

Alma Mater Studiorum - Università di Bologna

**DOTTORATO DI RICERCA IN  
CHIMICA**

Ciclo XXVII

Settore Concorsuale di afferenza: 03/A1 - CHIMICA ANALITICA

Settore Scientifico disciplinare: CHIM/12 - CHIMICA DELL'AMBIENTE E DEI BENI  
CULTURALI

**ASSESSMENT AND OPTIMIZATION OF CHEMICAL  
INDUSTRIAL PROCESSES FROM A LIFE CYCLE PERSPECTIVE**

Presentata da: **Daniele Cespi**

**Coordinatore Dottorato**

**Prof. Aldo Roda**

**Relatore**

**Prof. Dr. Fabrizio Passarini**

**Correlatore**

**Prof. Dr. Fabrizio Cavani**

**Esame finale anno 2015**

*Dedicated to my parents, Giorgio and Patrizia,  
and to my best friends for all your support during the hard days*



# Acknowledgement

Thanks to Fabrizio, for having always trusted in me and in mine abilities during the years of the PhD program. Thanks for all your time, support, suggestions, help and all the efforts you made.

Thanks to Prof. Fabrizio Cavani, for having involved us in these interesting projects, shared his knowledge and dedicated his time to some “*crazy environmental chemists*”.

Thanks to the undergraduate students, Esmeralda and Giada, without you I’ve never reached these results.

Thanks to Ivano, for his help, his time and his precious suggestions to each work.

Thanks to all the members of the group, Antonella, Asma, Chiara, Claudio, Elena, Elisa, Fabio, Federica, Francesca, Lara, Laura, Luca, Maywin, Michael, Michela, Monica, Nicola, Roberta, Silvia, Simona. I’ll never forget all the beautiful time we spent together.

Thanks to the Professors Paul T. Anastas and Julie B. Zimmerman and to all the Yale guys, in particular Chiara, Laurene, Sam and Shida. You were my family in the US and I’ve never felt alone with you.

Last but not least...

Thanks to Prof. Luciano Morselli, for his efforts to create the research group in Environmental and Cultural Heritage Chemistry at the University of Bologna.



*“Emancipate yourselves from mental slavery*

*None but ourselves can free our minds*

*Have no fear for atomic energy*

*‘Cause none a them can stop the time*

*How long shall they kill our prophets*

*While we stand aside and look*

*Some say it’s just a part of it*

*We’ve got to fulfill the book [...]”*

Bob Marley, Redemption Song 1980

*There are those who look at things the way they are,*

*and ask why...*

*I dream of things that never were, and ask why not?*

Robert F. Kennedy, 1968

## Candidate presentation

Daniele Cespi's work carried out during his triennium of PhD in Chemistry mainly dealt with the assessment and optimisation of industrial processes, by means of the application of analytical methodologies as *Life Cycle Assessment (LCA)*, able to perform environmental evaluation from a systemic standpoint.

During the first year, the attention has been oriented partially on domestic heating sector, comparing systems that employ renewable fuels as pellet and wood, with alternative techniques (as heating pump, solar panels, gas boiler); another aspect considered has been the assessment of sustainability in industrial chemistry. The latter represented the main topic of Daniele Cespi's work during the three year of PhD course. Two case studies have been particularly investigated, choosing among the most important industrial production.

The first example concerned the industrial synthesis of acrylonitrile by means of an ammoxidation reaction. Two different ways of synthesis have been studied comparing, with a *from cradle-to-industrial gate* approach, the traditional process from propylene, with the alternative one from propane, which is considered more sustainable, at least from an economical point of view.

Furthermore, the way from propane involves a reduction of stages, since the alkane is obtained via direct distillation of oil and does not require further cracking processes as olefin. Notwithstanding these observations, the use of propane as a feedstock revealed a greater environmental burden, mainly noticeable in terms of climate change and fossil fuel depletion. This trend is mainly due to the lower efficiency of the catalytic system employed in propane ammoxidation, which implies a higher consumption of reagents and auxiliaries, for the same amount of product.

In the second case study, LCA methodology has been applied to verify the principle of *Green Chemistry*, which suggests substituting fossil raw materials with renewable ones. Acrolein industrial production has been especially investigated comparing the consolidated way from propylene with the alternative one from glycerol, obtained as a by-product of the trans-esterification and hydrolysis of triglycerides, in order to assess the sustainability of its potential reuse as a platform molecule for the synthesis of chemicals. The results of LCA, also in this case expressed in terms of resource consumption, damage to human health and ecosystem quality, confirm the lower sustainability of the way from glycerol, in the case the latter is produced from

dedicated crops. Indeed, rapeseed cultivation, the most employed seed for biodiesel production via transesterification, implies a high consumption of energy and resources related to cultivation phase: use of fertilisers, land occupation and exploitation. On the contrary, starting from tallow and hydrolysing triglycerides in order to obtain fatty acids, dedicated crops are avoided, thus this glycerol is without impacts associated to cultivation and land exploitation. This results in a greater sustainability of this way even when compared to the traditional one.

Furthermore, during the PhD course, Daniele Cespi spent 8 months for a period of research at the Yale University - Center for Green Chemistry and Green Engineering (Connecticut, United States) as a *Visiting Assistant in Research (VAR)*, under the supervision of Prof Dr Paul Anastas and of Dr Evan Beach. There, he had the opportunity of studying the application of sustainability assessment tools as LCA to topics related to Green Chemistry and Green Engineering. Moreover, he started a collaboration with Pfizer Inc. (Dr. Peter J. Dunn) and the Center for Industrial Ecology (Dr. Thomas E. Swarr) with the aim of assess the sustainability also in the Pharma sector, identifying benefits and drawbacks related to the application of tools as *green metrics* and LCA. This collaboration resulted in a scientific paper which will be submitted prior a revision by the transnational company.

During the triennium, the candidate distinguished himself by contributing to the publication of the following articles on scientific peer-reviewed journals:

- Cespi D., Passarini F., Mastragostino G., Vassura I., Larocca S., Iaconi A., Chiericato A., Dubois J.-L., Cavani F., *Glycerol as feedstock in the synthesis of chemicals: a life cycle analysis for acrolein production*, *Green Chem.*, 2015, 17, 343-355;
- Cespi D., Passarini F., Neri E., Vassura I., Ciacci L., Cavani F., *Life Cycle Assessment comparison of two ways for acrylonitrile production: the SOHIO process and an alternative route using propane*, *J. Clean. Prod.*, 2014, 69, 17-25;
- Cespi D., Passarini F., Cavani F., Neri E., Vassura I., *Comparison of Different Chemical Processes from a Life Cycle Perspective*, *Engineering Chemical Transaction*, 2014, 36, 169-174;
- Cespi D., Passarini F., Ciacci L., Vassura I., Castellani V., Collina E., Piazzalunga A., Morselli L., *Heating systems LCA: comparison of biomass-based appliances*, *Int. J. LCA*, 2014, 19, 89-99.



He also was co-author of 14 contributions (oral or posters) to national and international congresses and attending a national school in environmental and cultural heritage chemistry. Overall, the activity developed by the PhD student has been of excellent quality.

*The Board expresses a score of excellence on the activity carried out by the candidate during the whole cycle of doctorate and considers him worthy to attain the PhD in Chemistry.*

# Index

<b>Aknowledgement</b>	<b>i</b>
<b>Candidate presentation</b>	<b>iv</b>
<b>Index</b>	<b>vii</b>
<b>List of tables</b>	<b>x</b>
<b>List of figures</b>	<b>xi</b>
<b>Abbreviations</b>	<b>xiv</b>
<b>Abstract</b>	<b>xvii</b>
<b>1. Introduction</b>	<b>1</b>
1.1 Sustainability - introduction and background	1
1.2 Sustainability - the industrial chemical sector	2
1.2.1 Green Chemistry and Green Engineering principles	3
1.2.2 Tools to evaluate sustainability in the chemical sector	7
1.3 Motivation and structure of the work	9
References	11

<b>2.</b>	<b>Methodology</b>	<b>13</b>
2.1	LCA methodology - introduction and background	13
2.2	LCA methodology - framework and standardization	16
2.2.1	Goal and Scope Definition	17
2.2.2	Inventory Analysis	18
2.2.2.1	Allocation criteria	19
2.2.3	Impact Assessment	20
2.2.3.1	Analysis methods overview	22
2.2.4	Interpretation	25
2.2.4.1	Uncertainty analysis	25
2.3	Software and Database	26
	References	28
<b>3.</b>	<b>Life Cycle perspective in the chemical sector</b>	<b>29</b>
3.1	Life cycle thinking of chemicals production - a literature review	29
3.2	Reduction in the production steps - the case study of acrylonitrile synthesis	30
3.2.1	Background and motivation of the study	31
3.2.2	Amoxidation reactions to acrylonitrile	32
3.2.3	System boundaries and functional unit	35
3.2.4	LCI of acrylonitrile production scenarios	36
3.2.4.1	Scenario 1: the SOHIO process	37
3.2.4.2	Scenario 2: Propane ammoxidation to acrylonitrile, alternative synthetic process	39
3.2.5	Impact assessment and results interpretation	40
3.2.6	Personal conclusions and recommendation	45
3.2.7	Comparison with other chemical products	47

3.3	Use of renewable feedstock – glycerol as a raw material in synthesis of acrolein	49
3.3.1	Glycerol as a platform molecule - background motivation of the study	49
3.3.2	System boundaries and functional unit	53
3.3.3	Acrolein production scenarios – description and inventory	55
3.3.3.1	Glycerol dehydration process	55
3.3.3.1.1	Triglycerides trans-esterification process	57
3.3.3.1.2	Triglycerides hydrolysis process	59
3.3.3.2	Propylene oxidation process	61
3.3.4	Impact assessment and results interpretation	62
3.3.5	Personal conclusions and recommendation	71
3.3.5.1	Renewable feedstock in the domestic heating system – an LCA approach	72
3.3.5.1.1	Introduction, main results and conclusions	73
	References	82
<b>4.</b>	<b>Conclusions of the study</b>	<b>91</b>
4.1	Main results and personal considerations about the approach	91
4.2	Future developments	93
	References	95
	<b>Annex A</b>	<b>96</b>
	<b>Annex B</b>	<b>99</b>

# List of Tables

<b>Table 1.1</b>	E-factors in the chemical industry. Adapted from Sheldon 2007	8
<b>Table 2.1</b>	Description of the 14040 series, including year of update	16
<b>Table 3.1</b>	Comparison between two acrolein production scenarios in terms of ReCiPe I/A - Characterization analysis. Adapted from Cespi et al. 2015- by permission of The Royal Society of Chemistry	62
<b>Table 3.2</b>	Global Warming Potential for both scenarios (IPCC 2007, 20a). Adapted from Cespi et al. 2015- reproduced by permission of The Royal Society of Chemistry	67
<b>Table 3.3</b>	Acrolein production from propylene partial oxidation, ReCiPe I/A - Characterization analysis. Adapted from Cespi et al. 2015- reproduced by permission of The Royal Society of Chemistry	69
<b>Table 3.4</b>	Monte Carlo analysis - comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories. Adapted from Cespi et al. 2015- reproduced by permission of The Royal Society of Chemistry	70
<b>Table 3.5</b>	Process contributions to impact categories by percentage. Adapted from Cespi et al. 2014 - reproduced by permission of Springer	78

# List of Figures

<b>Figure 1.1</b>	The three pillars of sustainability. Adapted from Clift 1995	1
<b>Figure 1.2</b>	Production of hazardous waste in 2013 per industrial sector. Graphic adapted from data reported in literature	3
<b>Figure 2.1</b>	Historical evolution of LCIA methods. Adapted from Curran 2012	14
<b>Figure 2.2</b>	Chronological distribution of life cycle assessment research-related articles n Web of Science (1998-2013). Source Chen et al. 2014	15
<b>Figure 2.3</b>	LCA framework, adapted from ISO 14040	17
<b>Figure 2.4</b>	Description of the flows exchanged between process units and environment	19
<b>Figure 2.5</b>	Simplified example of environmental mechanism which links both levels of analysis for the case study of greenhouse gases. Adapted from Goedkoop et al. 2012	24
<b>Figure 3.1</b>	SOHIO process. Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	34
<b>Figure 3.2</b>	Propane ammoxidation, recycle/no recycle configuration. Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	35

<b>Figure 3.3</b>	System boundaries of the study. Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	36
<b>Figure 3.4</b>	Five ammoxidation scenarios compared in terms of ReCiPe 2008 single score. Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	43
<b>Figure 3.5</b>	Radar chart showing results in terms of single points (by percentage). Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	44
<b>Figure 3.6</b>	Monte Carlo Analysis in terms of midpoint impact categories. Source: Cespi et al. 2014 <sup>67</sup> - reproduced by permission of Elsevier	45
<b>Figure 3.7</b>	Comparison between ammoxidation scenario and other industrial production: ReCiPe single score. Source: Cespi et al. 2014 <sup>99</sup> - reproduced by permission of AIDIC	48
<b>Figure 3.8</b>	A selection of glycerol valorization pathways. Source: Katryniok et al. 2009 - reproduced by permission of the Wiley-VCH Verlag GmbH & Co. KGaA Wiley	50
<b>Figure 3.9</b>	Glycerol sources trend per year	51
<b>Figure 3.10</b>	Trend of glycerol price per year	51
<b>Figure 3.11</b>	Chemicals derived from acrolein. Source: Liu et al. 2012	52

<b>Figure 3.12</b>	System boundaries considered in the LCA study for the bio-based scenarios. Source: Cespi et al. 2015 <sup>101</sup> - reproduced by permission of The Royal Society of Chemistry	54
<b>Figure 3.13</b>	System boundaries considered in the LCA study for the scenario starting from propylene. Source: Cespi et al. 2015 <sup>101</sup> - reproduced by permission of The Royal Society of Chemistry	55
<b>Figure 3.14</b>	EU biodiesel production. Source: EBB - European Biodiesel Board, <i>Statistics - The EU biodiesel industry 2011</i> , <a href="http://www.ebb-eu.org/stats.php">http://www.ebb-eu.org/stats.php</a> (accessed November 2014)	59
<b>Figure 3.15</b>	Comparison between two acrolein production scenarios in terms of ReCiPe I/A - Single score. Source: Cespi et al. 2015 <sup>101</sup> - reproduced by permission of The Royal Society of Chemistry	63
<b>Figure 3.16</b>	Comparison between the three acrolein production scenarios, in terms of ReCiPe I/A - Single score (radar chart). Source: Cespi et al. 2015 <sup>101</sup> - reproduced by permission of The Royal Society of Chemistry	68
<b>Figure 3.17</b>	Monte Carlo analysis - comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories. Source: Cespi et al. 2015 <sup>101</sup> - reproduced by permission of The Royal Society of Chemistry	70
<b>Figure 3.18</b>	Radar chart showing results in terms of single point (by percentage). Impact categories are at vertexes of the radar, while the lines lay in correspondence of the share gained by each scenario. Source: Cespi et al. 2014 <sup>96</sup> - reproduced by permission of Springer	75
<b>Figure 3.19</b>	Comparison of biomass based scenarios and innovative domestic heating systems. Values are expressed in ReCiPe single scores (mPt). Source: Cespi et al. 2014 <sup>96</sup> - reproduced by permission of Springer	79



# Abbreviations

ABS	Acrylonitrile-Butadiene-Styrene
ACN	Acrylonitrile
ADIC	Associazione Italiana di Ingegneria Chimica
AKCC	Asahi Kasei Chemicals Corporation
ALO	Agricultural Land Occupation
ART	Agroscope Reckenholz-Tänikon Research Station
BATs	Best Available Technologies
BP	British Petroleum
CALCAs	Co-ordination Action for innovation in Life Cycle Analysis for Sustainability
CD	Climate Change
CE	Climate change damage on Ecosystem
CET	Chemical Engineering Transaction
CH	Climate change damage on Human health
CED	Cumulative Energy Demand
cEF	<i>complete</i> E-factor
CISAP 6	6th International Conference on Safety & Environment in Process & Power Industry
CSTR	Continuous Stirred Tank Reactor
DALYs	Disability-Adjusted Life Years
EATOS	Environmental Assessment Tool for Organic Syntheses
ED	Ecosystem Diversity
EIA	Energy Information Administration
EIO	Economic Input-Output
EMPA	the Swiss Federal Laboratories for Materials Testing and Research
EPA	Environmental Protection Agency
EPFL	Swiss Federal Institute of Technology Lausanne
ETH	Swiss Federal Institute of Technology Zürich
FAME	Fatty Acid Methyl Esters
FCC	Fluid Catalytic Cracking
FD	Fossil Fuel Depletion
FE	Freshwater Eutrophication

FET	Freshwater Ecotoxicity
FU	Functional Unit
GC	Green Chemistry
GE	Green Engineering
GWP	Global Warming Potential
HH	Human Health
HHV	Higher Heating Value
HT	Human Toxicity
IPCC	Intergovernmental Panel on Climate Change
IR	Ionising Radiation
ISO	International Organisation for Standardization
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCSA	Life Cycle Sustainability Analysis
LHV	Low Heating Value
NB	Nitrile-Butadiene
NLT	Natural Land Transformation
MCI	Marginal Cost Increase
MD	Metal Depletion
MCC	Mitsubishi Chemical Corporation
ME	Marine Eutrophication
MET	Marine Ecotoxicity
MMM	Multi Metal Molybdate
MRD	Mineral Resource Depletion
MRI	Midwest Research Institute
NMGO	Non-Glycerin Organic Matter
OD	Ozone Depletion
OECD	Organisation for Economic Co-operation and Development
PBR	Packed Bed Reactor
PDF	Potential Disappear Fraction of species
PEP	Process Economics Program
PERP	Process Economics and Research Planning
PhD	Doctoral of Philosophy
PMF	Particulate Matter Formation
POF	Photochemical Oxidant Formation
PSI	Paul Scherrer Institute
Pt	Points
RA	Resource Availability
RCS	Royal Society of Chemistry
REPA	Resource and Environmental Profile Analysis
SAN	Styrene-Acrylonitrile
SETAC	Society of Environmental Toxicology and Chemistry

SLCA	Social Life Cycle Assessment
TA	Terrestrial Acidification
TET	Terrestrial Ecotoxicity
ULO	Urban Land Occupation
WCED	World Commission on Environment and Development
WD	Water Depletion
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 sustainability of industry was investigated through the application of the LCA methodology. The efforts were focused on the chemical sector in order to investigate reactions dealing with the Green Chemistry and Green Engineering principles, evaluating their sustainability in comparison with traditional pathways by a life cycle perspective. The environmental benefits associated with a reduction in the synthesis steps and the use of renewable feedstock were assessed through a holistic approach selecting two case studies with high relevance from an industrial point of view: the synthesis of acrylonitrile and the production of acrolein. The current approach wants to represent a standardized application of LCA methodology to the chemical sector, which could be extended to several case studies, and also an improvement of the current databases, since the lack of data to fill the inventories of the chemical productions represent a huge limitation, difficult to overcome and that can affect negatively the results of the studies. Results emerged from the analyses confirm that the sustainability in the chemical sector should be evaluated from a *cradle-to-gate* approach, considering all the stages and flows involved in each pathway in order to avoid shifting the environmental burdens from a step to another. Moreover, if possible, LCA should be supported by other tools able to investigate the other two dimensions of sustainability represented by the social and economic issues.

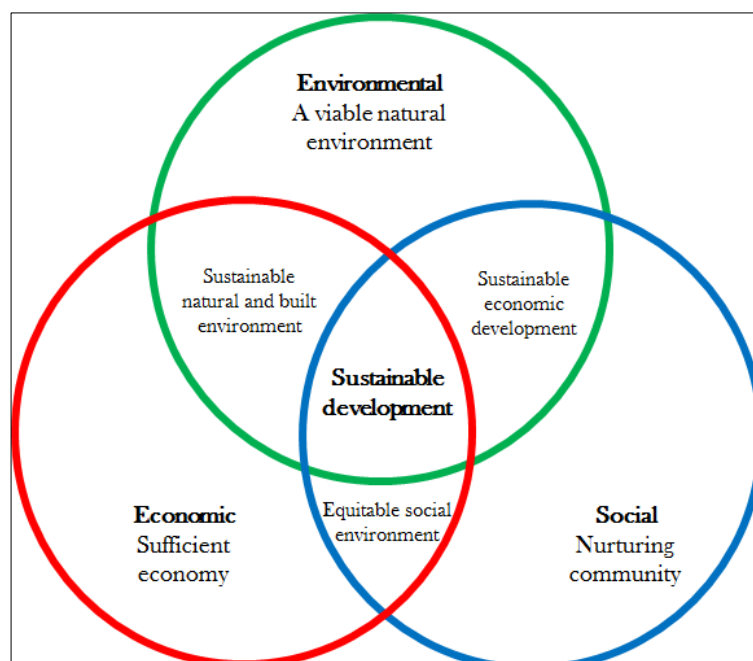
# 1. Introduction

## 1.1 Sustainability - introduction and background

It is not easy to find the exact words to express the wide meaning associated with the term “sustainability”. Therefore, it is common to refer to the concept of *sustainable development* in order to understand what sustainability is. Literature<sup>1</sup> reports that although the term sustainable development was first formulated during the 1980’s World Conservation Strategy,<sup>2</sup> its international recognition was associated with the release of the report “Our common future” (well known as “the Brundtland Report”), published by World Commission on Environment and Development (WCED) in 1987,<sup>3</sup> in which a simplified definition is reported as follow: “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs”.

Many commentators usually consider sustainability as the combination between three different dimensions and their constraints: the environment, the economy and the society.<sup>4</sup> Several attempts to display this deep relationship between the sub-categories were done. Among these, Mitchell<sup>5</sup> proposed three concentric and progressively nested circles. On the other hand, one of the most consolidated representation was released in 1995 by Clift,<sup>6</sup> who suggested the sustainable development as an intersection of the three sub-categories which results in a Venn diagram (Figure 1.1).

