		S	Pasta with pesto sauce	Blue shark with tomato sauce	Mixed salad
	W	W	Pasta with meat sauce or backed pasta	Cheese	Crudities with oil
		S	Pasta with meat sauce	Caprese salad	-
	T	W	Rice with tomato sauce and vegetables	Backed chicken thighs	Carrots
		S	Pasta with zucchini	Loin roll with vegetables	Mixed salad
	F	W	Spaghetti with garlic and oil	Fish croquettes or cutlets	Peas
		S	Pasta with oil and Parmigiano	Tuna, beans, potatoes and onions	Mixed vegetables
Week 2	M	W	Pizza Margherita	Raw or backed ham	Mixed salad
		S	Spaghetti with olives	Raw ham with melon	Mixed salad
	T	W	Soup pasta with legumes	Omelettes	Backed potatoes
		S	Pasta with vegetables	Aubergines rolls	Peas with butter and Parmigiano
	W	W	Risotto with artichokes	Hamburger sandwich	Carrots
		S	Pasta with oil and Parmigiano	Fish croquettes	Tomatoes gratin
	T	W	Gnocchi with tomato sauce	Turkey stew or milk loin	Mixed raw vegetables
		S	Pasta with tomato sauce	Loin roast or cold turkey	Crudities with oil
	F	W	Pasta with oil and Parmigiano	Codfish with lemon	Stew cabbage
		S	Pasta with tomato sauce	Boiled eggs or omelettes	Mixed salad
Week 3	M	W	Rice with tomato sauce and vegetables	Chicken breast	Mixed cooked vegetables
		S	Rice salad	-	Crudities with oil
	T	W	Lasagne	-	Crudities with oil
		S	Pizza Margherita	Vegetables parmigiana	-
	W	W	Pasta with pesto	Hamburger meat pizzaiola	Peas
		S	Risotto with fish	Hamburger meat pizzaiola	Mixed cooked vegetables
	T	W	Pasta or polenta with meat sauce	Cheese	Carrots
		S	Pasta with aubergines	Caprese salad	-
	F	W	Vegetables soup with pasta	Squid and potatoes salad	-
		S	Pasta with tomato sauce	Squid and potatoes salad	-
Week 4	M	W	Pasta with tomato sauce and olives	Fish or tuna	Mixed raw vegetables
		S	Pasta salad	Fish or tuna	Mixed raw vegetables
	T	W	Risotto Milanese	Escalope	Carrots
		S	Risotto parmigiana	Meatballs	Carrots
	W	W	Pasta with meat sauce and vegetables	Codfish with tomato sauce	Green beans
		S	Pasta with tomato sauce	Codfish with lemon	Mixed cooked vegetables
	T	W	Pasta with tomato sauce	Turkey stripes	Mixed raw vegetables
		S	Pasta with meat sauce and vegetables	Turkey stripes	Mixed raw vegetables
	F	W	Soup pasta with legumes	Vegetables parmigiana	-
		S	Pasta with peas	Vegetable pie/omelette	Mixed raw vegetables

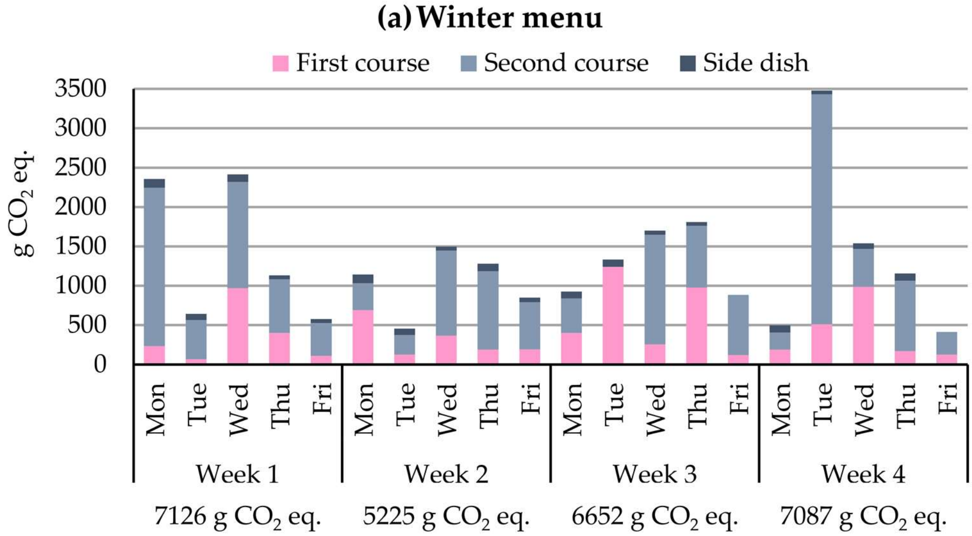
Climate change has been chosen as a representative impact category for this study, so the Greenhouse Gas Protocol method[97] was used. Through the measurement of the CF (kg CO_2 eq.) it is capable to quantify the total amount of GHGs emitted, directly and indirectly, during the production of canteen meals. In this study the GWPs considered are calculated over 100 years, according to the IPCC impact assessment method[98].

4.4.2. Results and discussion

The LCI of the study consists of 120 different foods and includes all the ingredients of the considered school menu. For each ingredient CF and food energy are reported, the ratio between these two characteristics has led to the creation of the Carbon-Footprint/Food Energy (CFE) index. The full list of foods is available in Table B7 in Annex B.

In order to properly investigate the environmental impact of meals, it is necessary to first take a look at the characteristics of the ingredients. The analysis shows that the most carbon intensive categories are "meat and fish" and "dairy products", whose CFs range from 3 g CO_2 eq./g to 24 g CO_2 eq./g. In particular, the highest values are attributable to veal, beef, yellowfin tuna, Parmigiano and Pecorino cheese, all of which have more than 16 g CO_2 eq. per g of product. "Oils, spices and sauces" category has CFs between 2 and 5 g CO_2 eq./g, while the other categories (fruit, cereals, legumes and vegetables) have a CF smaller than 2 g CO_2 eq./g. The analysis of their CFE index (g CO_2 eq./kJ), scatter plot shown in Figure B1 in Annex B, indicates that almost all foods tend to align or group with the ones of the category to which they belong. "Dairy products", "legumes" and "oils, spices and sauces" show a linear trend between CF and food energy. "Dairy products" have parameters that increase proportionally with each other, while "legumes" and "oils, spices and sauces" show a constant low CF although the energy content varies. Fruit, vegetables and cereals are grouped in areas with low environmental impact, distinguished by their food energy. "Fresh fruits" and "vegetables" have both the lowest CF and the lowest energy content (between 0 and 5 kJ/g), "cereals and pasta" are around 10-15 kJ/g, while "dry fruits" results to be the best category because it combines a low CF with a high food energy (25-30 kJ/g).

Moving from the GHG emissions of ingredients to those of canteen meals, the results, shown in Figure 4.12, indicate that the CF of the winter menu is slightly higher than that of the summer menu (26.1 kg CO_2 eq. vs 24.5 kg CO_2 eq.).



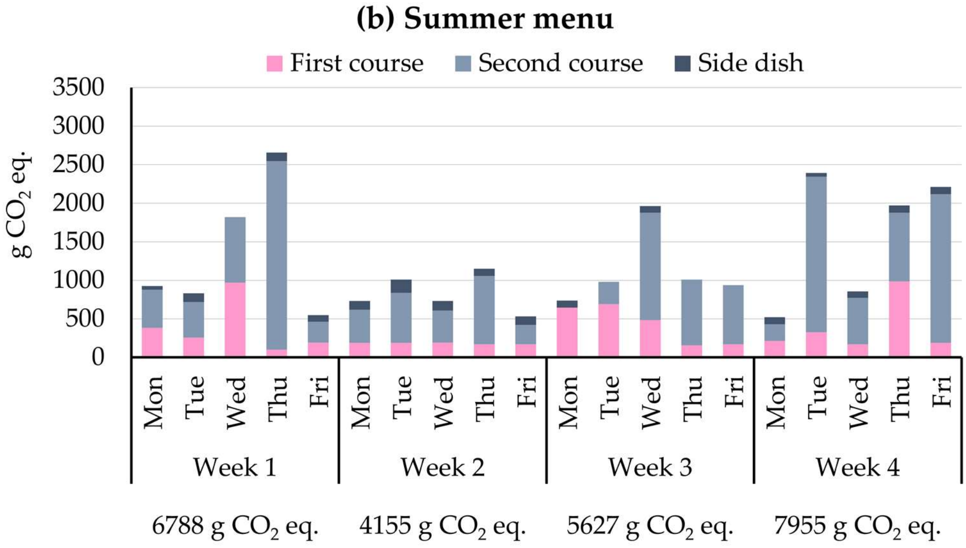


Figure 4.12 – Carbon Footprint of the (a) winter and the (b) summer menu analysed.

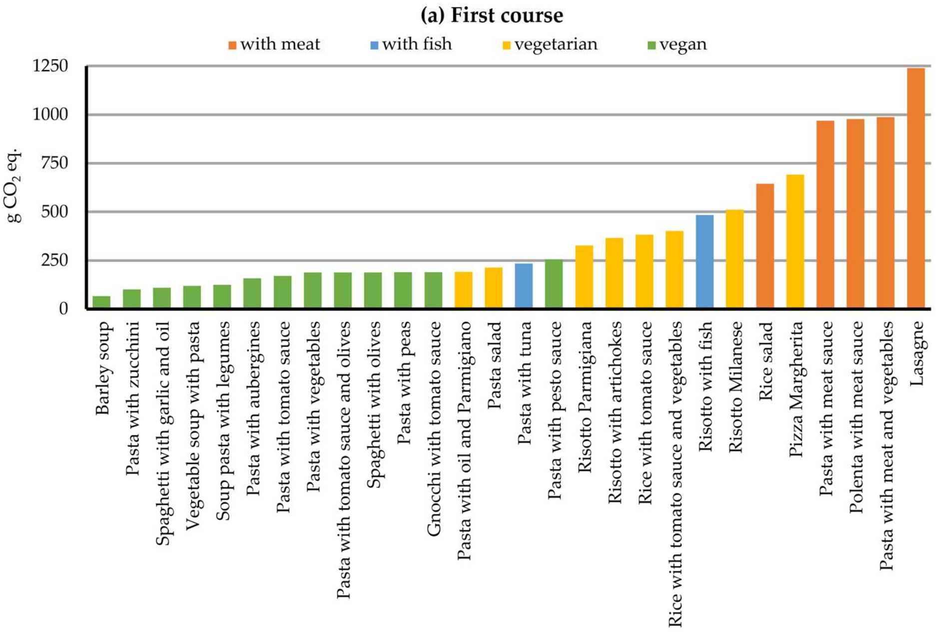
Analysing the differences between the two menus (Table 4.8), it emerges that in winter the consumption of meat and dairy products is higher than in the summer menu, which, in turn, provides for higher amounts of vegetables, fruit and cereals and pasta.

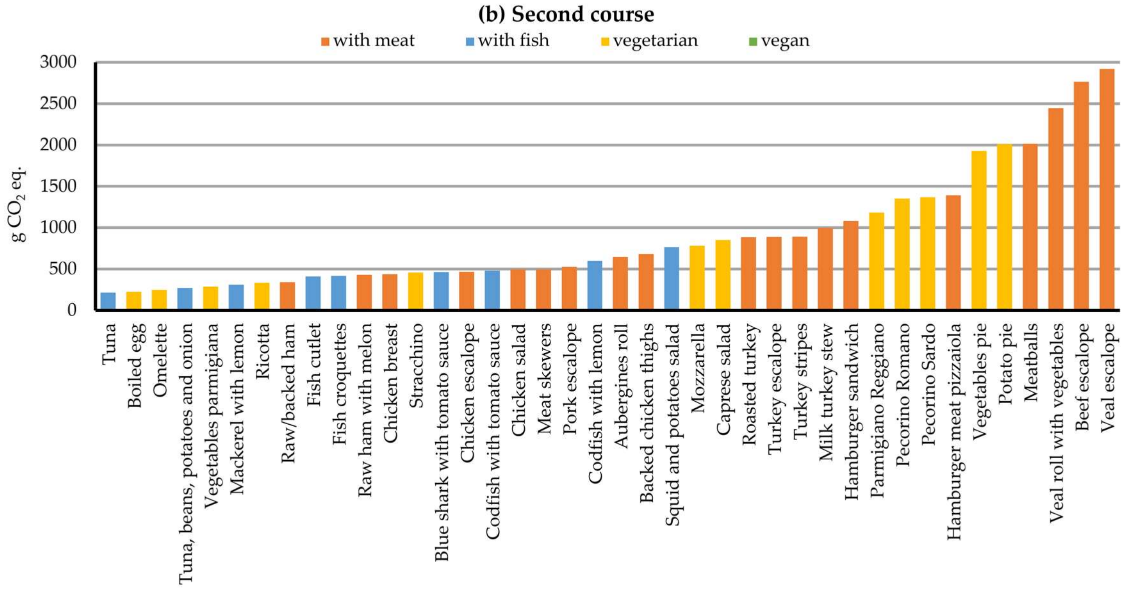
Table 4.8 – Total amount of ingredients (divided by course and category) used in the menus.

		Winter Menu			Summer Menu		
Food category	**Unit**	**First course**	**Second course**	**Side dish**	**First course**	**Second course**	**Side dish**
Meat and fish	g	170	1650	0	120	1460	0
Dairy, eggs and subs.	g	165	491	0	135	443	11
Vegetables	g	1065	560	2880	435	1465	2710
Fruits	g	0	0	0	0	300	0
Cereals and pasta	g	1465	80	0	1600	30	30
Oil, spices and sauces	g	920	200	132	974	346	90

This is consistent with the guidelines of the health care system and, based on the above findings, explains the reason for this higher CF. For the same reason, first courses are usually less impacting on the environment than second courses, as they contain less meat and dairy products but more cereal and pasta. On the other hand, side dishes are composed almost exclusively of vegetables and have the lowest environmental impact.

Among the school canteen dishes, the CF of first courses ranges from 67 g CO_2 eq. of barley soup to 1240 g CO_2 eq. of lasagne, the CF of second courses between tuna (not yellowfin, 215 g CO_2 eq.) and veal escalope (2919 g CO_2 eq.), while side dishes GHG emissions are lower and range from 49 g CO_2 eq. of carrots to 174 g CO_2 eq. of peas with butter and Parmigiano cheese. In Figure 4.13 all the 79 analysed dishes (28 first courses, 40 second courses and 11 side dishes) are listed by their CF and labelled according to four categories of food: with meat, with fish, vegetarian and vegan.





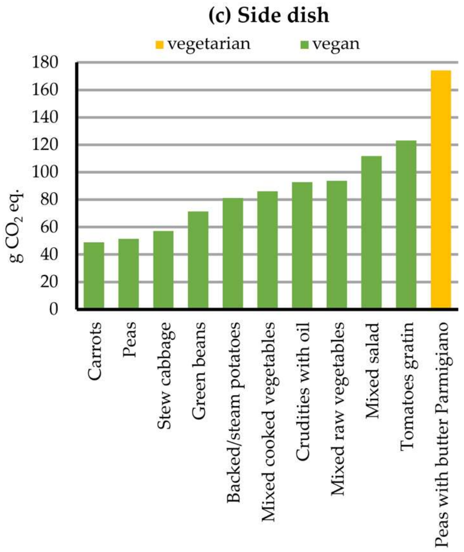


Figure 4.13 – Carbon Footprint of the analysed meals: first courses, second courses and side dishes

The results reflect the findings of the individual ingredient impacts, so dishes containing meat or fish are those that are assigned a higher CF. For instance, pasta with tomato sauce and pasta with meat sauce, which differ only by 35 g of beef meat, have a CF of 171 and 968 g CO_2 eq. respectively. Within the menus, the biggest impacts (Tuesday fourth week in the winter menu and Thursday first week in the summer menu, Figure 4.12) come from second courses that include veal: escalope and roll with vegetables. Moreover, meat dishes tend to have a higher GHG emission than fish dishes, dairy products (such as ripened cheeses or mozzarella) significantly increase the CF of the dishes, while vegan foods are confirmed to have the lowest impact.

When the CF of meals is related to their food energy they tend to cluster as in the case of ingredients. Figure 4.14 allows an easy comparison of the CF of various meals containing the same food energy, making the CFE index (g CO_2 eq./kJ) deductible. If a meal has a low index value means that it provokes low GHG emission related to its food energy.

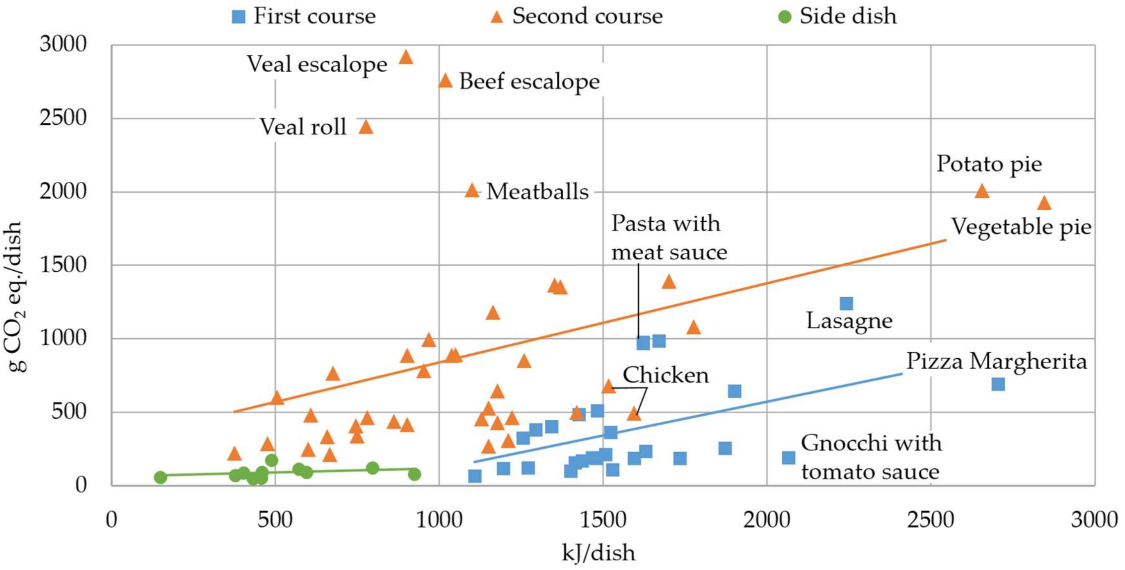


Figure 4.14 – Carbon-Footprint/Food Energy (CFE) index for the meals of the study.

The graph shows that first and second courses have a direct proportionality between CF and food energy (with a few exceptions especially among second courses) with a similar trend line slope. However, first courses are generally characterised by higher food energy, which, combined with the lower CF already emerged, makes the average CFE index of this category (0.23) closer to that of side dishes (0.20) than to that of second courses (0.85).

Semolina pasta is the main source of food energy for first courses and the reduced use of meat ensures a low level of environmental impact. The large CF of lasagne is partially justified by the high food energy of the dish, while pasta with meat sauce (or with meat sauce and vegetables) does not compensate so well for its environmental impact. Pizza Margherita and gnocchi with tomato sauce are, among the first courses, those that best combine CF and food energy.

On the other hand, veal and beef meals (such as meatballs) are confirmed to be the worst choices since high CF is not associated with high food energy. Indeed, there are many second courses that can guarantee the same (or greater) nutrient supply to the individual and that are associated with a lower GHG emission. Vegetable and potato pie depend, both for food energy and CF, on the Pecorino Romano cheese with which they are made, while chicken meals are the second courses that marry the two characteristics in the best way.

Side dish is the category that shows the lowest values, which is an advantage for CF but a negative point for food energy. Among these meals there is more variability in terms of energy than impact, with baked potatoes and tomatoes gratin at the maximum and stew cabbage at the minimum.

4.4.3. Conclusions

In this work, GHG emissions of meals provided in school canteens have been analysed and the results can be used to provide an additional supporting aspect to the costumer. Often in the menus the caloric intake of food is indicated to inform customers about dietary aspects; in the same way, following a life cycle perspective, it would be possible to offer a CF-based choice too. However, it must considered as well that a diet would be complete, also considering the balanced apportion of different nutrients.