**Figure 1.1** - The three pillars of sustainability. Adapted from Clift 1995.<sup>6</sup>



In this representation, the sustainable development fills the central region of three subordinate concepts of sustainability, each of them includes a wide set of several aspects: from the capacity of our planet to sustain us, with our needs, expectations and aspirations, up to all the human expertise and the economic system within they are deployed.<sup>1</sup>

Although the concept of sustainability can be subjected to several interpretations, the ecological limits should be evaluated considering the whole system (planet) and not as a changing variables which depend on different point of views. Therefore in order to make possible this assessment, researchers developed tools such as the *environmental space* and the *ecological footprint*. While the first was released to address the sustainable level of consumption per capita and to set practical targets of sustainability by the identification of mainly parameters (e.g. land occupation, resources exploitation, CO<sub>2</sub> absorption rate, etc.); the second (more widespread) is useful to define how much resources are needed to support a certain economy expressing results in terms of hectares (ha).<sup>1</sup> Recent studies have categorized our system as "unsustainable", due to the fact that the world average ecological footprint (2.3 ha) exceeds of almost 20% the world productive space per person (1.9 ha).<sup>7</sup>

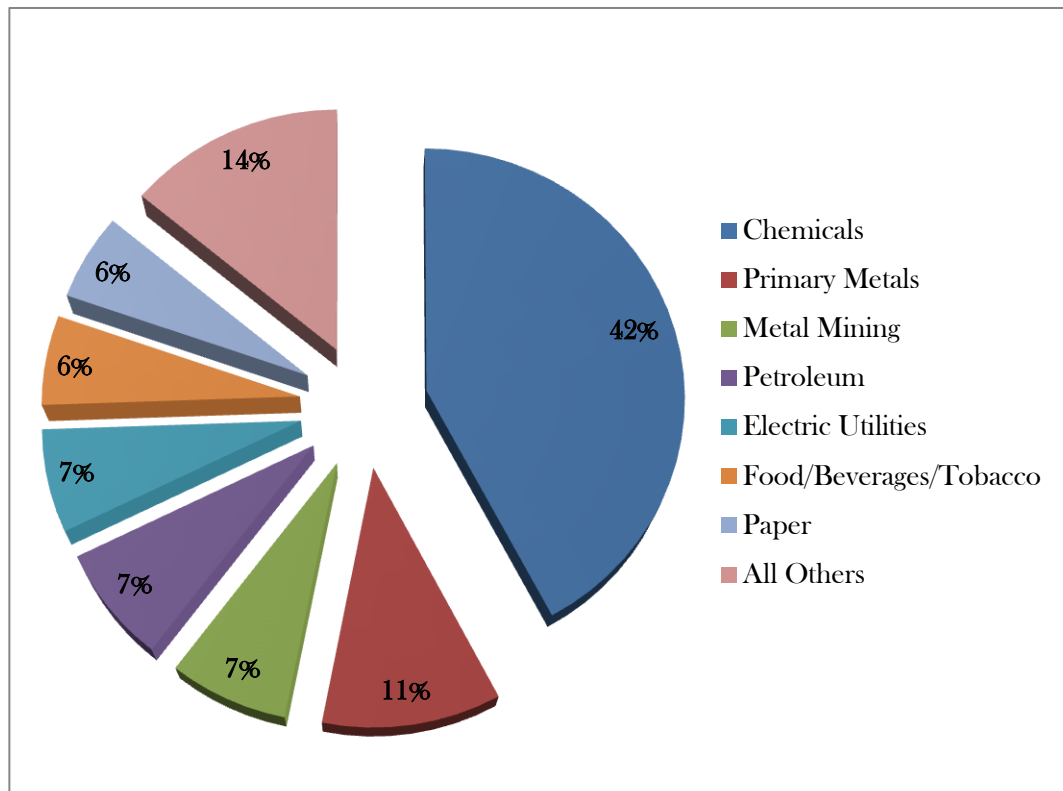
Therefore it looks evident that the achievement of goals proposed by the sustainable development involve a hard work which can be completed just by common efforts, the application of screening tools and best available technologies.

## 1.2 Sustainability - the industrial chemical sector

The US Energy Information Administration (EIA)<sup>8</sup> evaluated that the industrial sector reached in 2010 a world energy consumption around 200 quadrillion Btu and it is expected to grow up to 307 quadrillion Btu in 2040 with an estimated average annual growth of 1.8% for the Non-OECD (Organisation for Economic Co-operation and Development) countries. Moreover, the production of chemicals (including feedstock) represents the major energy-intensive industry with a consumption around 40 quadrillion Btu in 2010, which represent almost the 20% of the total energy usage by the year.<sup>8</sup> Therefore, these numbers suggest that in order to reach targets promoted by sustainable development the chemical industry and the other energy-intensive sectors, such as the iron and steel production, need to be re-thought in a more sustainable way. Furthermore, in addition to the resources depletion and the greenhouse gases emissions associated with the energy consumption, the chemical industry is also

characterized by the usage and the release of toxic substances. This also has not negligible repercussions on the waste streams. In fact, in 2013, the US chemical industry has represented the higher producer of hazardous wastes if compared with the other industrial sectors (Figure 1.2).

**Figure 1.2** - Production of hazardous waste in 2013 per industrial sector. Graphic adapted from data reported in literature.<sup>9</sup>



Therefore, in the last 20 years the awareness of researchers, industries and non-governmental institutions toward these environmental issues increased leading to the development of innovative disciplines and tools aimed to express and assess the sustainability.

### 1.1.1 Green Chemistry and Green Engineering principles

As a consequence of the Pollution Prevention Act release,<sup>10</sup> the 1990 is well recognized as the year in which the US environmental protection strategy moved away from the "command and control" approach to a more innovative plan aimed to pollution prevention. Indeed, while the first was based on the application of the set of strategies so-called *end-of-pipe*, which include all technologies able to reduce or neutralize the pollutants before their release into environment, the new approach focused on the

*front-of-pipe* strategies. The latter included the development of production processes which prevent the pollutants formation by also a source reduction criteria.<sup>11,12</sup> Several areas were involved in this prevention strategy, in particular relevant efforts were done in the chemistry sector in which a new discipline called *Green Chemistry* arose. Although, in the first half of 1990s countries such as Italy and United Kingdom have already promoted several initiatives around green chemistry issues,<sup>11</sup> Paul T. Anastas - chief of the Industrial Chemistry Branch at EPA (US Environmental Protection Agency)- is well recognized as the father of Green Chemistry (GC) for having coined the name<sup>13</sup> and developed together with John C. Warner the 12 principles of GC, which are listed below:<sup>14</sup>

1. Prevention

It is better to prevent waste than to treat or clean up it after its creation.

2. Atom economy

Design synthetic methods in order to maximize the incorporation of all materials used in the process into the final product.

3. Less hazardous chemicals syntheses

Develop new synthetic methods which use and generate substance with little or no toxicity to human health and environment.

4. Design safer chemicals

Design chemical product minimizing their toxicity.

5. Safer solvents and auxiliaries

Make unnecessary the use of chemical auxiliaries wherever innocuous alternatives are possible.

6. Design for energy efficiency

Minimize energy requirements for chemical processes recognizing their environmental and economic impacts. Preference reaction conducted at room temperature and pressure.

7. Use of renewables feedstock

Raw materials and feedstock should be selected on the basis of their renewability.

8. Reduce derivatives

Minimize or avoid the use of unnecessary derivatives (e.g. blocking\protection\deprotection groups, etc.), because of the can involve further reagents and produce waste.



9. Catalysis

Prefer the use of catalytic reagents (as selective as possible) instead of stoichiometric.

10. Design for degradation

Design chemical products in order to avoid the release of persistent and dangerous substances in the environment at the end of their function.

11. Real-time analysis for pollution prevention

Use of real-time, in-process monitoring and prior methodologies which allow to control the formation of hazardous substances.

12. Inherently safer chemistry for accident prevention

Minimize the potential for chemical accidents, releases, explosions and fires using proper substances and form of them.

As can be noticed, each principle underlines the main goal of GC which incorporates the prevention of resources and pollutants as well as the minimization of hazardous substances in order to develop processes intrinsically more safely.

A brief and explicative definition of GC goals is well summarized in the words of Roger A. Sheldon<sup>15</sup> who defined Green Chemistry as the discipline which “*efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products*”.

After its introduction as a new discipline able to deal with environmental issues, GC was recognized by international initiatives such as the release of the first Green Chemistry program so-called the "US Green Chemistry Program" (1993) or the launch of the Green Chemistry journal sponsored by RSC Publishing (1999).<sup>11</sup>

Simultaneously to GC a new science became established under the branch of technology. The concept of *Green Engineering* (GE) was developed in 2000 by Anastas, Lauren G. Heine and Tracy G. Williamson and defined as “*the design of systems and unit processes that obviate or reduce the need for the use of hazardous substances while minimizing energy usage and the generation of unwanted by-product.*”<sup>16</sup> Moreover, as already done for the GC, the GE aims were embodied into further twelve principles, which are reported in literature<sup>17</sup> as follow:

1. Inherent rather than circumstantial

Designers need to ensure all the materials and energy inputs and outputs are as inherently as possible.

2. Prevention instead treatment

It is better to prevent waste than to treat or clean up it after its creation.

3. Design for separation

Minimize energy consumption and material use during separation and purification procedures.

4. Maximize efficiency

Design products, processes and systems in order to maximize mass, energy, space and time efficiency.

5. Out-put versus Input-pushed

Products, processes and systems should be out-pulled rather than input-pushed through the usage of energy and materials.

6. Conserve complexity

Embedded entropy and complexity must be considered as an investment when making design choices on recycle, reuse or beneficial disposition.

7. Durability rather than immortality

Durability should be the target of designers, not immortality.

8. Meet need, minimize excess

Avoid to design unnecessary capacity or capability solutions.

9. Minimize material diversity

Promote disassembly and value retention by the reduction of material diversity in multicomponent product.

10. Integrate material and energy flow

Integration and interconnectivity with available energy and material flows must be included in the design of products, processes and systems.

11. Design for commercial “afterlife”

Products, processes and systems should be designed for performance in a commercial “afterlife”.

12. Renewable rather than depleting

Material and energy inputs should be renewable, not depleting.

Paraphrasing the GE principles is obvious that both disciplines are strictly related by the common aim of sustainability. However, the concept of GE implies a wider audience since it points the attention to all the branches of engineering even if chemical engineers can be considered as the main beneficiaries due to their capacity to prevent pollutants formation and to develop inherently safe processes without the use of hazardous substances.<sup>16</sup> Moreover, as outlined by literature<sup>17</sup> the principle of inherency (for both sustainability and safety) implies to take into account the products life cycle in order to evaluate all the materials and energies involved in the production processes.

### 1.1.2 Tools to evaluate sustainability in the chemical sector

The establishment of Green Chemistry and Green Engineering led to the release of several approaches aimed to assess sustainability in the chemical sector. Among these, the *E-factor* developed by Sheldon<sup>18,19</sup> represents an easy and understandable tool able to address the environmental load associated with the industrial production. Together with Chemical Yield, Atom Economy, Process Mass Intensity, etc., it belongs to the *green chemistry process metrics* category<sup>20</sup> and is defined as the ratio between the amount of waste and the quantity of desired product (see equation 1.1).

$$E\text{-factor} = \frac{\text{kg of waste}}{\text{kg of product}}$$

1.1

The expression was developed in order to take into account all the substances involved in the process such as reagents, solvents (including losses), auxiliaries and fuels. However, although the quantity of inorganic and organic substances in the waste streams are included in the calculation, the amount of water is voluntarily excluded in order to avoid higher E-factor values and make comparison easier.<sup>21</sup> However, this is not an absolute rule but should be evaluated case by case. For example in the pharmaceutical industry could be helpful address sustainability using a *complete E-factor* (cEF)<sup>20</sup> which also takes into account process water.

As suggested by the equation the ideal E-factor is equal to zero, even if obtaining such value is not so easy. Below Table 1.1 collects the common E-factors values for several chemical industrial sectors as reported in literature.<sup>22</sup>

**Table 1.1** - E-factors in the chemical industry. Adapted from Sheldon 2007.<sup>22</sup>

Industry segment	Product tonnage	E-factor (kg waste / kg product)
<b>Oil refining</b>	$10^6$ - $10^8$	< 0.1
<b>Bulk chemicals</b>	$10^4$ - $10^6$	< 1-5
<b>Fine chemicals</b>	$10^2$ - $10^4$	5 ->50
<b>Pharmaceuticals</b>	$10$ - $10^3$	25 -> 100

Values reported above show a direct relationship between the chemistry complexity of the process and the E-factors. In fact higher scores are achieved in the case of pharmaceuticals, which involves several stages in the production chains of drugs and higher amount of waste. On the other hand, lower values are achieved by the oil refining class. Although this sector reaches the higher annual productivity, the absence of multi-step synthesis involved a lower process complexity and this reflects in an inferior waste amount.

However, the E-factor has several limitations: i) the need of a clear definition concerning what is considered and not as a waste, ii) as suggested by Tufvesson et al.<sup>23</sup> as the other green metrics (e.g. mass intensity) it does not make distinction between the different types of waste produced, iii) furthermore, it does not provide any info regarding the potential effects associated with the use and the release of certain substances in the environment, but it takes into account one environmental load as the production of waste. Therefore, it seems necessary the use of dedicated software able to associate potential environmental burdens to each input and output of a chemical process. Among these, *EATOS (Environmental Assessment Tool for Organic Syntheses)*,<sup>24</sup> released by Marco Eissen (Swiss Federal Institute of Technology Zürich - ETH) and Jürgen O. Metzger (Carl von Ossietzky Universität Oldenburg), deserves to be mentioned. Different from the other green chemistry metrics, it evaluates the sustainability of substance by the comparison of alternative synthesis routes on a laboratory scale. In fact, through mass balances researchers identify all reagents and auxiliaries involved in the processes as well as the recovery and waste streams, thus the software is able to express each environmental load in terms of several impact categories such as human toxicity, ecotoxicity, air pollution, resources claiming, etc. Moreover, it provides the function to estimate the E-factor value for each route.

Although EATOS has a lot of valid functions that can help in a screening analysis, it is considered a “simple model”<sup>23</sup> with several drawbacks such as the restriction of its

database (around 60 chemicals) and even more its limitation to the organic syntheses only.

Furthermore, the high limitation that affects both green chemistry metrics and tools as EATOS is the lack of standardization. In fact, in order to have a crucial effect on the community is necessary to point the attention on the application of standardized methodology well recognized internationally, which can be applied both to organic and inorganic chemistry as well as to the more innovative fields such as biobased and nanomaterials.

Given these motivations, the Life Cycle Assessment (LCA) represents the more suitable methodology to address the environmental sustainability in the chemical sector. A detailed description of LCA is reported in the further section.

## 1.2 Motivation and structure of the work

As discussed above, the sustainability in the chemical industry represents one of the primary target of our society mainly because of its environmental footprint is not limited to a defined area but it has serious repercussions all over the world. This entails that corporates and intergovernmental organizations have invested in research with the aim to mitigate these aspects and provide new solutions. All the efforts done in this sector during the last 20 years led to the promotion of several initiatives and to the development of new disciplines, as outlined above. Academia in this context did not remain aloof, but it participated in active way promoting different research topics aimed to the continuous improvement. Among the various academy positions, a figure such as an industrial chemist with an environmental background is perfectly in the middle between a green chemist and engineer and hence gives a significant contribution toward several themes. For this reason the research conducted during my Doctoral of Philosophy (PhD) program at the Department of Industrial Chemistry “Toso Montanari” - University of Bologna, under the supervision of Prof. Dr. Fabrizio Passarini and the co-supervision of Prof. Dr. Fabrizio Cavani, was aimed on the valorization and optimization of chemical processes from a life cycle perspective. The main goal was to investigate in depth the LCA methodology, understanding the strengths and gaps of its application in the sector of industrial chemistry and to develop an innovative approach to compare alternative routes in order to discover which one is the more sustainable. The overall idea was to use the LCA as a screening tool in order to support the procedure of decision making by enterprises and furnish a tool to

develop processes inherently more efficient. The life cycle thinking approach was applied to several case studies choosing those which represent the most developed and consolidated from an industrial point of view. In each example, a comparison with the alternative path, suggested by the green chemistry and sustainable development principles, was carried out verifying the preferred route on different environmental issues. Therefore, in our opinion, just the use of a holistic approach as that proposed by the LCA is able to address sustainability during all the production chain (from cradle-to-gate) and evaluate the effective benefits associated with the substitution of a certain substance with others considered lower energy and mass intense.

Thus, in order to provide an overview of the work carried out during the three years program, all the studies were collected in this single dissertation, which also represents my PhD thesis. The structure of the dissertation is as follow:

- Chapter 1 consists in a briefly introduction about the sustainability themes was done focusing the attention on the industrial chemical sector and on the different approaches developed;
- Chapter 2 is dedicated to an in-depth description of the LCA methodology - background, structure and tools;
- Chapter 3 represents the main part of the work in which each case study and its main results are presented and discussed in detail;
- Chapter 4 collects the main conclusions of the dissertation in which also some suggestions for future work are provided.

## References

---

- 1 A. Azapagic, S. Perdan, R. Clift, *Sustainable Development in Practice - Case Studies for Engineers and Scientists*, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2004.
- 2 UNEP/WWF/IUCNNF, *World Conservation Strategy*, International Union for Conservation of Nature and Natural Resources, Gland, 1980.
- 3 WCED, *Our common future*, World Commission on Environment and Development, Oxford University Press, Oxford, 1987.
- 4 A.L. Carew, C.A. Mitchell, *J. Clean. Prod.*, 2008, **16**, 105-115.
- 5 C.A. Mitchell, *Trans. IChemE.*, 2000, **78**, 237-242.
- 6 R. Clift, *The challenge for manufacturing*, Engineering for sustainable development, J. McQuaid editor, London: The Royal Academy of Engineering, 1995.
- 7 Redefining Progress, *Ecological footprint 2003*, available on <http://www.rprogress.org/programs/sustainability/ef%20/>
- 8 US Energy Information Administration (EIA), *International Energy Outlook 2013 - with projections to 2040*, <http://www.eia.gov/ieo/>.
- 9 Office of Pollution Prevention and Toxics - EPA (US Environmental Protection Agency), *2013 Toxics Release Inventory*, available on <http://www2.epa.gov/toxics-release-inventory-tri-program/2013-toxics-release-inventory-national-analysis>.
- 10 Pollution Prevention Act of 1990. 42 U.S.C., Sections 13101-13109, 1990.
- 11 P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686-694.
- 12 S. E. Manahan, *Green chemistry and the ten commandments of sustainability*, ChemChar Research, Inc. Publishers, Columbia, Missouri, 2005.
- 13 R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2007.
- 14 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
- 15 R. A. Sheldon, *C. R. Acad. Sci. Paris*, 2000, **3**, 541-551.
- 16 P. T. Anastas, L. G. Heine, T. C. Williamson, *Green Engineering*, Eds. American Chemical Society, Washington, DC, 2000.
- 17 P.T. Anastas, J. B. Zimmerman, *Env. Sci. Tech.*, 2003, **37**, 94-101.
- 18 R. A. Sheldon, *Chem. Ind.*, 1992, **23**, 903-906.
- 19 R. A. Sheldon, *Chem. Ind.*, 1997, **1**, 12-15.
- 20 F. Roschnager, R. A Sheldon and C. H. Senanayake, *Green Chem.*, Advance article. DOI 10.1039/c4g01563k.

---

21 M. Lancaster, *Green Chemistry: An Introductory Text*, Royal Society of Chemistry, Cambridge, 2002.

22 R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273-1283.

23 L.M. Tufvesson, P. Tufvesson, J.M. Woodley, P. Börjesson, *Int. J. Life Cycle Assess.*, 2013, **18**, 431-444.

24 <http://www.metzger.chemie.uni-oldenburg.de/eatos/>



## 2. Methodology

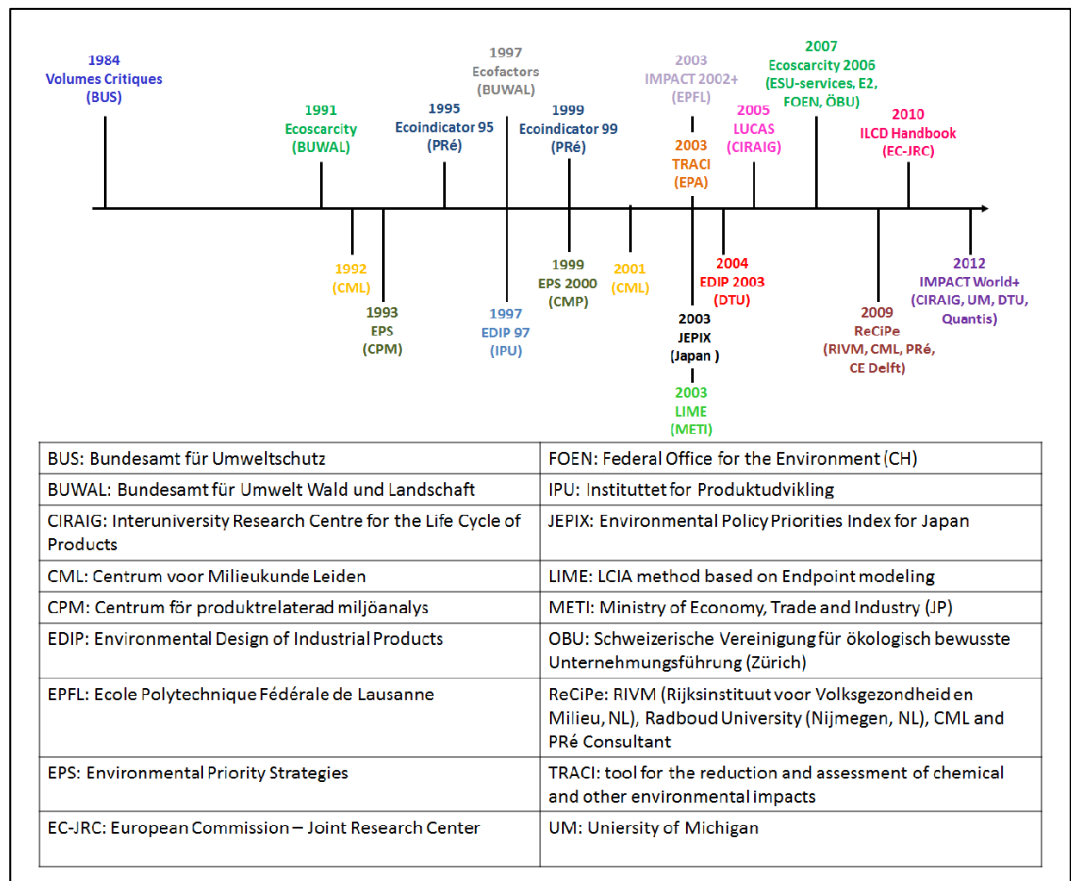
### 2.1 LCA methodology - introduction and background

Although the life cycle thinking is considered a recent concept, this belief is not correct at all. It could be hard to identify the year in which LCA methodology was used for the first time; however literature<sup>1</sup> reports that the exploration of the life cycle of product was started around the fifties and sixties in the United States and that the first mention to the life cycle concept is ascribable to the internal report produced by Novick in 1959<sup>2</sup> for the RAND Corporation, which focused on the life cycle cost of weapons. This reflects the trend of that period when the first examples of Life Cycle Analysis (the term "Assessment" was introduced later) were more inclined in the evaluation of budget management than in the environment. The transition from a cost analyses to an environmental oriented evaluations just occurred at the end of Sixties, when environmental issues became established in industrialized societies. The first example of LCA (how we view it today) is considered the work conducted by the Midwest Research Institute (MRI) for the Coca Cola Company in 1969.<sup>1</sup> The acronym they used to refer to this kind of study was REPA (Resource and Environmental Profile Analysis). It referred to a modern "*from cradle to gate*" analysis which investigated all the production chain of products. Unfortunately the assessment carried out by MRI remained unpublished as a lot of other studies up the early 1980s. In 1984 EMPA (the Swiss Federal Laboratories for Materials Testing and Research)<sup>3</sup> released a report in which they selected the data needed to carry out a general LCA and then launched the first impact assessment method, distinguishing airborne and waterborne emissions starting from semi-political standards for them.<sup>1</sup>

Although the interest for aspects concerning the life cycle application grew during the 1990s (e.g. workshops, forums, publications on scientific journals, etc.), there was none international recognized platforms and networks able to start a discussion on how to carry an LCA. Therefore, the combination of SETAC (Society of Environmental Toxicology and Chemistry) and ISO (International Organization for Standardization) efforts resulted in a harmonization of the methodology, thorough the definition of general LCA

framework. For that reason, the period 1990-2000 is broadly recognized as the *decade of standardization* in the LCA history.<sup>1</sup> However, it should be noted that the ISO approach was not aimed to identify the ideal method to run LCA, but to harmonize the methodology in general through also the implementation of analysis method database. As shown by the Figure 2.1 a lot of them, still used today, were developed during that decade.