From the analysis of the ingredients it was found that meals containing meat, fish and dairy products are the most impacting in terms of GHG emissions. Dairy products have high CF when cheese and butter are involved, lower in the case of milk and eggs. In general, fresh fruit, vegetables, cereals and legumes are the foods with the lowest CO_2 eq. contribution, although dry fruit should be considered the best option, because it combines a low CF with a high food energy (low CFE index). However, it must be kept in mind that a proper diet must include all the different types of food to ensure the correct caloric and nutritional intake. For this reason, this environmental analysis was not limited to the ingredients but considered meals. Dividing canteen meals distributed at school into three groups (first courses, second courses and side dishes), it emerged that second courses, which generally contain more meat than the others, have the highest CF, while side dishes are the lowest as they are composed almost exclusively of vegetables. When the CF is linked to the food energy of meals, the first courses have the best combination of the two parameters, because many of them have a high energy content that justify the environmental impact. Side dishes have an even smaller CF, but their caloric contribution to the person is also lower, resulting in a CFE index similar to that of first courses. On the contrary, second courses generally have high CF value but intermediate food energy, which makes them the most discouraged choice from an environmental and nutritional point of view. Among these, it is preferable to consume more white meat (such as chicken or turkey) than red (beef, veal, pork, lamb…), both considering the environmental results of this study and for health reasons already widely documented[99].

In conclusion, results on the carbon footprint of meals and ingredients used in school canteens could be useful for further changes in school food policy in light of environmental sustainability, nutritional aspects and educational purposes.

An article, currently under review in the Journal of Cleaner Production (Elsevier), has been written on this project, and future developments will be aimed at extending the life cycle boundaries to provide a better knowledge about the environmental sustainability of food and meals.

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5. Conclusions of the study

In this thesis, entitled "*Environmental assessment of industrial chemical and primary sector processes from a life cycle perspective*", several production systems have been investigated in the context of sustainable development. The activity carried out during the three years of the PhD program, in line with the professional figure of an industrial chemist, was aimed at analysing different technological solutions with the purpose of identifying the most suitable one from an industrial and environmental point of view.

Sustainability assessments were carried out using the Life Cycle Assessment methodology, whose characteristics and properties were explored in depth during the various case studies. The discussion of environmental sustainability in industrial chemical production was developed in three projects concerning: *i*) the production of a chemical commodity (terephthalic acid, a precursor of PET) from renewable sources, *ii*) the environmental study of an innovative biogas upgrading process to syngas and *iii*) the environmental characterization of ionic liquids. Although belonging to different sectors of industrial chemistry, these three projects have in common the fact that they have evaluated processes currently under development. This type of approach, called At Early Stage, aims to assess the possible impacts of processes before they are transferred on an industrial scale, in order to identify any critical issues before energy, time and resources are spent on their development[1]. This aspect is of particular importance because it is estimated that about 80% of all the environmental effects associated with a product are determined in the design phase of development[2]. Determining where improvements can be made while a process is still at the laboratory stage can be the key to unlocking the environmental improvement potential, forming the basis of eco-design.

The evaluation of terephthalic acid production showed that renewable resources can provide significant benefits for the environmental balance only when waste biomass is involved. Dedicated crops, in fact, have shown both great impacts and great demands for resources linked to the cultivation phases that compromise their environmental performance. The analysis of the biogas reforming process has shown that the innovative Steam/Dry Reforming technology has the potential to guarantee savings in CO_2 emissions, thus acting as Carbon Capture technology. This is an important strength of the process that can guide and justify its development. Finally, with the environmental characterization of ionic liquids, the basis for the development of an environmental impact prediction methodology has been set. The first obtained results are encouraging and the road taken seems to go in the right direction, but the dataset must certainly be expanded to obtain more reliable answers.

The study of these processes has revealed a strong link with the primary production sector and this has opened a new line of research focused on environmental assessment in this field. The production of raw materials (including those for the chemical industry) is linked to the challenges of the primary sector and a better understanding of them also involves the analysis of upstream processes. The studies carried out in this area are: *i*) the environmental sustainability analysis of some organic vineyard cultivation practices, *ii*) the evaluation of a parameter for the comparison of different crop rotations and *iii*) the study of the environmental impact of food served in school canteens.

Both the study of vineyards and the study of crop rotation have shown that agricultural machinery is one of the main sources of crop impact. This means that the environmental problem is linked to the movement technologies of such machinery rather than to the other phases of cultivation and to be solved it is necessary to upgrade the engines and/or use of renewable sources. However, this is often not directly dependent on the farmer or farm, so the suggestion is to use the machinery as efficiently as possible, avoiding waste or preferring manual work (as long as the same productivity is maintained). The work on canteen food has the peculiarity of comparing complete meals, thus including within the system boundaries also the aspects related to nutritional balance on which school menus are built.

The cross-application of the LCA methodology proposed in this doctoral thesis has shown, in general, that traditional production technologies are often quite well optimized, so it is quite challenging to find new, more sustainable alternatives. Both when fossil resources are used (see the case of terephthalic acid and biogas reforming) and conventional production techniques (chemical fertilizers or rotations) are analysed, the impacts of innovative processes are not always lower than those of traditional ones. However, this aspect represents an even greater challenge for those working on sustainable development and underlines how LCA assessments are an essential tool for understanding all aspects of the life cycle of products and/or processes. Through it, it is possible to identify weak links in production chains and act where it is most urgent to do so.

Finally, having covered topics belonging to different areas provides additional evidence of the flexibility of the LCA methodology, suitable for any field of research.

As seen, it is not only the environmental sphere, but also the social and economic sphere that defines sustainable development, and it is in this sense that future developments of the work presented in this thesis will be projected. It can be done by following the updates of the methodology, which have led to the definition of a new approach called Life Cycle Sustainability Analysis[3]. The use of a combined approach is particularly important where the decision-making process is mainly driven by economic feasibility and social acceptance, as in the case of industrial production.

Future developments will also include the investigation of other case studies related to the use of renewable sources in industrial chemistry and the extension of the field of interest to other sectors such as environmental assessment of different water supply strategies in a perspective of resource optimisation.

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Annex A

Table A1 – LCI Scenario A: PTA from isobutanol.

Stage	Process	Amount	Unit
Cultivation phases			
	Maize grain	4.2E+03	kg
ABE fermentation			
Input	Calcium carbonate	2.4E+01	kg
	Sulphuric acid	8.1E+00	kg
	Sodium hydroxide	2.8E-01	kg
	Ammonium sulfate	9.4E+00	kg
	Phosphate fertiliser	4.1E+01	kg
	Electricity	2.2E+02	kWh
	Steam	2.5E+03	kg
Avoided products	Acetone	5.1E+01	kg
	Ethanol	4.4E+00	kg
	DDGS	4.2E+01	kg
p-Xylene production			
Input	Heat	8.2E+02	MJ
	Cooling energy	8.1E+02	MJ
	Electricity	5.6E+01	MJ
Emission & Waste	Wastewater	5.4E+01	kg
Oxidation to PTA			
Input	Oxygen	5.9E+01	kg
	Carbon dioxide	3.5E-01	kg
	Acetic acid	5.4E-01	kg
	Heat	6.9E+02	MJ
Emission & Waste	Oxygen	1.5E+00	kg
	Carbon dioxide, biogenic	6.0E-01	kg
	Wastewater	2.2E+01	kg

Table A2 – LCI Scenario B: PTA from HMF and ethylene.

Stage	Process	Amount	Unit
Bio-ethylene production			
Input	Ethanol, from maize	2.0E+01	kg
	Electricity	2.1E+01	MJ
	Fuel oil	6.6E+01	MJ
Emission	Methane	1.8E-02	kg
	Carbon monoxide	2.3E-03	kg
	Carbon dioxide	3.8E+00	kg
	NMVOC	1.3E-04	kg
	Sulphur dioxide	1.2E-03	kg
	Nitrogen oxides	1.8E-02	kg

	Dinitrogen monoxide	1.4E-04	kg
p-Xylene production			
Input	Sugar, from sugar beet	1.0E+02	kg
	Hydrogen	2.9E+00	kg
	Water	2.7E+00	m^3
	Electricity	3.4E+01	MJ
	Steam	1.0E+03	kg
Emission & Waste	Carbon dioxide	2.3E+00	kg
	Wastewater	4.7E+01	kg
Oxidation to PTA			
Input	Oxygen	5.9E+01	kg
	Carbon dioxide	3.5E-01	kg
	Acetic acid	5.4E-01	kg
	Heat	6.9E+02	MJ
Emission & Waste	Oxygen	1.5E+00	kg
	Carbon dioxide, biogenic	6.0E-01	kg
	Wastewater	2.2E+01	kg

Table A3 – LCI Scenario C: PTA from orange peels.

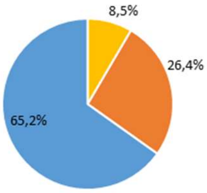
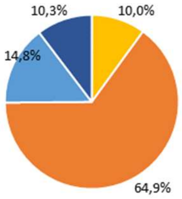
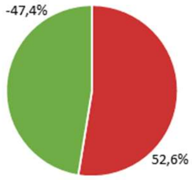
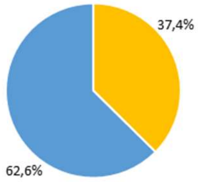
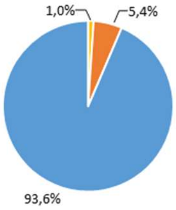
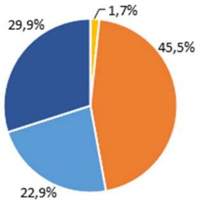
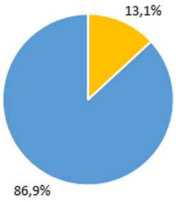
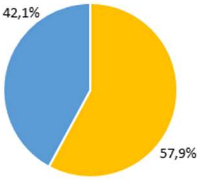
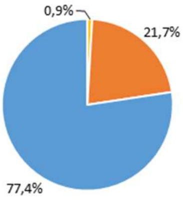
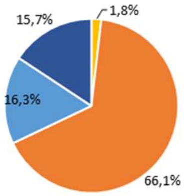
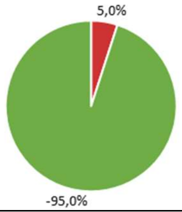
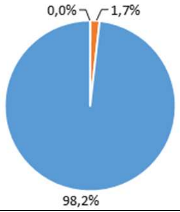
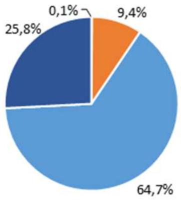
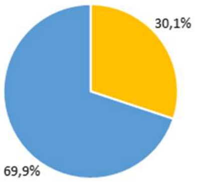
Stage	Process	Amount	Unit
p-Cymene production			
Input	Orange peels	4.1E+03	kg
	Water	4.1E+02	kg
	Electricity	3.6E+02	kWh
	Steam	2.3E+02	kg
	Water	5.2E+01	m^3
Waste	Wastewater	3.5E+03	kg
Avoided product	Composting of wastes	1.7E+04	kg
Oxidation to PTA			
Input	Oxygen	1.7E+01	kg
	Heat	5.1E+01	MJ
	Cooling energy	3.3E+02	MJ
	Electricity	4.8E+01	MJ
Emission & Waste	Wastewater	7.3E+00	kg

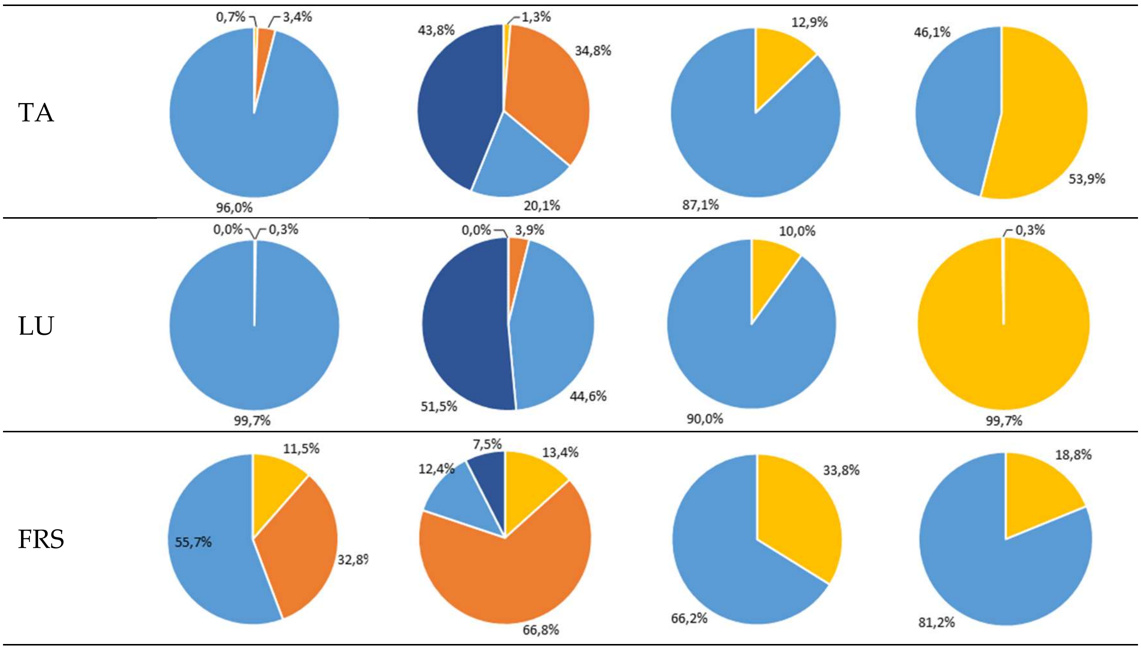
Table A4 – LCI Scenario D: PTA from crude oil.

Stage	Process	Amount	Unit
PTA production			
Input	Xylene	6.6E+02	kg
	Water	3.4E-01	m^3
	Acetic acid	5.0E+01	kg

	Electricity	4.7E+02	kWh
	Heat	1.6E+03	MJ
	Nitrogen	4.9E+01	kg
	Sodium hydroxide	1.5E+00	kg
	Steam	6.4E+02	kg
	Water	4.3E+02	kg
Emission & Waste	Hydrocarbons, aromatic	0.378	kg
	NMVOC	0.11	kg
	PM2.5	0.02	kg
	PM10	0.03	kg
	Water	0.22	m³
	Average incineration residue	6.00	kg
	Hazardous waste	0.20	kg

Table A5 – Contribution of the phases of the processes on the impact of scenarios.

Impact category	Scenario A	Scenario B	Scenario C	Scenario D
GW				
FPMF				
HT				
WC				



General legend:

🟨 Final oxidation steps (*Amoco process* or *Oxidation to PTA*)

🟧 Transformations to p-Xylene (*GEVO process* or *Diels-Alder reaction*)

🟦 🟦 Raw materials (*Isobutanol*, *Ethylene*, *HMF*, *p-Cymene* or *p-Xylene*)

🟩 Negative impacts (*p-Cymene production*)

🟥 Positive impacts (*Oxidation to PTA*)

Table A6 – Comparison between PTA production scenarios in terms of ReCiPe 2016 H/A – Single Score.

Impact category	**Unit**	**Scenario A**	**Scenario B**	**Scenario C**	**Scenario D**
Total impact	Pt	746.13	558.89	96.58	372.46
GW	Pt	143.63	123.20	1.16	47.10
FPMF	Pt	116.94	73.34	21.73	24.42
HT	Pt	18.83	10.60	-27.53	9.31
WC	Pt	32.35	14.26	15.60	1.99
TA	Pt	20.39	10.35	2.39	2.55
LU	Pt	38.58	20.43	0.63	0.55
FRS	Pt	375.40	306.71	82.60	286.54

Figure A1 – Contribution analysis for Scenario B (a) and Scenario C (b) (ReCiPe 2016 H/A).

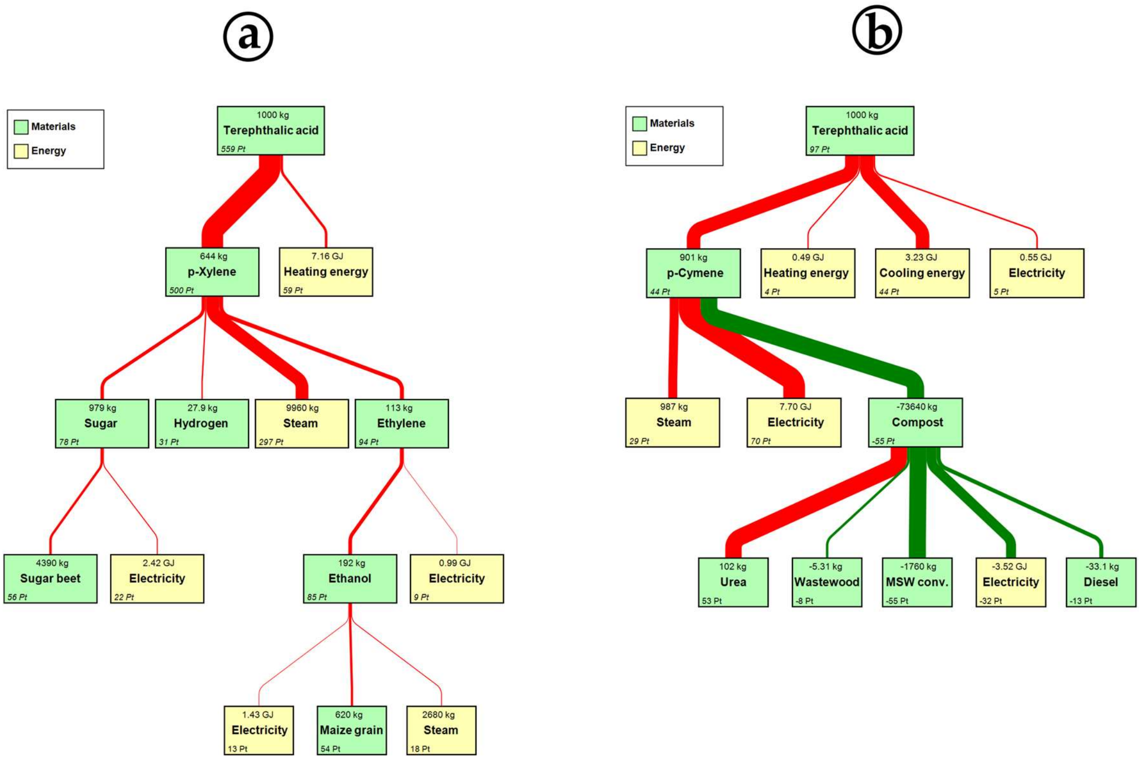


Figure A2 – Carbon formation curves at thermodynamic equilibrium calculated at 5 bar and 30 bar with an equimolar mixture of CH_4 and CO_2 in the inlet stream, as a function of temperature and S/CH_4 ratio (DR condition, $S/CH_4 = 0.0$).

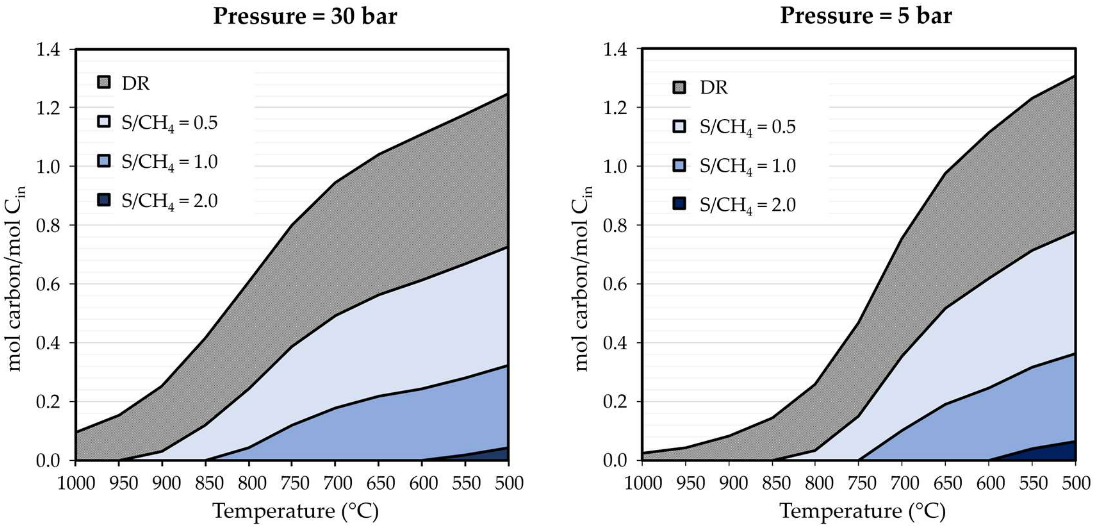


Figure A3 – Process flow diagram for (a) the ATR of pure methane (Scenario A), (b) the ATR of biogas (Scenario B) and (c) the S/DR of biogas using pure methane as heating medium (Scenario C).