**Figure 2.1** - Historical evolution of LCIA methods. Adapted from Curran 2012.<sup>1</sup>

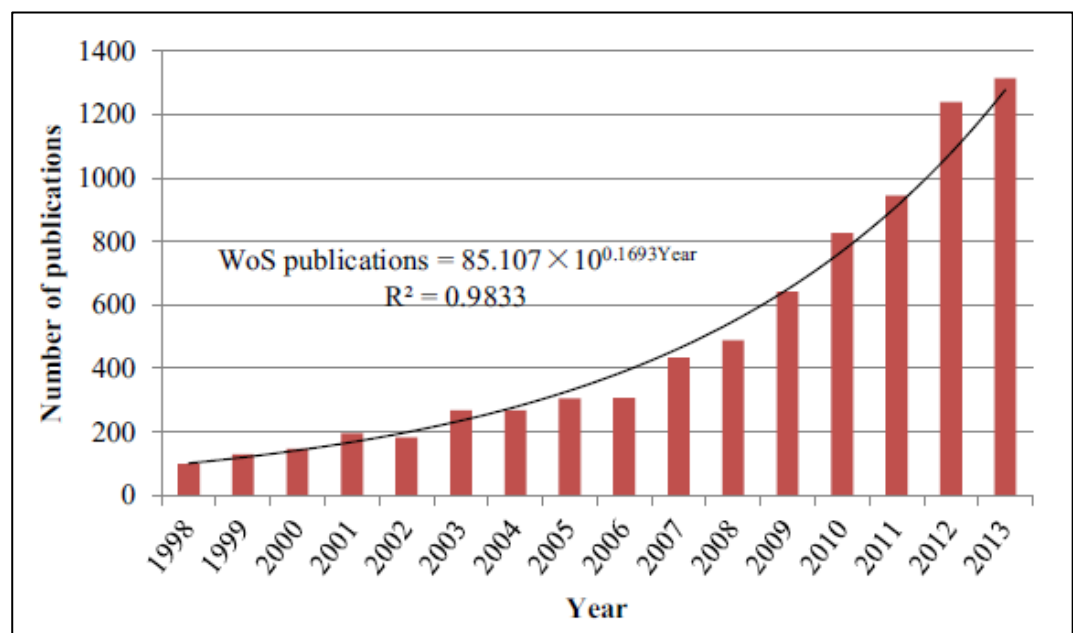


The most recent history of LCA, from 2000 up to 2010 is defined by literature as the *decade of elaboration*.<sup>1</sup> Life cycle thinking became the keystone in order to start to talk about environmental sustainability. As a confirmation of that several international partnerships were developed, the Life Cycle Initiative is an example,<sup>4</sup> as well as national networks (e.g. Australian LCA Network)<sup>5</sup>. Moreover, the concept of evaluate the environmental footprint in a life cycle approach was incorporated in the strategies oriented to a better and sustainable resources management and waste prevention. Thus, different kind of LCA approaches have caught on. All of them have the life-cycle basis in common, but they differ in the elaboration and target: from a more social oriented analysis

(SLCA) up to dynamic LCA, as well as life cycle costing (LCC) and Economic Input-Output LCA (EIO-LCA).

This large amount of different ways to consider LCA increased its popularity. As a confirmation of that, in the recent years a dramatic increase of life cycle research-article was occurred. An overview of this trend, which also confirmed the importance related with life cycle issues, was extrapolated from Chen et al. 2014<sup>6</sup> and reported below in Figure 2.2.

**Figure 2.2** - Chronological distribution of life cycle assessment research-related articles in Web of Science (1998-2013). Source Chen et al. 2014<sup>6</sup> - with kind permission of Springer Science+Business Media.



Moreover, the CALCAs (Co-ordination Action for innovation in Life Cycle Analysis for Sustainability) project,<sup>7</sup> commissioned by the EU in 2006, released the framework for future LCA, called LCSA (Life Cycle Sustainability Analysis), which will occur in the next decade 2010-2020.<sup>1</sup> The framework for a future LCSA will be different from the structure of a common LCA. Main innovations regard i) the scope, which will cover all three dimensions of sustainability (people, planet and prosperity); ii) the target of the study that will be more process or sector than product related; iii) the necessity to also include physical, economic and behavioral relations in the analysis in addition to technological; iv) the incorporation of normative in the LCSA. Different from a common LCA, LCSA could be considered as a “trans-disciplinary integration framework of models rather than a model in itself”.<sup>1</sup>

## 2.2 LCA methodology - framework and standardization

As outlined, LCA is a tool able to evaluate the sustainability of product and processes considering each stage involved in the life cycle. Differently from other approaches, it received the standardization by ISO during the already mentioned decade. Starting from 1996 up to 2006, a series of standard and technical reports were issued by the ISO. It is usual to refer to them as "the 14040 series". They are briefly listed below in Table 2.1, which was extrapolated from literature.<sup>1</sup>

**Table 2.1** - Description of the 14040 series, including year of update.

Number	Type	Title	Year
14040	International standard	Principles and framework	1996, 2006
14041	International standard	Goal and scope definition and inventory analysis	1998 <sup>1</sup>
14042	International standard	Life cycle impact assessment	2000 <sup>1</sup>
14043	International standard	Life cycle interpretations	2000 <sup>1</sup>
14044	International standard	Requirements and guidelines	2006
14047	Technical report	Examples of application of ISO 14044	2012
14048	Technical report	Data document format	2002
14049	Technical report	Examples of application of ISO 14044	2012

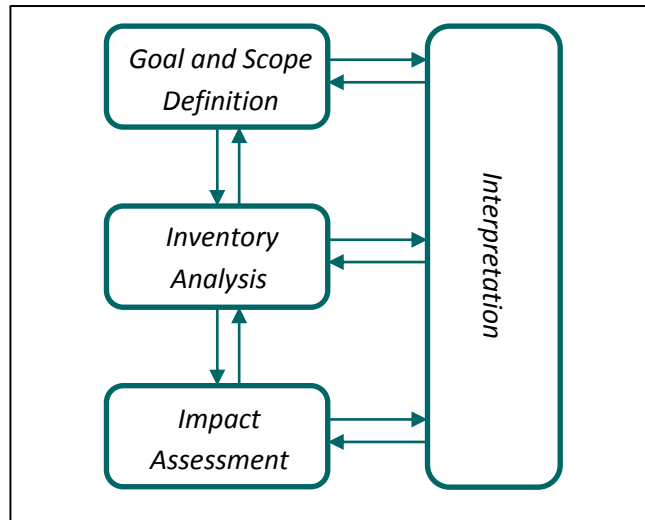
<sup>1</sup> updated in 2006 with the introduction of 14044.

Figure 2.3 reports the general methodological framework of a common LCA as described by the ISO 14040 series. As shown by the figure, which also represents the typical logo of LCA,<sup>1</sup> four conceptual phases can be identified:

1. Goal and scope definition
2. Inventory analysis
3. Impact assessment

#### 4. Interpretation

**Figure 2.3** - LCA framework, adapted from ISO 14040.<sup>8</sup>



Below a briefly description of each phase is reported. Further details can be found in literature.<sup>8,9</sup>

##### 2.2.1 Goal and Scope Definition

Although ISO does not explicit which is the first stage of LCA the goal and scope definition should be considered as such, since the choices made during this phase will influence the entire analysis. As outlined by the name, the main topics of this stage are to define explicitly the aim of the work through the identification of:

- the intended application (e.g. marketing, research, ecodesign, etc.);
- the reasons of the study;
- the intended audience;
- how to use the results of the study (e.g. internal purpose or not)

In order to fill of these aspects is first necessary to define the *system boundaries* and the *functional unit*. The former term indicates what wants to be investigated through LCA methodology and for that reason it is usual to refer to several different kinds of boundaries: physical, geographical, technological, temporal, etc. Often, when talking about LCA, expressions as *from cradle-to-grave* or *from cradle-to-gate* indicate how much extended are the boundaries. The first one refers to the entire life cycle of a product or system, including the usage and the

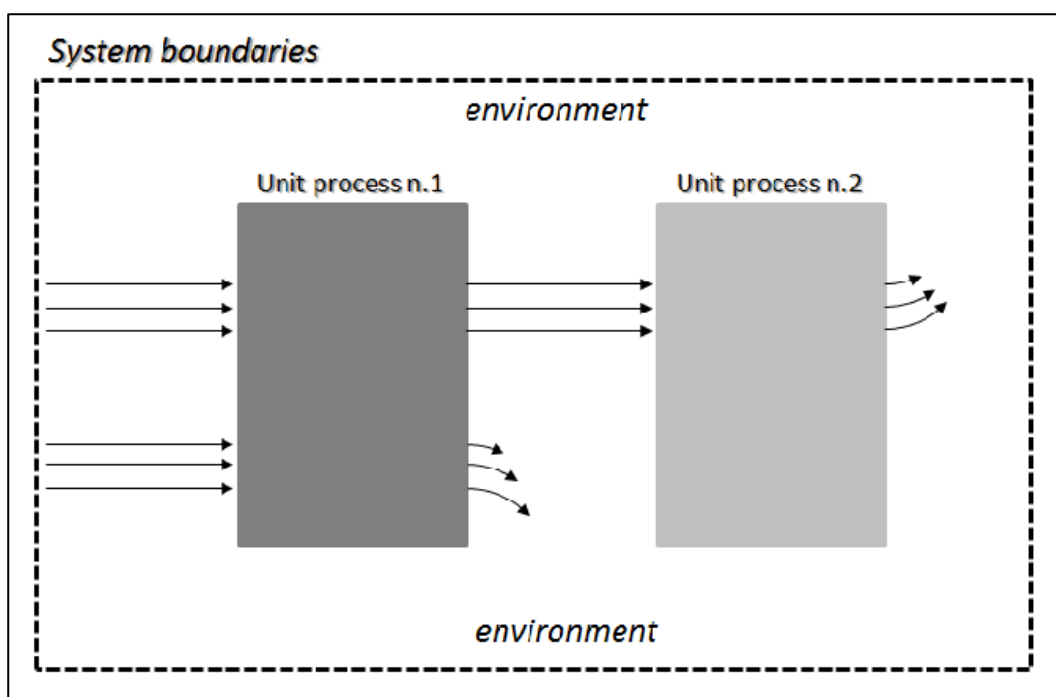
end of life; the latter only includes from the raw materials extraction up to the industrial gate. Other further system boundaries can be identified depending on who commissions the study and its purpose. As outlined above, another fundamental aspect of LCA is the identification of the functional unit. It expresses a function of the product or system under investigation (e.g. a defined amount, a mass or energy quantity, etc.) and it is used to create and compared different models. In order to equalize differences and allow comparisons, all the input and output flows as well as the results of evaluation are referred to it. The choice of functional unit (FU) is not always an easy procedure, different aspects should be taken into account:

1. it should be common to all the models;
2. it should be coherent with the models (e.g. LCA concerns energy production should consider amount of energy as FU);
3. it is better to choose a FU able to simplify the inventory analysis step through the reduction and simplification of the evaluation.

### 2.2.2 Inventory Analysis

Second stage of LCA is the Inventory Analysis, sometimes written as Life Cycle Inventory (LCI). It represents the more time-consuming phase of the entire methodology, due to data search and utilization to create models as snapshot of the system. Each model can be considered as a *unit process* that exchanges flows with other units and the environment. These input and output flows can have different nature: natural resources and raw materials, energy, products and co-products, waste (material and energy), emissions and released in compartments (air, water and soil), etc. An example of this exchange is reported below in Figure 2.4. Therefore, considering LCA as a quantitative methodology,<sup>1</sup> the practitioners should fill the inventory with all the flows involved between each unit process and environment in order to assess what happens in the system studied (system boundaries).

**Figure 2.4** - Description of the flows exchanged between process units and environment.



Information necessary to complete the LCI phase can be obtained from a higher range of sources. Therefore different classes of data can be identified:

- Primary, which represents the higher quality data. It includes all the information obtained by direct measurements as well as data furnished by company through internal reports or personal communications of expert.
- Secondary, all the information reported in literature such as database, journals, books, patents, encyclopedias, etc. Sources with a strongly peer-review process implies higher data quality.
- Tertiary, this class represents a set of information with the lower quality, such as: data extrapolated from other case studies which are assumed to be similar to the model under investigation or data extrapolated from not peer-review literature (e.g. not accredited websites).

Certainly, using primary and/or appropriate information obtained by literature results in a high quality of the study.

### 2.2.2.1 *Allocation Criteria*

Often it happens that the product under study represents just a part of a multi-output process. Main examples are the farms, where several commodities can

obtained starting from animals (e.g. milk, leather, meat, fat, bones, etc.), as well as the chemical industry, in which the co-products of the reactions can be sold or used for other lines. On these cases ISO 14044 suggests to apply the system boundaries expansion, in order to include in the analysis the greatest number of possible co-products. If this approach is not applicable, the adoption of allocation criteria is necessary. ISO provides the hierarchy to run allocation procedure, where they are not avoidable:

1. Allocate all the inputs and outputs on the base of physical relationship with the interested product - *mass allocation*
2. If is not possible to apply mass allocation, choose different kind of relationships (e.g. *economic allocation*).

### 2.2.3 Impact Assessment

ISO 14040 series defines the Life Cycle Impact Assessment (LCIA) as “the phase aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product”.<sup>8,9</sup> It represents the third stage of a common LCA and was introduced since the understanding and interpretation of all the inputs and outputs involved in the inventory require too much time and wide knowledge.<sup>1</sup> Therefore, the characterization procedure, ran by several LCA software, is able to translate all the choices made during the LCI phase into impact categories defined by ISO 14040 series as “class representing environmental issues of concern to which life cycle inventory analysis results may be assigned”.<sup>8,9</sup> Obviously, each input and output of a material and substance can have different kind of causal effects on the ecosystem. Two are the main impact mechanisms well recognized by LCA community: i) the front-end, so-called *midpoint* approach, and ii) the back-end, also known as *endpoint* approach.<sup>1</sup> In the case of CO<sub>2</sub> emission a typical example of midpoint effect is the change in radiation balance, on the other hand change of biodiversity can represent a good explanation of endpoint approach. In order to convert the results from LCI into impact indicators (both on midpoint and endpoint level) ISO 14040 series provides a six step procedure. The *choice of the impact categories*, which is strictly related with the aim of the study and the analysis method selected by



researchers, represents the first step of LCIA. After the *classification procedure*, which consists on the assignment of LCI results to specific impact indicators, the subsequent stage is the *characterization* phase, which can be summarized as follow

$$I_c = \sum_s CF_{c,s} \cdot m_s$$

2.1

where  $I$  represents the impact indicator for a defined impact category  $c$ ,  $CF$  stands for the *characterization factor* which is different for each category and substance  $s$ . The  $m$  represents the amount of that substance. As outlined above, the impact indicator  $I$  can refer both to midpoint, such as climate change, human toxicity, acidification, ozone layer depletion, etc., as well as endpoint categories, which represent the damage on the main receptors: human health, ecosystem quality and resource depletion. As shown by the expression, each substance and impact indicator has its own  $CF$  such as the Global Warming Potential (GWP) for greenhouse gases and the climate change category. After the characterization procedure two optional steps could occur: i) the *normalization* procedure, in which results are normalized using some reference information (e.g. the total impact in a region in a defined period of time)<sup>1</sup> in order identify to which categories the product under study has the higher contribution; and ii) the *grouping* defined by ISO as “the assignment of impact categories into one or more sets”.<sup>8,9</sup> Although normalization equalizes all the units, these scores cannot be added. So a further step called *weighting* is necessary to convert results obtained from either the characterization (or normalization) procedure and show them in terms of aggregate scores. Literature<sup>1</sup> reports a general expression for the weighting as follow

$$W = \sum_c WF_c \cdot I_c$$

2.2

where the weighting result  $W$  is obtained by the product between the impact or normalized score  $I$  and the weighting factor  $WF$  for each impact category  $c$ . Typical example of aggregate scores for LCIA phase is the *eco-indicator* which

shows results in terms of points (Pt). Below, a briefly overview of the analysis methods used in our case studies is reported.

### ***2.2.3.1 Analysis methods overview***

As shown previously by the Figure 2.1, the first examples of LCIA methodologies arose from the beginning of 90s during the so-called decade of standardization. Although the historical overview shows a big variety of LCIA methodologies which came out, some of them did not receive any further upgrade. Therefore, their usage looks like obsolete and as asserted by Curran<sup>1</sup> “any given LCIA methodology older than 10 years is no longer likely to reflect the state of the art, thereby, showing serious methodological weaknesses”. Moreover, the update procedures have made the LCIA methodologies more oriented to the current environmental problems through the improvement of their impact indicators lists from few to over 30 categories (e.g. ReCiPe and IMPACT World+).<sup>1</sup> This represents a further confirmation of the growing interest of researchers toward LCA-related studies.

This section reports just a brief overview of methods used in our works. They were selected considering the goals of the studies, trying to find methods which cover the main impact categories, and on the base of their upgrades. Among these ReCiPe and IPCC are described below.

- **ReCiPe** was developed in 2008 by the joint efforts of different institutions such as the RIVM (Rijksinstituut voor Volksgezondheid en Milieu), CML (Centrum Voor Milieukunde), Pré Consultants, Radboud Universiteit Nijmegen and CE Delft.<sup>1,10</sup> ReCiPe represents a combination between the midpoint approach proposed by CML<sup>11</sup> and the more damage oriented Eco-indicator99,<sup>12</sup> so-called endpoint approach. The name is an acronym derived from the initials of the institutes that were the main contributors to this project (RIVM and Radboud University, CML, and PRé) and also was selected in order to provide a "recipe" life cycle impact category indicators.<sup>10</sup>

The overall structure of ReCiPe provides two sets of impact indicators at midpoint and endpoint levels.

The eighteen midpoint categories are:

1. Climate Change (CD)

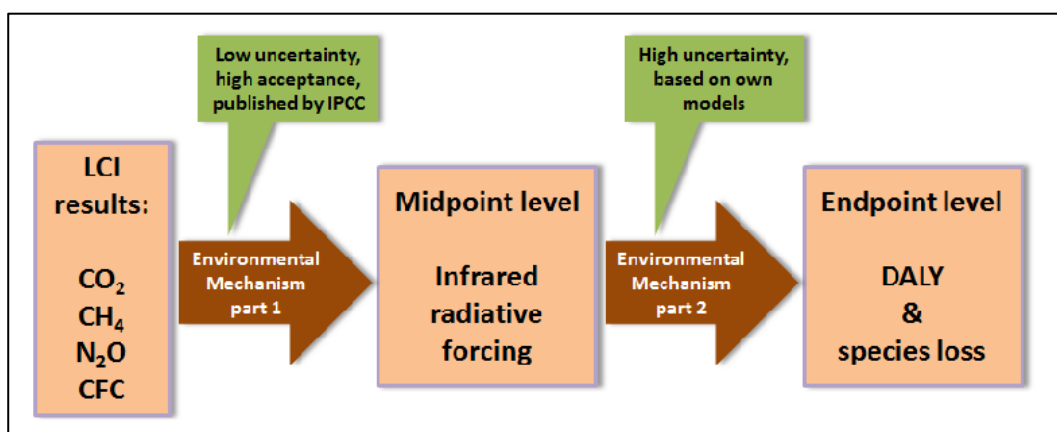
2. Ozone Depletion (OD)
3. Terrestrial Acidification (TA)
4. Freshwater Eutrophication (FE)
5. Marine Eutrophication (ME)
6. Human Toxicity (HT)
7. Photochemical Oxidant Formation (POF)
8. Particulate Matter Formation (PMF)
9. Terrestrial Ecotoxicity (TET)
10. Freshwater Ecotoxicity (FET)
11. Marine Ecotoxicity (MET)
12. Ionising Radiation (IR)
13. Agricultural Land Occupation (ALO)
14. Urban Land Occupation (ULO)
15. Natural Land Transformation (NLT)
16. Water Depletion (WD)
17. Mineral Resource Depletion (MRD)
18. Fossil Fuel Depletion (FD)

Further details about midpoint indicators are reported in literature.<sup>10</sup> Some of these midpoint indicators can also be expressed in aggregated form showing them in terms of endpoint level which represent damage on:

1. Human Health (HH)
2. Ecosystem Diversity (ED)
3. Resource Availability (RA)

In order to understand the mechanism which links both levels of analysis, the example of greenhouse gases is reported in Figure 2.5.

**Figure 2.5** – Simplified example of environmental mechanism which links both levels of analysis for the case study of greenhouse gases. Adapted from Goedkoop et al. 2012.<sup>10</sup>



ReCiPe method uses different units in order to show damage on different receptors. Disability-Adjusted Life Years - *DALYs*, obtained by the sum between the years of life lost (*YLL*) and the years life lives as disabled (*YLD*) due to the onset of a disease (e.g. cancer), was chosen to express damages on HH

$$DALY = YLL + YLD$$

2.3

*YLD* values are obtained by the product between the severity factor  $w$ , which varies between 0 and 1, and the duration of disease  $D$

$$YLD = w \times D$$

2.4

Damages on ED are measured using the *Potential Disappear Fraction of species* (PDF), expressing results in terms of *number of disappear species per year* (*species · yr*) in all the compartments: terrestrial, freshwater and marine water) due to anthropogenic factors.

RA is measured starting from the Marginal Cost Increase (MCI) associated with a resource consumption and the amount of the resource consumed. It is expressed in terms of increased extraction costs - \$.

ReCiPe v.1.06 released on 2011 was used as analysis method. Latest update version of the method is 1.11 and was released in 2014.

- **IPCC**, different from ReCiPe, is a single issue LCIA method able to assess the GWP associated with the emissions of greenhouse gases. It was released in 2001 by the Intergovernmental Panel on Climate Change in order to provide a tool

for LCA practitioners which was able to evaluate climate change expressing the magnitude in a more comprehensive way: kg of CO<sub>2</sub> equivalent. IPCC 2007 v.1.03,<sup>13</sup> updated in 2009, was used to make evaluations of GWP. In 2013 was release the update version of the method: IPCC 2013 (v. 1.00).