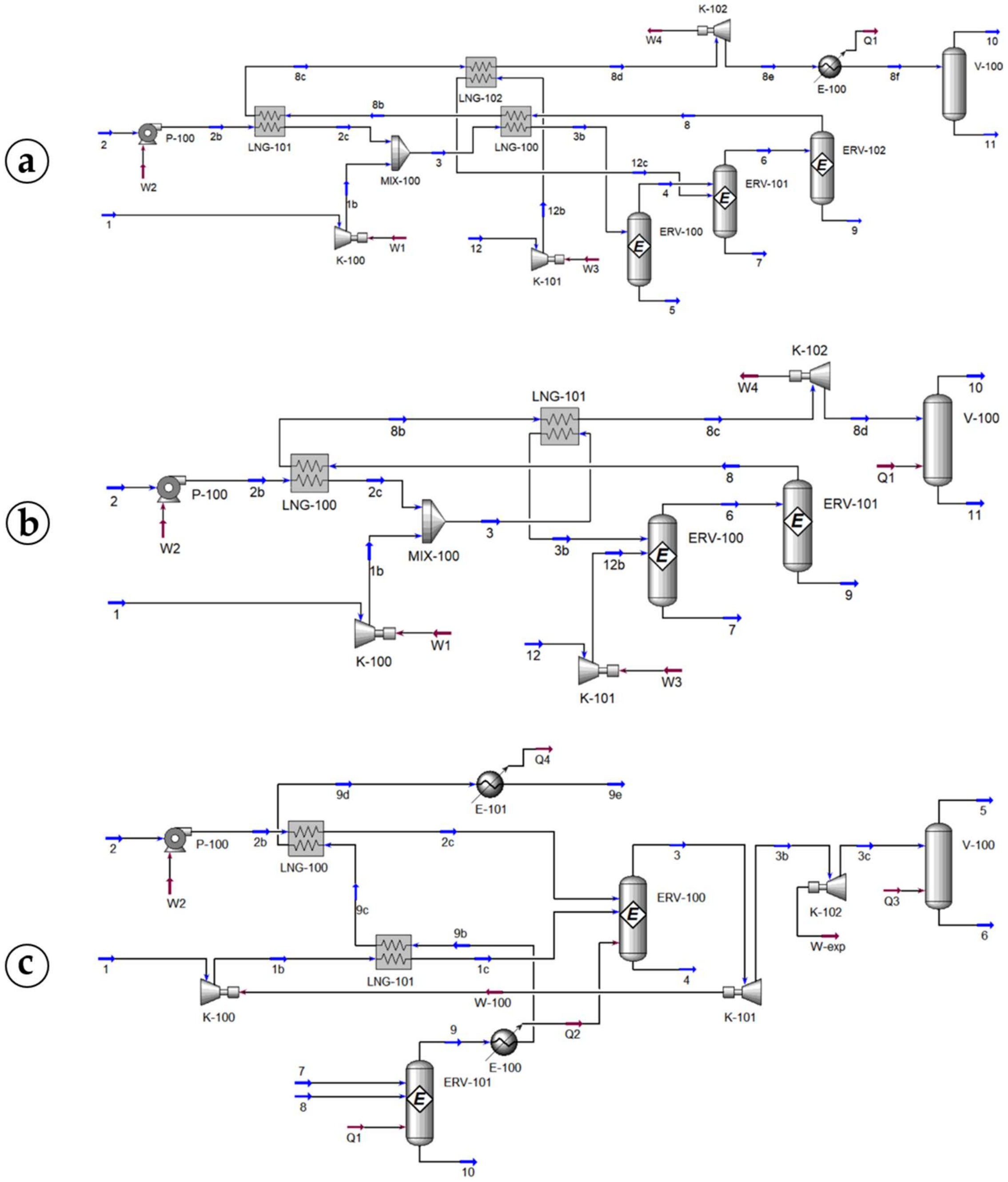


Table A7 – Full environmental results of 1 mol of imidazolium chlorides ILs.

Impact category	**Unit**	**[Hmim] Cl**	**[C$_2$mim] Cl**	**[C$_4$mim] Cl**	**[C$_6$mim] Cl**	**[C$_{10}$mim] Cl**	**[Amim] Cl**	**[PhC$_2$mim] Cl**	**[C$_4$dmim] Cl**
Abiotic depletion potential	kg Sb eq.	5.9E-06	8.6E-06	9.7E-06	1.1E-05	1.3E-05	8.2E-06	1.1E-05	1.0E-05
Abiotic depletion potential (fossil fuels)	MJ	1.4E+01	1.7E+01	1.8E+01	1.9E+01	2.1E+01	1.8E+01	2.4E+01	2.0E+01
Global warming potential	kg CO$_2$ eq.	7.9E-01	9.8E-01	1.0E+00	1.1E+00	1.2E+00	9.9E-01	1.2E+00	1.1E+00
Ozone layer depletion potential	kg CFC-11 eq.	8.3E-07	8.9E-07	9.0E-07	9.2E-07	9.5E-07	8.8E-07	9.1E-07	9.0E-07
Human toxicity potential	kg 1,4-DCB eq.	6.2E+00	6.4E+00	6.4E+00	6.5E+00	6.6E+00	6.4E+00	6.5E+00	6.5E+00
Fresh water aquatic ecotoxicity potential	kg 1,4-DCB eq.	2.5E-01	3.3E-01	3.7E-01	4.0E-01	4.8E-01	3.3E-01	4.1E-01	4.1E-01
Marine aquatic ecotoxicity potential	kg 1,4-DCB eq.	4.5E+02	6.0E+02	6.7E+02	7.3E+02	8.6E+02	6.1E+02	7.7E+02	7.9E+02
Terrestrial ecotoxicity potential	kg 1,4-DCB eq.	1.6E-03	2.1E-03	2.3E-03	2.5E-03	2.9E-03	2.1E-03	2.4E-03	2.5E-03
Photochemical oxidation potential	kg C$_2$H$_4$ eq.	1.5E-04	1.7E-04	1.8E-04	1.9E-04	2.1E-04	1.8E-04	3.8E-04	1.9E-04
Acidification potential	kg SO$_2$ eq.	2.7E-03	3.2E-03	3.4E-03	3.5E-03	3.9E-03	3.3E-03	4.0E-03	3.9E-03
Eutrophication potential	kg PO$_4^{3-}$ eq.	6.1E-04	7.9E-04	8.6E-04	9.3E-04	1.1E-03	8.2E-04	1.1E-03	1.0E-03

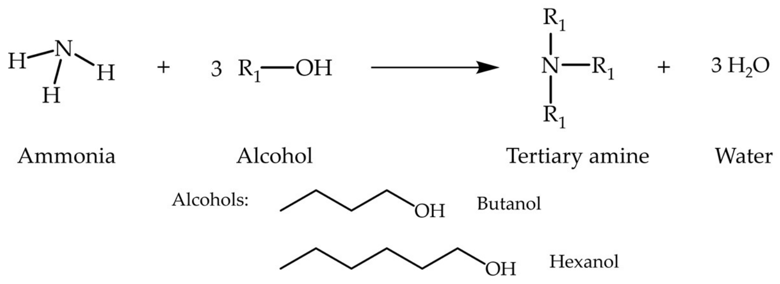
Table A8 – Full environmental results of 1 mol of imidazolium tetrafluoroborate ILs.

Impact category	**Unit**	**[Hmim] BF$_4$**	**[C$_2$mim] BF$_4$**	**[C$_4$mim] BF$_4$**	**[C$_6$mim] BF$_4$**	**[C$_{10}$mim] BF$_4$**	**[Amim] BF$_4$**	**[PhC$_2$mim] BF$_4$**	**[C$_4$dmim] BF$_4$**
Abiotic depletion potential	kg Sb eq.	1.4E-04	1.4E-04	1.5E-04	1.5E-04	1.5E-04	1.4E-04	1.5E-04	1.5E-04
Abiotic depletion potential (fossil fuels)	MJ	3.5E+01	3.9E+01	3.9E+01	4.0E+01	4.3E+01	3.9E+01	4.6E+01	4.1E+01
Global warming potential	kg CO$_2$ eq.	2.1E+00	2.3E+00	2.4E+00	2.4E+00	2.5E+00	2.3E+00	2.6E+00	2.4E+00
Ozone layer depletion potential	kg CFC-11 eq.	1.1E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06
Human toxicity potential	kg 1,4-DCB eq.	8.6E+00	8.8E+00	8.8E+00	8.9E+00	9.0E+00	8.7E+00	8.9E+00	8.9E+00

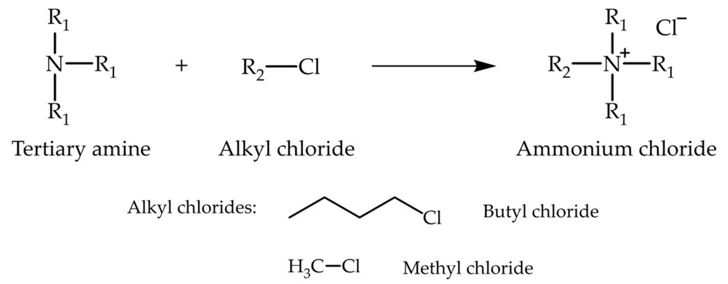
Fresh water aquatic ecotoxicity potential	kg 1,4-DCB eq.	1.2E+00	1.3E+00	1.3E+00	1.4E+00	1.4E+00	1.3E+00	1.4E+00	1.4E+00
Marine aquatic ecotoxicity potential	kg 1,4-DCB eq.	9.1E+03	9.3E+03	9.4E+03	9.5E+03	9.6E+03	9.3E+03	9.5E+03	9.5E+03
Terrestrial ecotoxicity potential	kg 1,4-DCB eq.	4.4E-03	5.0E-03	5.2E-03	5.4E-03	5.8E-03	5.0E-03	5.4E-03	5.4E-03
Photochemical oxidation potential	kg C_2H_4 eq.	5.5E-04	5.7E-04	5.9E-04	5.9E-04	6.1E-04	5.8E-04	8.0E-04	5.9E-04
Acidification potential	kg SO_2 eq.	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.3E-02	1.2E-02	1.3E-02	1.3E-02
Eutrophication potential	kg PO_4^{3-} eq.	3.0E-03	3.2E-03	3.3E-03	3.4E-03	3.5E-03	3.2E-03	3.5E-03	3.4E-03

Table A9 – Full environmental results of 1 mol of imidazolium hexafluorophosphate ILs.

Impact category	**Unit**	**[Hmim] PF_6**	**[C_2mim] PF_6**	**[C_4mim] PF_6**	**[C_6mim] PF_6**	**[C_{10}mim] PF_6**	**[Amim] PF_6**	**[PhC_2mim] PF_6**	**[C_4dmim] PF_6**
Abiotic depletion potential	kg Sb eq.	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04	1.3E-04
Abiotic depletion potential (fossil fuels)	MJ	5.2E+01	5.6E+01	5.7E+01	5.8E+01	6.0E+01	5.7E+01	6.3E+01	5.9E+01
Global warming potential	kg CO_2 eq.	3.9E+00	4.1E+00	4.2E+00	4.2E+00	4.3E+00	4.1E+00	4.4E+00	4.2E+00
Ozone layer depletion potential	kg CFC-11 eq.	1.3E-06	1.4E-06	1.4E-06	1.4E-06	1.4E-06	1.4E-06	1.4E-06	1.4E-06
Human toxicity potential	kg 1,4-DCB eq.	1.4E+01	1.4E+01	1.4E+01	1.4E+01	1.5E+01	1.4E+01	1.5E+01	1.4E+01
Fresh water aquatic ecotoxicity potential	kg 1,4-DCB eq.	2.6E+00	2.7E+00	2.8E+00	2.8E+00	2.9E+00	2.7E+00	2.8E+00	2.8E+00
Marine aquatic ecotoxicity potential	kg 1,4-DCB eq.	5.8E+04	5.8E+04	5.8E+04	5.8E+04	5.8E+04	5.8E+04	5.8E+04	5.8E+04
Terrestrial ecotoxicity potential	kg 1,4-DCB eq.	1.1E-02	1.1E-02	1.1E-02	1.2E-02	1.2E-02	1.1E-02	1.2E-02	1.2E-02
Photochemical oxidation potential	kg C_2H_4 eq.	1.8E-03	1.8E-03	1.8E-03	1.9E-03	1.9E-03	1.8E-03	2.1E-03	1.8E-03
Acidification potential	kg SO_2 eq.	3.1E-02	3.2E-02	3.2E-02	3.2E-02	3.2E-02	3.2E-02	3.2E-02	3.2E-02
Eutrophication potential	kg PO_4^{3-} eq.	6.0E-03	6.2E-03	6.3E-03	6.4E-03	6.5E-03	6.2E-03	6.5E-03	6.5E-03



eq. 3.8



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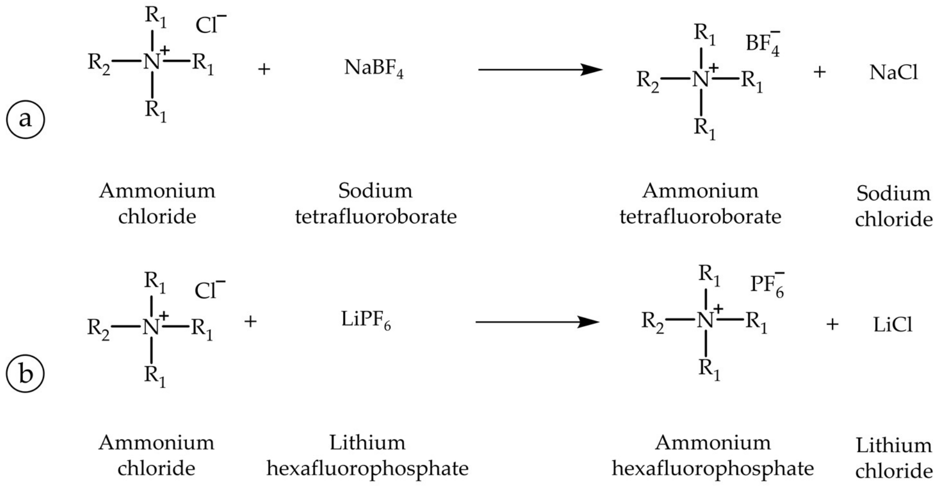

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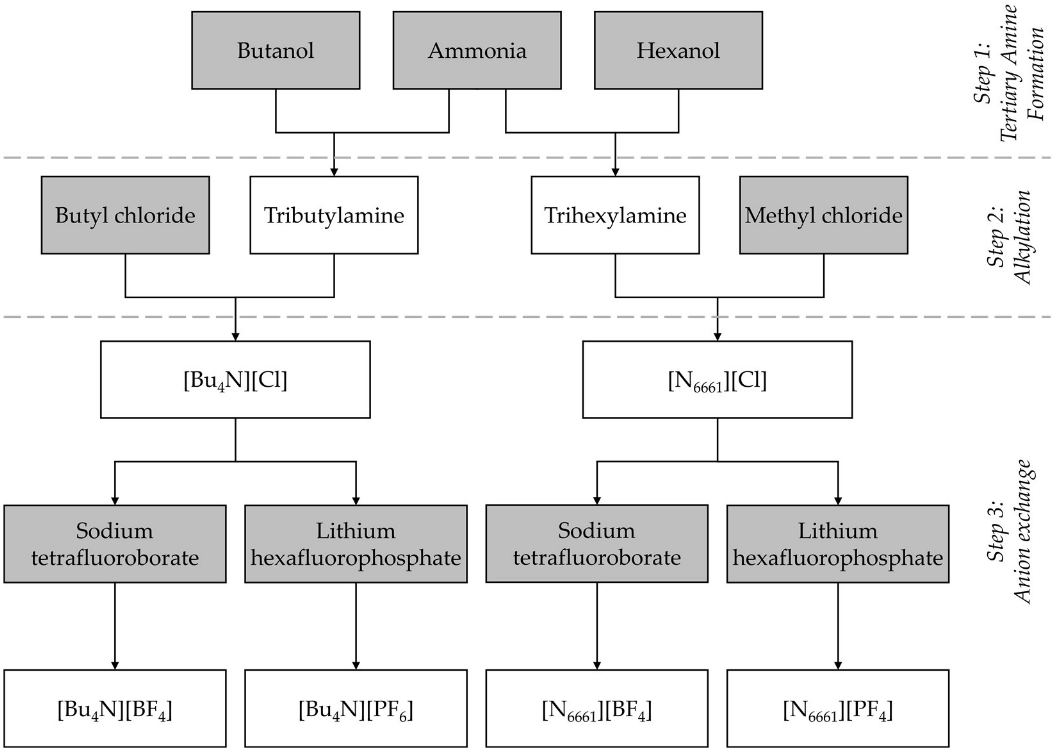
Table A10 – Comparison between PTA production scenarios in terms of ReCiPe 2016 H/A – Single Score.

Synthesis step	Reactants	Co-products and waste	Unit	[Bu$_4$N]$^+$	[N$_{6661}$]$^+$
Tertiary amine production	Ammonia		g/mol	21	24
	Butanol		g/mol	313	-
	Hexanol		g/mol	-	432
	Heat		MJ/mol	6	7
		Water	g/mol	61	61
		Organic waste	g/mol	67	91

Menshutkin reaction	Tertiary amine		g/mol	209	304
	Butyl chloride		g/mol	167	-
	Methyl chloride		g/mol	-	91
	Cooling		MJ/mol	0.3	0.1
		Organic waste	g/mol	70	43
Anion exchange $[BF_4]^-$	Ammonium chloride		g/mol	305	352
	Sodium tetrafluoroborate		g/mol	121	121
	Heat		MJ/mol	6	6
		Sodium chloride	g/mol	58	58
		Organic waste	g/mol	38	43
Anion exchange $[PF_6]^-$	Ammonium chloride		g/mol	305	352
	Lithium hexafluorophosphate		g/mol	167	167
	Heat		MJ/mol	8	8
		Lithium chloride	g/mol	42	42
		Organic waste	g/mol	43	47

Figure A4 – Generic life cycle tree for the production of ammonium-based ILs selected in the study.



Annex B

Table B1 – Analysis of environmental impacts of 1 kg of manure with or without inclusion of animal feed production (ReCiPe 2016 H/A – Single Score).

Impact category	Unit	With feed impacts	Without feed impacts
Total	**mPt**	1.68E+00	5.71E-01
GW	mPt	5.95E-01	2.95E-01
FPMF	mPt	3.42E-01	1.39E-01
HT	mPt	2.71E-02	2.08E-02
WC	mPt	3.38E-02	2.10E-03
FRS	mPt	2.54E-01	6.89E-02
Others	mPt	4.28E-01	4.52E-02
Contribution in Scenario B2	**Pt**	**33.64**	**11.43**

Table B2 – Impacts of all considered scenarios in terms of ReCiPe 2016 H/A – Single Score.

Impact category	Unit	Scenario A1	Scenario A2	Scenario B1	Scenario B2	Scenario C
Total impact	**Pt**	**43.8**	**49.8**	**12.6**	**20.3**	**1245.1**
GW	Pt	1.5	1.6	0.4	6.2	55.9
SOD	Pt	8.5E-04	9.4E-04	1.8E-04	1.4E-02	3.3E-02
IR	Pt	6.9E-04	7.7E-04	1.4E-04	6.8E-04	5.1E-02
OF	Pt	7.2E-02	7.8E-02	1.7E-02	3.8E-02	3.8
FPMF	Pt	3.4	3.6	0.5	3.1	333.8
TA	Pt	3.7E-01	3.9E-01	5.9E-02	6.5E-01	35.9
FE	Pt	1.6E-01	1.6E-01	2.7E-03	3.0E-02	29.7
ME	Pt	2.5E-05	2.5E-05	9.6E-07	8.1E-06	4.2E-03
TET	Pt	6.6E-02	6.6E-02	5.5E-04	4.6E-03	11.8
FET	Pt	2.9E-02	2.9E-02	2.9E-04	3.5E-03	5.1
MET	Pt	6.3E-03	6.3E-03	6.8E-05	7.3E-04	1.1
HT	Pt	3.5	3.5	4.6E-02	4.5E-01	614.0
LU	Pt	2.2E-02	2.3E-02	3.0E-03	2.0E-01	2.7
MRS	Pt	2.3E-01	2.3E-01	4.0E-03	3.8E-02	43.8
FRS	Pt	34.2	37.9	11.5	9.5	103.6
WC	Pt	2.3E-01	2.3E+00	1.0E-02	5.0E-02	3.9

Table B3 – Distribution, calculation of CU factors and prices of the agricultural products of the two crop rotations.