## 2.2.4 Interpretation

The interpretation phase should not be considered as the fourth and last step of LCA, but as also shown by the ISO logo (Figure 2.3) it occurs all over the entire methodology. Indeed, findings of LCI and LCIA stages as well as decisions made during the goal and scope definition are revised evaluating study limitations and reliability. The work completeness and consistency are checked by the identification of the several issues. The main conclusions are addressed and further recommendations for future works and update are suggested.<sup>1</sup>

In the case in which the interpretation phase reveals strong inconsistency and high data uncertainty the study should be rethought in terms of different functional unit or system boundaries expansion as well as the changing in data sources. This iterative approach, also shown by the ISO logo, reveals that the goal of the methodology is aimed at the continuous improvement.

Moreover, in order to validate models and results ISO suggests to run an uncertainty analysis. Although ISO 14040 series does not provide any detail and guide to complete this procedure, literature<sup>1</sup> suggests two main approaches:

- the *procedural approaches*, which consists in comparing the results with others extrapolated from further data sources (e.g. expert judgement and internal reports);
- the *numerical approaches*, which differ from the previous set of procedures since they imply the application of algorithms and statistical techniques to evaluate uncertainty (e.g. Monte Carlo analysis). In the next section further details about Monte Carlo method are reported.

### 2.2.4.1 *Uncertainty analysis*

As well known, LCA studies are characterized by a large use of data in order to complete the inventories. Each data is in general affected by a wide range of

uncertainty due to the kind of source used: lower is the class of data higher is the uncertainty associated with them. Further details about the several classes were above in section 2.2.2. Therefore, in order to fight the data uncertainty and provide more reliable results, literature<sup>1</sup> strictly recommends the use of sensitivity analyses. For this reason, we selected the procedures reported so-called numerical approaches in order to support our LCA studies. Among these Monte Carlo method, incorporated in our software license, was chosen. All the procedure is characterized by five steps. First, researchers have to evaluate the results uncertainty values. In our case studies the peer-reviewed procedure developed by Weidema and Wesnæs was applied.<sup>14</sup>

Second, information about uncertainty should be translated into a standard distribution type.<sup>15</sup> The lognormal distribution was selected for our case studies. Then, in order to recalculate the results a variable for each value within the uncertainty range specified is selected randomly by software.<sup>15</sup> Finally, scores obtained are stored before repeating the simulation using different values in the range each time. Statistical approach and results robustness are guaranteed by the repetition of this procedure for a higher number of runs (e.g. 10,000).

Usually Monte Carlo analysis is a further confirmation of the results achieved previously. Where there is no consistency between results achieved in the uncertainty analysis and those obtained during the LCIA phase further investigations are necessary, such as the contribution analysis, the network tool, etc.

## 2.3 Software and Database

Studies presented in this dissertation were carried out using one of the most diffused LCA software: the SimaPro (version PhD 7.3.3) developed by the PRÉ Consultants.<sup>16</sup> The license incorporates database, list of substances and different analysis methods. It also provides the possibility to show results in a different way (e.g. single score, characterization, normalization, damage assessment) in addition to several tools, such as the contribution analysis, the network and tree visualization and the Monte Carlo method. SimaPro structure is organized in *product stage* and *processes*. The first one provides the general layout in order to build LCA of a product, giving the possibility to make distinction between

each life cycle stage: production, usage, end of life, disassembling and reuse. On the other hand, the latter collects all the default processes provided by several databases, dividing them in macro categories like: material, energy, transport, processing, use, waste scenario and waste treatment. Each macro sector is also divided in subcategories.

Ecoinvet<sup>17</sup> represents one of the most diffused library among LCA practitioners. It was developed starting from 1998 by the joint efforts of several institution such as the Agroscope Reckenholz-Tänikon Research Station (ART), the Paul Scherrer Institute (PSI), the Swiss Federal Institute of Technology Lausanne (EPFL), the Swiss Federal Institute of Technology Zürich (ETH) and the Swiss Federal Laboratories for Materials Testing and Research (EMPA) and released around 2003.

The database provides a huge number of default processes in order to cover all the sectors identified by each macro and subcategory. A distinction between *unit* and *system* processes was introduced by the developers. The first category includes all the default processes for which the inputs and outputs are shown in aggregated way under the main stages. The other class comprises processes for which inventory is reported just in terms of resources list. Ecoinvent v.2.2 (released in 2009) was used as default database in order to build the inventories for our studies.

## References

---

- 1 M.A. Curran, *Life Cycle Assessment Handbook*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2012.
- 2 D. Novick, *The federal budget as an indicator of government intentions and the implications of intentions*. Santa Monica, CA: Rand Corporation, publication P-1803, 1959.
- 3 Ökobilanzen von Packstoffen. Schriftenreihe Umweltschutz no. 24; Bundesamt für Umweltschutz: Bern, Switzerland, 1984.
- 4 UN Environment Programme Life Cycle Initiative website; <http://lcinitiative.unep.fr/>.
- 5 ALCAS Australian Life Cycle Assessment Society Website; <http://www.alcas.asn.au/>.
- 6 H. Chen, Y. Yang, Y. Yang, W. Jiang, J. Zhou, *Int J Life Cycle Assess*, 2014, **19**, 1674-1685.
- 7 CALCAS Co-ordination Action for innovation in Life-Cycle Analysis for Sustainability <http://www.calcasproject.net/>.
- 8 EN ISO 14040 *Environmental Management, Life Cycle Assessment, Principles and Framework*, International Organization for Standardization, Geneva, Switzerland, 2006.
- 9 EN ISO 14044 *Environmental Management, Life Cycle Assessment, Requirements and Guidelines*, International Organization for Standardization, Geneva, Switzerland, 2006.
- 10 M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs, R. van Zelm, *ReCiPe 2008 - A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level, First edition (version 1.07)*, Ministry of Housing, Spatial Planning and the Environment (VROM), Netherlands, 2012.
- 11 J.B. Guinée, M. Gorrée, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, L. van Oers, A. Wegener Sleeswijk, S. Suh, H. A. Udo de Haes, H. de Bruijn, R. van Duin, M.A.J. Huijbregts, *Handbook on life cycle assessment. Operational guide to the ISO standards*, Kluwer Academic Publishers, Dordrecht, 2002.
- 12 M. Goedkoop, R. Spriensma, *The Eco-indicator 99. A damage oriented method for life cycle impact assessment. Methodology report and annex*, Pré Consultants, Amersfoort, The Netherlands, 1999.
- 13 IPCC - Intergovernmental Panel on Climate Change, *Climate Change 2007. Fourth Assessment Report. The Physical Science Basis*, Cambridge University Press, United Kingdom, 2007.
- 14 B. P. Weidema and M. Wesnaes, *J. Cleaner Prod.*, 1996, **4**, 167-174.
- 15 M. Goedkoop, M. Oele, J. Leijting, T. Ponsioen, E. Meijer, *Introduction to LCA with SimaPro*, v.5.1, PRé, 2013.
- 16 PRé Consultants, SimaPro7, PhD version 7.3.3, Amersfoort, The Netherlands, 2013.
- 17 Ecoinvent Centre (formerly Swiss Centre for Life Cycle Inventories), Ecoinvent 2.2 Database, 2009.



### 3. Life Cycle perspective in the chemical sector

#### 3.1 LCA of chemicals production – a literature review

Although during the first part of the 20<sup>th</sup> century the industry was reluctant to accept the LCA approach, its application in this sector grew throughout the last decades and was launched firstly by the producers of plastics, detergents, personal care and automobiles which are recognized as the pioneers.<sup>1</sup> After this early approach to the methodology, it became more established also among the other branches of industry, furthermore, as suggested by literature,<sup>2,3</sup> the interest was moved from the products to the study of the production processes. LCA is now a well-established tool since it represents an integral part of decision-making in industry<sup>4</sup> to make environmental considerations which effect process design and optimization.<sup>1</sup> Efforts made by Jacquemin et al.<sup>1</sup> to collect the works in which LCA is applied as a tool to investigate sustainability in the industry has revealed that different sectors were already covered such as the waste management and the emissions abatement,<sup>5,6,7,8</sup> the metal industry,<sup>9,10</sup> the areas of fuel and the energy production.<sup>11,12,13</sup>

Moreover, an interesting field of application of the LCA is the chemical sector and its several aspects such as: i) the production process and the best recovery option of the products (e.g. polymer materials,<sup>14</sup> dimethylcarbonate,<sup>15</sup> maleic anhydride,<sup>16</sup> cellulose nanowhiskers,<sup>17</sup> carbon nanotubes,<sup>18</sup> acrylic acid,<sup>19</sup> sodium chromate<sup>20</sup> and astaxanthin<sup>21</sup>), ii) the oil refining and the pharmaceutical sectors.<sup>22,23,24</sup>

In addition, literature<sup>25,26,29</sup> recognized the LCA as a valuable tool to assess the sustainability of the disciplines of chemistry which concern the environmental issues such as the GC. The crucial role of the LCA into GC is well summarized by Gustafsson and Börjesson in the conclusion of their work<sup>27</sup> when they affirmed “...the importance of investigating the environmental performance of a product from cradle-to-grave and not only consider it ‘green’ because it is based on renewable resources or is produced based on the principles of Green Chemistry.” This increased interest of the research community toward this field was also proved by the fact that in 2012 the International Journal of Life Cycle Assessment (edited by Springer) launched a call for paper concerning studies which apply life cycle approach to GC.<sup>28</sup> In addition several reviews<sup>4,29</sup> were written with aim to collect the more relevant articles which deal with some of the emerging aspects, such as: biopolymers,<sup>30,31,32,33,34,35,36,37</sup> biofuels and land use,<sup>38,39,40,41,42,43,44,45</sup> biorefinery,<sup>46,47</sup> green pharmaceutical processes,<sup>48,49,50,51,52,53,54,55</sup> solvents and CO<sub>2</sub>,<sup>56,57,58,59,60,61,62</sup> nanotechnology,<sup>63,64,65</sup> etc.

However, as suggested by Jiménez-González and Constable<sup>66</sup> the life cycle approach is not only restricted to the GC, but it should be extended to each activity which is considered «sustainable»: *“a process or activity to be considered green it is necessary to assess the cumulative environmental impacts across the entire life cycle of the product: raw material extraction, manufacturing, use, maintenance, reuse, transportation and final fate. This is done using life cycle inventory and assessment concepts [...]”*.

Therefore, in the following sections, a description of the research activity carried out during the PhD program in chemistry (curriculum environmental chemistry) will be presented in detail. Two are the aspects investigated through LCA, both concern some aspects of GC and GE as well as the sustainable development: i) the reduction in the production steps and ii) the use of renewable raw materials. The research activity led to the publication of several peer-review papers, thus, according with the copyright of each editor, the description will be disclosed using part of the manuscripts (text, figures and tables). No significant change will be applied to the already published materials, with the exception of some stylistic adjustment in line with the format of the work.

### **3.2 Reduction in the production steps – the case study of acrylonitrile synthesis**

The reduction in steps involved in the overall production chain is not considered as a fundamental principle of GC and GE, since reducing the number of stage could entail the use of some hazardous substance (e.g. as a solvent). However, usually, lower is the number of phases involved lesser is the amount of energy consumed during the entire process, especially when reduction concerns the production of feedstock and/or the purification procedures. This aspect seems to be perfectly in line with the concepts of energy requirement minimization and energy efficiency maximization expressed by the 6<sup>th</sup> GC and the 4<sup>th</sup> GE principles (section 1.1.1). Therefore, LCA methodology was used as a screening tool to investigate the environmental performances associated with the reduction in steps occurred during the production chain. The work resulted in a publication on the Journal of Cleaner Production edited by Elsevier,<sup>67</sup> hence text, figures and tables were reproduced by permission of the editor.

### 3.2.1 Background and motivation of the study

The chemical industry is one of the sectors that contribute most to the economy in terms of revenues, trade, and employment, while chemistry is considered to be at the forefront of the transition to a more sustainable development, as it takes part in all economies through the furnishing of products.<sup>68</sup>

The 20<sup>th</sup> century has been defined, among other ways, as the “plastic century” due to the primary role played by polymers in influencing the human culture and way of living. While considering the wide use of plastics and rubbers in our society as critical elements in the depletion of fossil fuels, it is not surprising that among the most promising fields of improvement for a greener chemistry is the study of alternative building blocks and innovative processes to replace traditional feedstock routes from oil.<sup>69</sup>

Acrylonitrile (ACN) is an example of a chemical whose use increased dramatically after its first application in plastic and rubber manufacturing in the 1930s. The production of acrylic fibers, acrylonitrile-butadiene-styrene (ABS), adiponitrile, nitrile-butadiene (NB) copolymers, acrylamide for water-treatment polymers, and carbon fibers are among the main applications that have determined the commercial significance of ACN.<sup>70</sup> In 2010, world ACN production amounted to 6 Mt, and a +3.7% annual growth over the years 2008-2018 – mainly driven by ABS and styrene-acrylonitrile (SAN) resin manufacturing – has been estimated.<sup>70,71</sup> About 90% of the total ACN production follows the Standard Oil of Ohio (SOHIO) process, which is based on the ammoxidation of propylene. The reaction is highly selective, fast, and leads to efficient yields of ACN requiring no further recycling steps.<sup>72</sup> In any case, the cost of ACN production has recently increased due to the market price of reagents, in particular propylene, which accounts for more than 70% of the total cost.<sup>73</sup> Thus there is an increasing interest in finding alternative, more economic ways to produce ACN. Specifically, propane ammoxidation seems to be the most promising alternative process.<sup>72</sup> In 2012 PTT Asahi Kasei Chemical Co. Ltd., a joint venture of PTT Asahi Kasei Chemical and Marubeni, started up the first acrylonitrile production facility in Thailand. The plant, which achieves an acrylonitrile productivity of about 200,000t/y, also includes in project the production of methyl methacrylate and ammonium sulfate (about 70,000t/y and 160,000t/y respectively).<sup>74</sup> Also, the use of propane would imply a significant cost advantage over propylene (the difference between propylene and propane was estimated in the range of 900-1000\$ per Mt in the year 2012).<sup>75</sup> Although

it might be argued that such a difference would not be stable enough, because it is influenced by the fluctuations in market prices, anyhow it is certain that the change from propylene to propane ammoxidation produces a reduction in the number of steps required, as the latter is commonly produced by a direct fractional distillation of petroleum, whereas with propylene, cracking or catalytic dehydrogenation operations are necessary. Moreover, it is reported that the direct transformation of the alkane into acrylonitrile affords a more rational use of energy, since the strongly endothermic process for propylene production is avoided.<sup>76</sup> Moreover, the development of new catalysts will lead to an improved exploitation of light alkanes, by means of processes conducted in mild conditions.<sup>77</sup>

Aiming to evaluate whether such a difference between processes might eventually entail a reduction of loads to the environment, or – in other words – whether the alternative ammoxidation process is greener than the conventional one, the LCA methodology was used to evaluate the cleaner production in terms of sustainability from a life cycle perspective. Specifically, in this study five scenarios describing different ACN production routes were modeled and compared in terms of contribution to midpoint impact categories: Climate Change (damage on human health, CH, and on ecosystem, CE), Fossil Fuel Depletion (FD) and Metal Depletion (MD). One kilogram of ACN was assumed as the reference flow, while the impact analysis was carried out using SimaPro 7.3.3 software, (Pré Consultant 2010) and the ReCiPe 2008 method v1.07.<sup>78</sup>

### 3.2.2 Ammoxidation reactions to acrylonitrile

Ammoxidation reaction consists of a catalytic oxidation of hydrocarbons in the presence of ammonia to produce organic nitriles and water, where mixed metal oxides, with or without support, are used as catalysts.<sup>79</sup> Typical reactants are alkenes. The reaction involves three main steps: hydrocarbons oxidation to form intermediates on the active sites, nitrogen insertion, and oxidative dehydrogenation of the N-bonded species.<sup>80</sup> A description of both the conventional SOHIO process and the most innovative routes for the production of ACN is reported hereafter.

## The SOHIO process - propylene-based scenario

The INEOS Technologies ACN technology, also known as the SOHIO process, involves the catalytic oxidation of propylene in the presence of ammonia and air, as schematically depicted in the equation 3.1. The classes of catalyst used in this process are: Multi Metal Molybdate (MMM), made up of Mo, Bi, Fe, Ni, Co, and additives (e.g. Cr, Mg, Rb, K, Cs, P, B, Ce, Sb, and Mn) dispersed in silica (50% w/w), and Antimonate with rutile structure, made up of four metal antimonate cations and a redox couple of Fe, Ce, U, and Cr.<sup>80</sup> These classes of catalyst led to an increase in the production of ACN starting from 1960,<sup>81</sup> for this reason they were deeply investigated in literature in order to identify their physical and chemical structures, and the proposed mechanisms for propylene and propane ammoxidation reaction.<sup>82</sup>

The reaction is conducted in a fluidized-bed reactor system operating at 30–200 kPa and with a temperature range of 400–500 °C.<sup>70</sup>

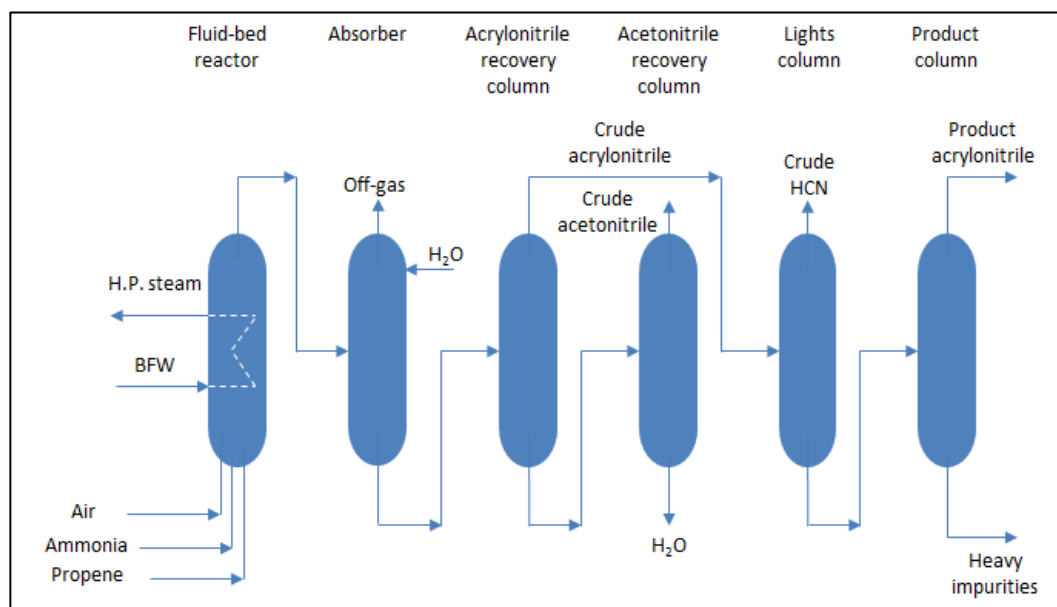


3.1

The reaction is highly exothermic ( $\Delta H^\circ = -515$  kJ/mol),<sup>79</sup> thus the fluidized-bed configuration is necessary to remove the heat in excess and achieve a propylene conversion higher than 95%, as well as a selective yield in ACN close to 80%. Also, numerous steam coils are contained inside the reactor to keep the temperature as constant as possible in order to prevent run-away phenomena.<sup>80</sup> Usually the heat recovered is used to produce high-pressure steam.<sup>72</sup> Reactants are fed separately – in order to avoid homogeneous reactions – with high purity (e.g. > 90% for propylene and 99.5% for ammonia)<sup>80</sup> and with a molar ratio close to the stoichiometric one (equation 3.1). Higher ammonia/propylene molar ratios are not common because of the occurrence of side reactions. The hot effluent outputs of the fluidized-bed reactor are quenched in a water absorber: here, unreacted ammonia is rapidly neutralized by sulfuric acid to produce ammonium sulfate,<sup>79</sup> while unreacted propylene is vented. The ACN produced is recovered from the organic phase and then purified of hydrogen cyanide and heavy impurities. The main byproducts are acetonitrile and hydrogen cyanide (0.02-0.11 kg and 0.15-0.20 kg per kg of ACN, respectively), which could be

recovered, and used for other applications (e.g. solvent, raw material).<sup>70</sup> A schematic view of the process is shown in Figure 3.1.

**Figure 3.1** – SOHIO process. Source: Cespi et al. 2014<sup>67</sup> – reproduced by permission of Elsevier.



### Alternative synthetic process – propane-based scenario

The general stoichiometry of the reaction based on propane feedstock is shown in equation 3.2.

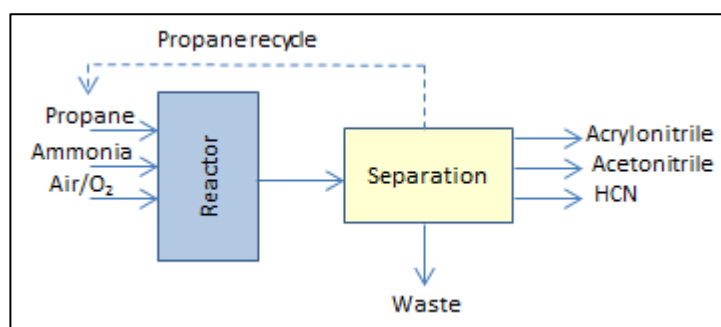


3.2

Many companies are involved in the industrial conversion of propane to ACN, and although the synthetic reaction is the same, each of them has undertaken different production routes with distinct process conditions. The first patent developed by Standard Oil (now BP plc) uses propane-rich conditions, while both the Mitsubishi Chemical Corporation (MCC) and Asahi Kasei Chemicals Corporation (AKCC) use propane-lean compositions.<sup>80</sup> Major differences between these two approaches lie in both the propane conversion – which is lower in the former case – and the choice of catalyst. MCC and AKCC use a molybdate-based catalyst, so that the system may achieve higher selectivity and yield, while BP has preferred an antimonate catalyst. However, in a later patent BP also suggested the use of propane-lean conditions, which, in any case, require higher temperatures (around 50°C higher). Both catalytic systems used are defined as belonging to the “multi-functional system” category, due to

their structure with different kinds of active sites that have the ability to produce ACN via a propylene intermediate. Nevertheless, the catalysts for propane ammoxidation differ from the systems used in the ammoxidation of propylene due to the presence of an oxidative enhancer (a halogen promoter or a strong oxidant such as Vanadium). Also, the propane ammoxidation reaction (equation 3.2) is extremely exothermic ( $\Delta H$  at reaction temperature is around  $-813\text{kJ/mol}$ ): it is conducted in a fluidized-bed reactor under the same process conditions (temperature and pressure) as the SOHIO process, as well as with the use of procedures that neutralize unreacted ammonia and recover acrylonitrile from byproducts. Figure 3.2 shows a simplified scheme of propane-based process to ACN. Both a higher performance in terms of selectivity and conversion from molybdate catalysts and the lower price of propane make the configuration without recirculation preferable (Figure 3.2). The recycling option may become interesting when a high propane conversion rate is not achieved.<sup>80</sup>

**Figure 3.2** - Propane ammoxidation, recycle/no recycle configuration. Source: Cespi et al. 2014<sup>67</sup> - reproduced by permission of Elsevier.