Product	Purpose	Distribution	Receptor	Share	ME [MJ/kg]	CU indexes [CU/kg]	CU factor [CU/kg]	Price [$/ton]
Soybean	Animal	85%	Ruminants	62%	14.8	1.20[3]	**1.23**	**180.7**
			Swine	17%	15.9			
			Poultry	18%	14.7			
			Fish	3%	17.9			
	Human	11%				1.25		
	Industrial	4%				1.86		
Corn	Animal	71%	Ruminants	55%	11.7	0.99[3]	**1.09**	**106.6**
			Swine	9%	14.2			
			Poultry	36%	13.1			
	Human	13%				1.14		
	Industrial	16%				1.48		
Wheat	Animal	-						
	Human	100%				2.86	**2.86**	**144.2**
	Industrial	-						
Sunflower	Animal	43%	Ruminants	100%	1.9	0.15[3]		
	Human	57%				1.54	**0.94**	**157.7**
	Industrial	-						
Rapeseed	Animal	-						
	Human	50%				2.11	**2.21**	**299.5**
	Industrial	50%				2.31		
Mung bean	Animal	-						
	Human	100%				3.33	**3.33**	**661.3**
	Industrial	-						

Table B4 – LCI of San Justo (SJ) Rotation.

		Unit	Wheat	Soybean 1st yr	Sunflower	Corn	Fallow	Soybean 3rd-6th yr
	Production	**kg**	**2800**	**2600**	**1300**	**3850**	**-**	**3200**
Land use	Occupation	ha·a	0.5	0.5	0.25	0.25	0.5	0.5
	Transformation from annual crop	ha	1.0	1.0	0.5	0.5	-	1.0
	Transformation to arable	ha	1.0	1.0	0.5	0.5	-	1.0
Machinery	Spraying machine	ha	4.0	5.0	1.5	1.5	-	6.0
	Sowing machine	ha	1.0	1.0	0.5	0.5	-	1.0
	Fertilizing machine	ha	1.0	1.0	0.5	0.5	-	-
	Combine harvester	ha	1.0	1.0	0.5	0.5	-	1.0
Seeds & growth	Seeds	kg	140.0	65.0	3.5	10.0	-	65.0

promotors	Carbendazim	g	40.5	21.0	-	-	-	21.0
	Thiram	g	40.5	21.0	-	-	-	21.0
	Metalaxyl	g	11.8	6.1	-	-	-	6.1
Fertilisers	Monoammonium phosphate, as N	kg	-	13.2	-	-	-	7.7
	Monoammonium phosphate, as P	kg	-	62.4	-	-	-	36.4
	Diammonium phosphate	kg	80.0	-	40.0	67.5	-	-
	Urea	kg	120.0	-	70.0	82.5	-	-
	Zinc phosphite	g	540.0	-	-		-	-
	Nitrogen fertiliser	g	320.0	-	-		-	-
	Calcium sulphate	kg	120.0	-	60.0	60.0	-	-
	Manganese	g	-	20.0	-	-	-	-
	Boron	g	-	100.0	50.0	-	-	-
	Zinc	g	-	-	-	80.0	-	-
Herbicides	Glyphosate	g	1536.0	3360.5	736.0	1547.0	-	4960.5
	Metsulfuron-methyl	g	0.07	-	-	-	-	-
	Dicamba	g	86.6	-	-	-	-	-
	Metolachlor	g	-	-	480.0	-	-	-
	2,4-D	g	-	520.0	300.0	400.0	-	800.0
	Haloxyfop	g	-	135.0	-	-	-	135.0
	Picloram potassium salt	g	-	-	-	13.9	-	-
	Diflufenican	g	-	125.0	62.5	-	-	125.0
	Flumioxazin	g	-	-	-	28.8	-	-
	Siliconed methyled oil	g	300.0	1200.0	200.0	150.0	-	1200.0
Insecticides	Lufenuron	g	-	10.0	-	-	-	10.0
	Cyhalothrin-gamma	g	-	-	1.9	-	-	-
	Fipronil	g	-	-	2.0	-	-	-
	Chlorantraniliprole	g	-	5.0	-	-	-	5.0
	Flubendiamide	g	-	-	-	12.0	-	-
	Triflumuron	g	-	-	12.0	-	-	-
	Tiametoxam	g	-	28.2	-	-	-	28.2
	Lambdacialotrina	g	-	21.2	-	-	-	21.2
Fungicides	Trifloxystrobin	g	82.5	45.0	-	-	-	56.3
	Cyproconazole	g	35.2	19.2	-	-	-	24.0
	Zinc Phosphite	g	540.0	135.0	-	-	-	-
	Nitrogen fertiliser	g	320.0	-	-	-	-	-

Table B5 – LCI of Evergreen (EG) Rotation.

		Unit	**Sunflower**	**Corn 1st yr**	**Rapeseed coverage**	**Soybean 2nd yr**	**Wheat**	**Corn 3rd yr**
	Production	**kg**	**2600**	**6300**	**-**	**3200**	**2800**	**6700**
Land use	Occupation	ha·a	0.5	0.5	0.5	0.5	0.5	0.5
	Transformation from annual crop	ha	1.0	1.0	1.0	1.0	1.0	1.0

	Transformation to arable	ha	1.0	1.0	1.0	1.0	1.0	1.0
Machinery	Spraying machine	ha	3.0	3.0	-	5.0	4.0	3.0
	Sowing machine	ha	1.0	1.0	1.0	1.0	1.0	1.0
	Fertilizing machine	ha	1.0	1.0	1.0	-	1.0	1.0
	Combine harvester	ha	1.0	1.0	-	1.0	1.0	1.0
Seeds & growth promotors	Seeds	kg	7.0	15.0	7.0	65.0	140.0	15.0
	Carbendazim	g	-	-	4.5	18.9	40.5	-
	Thiram	g	-	-	4.5	18.9	40.5	-
	Metalaxyl	g	-	-	1.3	5.5	11.8	-
	Imidacloprid	g	-	-	9.0	-	48.6	-
	Zinc	g	1.2	2.0	1.5	6.3	13.5	160.0
Fertilisers	Monoammonium phosphate, as N	kg	-	-	-	13.2	-	-
	Monoammonium phosphate, as P	kg	-	-	-	62.4	-	-
	Diammonium phosphate	kg	80.0	96.0	-	-	80.0	96.0
	Urea	kg	140.0	144.0	-	-	120.0	144.0
	Zinc phosphite	g	-	-	-	-	540.0	-
	Nitrogen fertiliser	g	-	-	-	-	320.0	-
	Calcium sulphate	kg	120.0	-	120.0	-	120.0	-
	Manganese	g	-	-	-	20.0	-	-
	Boron	g	100.0	-	-	100.0	-	-
	Zinc	g	-	160.0	-	-	-	160.0
Herbicides	Glyphosate	g	1920.0	3190.0	-	3360.5	1536.0	3190.0
	Metsulfuron-methyl	g	-	-	-	-	0.07	-
	Dicamba	g	-	-	-	-	86.6	-
	Metolachlor	g	960.0	-	-	-	-	-
	2,4-D	g	600.0	-	-	520.0	-	-
	Haloxyfop	g	-	-	-	135.0	-	-
	Picloram potassium salt	g	-	41.6	-	-	-	41.6
	Diflufenican	g	125.0	-	-	125.0	-	-
	Flumioxazin	g	-	57.6	-	-	-	57.6
	Clethodim	g	-	216.0	-	-	-	216.0
	Siliconed methyled oil	g	400.0	1200.0	-	1200.0	300.0	1200.0
Insecticides	Lufenuron	g	-	-	-	10.0	-	-
	Cyhalothrin-gamma	g	3.8	-	-	-	-	-
	Fipronil	g	4.0	-	-	-	-	-
	Chlorantraniliprole	g	-	-	-	5.0	-	-
	Flubendiamide	g	-	2.4	-	-	-	2.4
	Triflumuron	g	12.0	-	-	-	-	-
	Tiametoxam	g	-	-	-	28.2	-	-
	Lambdacialotrina	g	-	-	-	21.2	-	-
Fungicides	Trifloxystrobin	g	-	-	-	45.0	82.5	-
	Cyproconazole	g	-	-	-	19.2	35.2	-
	Zinc Phosphite	g	-	-	-	135.0	540.0	-
	Nitrogen fertiliser	g	-	-	-	-	320.0	-

		Unit	**Ryegrass coverage**	**Soybean 4th yr**	**Rapeseed**	**Soybean 5th yr**	**Corn 6th yr**	**Mung bean**
	Production	**kg**	**-**	**3200**	**1900**	**3200**	**7700**	**1200**
Land use	Occupation	ha·a	0.5	0.5	0.5	0.5	0.5	0.5
	Transformation from annual crop	ha	1.0	1.0	1.0	1.0	1.0	1.0
	Transformation to arable	ha	1.0	1.0	1.0	1.0	1.0	1.0
Machinery	Spraying machine	ha	-	5.0	3.0	5.0	3.0	3.0
	Sowing machine	ha	1.0	1.0	1.0	1.0	1.0	1.0
	Fertilizing machine	ha	1.0	-	1.0	-	1.0	-
	Combine harvester	ha	-	1.0	1.0	1.0	1.0	1.0
Seeds & growth promotors	Seeds	kg	25.0	65.0	7.0	65.0	20.0	33.0
	Carbendazim	g	-	18.9	2.1	18.9	-	7.5
	Thiram	g	-	18.9	2.1	18.9	-	7.5
	Metalaxyl	g	-	5.5	0.6	5.5	-	2.2
	Imidacloprid	g	-	-	4.2	-	-	9.0
	Zinc	g	2.0	6.3	0.7	6.3	2.0	2.5
Fertilisers	Monoammonium phosphate, as N	kg	-	13.2	-	13.2	-	5.5
	Monoammonium phosphate, as P	kg	-	62.4	-	62.4	-	26.0
	Diammonium phosphate	kg	-	-	90.0	-	135.0	-
	Urea	kg	-	-	-	-	165.0	-
	Nitrogen fertiliser	g	-	-	47.4	-	-	-
	Calcium sulphate	kg	120.0	-	120.0	-	120.0	-
	Sulphur	g	-	-	4108.0	-	-	-
	Manganese	g	-	20.0	-	20.0	-	20.0
	Boron	g	-	100.0	-	100.0	-	100.0
	Zinc	g	-	-	-	-	160.0	-
Herbicides	Glyphosate	g	-	3040.5	1280.0	2400.5	3094.0	-
	Metsulfuron-methyl	g	0.006	-	-	-	-	-
	Dicamba	g	-	-	115.4	-	-	-
	2,4-D	g	-	520.0	-	520.0	800.0	-
	Haloxyfop	g	-	135.0	-	135.0	-	-
	Picloram potassium salt	g	41.6	-	-	-	27.7	-
	Diflufenican	g	-	125.0	-	125.0	-	-
	Flumioxazin	g	-	-	-	-	57.6	-
	Glufosinate ammonium	g	-	-	-	-	-	400.0
	Imazethapyr ammonium	g	-	-	-	-	-	63.6
	Paraquat dichloride	g	-	-	552.0	-	-	552.0
	Clethodim	g	-	-	-	-	-	192.0
	Siliconed methyled oil	g	-	1200.0	300.0	1200.0	300.0	1000.0
Insecticides	Lufenuron	g	-	10.0	15.0	10.0	-	-
	Chlorantraniliprole	g	-	5.0	-	5.0	-	-
	Flubendiamide	g	-	-	-	-	24.0	-
	Triflumuron	g	-	-	-	-	-	24.0
	Bifentrin	g	-	-	-	-	-	10.0

	Tiametoxam	g	-	28.2	-	28.2	-	28.2
	Lambdacialotrina	g	-	21.2	-	21.2	-	21.2
Fungicides	Trifloxystrobin	g	-	45.0	-	45.0	-	37.5
	Cyproconazole	g	-	19.2	-	19.2	-	16.0
	Zinc Phosphite	g	-	135.0	-	135.0	-	135.0

Table B6 – Impact assessment of the rotations in terms of ReCiPe 2016 Midpoint H/H.

Impact category	**Unit**	**SJ Rotation**	**EG Rotation**	**Unit**	**SJ Rotation**	**EG Rotation**
GW	kg CO_2 eq./CU	1.6E-01	1.5E-01	kg CO_2 eq./$	1.4E+00	1.3E+00
SOD	kg CFC-11 eq./CU	2.2E-07	1.7E-07	kg CFC-11 eq./$	1.9E-06	1.4E-06
IR	kBq Co-60 eq./CU	4.3E-03	4.2E-03	kBq Co-60 eq./$	3.7E-02	3.7E-02
OF	kg NOx eq./CU	7.6E-04	7.0E-04	kg NOx eq./$	6.5E-03	6.0E-03
FPMF	kg $PM_{2.5}$ eq./CU	3.8E-04	3.7E-04	kg $PM_{2.5}$ eq./$	3.2E-03	3.2E-03
TA	kg SO_2 eq./CU	8.4E-04	8.9E-04	kg SO_2 eq./$	7.1E-03	7.7E-03
FE	kg P eq./CU	4.9E-05	4.3E-05	kg P eq./$	4.2E-04	3.7E-04
ME	kg N eq./CU	3.9E-05	3.0E-05	kg N eq./$	3.3E-04	2.6E-04
TET	kg 1,4-DCB/CU	6.0E-01	6.7E-01	kg 1,4-DCB/$	5.1E+00	5.8E+00
FET	kg 1,4-DCB/CU	4.4E-03	4.3E-03	kg 1,4-DCB/$	3.7E-02	3.8E-02
MET	kg 1,4-DCB/CU	6.0E-03	6.2E-03	kg 1,4-DCB/$	5.1E-02	5.3E-02
HT	kg 1,4-DCB/CU	4.6E-03	4.4E-03	kg 1,4-DCB/$	3.9E-02	3.8E-02
LU	m^2·a crop eq./CU	1.9E+00	1.2E+00	m^2·a crop eq./$	1.6E+01	1.0E+01
MRS	kg Cu eq./CU	1.9E-03	2.0E-03	kg Cu eq./$	1.6E-02	1.7E-02
FRS	kg oil eq./CU	4.4E-02	4.8E-02	kg oil eq./$	3.8E-01	4.2E-01
WC	m^3/CU	4.7E-03	5.4E-03	m^3/$	4.0E-02	4.7E-02

Table B7 – Carbon footprint (CF), energy content and Carbon-Footprint/Energy index (CFE index) of the food items.

Meat and fish	**CF [g CO_2/g]**	**Energy content [kJ/g]**	**CFE index [g CO_2/kJ]**
Beef	22.80	5.48	4.16
Beef (hamburger)	10.20	11.03	0.92
Blue shark	3.37	4.40	0.77
Chicken	3.65	7.17	0.51
Codfish	3.51	2.96	1.19
Cuttlefish	7.13	3.02	2.36
Fish (generic)	4.41	4.40	1.00
Mackerel	1.80	7.10	0.25
Mussels	9.51	3.51	2.71

Dairy, eggs, subs.	**CF [g CO_2/g]**	**Energy content [kJ/g]**	**CFE index [g CO_2/kJ]**
Butter	9.25	31.71	0.29
Coconut milk	0.42	14.97	0.03
Cream	5.90	9.74	0.61
Eggs	3.20	5.35	0.60
Gorgonzola	10.70	13.56	0.79
Mascarpone	7.11	19.02	0.37
Milk	1.8	2.65	0.68
Mozzarella	8.70	10.58	0.82
Parmigiano	16.90	16.61	1.02

Octopus	7.13	2.37	3.01
Pilchard	1.10	9.43	0.12
Pork (generic)	5.77	8.58	0.67
Pork (ham)	4.25	9.36	0.45
Pork (minced meat)	4.22	10.80	0.39
Pork (tenderloin)	4.17	6.58	0.63
Pork (sausages)	4.22	12.73	0.33
Pork (bacon)	4.23	22.19	0.19
Shrimps	7.80	2.96	2.64
Squid	7.13	2.84	2.51
Tuna	2.15	6.66	0.32
Tuna (yellowfin)	20.45	6.66	3.07
Turkey	7.17	5.64	1.27
Veal	24.10	4.48	5.38

Vegetables	**CF [g CO_2/g]**	**Energy content [kJ/g]**	**CFE index [g CO_2/kJ]**
Artichokes	0.48	1.38	0.35
Aubergines	1.35	0.94	1.44
Beans	0.43	13.62	0.03
Beans (borlotti)	1.06	4.26	0.25
Cowpeas	0.49	13.32	0.04
Broccoli	0.60	1.40	0.43
Cabbage	0.23	1.00	0.23
Carrots	0.20	1.71	0.12
Cauliflower	0.36	1.24	0.29
Celery	0.18	0.97	0.19
Chard	0.10	1.03	0.10
Chickpeas	0.77	4.65	0.17
Cucumber	0.23	0.65	0.35
Fava beans	0.56	2.15	0.26
Fennel	0.48	0.62	0.77
Garlic	0.57	2.22	0.26
Green beans	0.31	1.01	0.31
Leek	0.09	1.45	0.07
Legumes (generic)	0.51	13.56	0.04
Lentils	1.03	13.35	0.08
Lettuce	0.37	0.92	0.40

Pecorino Romano	16.90	17.10	0.99
Pecorino Sardo	17.10	16.90	1.01
Rice milk	0.66	2.22	0.30
Ricotta	3.33	6.58	0.51
Soy milk	0.69	1.33	0.52
Stracchino	5.08	12.55	0.40
Yogurt	2.73	2.78	0.98

Cereals and pasta	**CF [g CO_2/g]**	**Energy content [kJ/g]**	**CFE index [g CO_2/kJ]**
Barley	0.43	14.47	0.03
Bread (sliced)	1.03	11.20	0.09
Breadcrumbs	1.03	14.96	0.07
Burghul	0.52	12.77	0.04
Corn flour	0.93	14.26	0.07
Cous cous	0.52	15.09	0.03
Croutons	1.44	11.52	0.12
Quinoa	1.15	15.72	0.07
Rice	2.55	14.15	0.18
Seitan	0.51	15.49	0.03
Semolina pasta	0.82	14.26	0.06
Tagliatelle (egg pasta)	2.46	14.49	0.17
Wheat	0.52	13.76	0.04
Wheat flour	0.31	13.52	0.02

Fruits	**CF [g CO_2/g]**	**Energy content [kJ/g]**	**CFE index [g CO_2/kJ]**
Almonds	1.54	26.29	0.06
Apples	0.15	1.82	0.08
Apricot	0.43	1.77	0.24
Banana	0.72	3.19	0.23
Blueberries	0.92	2.07	0.44
Cashew nut	1.44	25.26	0.06
Cherries	0.39	2.01	0.19
Chestnut	0.43	7.28	0.06
Figs	0.43	2.62	0.16
Hazelnuts	0.97	28.08	0.03
Kiwi	0.36	2.02	0.18
Lemon juice	0.70	0.43	1.63

Mushrooms	0.27	1.28	0.21
Olives	0.63	10.17	0.06
Onion	0.17	1.18	0.14
Peas	0.38	3.28	0.12
Pepper	0.66	1.08	0.61
Potatoes	0.25	3.03	0.08
Pumpkin	0.25	1.23	0.20
Savoy cabbage	0.23	1.21	0.19
Soybean	0.49	18.00	0.03
Spinach	0.54	1.45	0.37
Sweetcorn	0.47	4.39	0.11
Tofu	0.49	3.27	0.15
Tomatoes	0.45	0.80	0.56
Vegetables (generic)	0.37	0.96	0.38
Zucchini	0.21	0.66	0.32

Melon	0.30	1.43	0.21
Oranges	0.33	1.55	0.21
Peaches	0.43	1.19	0.36
Peanut	0.83	25.93	0.03
Pears	0.31	2.16	0.14
Raspberries	0.84	2.03	0.41
Strawberries	0.58	1.27	0.46
Watermelon	0.32	0.67	0.48
White wine	0.76	2.93	0.26

Oil, spices, sauces	**CF [g CO2/g]**	**Energy content [kJ/g]**	**CFE index [g CO2/kJ]**
Mustard	2.09	24.28	0.09
Olive oil	4.14	37.62	0.11
Peanuts oil	4.72	37.62	0.13
Pesto sauce	2.72	10.44	0.26
Ragù sauce	4.41	8.18	0.54
Saffron	3205.13	13.77	232.73
Tomato sauce	1.14	0.89	1.28

Figure B1 – Carbon-Footprint/Food Energy (CFE) index graph for the analysed ingredients.