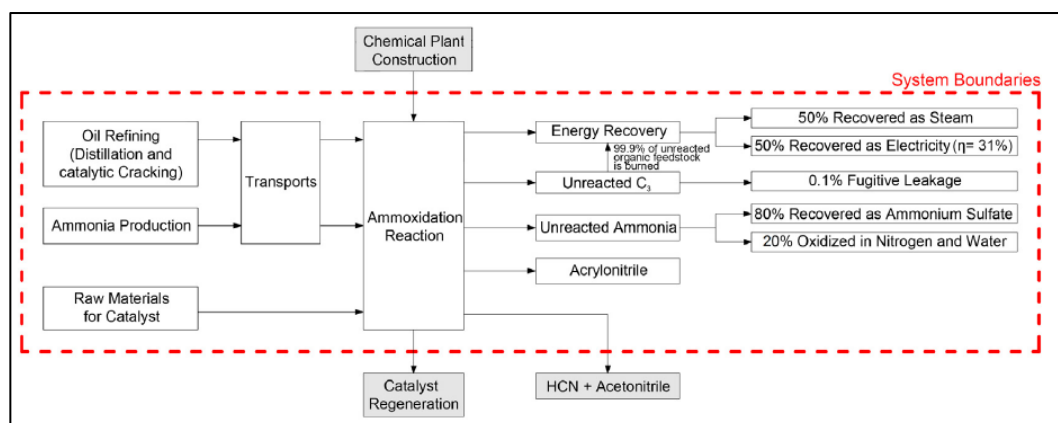


### 3.2.3 System boundaries and functional unit

In this study LCA methodology was applied as a scientific tool aimed at the identification of the cleaner technology in the production of ACN. For this reason, the system boundaries cover single unit processes involved in each scenario for the ACN production. Specifically, they include energy and mass flow into and out of the reactor (reactants, auxiliary chemicals, electricity and heat consumed for utilities), emissions into the air and water, energy dissipation, all mass and energy flows into and out of the heat exchanger of the fluidized-bed, the amount of raw material for the production of catalysts, transportation processes, and benefits resulting from energy and mass recovery (expressed as avoided impacts). Average infrastructure processes were not considered because of their low representativeness in quality for database data. Also,

the typical lifetime of a chemical plant is commonly very long, so any environmental loads connected with the functional unit chosen would in this case be negligible. System boundaries are plotted in Figure 3.3. One kilogram of ACN produced was assumed as the reference flow and thus used as a base to measure inputs and outputs of the systems studied. As reported previously, the ammoxidation processes produce acetonitrile and HCN as main by-products. Both species are recovered and used in downstream applications, either as a solvent (acetonitrile) or as a reactant for the synthesis of other chemicals, such as acetone cyanhydrine, which is the intermediate for methylmetacrylate synthesis. However, although the integration with other processes may greatly contribute to the success of a chemical production, the further extension of the system boundaries, including also the downstream use of by-products, would greatly increase both the system complexity and the uncertainty of the final result, due to the lack of detailed data for the additional inputs. This extension would require a specific study, which is intended to be tackled as a widening of the present work. Therefore, on the basis of each selectivity rate for ACN, it has been decided to apply mass allocation criteria to ACN production only, thus including any upstream transformation but without taking into account acetonitrile and HCN management and related burdens. Mass shares for each scenario investigated were estimated in accordance with both company reports and process specifications reported in patents.

**Figure 3.3** - System boundaries of the study. Source: Cespi et al. 2014<sup>67</sup> - reproduced by permission of Elsevier.



### 3.2.4 LCI of acrylonitrile production scenarios

In this case study LCI includes data collection for five scenarios, by modeling different ACN production routes: the first scenario describes the conventional SOHIO process



from propylene, while the others focused on alternative processes having propane as the raw material. Each scenario is characterized by different catalytic systems and process specifications (e.g. selectivity, conversion, and yield) that influence mass and energy balances. The modeling phase was carried out using SimaPro 7.3.3 software. (Pré Consultant 2010) A further description of the scenarios is reported below.

### 3.2.4.1 Scenario 1: the SOHIO process

Two propylene production methods were primarily investigated: one in which the olefin is produced by naphtha steam cracking (known also as thermal cracking), and the other in which propylene is synthesized by catalytic cracking (Fluid Catalytic Cracking, FCC). The former entails the use of heat to obtain the desired product: the Ecoinvent process “Propylene, at plant/RER” is set up as a default process for propylene production in the SimaPro software.<sup>83</sup> The FCC process is characterized by lower process temperatures, while the cracking reaction is carried out using zeolite as the catalyst. As the process was not present in the database, a specific inventory was created by using mass and energy balances,<sup>84</sup> and the Ecoinvent process “Zeolite, powder, at plant/RER” was used to model the catalyst production.<sup>83</sup> An average amount of catalyst was estimated on the basis of literature reports (0.97kg/ton of propylene produced).<sup>85</sup> No catalyst regeneration stages were included.

The screening comparison between the two propylene production procedures showed for the FCC process a 10% reduction of total impacts thanks to a lower operating temperature; thus catalytic cracking was used in Scenario 1 to simulate the production process for propylene supply. Data inventory for the ammoxidation of propylene to ACN was collected from literature which refers to an existing plant. At the industrial scale, a small excess of ammonia with respect to the stoichiometric procedure is necessary: ammonia-to-propylene molar ratio varies between 1.05 and 1.2, while the range 1.9-2.1 applies to the air/propylene share (usually oxygen-enriched air is used).<sup>80</sup> The catalyst was modeled considering the typical empirical structure of molybdates:  $(K,Cs)_{0.1}(Ni,Mg,Mn)_{7.5}(Fe,Cr)_{2.3}Bi_{0.5}Mo_{12}O_x$ . The excess of molybdenum is important for the catalyst performance because it functions as a molecular bridge from the molybdates and provides a reserve of the metal that is partly depleted during the redox cycle.<sup>80</sup> This type of active phase is supported over  $SiO_2$ , typically in the range of 50% of the entire catalyst weight. Considering data on the plant productivity and catalyst

make-up (0.7kg/t of ACN),<sup>86</sup> an amount of 1g of catalyst per kg of acrylonitrile produced was estimated. The model designed for the catalyst assumed raw material inputs necessary for assembling the system, while the amount of each element was calculated on the basis of the catalyst stoichiometry. As the model, the composition of the catalyst C49MC developed by Standard Oil in 1991 was chosen:<sup>87</sup>  $K_{0.15} Cs_{0.05} Ni_{4.0} Co_{0.5} Mg_{2.5} Fe_{2.0} Bi_{0.5} W_{0.5} Mo_{12} O_x$  and  $SiO_2$  (50% w/w). The process includes the extraction phase only. No information was available on production steps, for which impacts and flows were assumed to be negligible from the perspective of the entire life cycle. Again, the phase of catalyst regeneration was not taken into account due to its negligible impact on the total value. ACN selectivity and propylene conversion yield were assumed to be equal to 83% and 98%, respectively,<sup>70</sup> determining an 81% molar yield for ACN. Molar proportions and process specifications were used to calculate the reactant amounts put into the reactor, i.e. 0.86kg of propylene and 0.39kg of ammonia per kg of product. Furthermore, emissions were estimated by assuming that the unreacted olefin is burnt with 99.9% combustion efficiency (about 0.02kg), while the remaining fraction escapes into the air as fugitive leakage (1.72E-05kg). In order to evaluate the cleaner production, we performed the comparison on the basis of the best available techniques on the market, and we assumed that the heat from combustion is recovered and used for plant utilities (i.e. steam and electricity): the model counts environmental benefits from energy recovery, such as avoided impacts from natural gas (0.022m<sup>3</sup>) extraction and use. Energy produced from the propylene combustion, and LHV (Low Heating Value) values were used to estimate the amount of natural gas avoided. Model assumed that 80% of unreacted ammonia is neutralized (0.04kg). Mass balances were used to calculate the amount of sulfuric acid consumed during the neutralization phase and the resulting ammonium sulfate produced (0.12kg and 0.16kg respectively). Considering that ammonium sulfate is recovered in a solution to about one third by weight, models include the energy consumed for the production of salt as a byproduct, deriving from the main operations (water evaporation, centrifugation, and dehydration).<sup>88</sup> It was assumed that ammonium sulfate is sold as a fertilizer, so the avoided impact deriving from the production of a nitrogen fertilizer was taken into account in our scenarios. Lastly, the remaining ammonia (around 20% of the unreacted amount, about 0.01kg) was assumed to be oxidized to produce  $N_2$  and  $H_2O$ . Both the heat exchanged and the water amount used in reactor coils were calculated by using energy balance (respectively 7.64kg and 1.30E+04kJ). The model created

assumes that the heat exchanged in coils is recovered with an efficiency of 50% (6.52E+03kJ), and is used for plant utilities: half of it to produce heat (3.26E+03kJ), and the rest converted into electricity (2.81E-01kWh), with a 31% conversion efficiency.<sup>89</sup>

More details about the SOHIO process inventory (Table 3.6) and the equations used for the enthalpy balanced are listed below in the Annex A.

### 3.2.4.2 Scenario 2: Propane ammoxidation to acrylonitrile, alternative synthetic process

As previously reported, shifting from propylene to propane involves a reduction in the production steps, which could produce an environmental benefit. In particular, a screening comparison shows a cut in the total impact of about 16%, if propane production is compared with the catalytic cracking operation to manufacture propylene; this difference is much more appreciable as concerns climate change, for which the environmental load is reduced of about 42%. Therefore, to assess whether this reduction is maintained even during ammoxidation reaction, different scenarios were created aiming to model alternative routes for ACN production from propane ammoxidation. As just mentioned, only the AKCC started to develop a commercial process for the production of ACN from propane ammoxidation by modifying an existing plant.<sup>80</sup> However, many companies are looking into the replacement of propylene with alkanes, mainly by exploring different combinations of catalytic systems and reaction conditions. Thus, four scenarios were modeled according to the most advanced results and called AKCC, MCC, BP poor (low-propane concentration), and BP rich (propane-rich concentration). Each of them refers to a specific process and to the catalysts developed by the companies. The modeling phase was performed using information and data reported on patents, which remain constant even on an industrial scale: reaction conditions, catalyst composition, process specifications (yield and selectivity), and feed molar ratio for each system. As reported in literature, a double catalyst make-up with respect to the scenario from propylene was assumed,<sup>90</sup> entailing a consumption of 1.7g of catalyst per kg of ACN produced. The amount of propane necessary for the reaction was estimated from the ACN yield reported. In the LCA model, alkane production as a fraction of the distillation of petroleum and naphtha was assumed, considering it to be a cheaper raw material for synthesizing ACN instead

of using it to produce propylene by dehydrogenation.<sup>80</sup> Molar ratios were used to calculate the mass balance of input and output flows. Also in this case, 99.9% unreacted propane is sent to combustion, and avoided impacts from heat recovery are taken into account similarly to previous scenario (avoided extraction and combustion of natural gas). As previously assumed for the process from propylene, byproducts (acetonitrile and hydrogen cyanide) were not considered in these models. Mass allocation for each scenario was obtained using selectivity values, as reported in Table 3.7. Energy consumption for the production of ammonium sulfate, and the avoided impacts derived from N fertilizer production were included in each model. The remaining unreacted ammonia (about 20%) is assumed to be oxidized to produce N<sub>2</sub> and H<sub>2</sub>O. Equation 3.3 was used to estimate the energy exchanged in reactor coils, by assuming that 50% of the total is recovered and reused for the plant utilities (e.g. steam and electricity). Further details on these scenarios are listed in the in the Annex A (Table 3.7).

### 3.2.5 Impact assessment and results interpretation

Impact analysis was carried out using the ReCiPe 2008 method v1.07, which was followed for the assessment of environmental burdens for the midpoint categories CH, CE, FD, and MD.<sup>78</sup> The decision to neglect other midpoint impact categories is related to aim of the study. In fact chemical processes involve very wide geographical areas, considering those in which raw materials are extracted and sold, transportation, and the final use for synthetic purposes. So, in our opinion fossil fuel depletion, metal depletion and climate change are the main important categories for this study, since they represents damages on a global scale. These midpoint scores may further be grouped into three endpoints based on Damages to Human Health (units of measurement: disability adjusted life years - DALYs), Ecosystem Quality (measured in potentially disappeared fractions of species - species·yr), and Resource Consumption (in terms of increased costs of extraction - \$). The results of the characterization analysis at the midpoint level are reported in Table 3.8 (Annex A). Figure 3.4 shows the results of the characterization analysis in a radar chart, while Figure 3.5 offers a comparison among the five ammoxidation scenarios in terms of ReCiPe single score. The Climate Change category includes process contributions to both human health and the ecosystem damage categories. Each impact category is described in detail in the following paragraphs.

- **Climate Change and Fossil fuel Depletion**

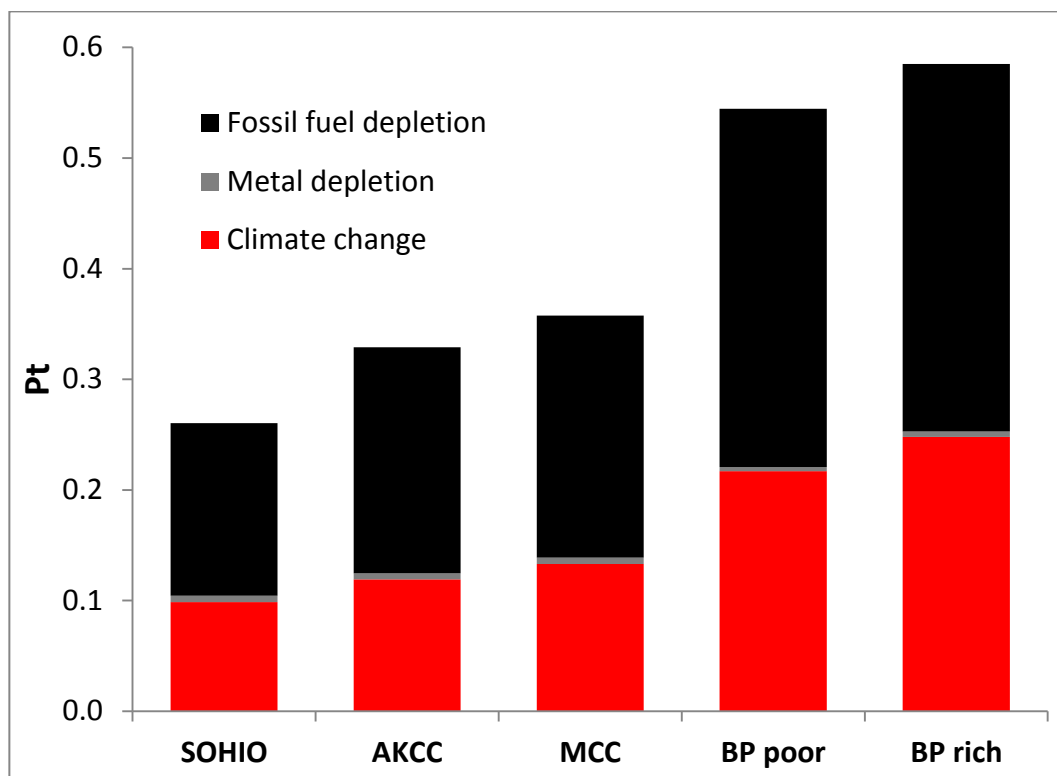
The impact on climate change and fossil fuel depletion categories is closely linked: the use of fossil fuels to generate energy produces relevant carbon dioxide emissions and entails greenhouse effects. In fact, both categories show a growing trend, moving from the SOHIO process to propane ammoxidation scenarios. The increase in impacts is mainly due to the amounts of input and output substances of the models (Table 3.7). There are two major causes: first, moving from the SOHIO process to the systems involving propane ammoxidation, a decrease in yield occurs: 81% for propylene ammoxidation, and around 60% for Asahi and Mitsubishi processes, down to the lowest values for the BP processes (from 9 to 40%). Consequently, the amount of organics introduced into the reactor changes: for instance, in the case of the BP-rich scenario, the amount of propane used is more than ten times higher than the propylene in the SOHIO process. The large amount of reactants means that a higher quantity of organics has to be extracted to satisfy supply requirements. The second reason is the higher amount of the ammonia necessary for running the process, which is determined on the basis of different molar ratios for each process. According to literature,<sup>91</sup> the designed model assumed that 85% of ammonia synthesis gases ( $N_2$  and  $H_2$ ) are produced by the reforming of natural gas, while the rest is obtained from the partial oxidation of heavy fuel oil at high temperature and pressure conditions (about  $500^\circ C$  and 300atm, respectively).<sup>92</sup> All process stages are energy-intensive and entail a high consumption of fossil fuels. Nevertheless, a significant contribution to the results is due to the avoided impact thanks to material and energy recovery. The electrical and thermal energy recovered from the exothermal reactions results in avoiding the extraction and consumption of fossil fuels, which contributes to reducing the overall impact score significantly. In particular, a low percentage of propane conversion means that a great deal of unconverted reagent (a light alkane) is burned: this translates into a direct contribution to methane savings. Furthermore, the avoided impacts deriving from the production of ammonium sulfate contribute to reducing the global environmental load for the two midpoint categories. As expected, the higher amount of ammonium sulfate is produced by the BP scenario with propane lean conditions, and the consequent excess of ammonia in feeding (Table 3.7). As already mentioned, unreacted ammonia is neutralized by sulfuric acid to produce salt; the greater the

amount of unreacted base, the greater the quantity of sulfate produced, and consequently the greater the avoided impact.

- **Metal depletion**

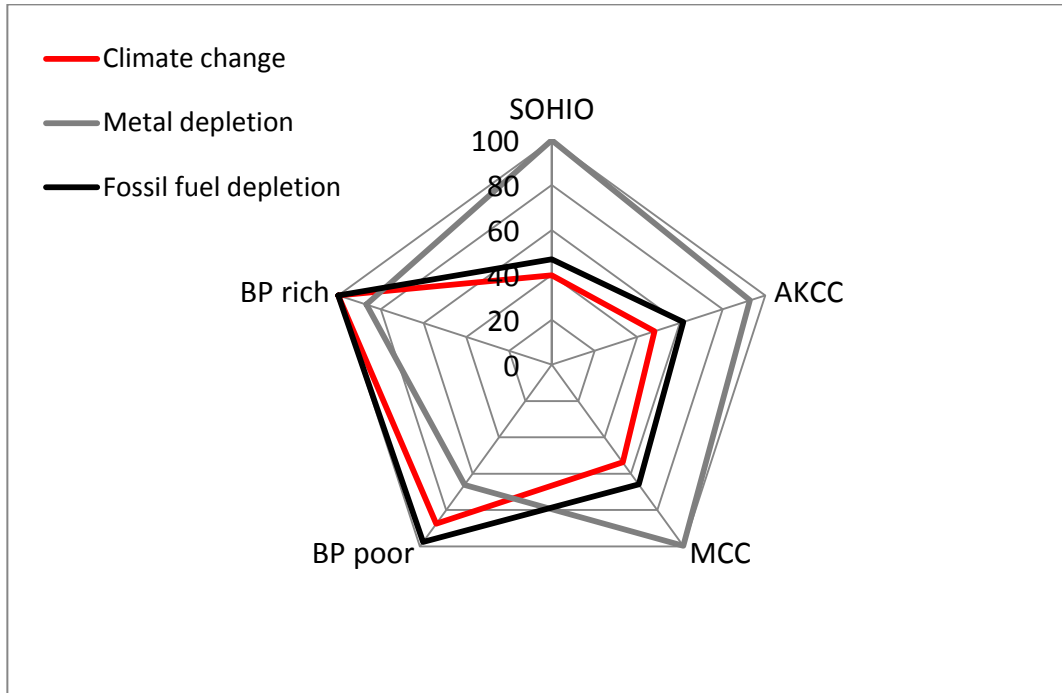
As known the catalyst efficiency influences the product yield, and so the feasibility of processes on industrial scale, aspect considered in the study through the evaluation of reactants amount consumed per kg of ACN produced. However, also the impacts associated with each catalyst system were evaluated. As reported in the inventory analysis no information about the production steps were available (e.g. energy consumption on industrial scale during the manufacture), due to the confidential information linked with the catalyst making (corporate know-how). Nonetheless, to have a simplified evaluation of impacts of the catalyst manufacture, we assessed the environmental load only in terms of resources extraction required for each system. Results, expressed in form of metal depletion impact category, show the worst performance for the SOHIO process scenario. Reasons must be sought in the use of two catalyst systems for this scenario: the first one (zeolite) is needed for the cracking, while the second is used in the ammoxidation step. Catalysts developed by Mitsubishi Chemicals Corporation and Asahi Kasei Chemical Corporation seem to have similar empirical composition, identified by means of a combinatorial methodology (Table 3.7). Molybdate systems are prepared preferably by hydrothermal synthesis, which results in nucleation and the growth of two phases: M1, which is able to independently convert propane into acrylonitrile, and the co-catalyst M2, which is necessary for increasing selectivity (the promotion of intermediately formed propylene ammoxidation into acrylonitrile).<sup>80</sup> These M1 and M2 compositions are reported in literature:  $\text{Mo}_{0.78} \text{V}_{1.2} \text{Nb} \text{Te}_{0.94} \text{O}_{28.9}$  and  $\text{Mo}_{0.67} \text{V}_{1.33} \text{Te}_{1.82} \text{O}_{19.82}$ , respectively.<sup>80</sup> As already mentioned, Figure 3.4 shows the results of the characterization analysis in the form of a radar chart: at each vertex of the pentagon a scenario is reported, and colored lines represent the percentage ratio for every impact category. The closer the lines are to vertices (100%), the higher the impact of the considered scenario. The red line represents the climate change category, which includes process contributions to both the human health and the ecosystem damage categories, the black line indicates the fossil fuel depletion and, lastly, the grey line shows metal consumption scores.

**Figure 3.4** - Five ammoxidation scenarios compared in terms of ReCiPe 2008 single score. Source: Cespi et al. 2014<sup>97</sup> - reproduced by permission of Elsevier.



The results obtained through the comparison of the five ammoxidation scenarios were also expressed in terms of a ReCiPe single score (Figure 3.5). Histograms show the overall results for the five scenarios, which were obtained from the cumulative sum of each impact category after conversion to a single point. The comparison shows how the alternative synthetic routes starting from propane have total impacts higher than those of the conventional SOHIO process. The cumulative results give overall measures of the environmental performance for scenarios, and permit weighting the relevance of each impact category in the total load on the environment. As shown, the fossil fuel depletion and climate change categories make the highest ReCiPe Pt contribution to the total impact, while the lowest contribution comes from metal depletion. Although this might make it seem environmental implications from that midpoint category are negligible, a further discussion is necessary. Indeed, the importance of taking into account the use of metals in catalytic systems is confirmed by literature,<sup>93</sup> as the situation for most metals (e.g. platinum, palladium, and rhodium) is critical because of supply risk, environmental implications, and vulnerability to supply restrictions,<sup>94</sup> and therefore their effects on the environment might be not negligible in the future.

**Figure 3.5** – Radar chart showing results in terms of single points (by percentage). Source: Cespi et al. 2014<sup>97</sup> – reproduced by permission of Elsevier.

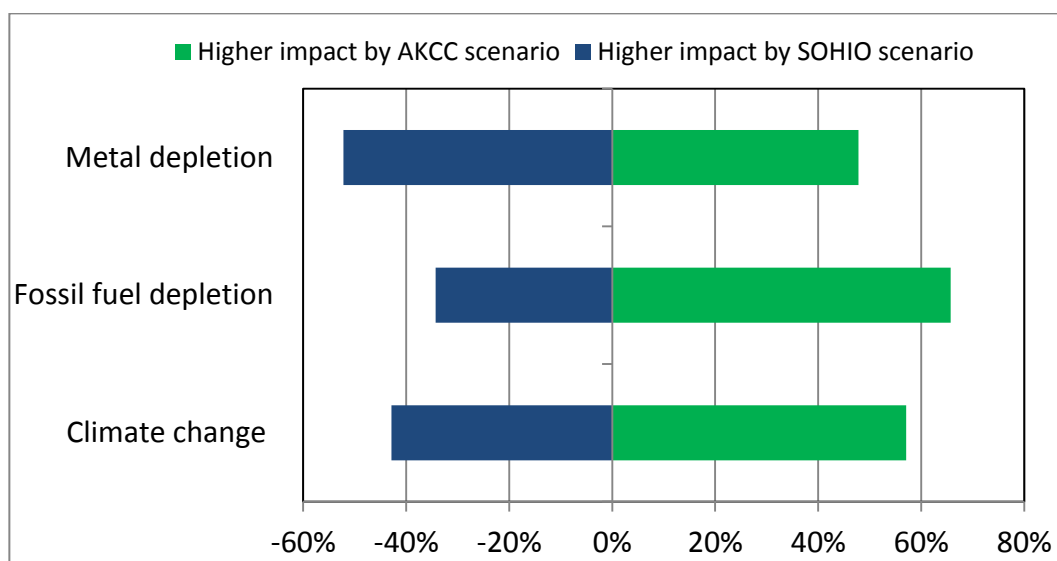


- **Sensitivity analysis**

LCA studies are commonly influenced by data quality used in the inventory analysis. As reported, SOHIO process scenario was created using data reported in literature, instead no information for alternative route starting from propane are available except in the patents. Also, some information about several aspects are not available for all scenarios, as for example: detailed input and output compositions, catalyst make-up and regeneration, energy consumed during the several stages, etc. These information often represent corporate know-how so they are confidential, and it is not possible obtain them from literature. So a sensitivity analysis was performed to evaluate the robustness of the model created, by focusing on the two scenarios fully operating at an industrial scale: the SOHIO process, and the AKCC process. Uncertainty ranges for data used in the inventory analysis were determined by using the data pedigree matrix developed by Weidema and Wesnaes,<sup>95</sup> as reported in a previous study.<sup>96</sup> The values obtained were used to perform a Monte Carlo analysis, which is a statistical method for evaluating the model's sensitivity. Lognormal statistical distribution, with a 95% confidence interval and an iterative calculation number of 1,000 simulations, was applied. The results of this comparison are reported in Figure 3.6.



**Figure 3.6** – Monte Carlo Analysis in terms of midpoint impact categories. Source: Cespi et al. 2014<sup>67</sup> – reproduced by permission of Elsevier.



The three impact categories considered in this study are shown on the y-axis, while the x-axis shows the percentage values achieved by the scenarios at the end of iterative simulations. Green bars show the number of times the AKCC process has higher impact than the SOHIO process; conversely, the blue bars represent the opposite situation. As shown, the Monte Carlo method confirms the reliability of the results obtained in the characterization analysis: the AKCC process proves to have higher impacts with regard to fossil fuel consumption and climate change, whereas the SOHIO process has a poorer performance in the metal depletion category. A marked preference between the two scenarios at a 95% confidence level cannot be clearly identified: the scores show that the poorer results achieved by the AKCC process are frequently confirmed in the range of 60-66% (climate change and fossil fuel depletion, respectively). Conversely, in the case of the metal depletion category, the SOHIO process seems to have a negligibly higher impact: about 48% for the Asahi process and 52% for the SOHIO process. These scores are due mainly to the close results in the characterization analysis.

### 3.2.6 Personal conclusions and recommendation

The study presents a scientific approach through which investigate the environmental footprint of the chemical production sector. In particular, the industrial production of acrylonitrile was studied considering the main stage of the manufacturing process: mass and energy input/output from reactor, heat exchanger, mass and energy recovery, and the catalyst making. The LCA methodology was applied as a scientific tool to compare

the traditional synthesis of acrylonitrile, by propylene ammoxidation (SOHIO process), and the less expensive alternative routes that use propane as the precursor, also in terms of production steps: in fact, propane production is performed with a one-step process, the distillation of petroleum, whereas propylene production involves two steps, distillation and cracking (steam or catalytic). These savings in production steps may suggest that the alternative processes would be allegedly greener than traditional methods, thus leading to a reduction in the environmental load. However, in order to define the most sustainable and cleaner route, it is necessary to have a complete view of the entire process, while evaluating the main stages and flows involved. LCA answers well the need for quantitatively assessing the environmental sustainability of an industrial process in a life cycle perspective. According to Curran<sup>97</sup>, LCA is a fundamental supporting tool for the chemical industry, as it makes it possible to extend the assessment of environmental implications from the production process to the entire life cycle, thus avoiding the deduction of partial or limited evaluations. The model created was analyzed using ReCiPe 2008; midpoint oriented method able to assess environmental loads of each scenario in terms of climate change, fossil fuel depletion, and metal depletion categories. As shown by characterization analysis, alternative processes starting from propane generally seem to have higher impacts especially in terms of fossil fuel depletion, and climate change categories. Although not reported in the study, the comparison between the five scenarios was also done using Ecoindicator 99 as analysis method. Scores confirmed results obtained by ReCiPe 2008 method, underlining higher impacts of the alternative routes starting from propane, in particular in terms of fossil fuel depletion. This outcome is mainly due to the lower activity of the commercially developed catalyst systems, entailing both larger amounts of reactants and a heavier load on the ecosystem, thus resulting in the lower sustainability of alternative processes. Therefore, a very crucial role is played mainly by the commercially developed catalyst system, which can modify the yield of the entire process, thus influencing selectivity and conversion. As said in the inventory analysis, a model for different catalyst systems was created - including only the extraction phase of metals - starting from information about make-up and composition reported in patents. Nevertheless, to make this model complete, more details would be needed regarding catalyst production steps: for example, energy consumption and emissions, and the regeneration of catalysts, but this kind of information is often confidential as it is part of corporate know-how, to which there is limited access. As we said LCA

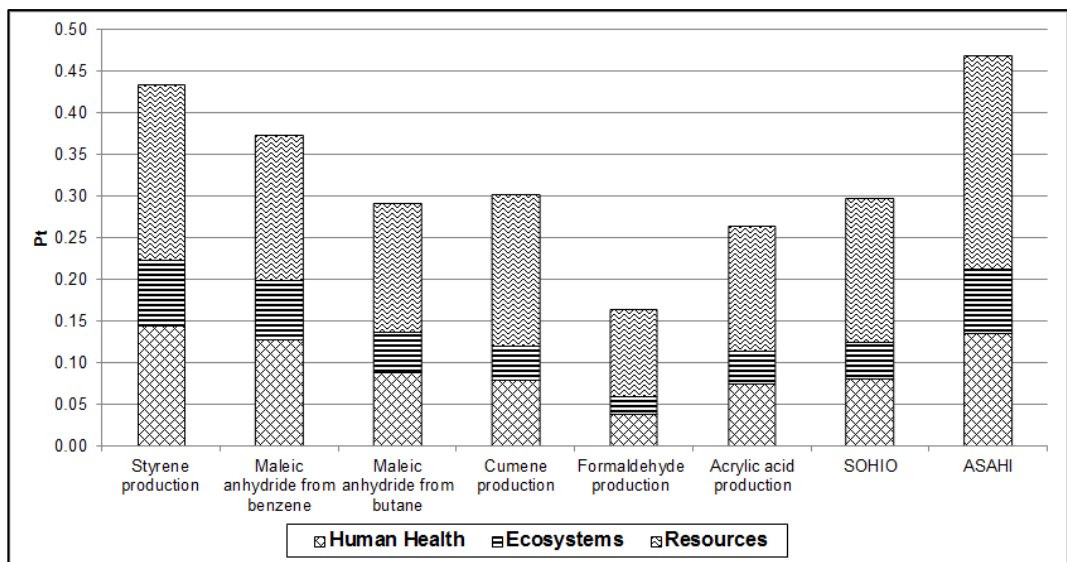
studies are influenced by data quality. In this study was no possible to obtain primary data for each scenario, so to evaluate the robustness of model created a sensitivity analysis using Monte Carlo method was performed. In order to enhance the potentiality of LCA applied to the chemical industry, it may be appropriate to discuss how to establish closer relationships between companies and research institutions, such as, for instance, the development of an accredited database, as well as a standardized approach to ensure a reliable inventory analysis and unambiguous assessment of environmental impacts.

### 3.2.7 Comparison with other chemical products

Usually, in the case in which the study concerns the life cycle of a wide use product, have a contextualization of the results obtained helps to understand better the meaning of each environmental load and the social repercussions associated. Therefore, a comparison with further industrial chemical productions was carried out. This work was presented at the 6th International Conference on Safety & Environment in Process & Power Industry (CISAP 6)<sup>98</sup> and then published on the special issue of the Chemical Engineering Transaction (CET) journal,<sup>99</sup> edited by ADIC (Associazione Italiana di Ingegneria Chimica). Six industrial productions were chosen as reference processes: the styrene production, the synthesis of maleic anhydride (both from benzene and from butane), the production of cumene, and the manufacturing processes for formaldehyde and acrylic acid, each of which was already contained in the Ecoinvent database. The comparison with the ammoxidation scenarios (SOHIO and ASAHI) was done on the base of the same amount of synthesized product (1kg). This confrontation was not extended to the other ammoxidation processes, because they have not yet been industrially developed. The results of the comparison, expressed in terms of endpoint categories (damage on human health, ecosystem quality, and resources depletion), are reported below in Figure 3.7. In this visualization histograms depict the global impact reached by each scenario. These cumulative results give the overall measures of the environmental performance and are able to weight the relevance of each endpoint category in the total load on the environment. In brief, the SOHIO process seems to have global impact similar to the production of cumene and maleic anhydride from butane; it is also not so far from the industrial synthesis of acrylic acid. The production of formaldehyde seems to have lower environmental load compared to traditional route. On the other hand, scores achieved by other syntheses,

such as for the styrene and maleic anhydride (from benzene), appear higher. On the contrary, the alternative route from propane seems to achieve the higher global impact, if compared with the six reference scenarios. This is mainly due to the result reached for the resources depletion category, which is influenced by the large consumption of fossil fuels; the rest is associated with the PMF and the climate change categories. Although these results can be considered as a good estimation of the real case, they should not be considered as an absolute due to the lack of primary data for the alternative chemical productions. However, it could represent a simple tool able to show the environmental load in a broader industrial context and to identify possible improvements.

**Figure 3.7** - Comparison between ammoxidation scenario and other industrial production: ReCiPe single score. Source: Cespi et al. 2014<sup>99</sup> - reproduced by permission of AIDIC.



### 3.3 Use of renewable feedstock - glycerol as a raw material in synthesis of acrolein

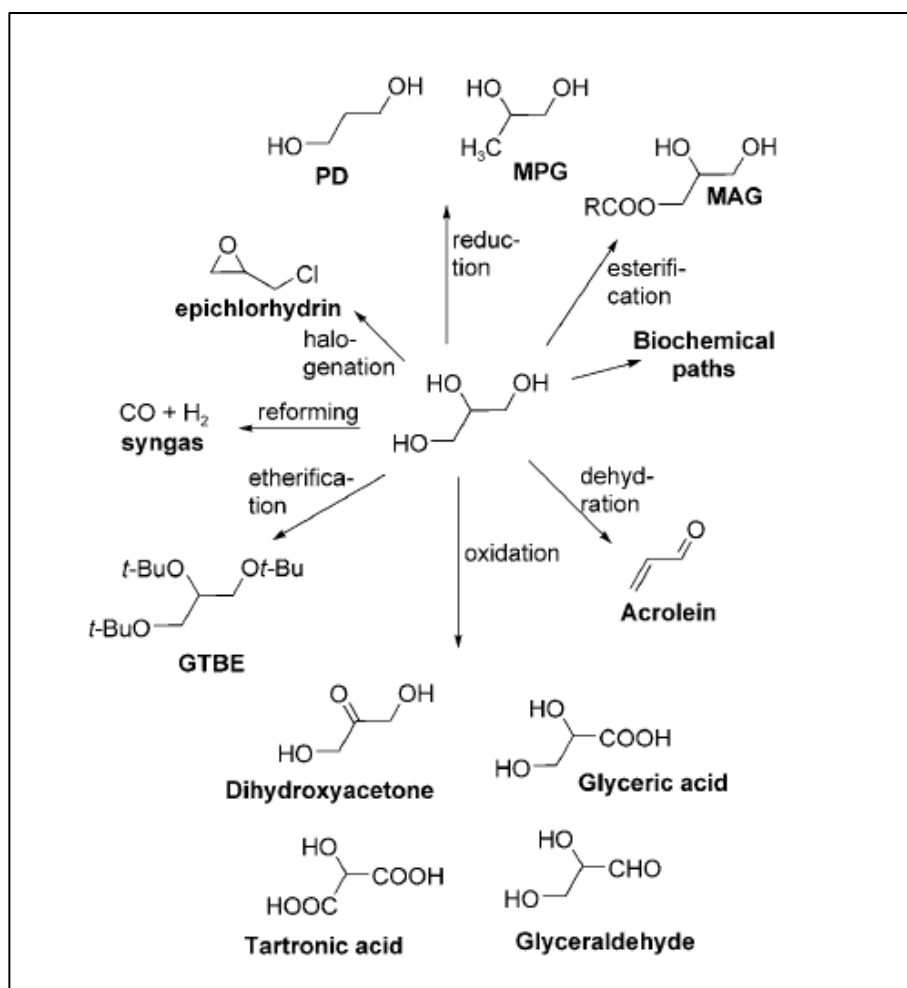
As outlined by Anastas and Warner in their book,<sup>100</sup> the main relevant difference between a fossil and renewable resources is the *time*, since substances such as fossil fuels need several millions of years to occur. Moreover, in addition to their inability to regenerate in a reasonable temporal frame, several other issues characterize their exploitation. The direct and indirect environmental effects such as the land destruction related to coal mining, the air pollution and the contribution to the greenhouse effect or the use of hazardous substances in order to promote the oxidation reaction to obtain building block for chemistry (e.g. chromium).<sup>100</sup> Furthermore, fossil fuels are affected by a not equal distribution which leads to political and economic instability in different regions in the world. Therefore, in order to fight these issues a shifting toward a more sustainable society based on renewables seems desired. The term "renewable feedstock" should be assigned both to the biobased materials and fuels as well as to substances which are easily regenerated within time frame accessible to human lifetime (e.g. CO<sub>2</sub> and CH<sub>4</sub>).<sup>100</sup> However, renewable feedstock are not free from economic and environmental concerns. Different from fossil fuel, renewables could be affected by the seasonal of the supply chain, especially when they are used in a large scale production, furthermore, the energy amount and the use of land for the cultivation phase could have severe repercussion on the ecosystem.<sup>100</sup> Therefore, the application of holistic analysis tool seems necessary in order to verify how the use of renewables influences our society. The use of biobased feedstock in the industrial chemistry was verified by the application of the life cycle approach. Results of the study were published in the journal of *Green Chemistry* - edited by the Royal Society of Chemistry (RCS publishing),<sup>101</sup> which allowed the reproduction of text, tables and figures.

#### 3.3.1 Glycerol as a platform molecule - background motivation of the study

In the coming decades, bio-based feedstocks are going to play a crucial role in the chemical and fuel industries, where their use is expected to grow and surpass that of fossil raw materials.<sup>102</sup> This sector, also known as bio-refineries, is expanding greatly and - in addition to the already well known environmental benefits - the coproduction of chemicals and biofuels may lead to a higher return on investment.<sup>103</sup> An important

emerging sector will be "glycerochemistry",<sup>104</sup> which consists of replacing oil with glycerol as a feedstock in several applications in the chemical industry, also as a solvent and fuel.<sup>105</sup> Indeed, glycerol is widely studied as a feedstock due to its chemical characteristics, which make it suitable as platform molecule for a wide range of different substances. An example of the huge amount of its potential application is shown below in Figure 3.8.

**Figure 3.8** - A selection of glycerol valorization pathways. Source: Katryniok et al. 2009<sup>106</sup> - reproduced by permission of the Wiley-VCH Verlag GmbH & Co. KGaA Wiley.



Moreover its exploitations is promoted by its abundance on the market. Nowadays, it is mainly generated as a co-product in processes which involve reactions with triglycerides, such as the production of fatty acids by hydrolysis, and the transesterification with methanol, which leads to the production of fatty acid methyl esters (FAME), also called biodiesel.<sup>107</sup> Every year about 20Mt of fats and oils are processed by the chemical industries; this leads to a great abundance of glycerol on the market: in 2012 its production was estimated at about 1.2 Mt,<sup>104</sup> and it is expected to rise to 1.54

Mt in 2015<sup>108</sup> and around 2.5 Mt in 2020.<sup>109</sup> Figure 3.9 and 3.10, which plot data already published in literature,<sup>109</sup> show which was the trend of glycerol production and of its price during the past decade respectively. As depicted, the amount of glycerol produced per year increased dramatically since the beginning of 2000s in correspondence to the growth of biodiesel usage as a fuel, which still is its main source. On the other hand, the amount generated as a by-product in the synthesis of fatty acids and alcohols remained almost the same; contrary to the quantity obtained through soaps or synthetically (from epichlorohydrin) which decreased drastically, due to the higher price in the case of synthetic glycerol (Figure 3.10).

Figure 3.9- Glycerol sources trend per year.

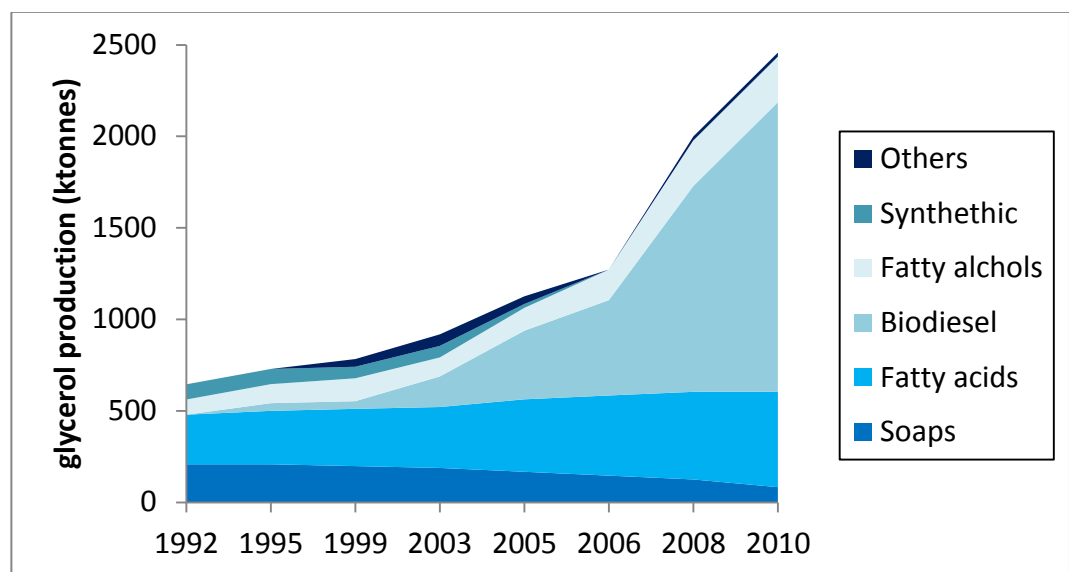
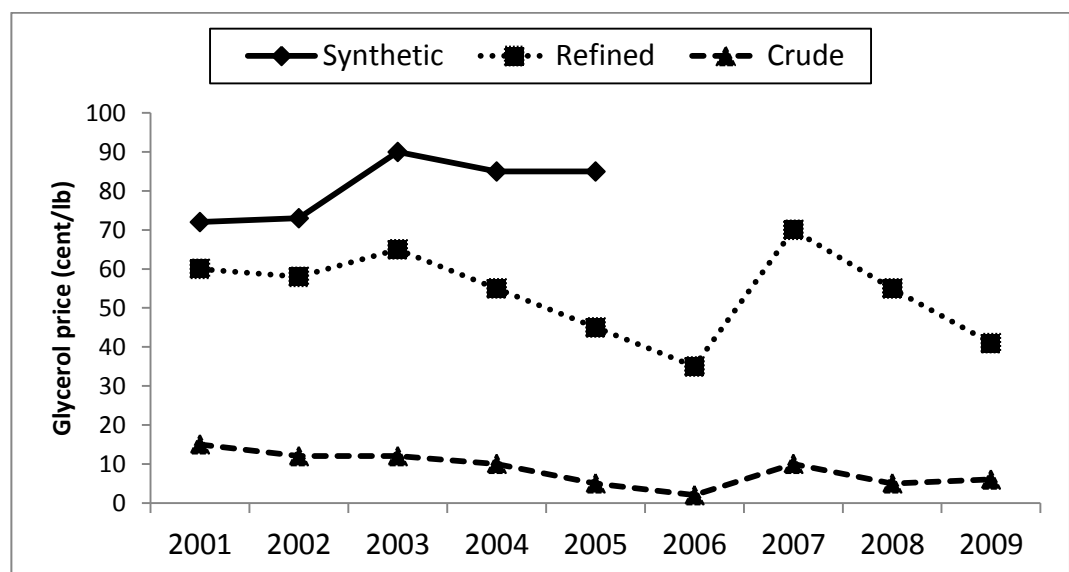
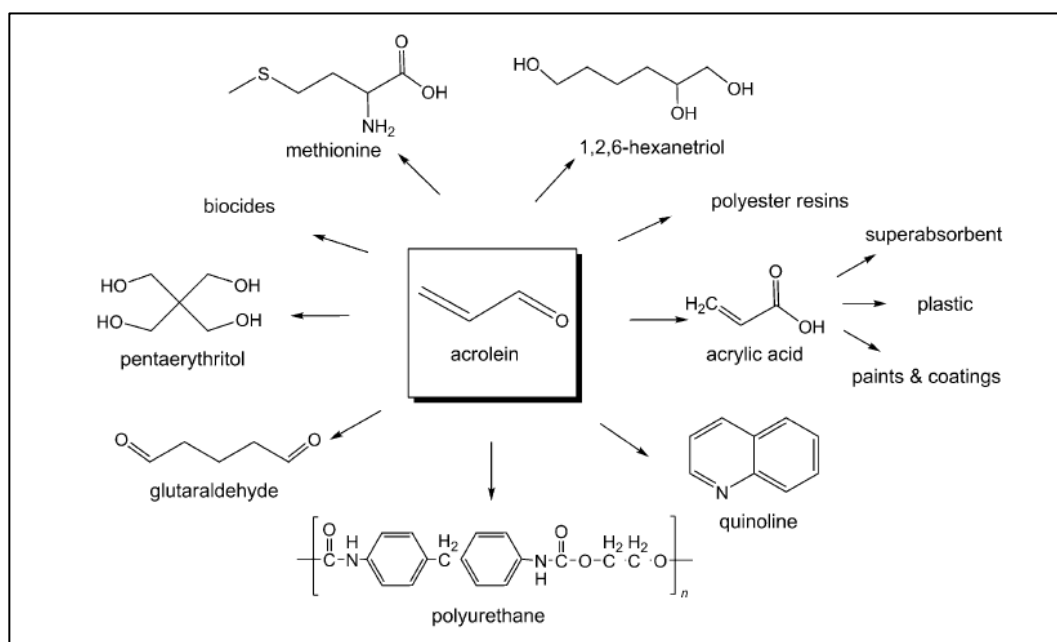


Figure 3.10 - Trend of glycerol price per year.



As previously stated, glycerol's chemical and physical properties make it an extremely versatile compound, which can be used as a feedstock for the synthesis of a high number of molecules (e.g. ethers, esters, carboxylic acids, ethylene glycol, epichlorohydrin, syngas, oligomers, polymers and many others).<sup>113,108,110,111,112</sup> The synthesis of acrolein by dehydration appears to be one of the most promising ways to valorize it,<sup>113</sup> therefore companies' efforts are focused substantially in that direction.<sup>114,115,116</sup> In fact, as shown in literature<sup>113</sup> acrolein produced starting from glycerol (with a purity grade around 92% wt) seems to have a good economic return and low raw material cost. Acrolein is an important drop-in chemical intermediate both in the industrial sector (e.g. acrylic acid)<sup>117,118,119</sup> and in the agricultural field (methionine, annual world-wide production of around 0.5 Mt).<sup>106</sup> The main applications of acrolein are well summarized by the Figure 3.11.

**Figure 3.11** – Chemicals derived from acrolein. Source: Liu et al. 2012<sup>120</sup> – reproduced by permission of the Wiley-VCH Verlag GmbH & Co. KGaA Wiley.



Although nowadays the common process to produce acrolein is the partial propylene oxidation, the issue of fossil fuels depletion needs consideration about alternative solutions: glycerol may represent a valuable feedstock. Before being used as a feedstock, however, crude glycerol obtained as a co-product needs to be treated to remove impurities in organic synthesis, but due to the high price of these processes (Figure 3.10) the availability of refined glycerol in Europe is now decreasing, with a



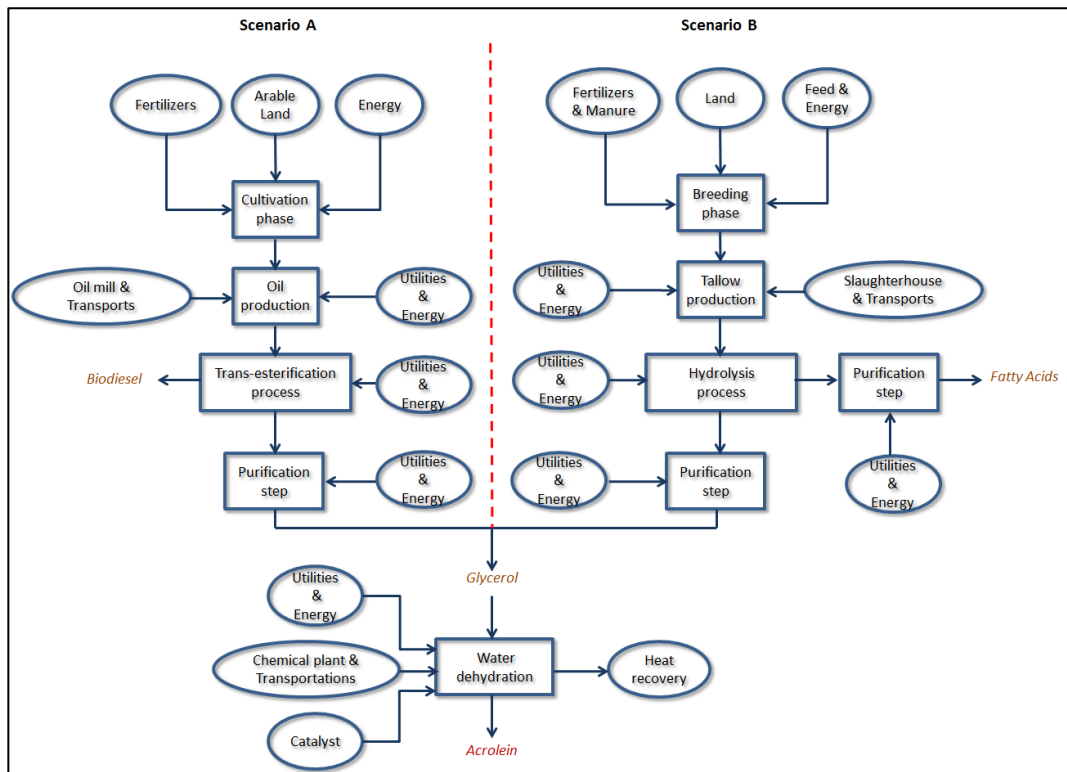
corresponding increase in the non-upgraded glycerol, which is addressed to the renewable energy market or even to poorer markets (e.g. animal feed). This end of life results in a loss of a valuable product that could be exploited in different ways, to make the most of its great potential. As well known the 7<sup>th</sup> principle of GC<sup>100</sup> encourages the use of renewable feedstock, in order to minimize fossil resources consumption, and to mitigate the greenhouse gases emissions associated to them. For this reason the aim of this study was to evaluate – from a life cycle perspective – the potential impacts on human health and the environment of the use of glycerol as an alternative and renewable feedstock in the production of acrolein. In fact, the glycerol production and its usage represent nowadays a crucial topic for chemical industry, in particular for companies with the aim of achieving a more sustainable production. For this reason, two main synthesis routes entailing glycerol generation as a co-product were compared: the trans-esterification process to produce biodiesel, and the production of fatty acid by triglycerides hydrolysis. This approach is able to identify both the environmental issues and the potential benefits connected with each production step considered in the study, and may be considered as a support for the companies involved in the chemical sector in achieving the target of sustainability promoted by the principles of GC.<sup>100</sup> Furthermore, a comparison was carried out with the traditional acrolein production process starting from propylene.

### 3.3.2 System boundaries and functional unit

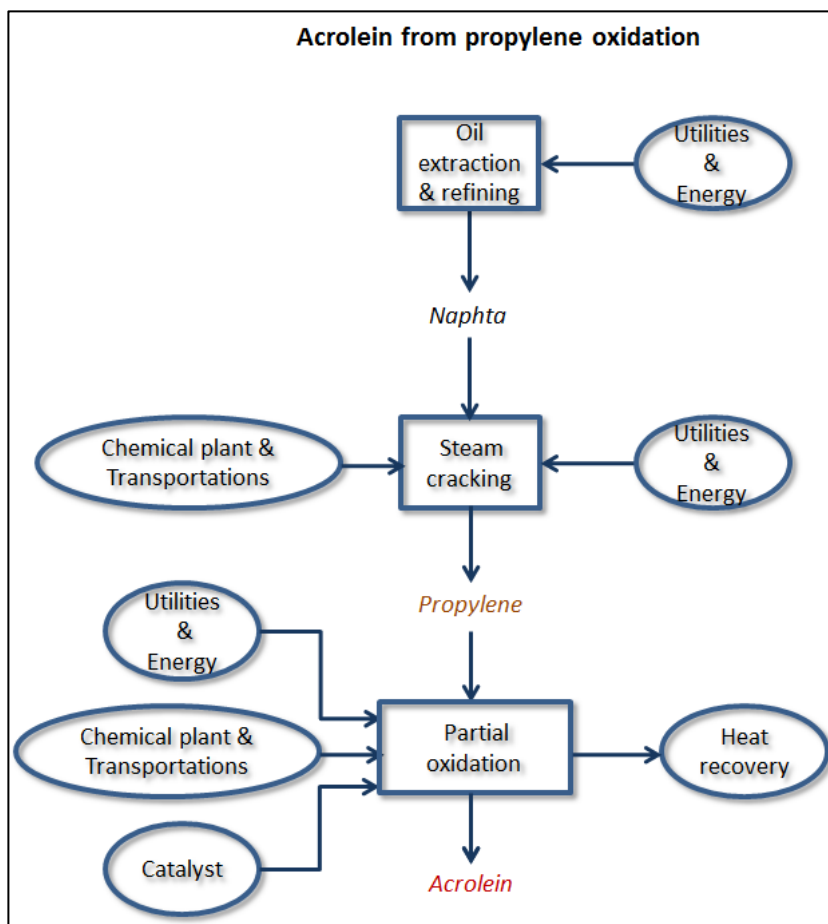
As is well-known, the effectiveness of an LCA study is strongly influenced by the quality of the input data used in the various systems considered. For this reason, in this work LCI was carried out using mostly primary data directly provided by two Italian oleochemical companies and one French company: however, when not available, data were collected from literature such as patents, encyclopaedia, and the Ecoinvent<sup>83</sup> database (v. 2.2). LCA was conducted using the software developed by PRé Consultants, SimaPro<sup>121</sup> (v.7.3.3). ReCiPe 2008<sup>78</sup> (I/A, v 1.07) and IPCC 2007<sup>122</sup> (20a) were used as LCIA analysis methods, both able to predict results with a twenty-year time horizon. The decision to choose these two methods stemmed from the need to express results in terms of midpoint categories, as well as in the forms of the most consolidated way, using CO<sub>2</sub>-equivalents. Scenario modelling and their comparisons were carried out using the same amount of acrolein produced (1kg) as a functional unit. A *from-cradle-to-gate* perspective was applied, considering the whole production

chain for both scenarios: from raw material production (oil and fat) up to the synthesis of acrolein by glycerol dehydration, including the main intermediate stages such as triglycerides reaction processes and purification steps (if required). System boundaries are schematically depicted in Figure 3.12 and Figure 3.13. In the next section a detailed description of each process and inventory is reported.

**Figure 3.12** - System boundaries considered in the LCA study for the bio-based scenarios. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



**Figure 3.13** - System boundaries considered in the LCA study for the scenario starting from propylene. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



### 3.3.3 Acrolein production scenarios - description and inventory

#### 3.3.3.1 Glycerol dehydration process

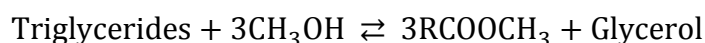
Due to its importance as a chemical intermediate, mainly in the synthesis of acrylic acid and methionine, different acrolein production routes have been investigated in the past. In 1942, Degussa developed the first industrial synthesis process starting from acetaldehyde and formaldehyde through an aldol condensation reaction; this was subsequently replaced by partial propylene oxidation because of conversion and product separation problems.<sup>120</sup> Given the affordability of propylene, today the latter process is still the most widespread manufacturing synthesis process despite the investigation into other routes - such as the partial oxidation of propane and the biological one.<sup>120</sup> Nevertheless, the availability of a great abundance of glycerol as a co-product has led companies and research efforts to look into new synthesis procedures. Among these, the dehydration of glycerol is studied in depth in literature,<sup>123,124,125,126</sup> due to the fact that it represents one of the most promising and easiest ways to valorize

it.<sup>113,112</sup> The dehydration process generally occurs in a Packed Bed Reactor (PBR) at 280°C and 101kPa in the presence of an acid catalyst.<sup>120</sup> In this study, a heteropoly acid catalyst with an empirical structure of  $H_4SiW_{12}O_{40}/TiO_2$  was taken into account.<sup>123</sup> Experimental data demonstrated<sup>123</sup> that it leads to a 79% yield and selectivity of acrolein, with a glycerol conversion of 100%. As already stated, acrolein is the main intermediate in the production of acrylic acid; therefore, some data regarding utilities consumption (e.g. electricity, natural gas, cooling and process water) as well as the amount of inert gas were assumed to be the same as the glycerol dehydration to acrylic acid and extrapolated from an internal report of a company.<sup>127</sup> Instead, general information regarding infrastructure (chemical plant), chemical auxiliary usage (e.g. hydroquinone as a stabilizing agent and ethyl acetate as a solvent for the extraction process) and average transportation, was assumed to be the same as for the process *Acrylic acid, at plant/RER U*.<sup>83</sup> Moreover the same average catalyst consumption for the synthesis of acrylic acid was assumed (0.3g per functional unit)<sup>83</sup> by modelling its structure on the basis of the already explained procedure reported in literature.<sup>67</sup> No information on regeneration and makeup, as well as on industrial energy consumption for the catalyst production, was available because such information usually constitutes corporate know-how. Therefore they were not included, assuming that their contribution to the overall impact is negligible, as reported in literature.<sup>67</sup> The amount of water in the form of steam, inlet into the reactor (necessary to maintain the desired temperature), was estimated by using the molar ratio reported in literature.<sup>123</sup> In order to limit the energy cost associated to the dehydration phase and to avoid side reactions, a concentrated solution of 50 wt % in glycerol is recommended as inlet to the reactor.<sup>123,128</sup> An energy recovery of half the heat exchanged in the reactor coils was assumed, calculating its amount through the enthalpy balance and the assumptions reported in literature:<sup>67</sup> half is recovered as heat and the rest as electricity (with a conversion efficiency of 31%). Lastly, the amount of steam for the purification steps of acrylic acid (reported in a previous study)<sup>129</sup> was assumed to be the same as in the case of acrolein. As can be seen, because of the lack of data due to corporate confidentiality, it was only possible to model the dehydration process by using some proxy information, but it does not seem to affect the result of the study. Moreover, for the sake of prudence, it has been deliberately overestimated. A more detailed description of the life cycle inventory for the dehydration process is shown in the

Annex B, see Table 3.9. Below a description of both biobased routes to obtain glycerol is stated.

### 3.3.3.1.1 Triglycerides trans-esterification process

As reported in literature,<sup>130</sup> the use of vegetable oils as a diesel source was investigated long before the oil crisis of the 1970s and '80s. Rudolf Diesel himself, in his book *Liquid Fuel*, mentioned the use of peanut oil (also known as arachis oil) in a small diesel engine seen during the Paris Exposition in 1900.<sup>130</sup> However, the patent developed by Chavanne<sup>131</sup> in 1937 seems to have been the first example of what we now call biodiesel. Nowadays, biodiesel is considered the best candidate to replace fuels in diesel engines, despite the higher cost<sup>132</sup> and lower HHVs (higher heating values) than traditional fossil fuels.<sup>133</sup> Biofuel importance is related to: i) the possibility of applying it in a blend without involving any engine modification,<sup>134</sup> and ii) the benefits linked with its usage (e.g. greenhouse gases reduction).<sup>133</sup> Differently from Chavanne's work, which entailed the use of an acid catalyst, nowadays most industrial processes involve alkali-catalyst (NaOH or KOH) trans-esterification<sup>135</sup> conducted at 60°C under atmospheric pressure with a residence time of about 1 hour.<sup>130</sup> Catalyst usage is also necessary in order to enhance the solubility of alcohol in oils.<sup>2010</sup> Triglycerides and an alcohol (methanol is the most used due to its low cost) are normally combined in a molar ratio of 1:3<sup>136</sup> and then let react in continuous stirred tank reactor (CSTR).<sup>130</sup> Below, equation 3.3 represents the general reaction for the triglycerides trans-esterification process using methanol.



3.3

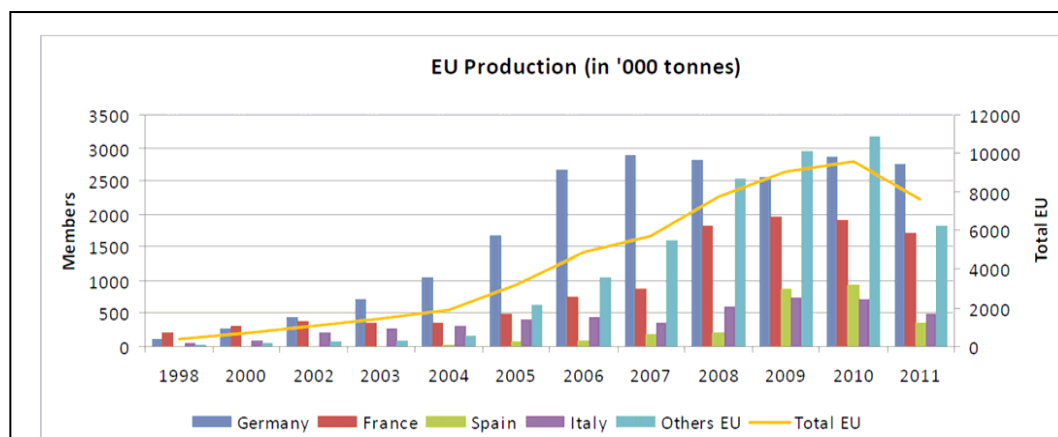
The process yield for glycerol is about 10 wt.%,<sup>109</sup> producing empirically 1 ton of biodiesel and 100 kg of crude glycerol per each ton of vegetable oil treated.<sup>136</sup> As previously stated, the crude glycerol, generally with a purity grade of 80-88%,<sup>109</sup> needs to be refined before its industrial usage. Generally speaking, the purification procedures require more processing steps and energy in respect to those used after hydrolysis, as salts and methanol have to be separated, and involve subsequent distillation steps until glycerol is obtained with the desired purity grade. Depending on salt content, the equipment may also use ion exchange or thin-film distillation.<sup>137</sup> As shown in Figure 3.12, the system boundaries for acrolein obtained by glycerol from the trans-esterification process scenario (hereafter called Scenario A) cover the entire

production chain: biomass cultivation and harvesting, oil production process, and trans-esterification to obtain biodiesel and glycerol purification. Rapeseed (*Brassica napus*) was chosen as representative of energy crops since it is the most common cultivation in Europe for obtaining biodiesel.<sup>138,139,140</sup> Furthermore, Europe represents the World's biggest producer of biodiesel,<sup>141,142</sup> with 178 thousand barrels/day in 2011<sup>143</sup> and thus rapeseed is now the dominant feedstock on a global scale.<sup>(FAO)</sup> *Rape oil, at mill/RER U* (Ecoinvent database) was chosen as the reference process to simulate both the rape cultivation and oil production phase. It includes all energy and mass flows used in rapeseed cultivation in Europe and all the utilities for treating seeds and extracting oil in an average European mill plant (included average seed transportation to the mill).<sup>83</sup> All these information were used in order to create two distinct models able to simulate both the Cultivation phase and the Oil production step. For more details see Table 3.10 in the Annex B. As shown in Figure 3.12, oil is then sent to the trans-esterification step. The default process considers that both plants are located in the same place (as in the case of hydrolysis). Spiga BD Srl, an Italian company which works in the field of biodiesel, glycerine, glycerine derivatives and renewable chemicals, provided the primary data needed to complete the life cycle inventory of trans-esterification and glycerol refining phases. The same operating conditions (temperature and pressure) described earlier were assumed. As suggested by the company, around 122kg of glycerol are generated from 1005kg of triglycerides treated to produce one ton of biodiesel. Moreover, the latter does not need to be refined: thus further purification steps were not included in the system boundaries. The use of glycerol as the starting raw material prevents its downgrading for energy uses. For this reason a process avoiding glycerol burning was introduced in both scenarios. The energy produced by the combustion was modelled by using the average values for glycerol LHV (18.74MJ/kg) reported in literature.<sup>144</sup> No reliable information on emissions was available, however in order not to neglect this environmental load, average air emissions from the combustion of natural gas<sup>83</sup> were used as proxy data. In addition, due to the fact that glycerol combustion would provide energy in the form of heat, the process includes this avoided energy recovery. Lastly, in order to take into account the environmental benefits connected with the production of biofuel, the model created for Scenario A assumed that biodiesel is used to replace the traditional fossil fuel and included the avoided extraction of the same diesel amount.

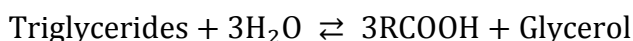
### 3.3.3.1.2 Triglycerides hydrolysis process

Despite the fact that a higher quantity of glycerol is commonly obtained as a co-product from FAME manufacturing,<sup>109</sup> biodiesel amounts produced in Europe during 2011 decreased by about 10% as compared to 2010.<sup>145</sup> A representation of this trend was extrapolated from literature<sup>145</sup> and depicted below in Figure 3.14.

**Figure 3.14** - EU biodiesel production. Source: EBB - European Biodiesel Board, *Statistics - The EU biodiesel industry 2011*, <http://www.ebb-eu.org/stats.php> (accessed November 2014).



This trend affects the availability of glycerol on the market; therefore triglycerides hydrolysis was investigated as an alternative route. As already depicted in Figure 3.9 fat splitting (followed by saponification) was the first source of glycerol in the past, until biodiesel production caught on. However, after a stagnant period, it is now considered to be the second major reserve of glycerol.<sup>109</sup> Also, due to the synthesis of fatty acids, its industrial importance makes it a secure reserve process for glycerol production. In fact, today fat splitting using water is the most common way of obtaining synthetic fatty acids. This process occurs in homogeneous conditions in which water is dissolved in the lipid phase.<sup>146</sup> The total equilibrium for the direct hydrolysis process is reported below in equation 3.4.



3.4

After the pre-treatment procedures to remove impurities and settle triglycerides sources (such as filtration under heat, acidification, and degassing), hydrolysis takes place in the presence of demineralized water as a splitting agent (to increase efficiency and prevent higher salt content).<sup>146</sup> Ernst Twitchell was the first scientist to attempt to improve the process performance by introducing the Twitchell reagent as a catalyst in

1898. Later, either different catalysts were used: lipases (cheaper due to lower process temperatures) or dibasic metal oxides (preferred over the acids, for corrosion prevention).<sup>146</sup> However, the majority of modern units operate without a catalyst in continuous splitting columns, in the presence of high pressure steam, to achieve higher temperature and pressure (average values are 210-260°C and 1.9-6.0MPa).<sup>146</sup> Fatty acids purity degrees obtained with the continuous processes splitting are generally higher than 98%; crude glycerol obtained achieves a purity grade of about 20% and needs to be at first concentrated up to about 90%, than purified (see procedure previously described, distillation or ion exchange).<sup>146</sup> As shown in Figure 3.12, the system boundaries for the production of acrolein starting from glycerol as a by-product of hydrolysis (Scenario B) cover the entire manufacturing chain: from the triglycerides source (beef tallow) up to the dehydration step to produce acrolein, also including the hydrolysis and purification procedures. As for the previous scenario, in this case, also, primary data regarding the triglycerides splitting and purification procedures were provided by SO.G.I.S. SpA. This oleochemical company synthesizes fatty acid starting mainly from animal fats or Palm Oil as triglycerides source. This raw material is obtained as a derivative from animal by-product of the meat production process and - as with other animal by-products - can be used in the industrial sector.<sup>147</sup> In particular, beef tallow was considered in the model. *Tallow, at plant/CH U* was taken as the reference process in the Ecoinvent database to describe average energy flows and other utilities (tap water, transportation, and infrastructure) involved in the production of tallow.<sup>83</sup> *Beef (farm type 23)*<sup>148</sup> was chosen as the reference process to describe all the inputs and outputs connected with animal rearing, such as, for example: the occupation of arable land dedicated to the growth of cows, the animal feeds, the use of artificial fertilizer and in part of manure as fertilizer, and all the energies usage during the breeding process. Given that tallow is considered a by-product, no mass flows and therefore no impacts related to animal rearing are included in the default process (*Tallow, at plant/CH U*).<sup>83</sup> However, for the sake of prudence and considering that tallow has its own market price, an economical allocation was done by including the beef growth in the model. Therefore the amount of tallow obtained from the mass balance (able to produce 1 kg of acrolein) was multiplied by an economic allocation factor of 1.02E-01 estimated from the ratio between the wholesale beef tallow price<sup>149</sup> and the price of beef meat.<sup>150</sup> In this way, tallow impact is proportional to its market price. As previously stated, hydrolysis and purification were modelled by using



information directly supplied by SO.G.I.S. SpA. According to this company, a production of around 90kg of glycerol (and 880kg of fatty acids) per ton of treated triglycerides was assumed. Also, inventory includes all the mass and energy flows involved in the fat splitting, as well as the utilities necessary for the purification step. In this case, the company suggests that refining procedures are necessary for both glycerol (from 20% to 99.5%) and fatty acids to reach market purity grade. As in the case of Scenario A, an avoided glycerol combustion was included in the model. Moreover, benefits deriving from fatty acids production starting from tallow were estimated by considering an avoided production of vegetable oil (*Rape oil, at oil mill/RER U*)<sup>83</sup> necessary for the synthesis of the same amount of acids. More details about the life cycle inventory are listed in Annex, see Table 3.11.

### 3.3.3.2 Propylene oxidation process

In 1959 Shell developed the first industrial synthesis of acrolein starting from propylene. The process was based on the vapour-phase oxidation of alkene using cuprous oxide as a catalyst. However, due to lower conversion of propylene, Sohio investigated a new class of catalyst based on bismuth molybdate.<sup>151</sup> These multicomponent metal oxide systems are still used nowadays, conducting oxidation process in a tubular fixed-bed reactor operated at 300-320°C and inlet pressure of 150-250 kPa.<sup>151</sup> Although the aim of the study was to evaluate the positive and negative aspects in the use of glycerol as renewable feedstock (as suggested by the GC principles),<sup>100</sup> a system boundaries expansion was carried out in order to perform a comparison with the traditional route starting from propylene. In order to match the requirements in the quality of data common to a LCA studies, an internal report provided by a company<sup>152</sup> was used to complete LCI for the Acrolein from propylene oxidation scenario. As for the dehydration scenario, data regarding chemical plant, average transportation, and catalyst amount were collected from Ecoinvent database (*Acrylic acid, at plant/RER U*).<sup>83</sup> On the other hand, the catalyst composition was evaluated from patent literature,<sup>153</sup> by assuming a yield of 75%<sup>152</sup> and a propylene conversion of 95%. Unreacted olefin was assumed to be released as CO<sub>2</sub>, with a combustion efficiency of 100%. As in the case of glycerol dehydration, enthalpy balances<sup>67</sup> were applied to estimate the amount of energy dissipated and recovered for plant utilities. This process was taken into account as a reference scenario for a comparison with the two bio-based routes described above. System boundaries are

depicted in Figure 3.13, while a detailed LCI description is reported in the Annex B (Table 3.12).

### 3.3.4 Impact assessment and results interpretation

As previously stated, the LCIA phase was carried out using ReCiPe 2008 (v 1.07),<sup>78</sup> selecting an *Average Individualist (I/A)* cultural perspective which considers a twenty-year time horizon. Results were expressed by selecting six midpoint impact categories, according to their significance with relation to the aim of the study: agricultural land occupation, terrestrial eco-toxicity, metal depletion, fossil fuel depletion, and climate changes with damage both on human health and ecosystem quality. Each impact category is related to a particular damage on Human Health, Ecosystem Quality and Resources Depletion, which is expressed with the units described above. Results from the “characterization analysis” are listed below in Table 3.1.

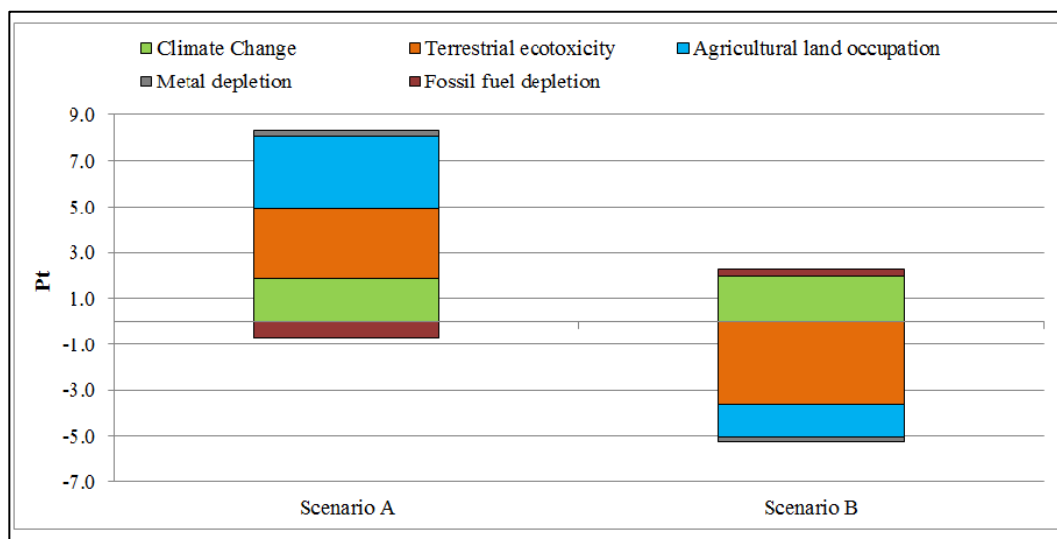
**Table 3.1** - Comparison between two acrolein production scenarios in terms of ReCiPe I/A - Characterization analysis. Adapted from Cespi et al. 2015<sup>101</sup> -by permission of The Royal Society of Chemistry.

Impact category	Unit	Scenario A	Scenario B
<b>Total Impact</b>	Pt	8.6E+00	-3.8E+00
<b>Agricultural land occupation</b>	species·yr	1.5E-06	-6.4E-07
<b>Terrestrial ecotoxicity</b>	species·yr	1.4E-06	-1.7E-06
<b>Climate change - Ecosystems</b>	species·yr	3.7E-07	3.9E-07
<b>Climate change - Human health</b>	DALY	5.6E-05	5.9E-05
<b>Fossil fuel depletion</b>	\$	-4.6E-01	1.8E-01
<b>Metal depletion</b>	\$	1.6E-01	-1.5E-01

However, in order to compare the two acrolein production scenarios showing which route is the preferable solution in terms of cumulative global impacts, it is necessary to convert damages in terms of score (Pt), also called “eco-indicator”, and sum up all of them obtaining the so-called “ReCiPe 2008 single score” (Figure 3.15). As shown, acrolein produced by glycerol obtained as a co-product of triglycerides transesterification is less sustainable compared to the route based on hydrolysis. The lower sustainability of Scenario A is mainly due to significant impacts in terms of land occupation, terrestrial eco-toxicity and climate change (which includes process

contributions to both human health and ecosystem damage categories), in spite of the benefits connected with an avoided fossil fuel consumption due to the avoided diesel extraction. This global negative trend is attributable to the high-intensity processes connected with the biomass growth phase as a source of triglycerides. On the other hand, Scenario B - based on hydrolysis - seems to have significant impacts on the climate change and the depletion of fossil fuels, which are related to the energy consumptions assumed in the scenario. In fact, both categories are strictly related to each other as well as to the energy need required by the system, for example during the very intensive phases of purification. In fact, as written previously in the description of LCI, the hydrolysis scenario implies a further purification stage than the transesterification scenario, in order to reach the market purity grade for fatty acids. This additional step leads to an increase of impacts related to energy use. Furthermore, although the just-mentioned negative effects are not negligible, the use of tallow as a substitute for vegetable biomass leads to potential environmental benefits in terms of avoided damage on land occupation and eco-toxicity. This cumulative representation shows a quick vision of the overall impacts of each scenario.

**Figure 3.15** - Comparison between two acrolein production scenarios in terms of ReCiPe I/A - Single score. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



However, considering only the figure above, it is not possible to clarify the environmental significance of each phase within both scenarios. Therefore, a contribution analysis was carried out in order to show the potential burdens on the environment which are associated with the system boundaries considered. To accomplish this, each scenario was split into its main phases and the analysis results are shown in terms of single score and characterization. The results from the analysis

carried out for Scenario A (Annex B, Figure 3.20 and Tables 3.13-3.14) show that the cultivation phase seems to contribute much more than the others to global impacts. As a confirmation of our previous suggestions, a detailed analysis conducted using the network tool provided by the software revealed that about 100% of global contribution for both categories of agricultural land occupation and eco-toxicity is associated with the cultivation phase. In particular, it was ascertained that the highest negative effect in terms of terrestrial eco-toxicity is related to the release of pesticides in soil, and that the exploitation of arable land contributes to its occupation. Also, Table 3.9 shows that the cultivation phase presents the highest negative load in terms of climate change. A contribution of approximately 77% was estimated for this impact category, associated with the energy consumptions during biomass growth. On the other hand the oil production phase has a contribution around 6% for the same category. Moreover, the trans-esterification, glycerol purification, and dehydration phases were estimated to make a non-negligible contribution to the same category (around 2-9% of the global impact) due to the energy flows involved. In particular, as previously described in the inventory analysis, mass and energy flows used to model the trans-esterification and purification processes were furnished directly by the company. For this reason the results may be considered a good simulation of the real case. Regarding the fossil fuel depletion category, the highest contribution is due to the cultivation phase (about 53%), followed by the trans-esterification process (22%), the oil production phase (10%), and the glycerol dehydration (7%) and refining (3%) phases. All these stages are energy-intensive, and industrial manufacturing involves higher consumption of fossil fuels for steam and electricity production. In particular, impacts regarding electricity generation are strictly related to the energy mix adopted by any country. In this case, according to the geographical system boundaries, an average energy mix for Italy was assumed (*Electricity, production mix IT/IT U*).<sup>83</sup> Also regarding fossil fuel depletion, a contribution of about 5% was calculated due to the avoided glycerol combustion. This trend is related to the assumptions made during the inventory phase: it was considered that glycerol was commonly burned in the industrial sector in order to produce heat, and that in the case in which it is not incinerated (but recovered as a feedstock) the same energy amount should be produced by traditional fuels. On the other hand, the avoided emission of greenhouse gases from the combustion of glycerol helps to prevent, in part, the negative effects on climate change. However, the highest positive contribution to the environment and human health proves to be from the use of

biodiesel in substitution for diesel. In fact, the avoided diesel extraction leads to significant benefits regarding both the climate change and the fossil fuel categories. The relative contribution of each life cycle phase for Scenario A, both in terms of Impacts and Avoided impacts, is reported in Annex B. Results from the contribution analysis for Scenario B are shown in Annex B (Figure 3.21 and Tables 3.15-3.16). The avoided use of rapeseed as a source of triglycerides entails several environmental benefits. First, the avoided burdens in terms of climate change (including damage to both human health and the ecosystem) and fossil fuels depletion are related to the lower energy consumption in the production of chemicals used as fertilizers. In particular, nitrogenous fertilizers produced by a synthesis starting from ammonia, whose manufacturing is highly energy-intensive, as well as the production of nitric acid, seem to be the major causes. Also, unlike in Scenario A, several advantages are linked to the avoided use of pesticides, and to the avoided occupation of arable areas which may be devoted to other agricultural activities. Moreover, the partial replacement of fertilizers with animal manure reduces the contribution of the breeding phase to the terrestrial ecotoxicity (around 4%), this latter category being highly influenced by both the release of substances and waste during the energy-consuming steps which characterize the tallow production (29%) and the other steps such as the fatty acids purification, that contributes for the 24%. However, even in this scenario the triglycerides supply is not without impacts. In fact, the phases of animal breeding and tallow production are the two steps with the highest environmental impacts along the entire manufacturing chain considered. As well known, animal rearing implies an intense use of resources and energy. In fact, despite the economic allocation of tallow, the breeding phase achieves the highest contribution in terms of agricultural land occupation (100%) and climate change (around 72%) categories. Also the contribution to the fossil fuel depletion is not negligible, around 17%. On the other hand, the intense energy consumption for the production of tallow is responsible for the highest contribution in terms of fossil fuel depletion (around 46%) and contributes for a 16% in terms of climate change category. Also, the energy consumption involved in the fatty acid purification stage is not so negligible as it contributes for 14% to the fossil fuel depletion and for 5% to the climate change category. Conversely, the energy used during hydrolysis and dehydration processes and for the glycerol refining procedure is not so significant as far as the contribution to climate change (2-3%) and fossil fuel depletion (5-7%) are concerned. However, as for Scenario A, the impacts related to

the production and purification of fatty acids and for glycerol refining should be considered a reliable approximation, since data were furnished directly by the enterprises. Also, it should be considered that the further purification stage of fatty acids increases the total impacts reached by Scenario B regarding both fossil fuel depletion and climate change categories of around 17% and 5% respectively. Moreover, this additional step entails an approximate 5% and 47% increases in impacts respectively on the same categories (fossil fuel depletion and climate change, including damage to both human health and the ecosystem), compared to results achieved by Scenario A for the same categories. As in the previous case, the contribution of each life cycle phase for Scenario B, both in terms of Impacts and Avoided impacts, is reported in Annex B. As shown by results, all energy consumptions involved in glycerol purification stage produce a contribution around 2% in terms of climate change and about 3-6% with regard to fossil fuel depletion (depending on the steps involved in refining). However, as reported in literature,<sup>154</sup> it seems not to be possible to avoid the glycerol purification stage, especially if glycerol is obtained as a co-product in the FAME process, due to the higher amount of impurities present in raw glycerol: water, salts deriving from basic medium neutralization, trace of methanol and NGOM (non-glycerin organic matter). A typical composition of various glycerol, produced at different industrial sites by trans-esterification was found in literature<sup>154</sup> and reported in Table 3.17. Basic compounds such as sodium and potassium salts might deactivate the acid catalyst used to dehydrate glycerol to acrolein, so prejudicing the entire process yield. Companies efforts are focusing on the developing of new technologies in order to solve this issue.<sup>154,155</sup> Moreover, NGOM includes several different substances extracted during the seeds crush (e.g., lignocellulosic materials, such as phenolic compounds), that end up in the oil and finally in glycerine. This material contributes to coke formation and accelerates catalyst deactivation. Therefore, in order to reduce the content of these compounds, a glycerol distillation process is necessary. These issues could be solved by technology improvements that lead to new processes able to use crude glycerol as the feedstock for dehydration. Therefore, in order to verify how the global impact of the entire process could change avoiding the purification stage for glycerol, the LCIA phase was repeated for both scenarios, excluding the steps of glycerol refining. As expected, due to the low contribution of the purification stage, results reported in Table 3.18 show that differences compared with the scores obtained previously were negligible. Moreover, the climate change category was also

investigated using IPCC 2007.<sup>122</sup> This analysis is able to assess the GWP while expressing results in terms of CO<sub>2</sub> equivalents. In agreement with the ReCiPe 2008 method, a perspective of a 20-year time horizon was chosen. Results from this study are shown in Table 3.2.

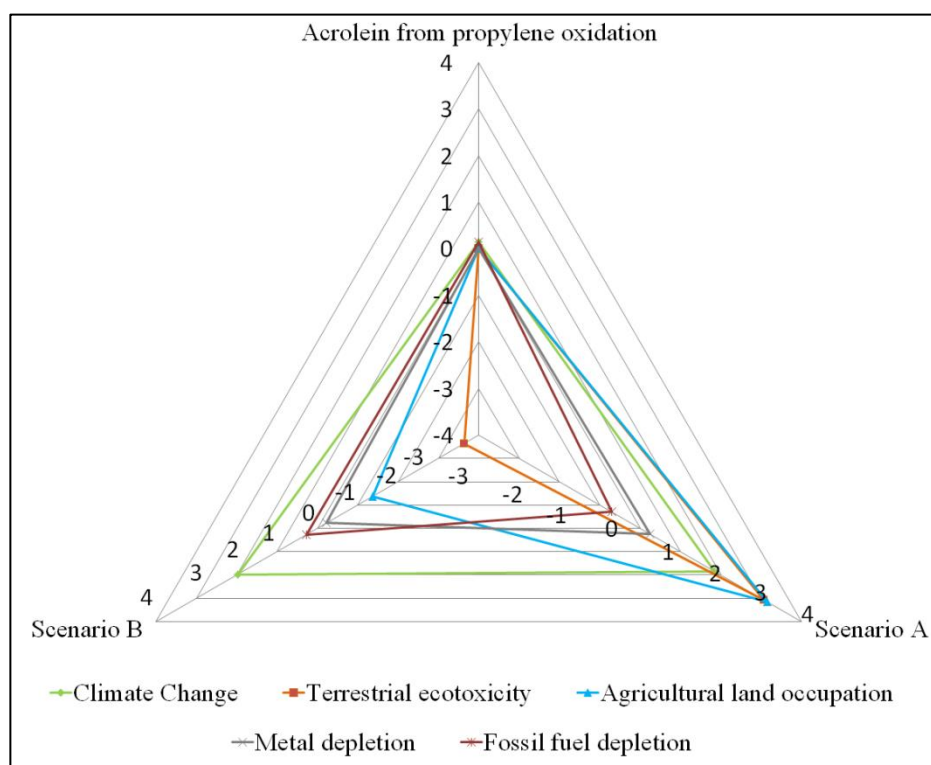
**Table 3.2** - Global Warming Potential for both scenarios (IPCC 2007, 20a). Adapted from Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Scenario A	kg CO <sub>2</sub> eq		Scenario B
<b>Tot</b>	45.2	49.7	<b>Tot</b>
<b>Cultivation phase</b>	42.5	70.0	<b>Breeding phase</b>
<b>Oil production</b>	3.6	16.6	<b>Tallow production</b>
<b>Triglycerides trans-esterification</b>	5.2	1.8	<b>Triglycerides hydrolysis</b>
<b>Glycerol refining (84%→100%)</b>	1.2	2.5	<b>Glycerol refining (20%→99.5%)</b>
<b>Avoided glycerine combustion</b>	-0.8	-0.8	<b>Avoided glycerine combustion</b>
<b>Avoided diesel extraction</b>	-9.4	-54.7	<b>Avoided rape oil production</b>
-	-	5.2	<b>Fatty acids purification</b>
<b>Dehydration process</b>	3.0	3.0	<b>Dehydration process</b>

In this table, IPCC confirms the scores achieved using ReCiPe 2008 as regards the climate change category. Furthermore, this method is able to quantify the exact amount of CO<sub>2</sub> emitted or saved during each stage of the manufacturing process. Although the scores are quite similar, Scenario B achieves higher results (49.7 kg of CO<sub>2</sub> eq.) than the trans-esterification-based scenario (45.2 kg of CO<sub>2</sub> eq.). In fact, despite the high CO<sub>2</sub> savings due to the avoided use of vegetable biomass as a source of triglycerides (-54.7 kg of CO<sub>2</sub> eq.), the emissions associated with the animal rearing (70.0 kg of CO<sub>2</sub> eq.) and energy consumption involved in tallow production (16.6 kg of CO<sub>2</sub> eq.) contribute to increasing the global amount. On the other hand, the cultivation (42.5 kg of CO<sub>2</sub> eq.) and oil production phases (3.6 kg of CO<sub>2</sub> eq.) achieve higher results than the total CO<sub>2</sub> amount emitted by Scenario A (46.1 kg of CO<sub>2</sub> eq.); however, the use of biodiesel as a substitute for traditional fuels seems to produce several environmental benefits (-9.4 kg of CO<sub>2</sub> eq.) by reducing their global amount. Lastly, the metal depletion category was also investigated. It was introduced at first to verify the overall environmental impact associated with metal extraction for the production of catalyst systems which are used for the dehydration process. However,

the contribution analysis conducted for both scenarios show that the catalyst assembly is not so significant for that category, which is mainly influenced by the consumption of metal in the form of salt used mainly as fertilizer (e.g. Ammonium Nitrate and Ammonium Nitrate Phosphate). In fact, the scores (Pt) achieved by both scenarios with regard to metal consumption are similar and, in both cases, the higher contribution (positive and negative) is due to phases which involve biomass cultivation. The rest may be attributable to the great quantity of infrastructure involved (e.g. chemical plant, oil mill, transportation). Therefore, catalyst contribution to the global impact seems to be negligible, even though, as previously described, the catalytic system was modelled using only proxy data regarding its amount of acrolein per kg. As stated above, in order to evaluate the environmental trends of both bio-based scenarios, a comparison with the traditional process for producing acrolein from the partial oxidation of propylene was also carried out using ReCiPe2008 as the test method. The results in terms of single scores are given in Figure 3.16.

**Figure 3.16** - Comparison between the three acrolein production scenarios, in terms of ReCiPe I/A - Single score (radar chart). Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



The radar chart is a quick representation to show scores achieved by each scenario for each impact category. The closer the line to the triangle vertex, the higher the score meaning a negative effect on the environment. This picture shows a considerable



difference between bio-based scenarios and that starting from olefin. The latter seems to have lower impacts compared to the scores achieved by Scenario A. The avoided use of dedicated crops entails no impacts related to land exploitation, occupation, or the use of pesticides. Contrary to the common opinion, that attributes higher impacts on fossil fuel depletion and climate change to propylene partial oxidation (due to the use of oil as a raw material), the high energy consumption mainly related to glycerol purification in bio-based scenarios greatly affects the results. In both categories (in particular the fossil fuel depletion) the impact of acrolein from partial oxidation is lower if compared with that of the two bio-based scenarios. This trend is ascribable to both the massive consumption of fossil fuels that characterizes all the purification steps (e.g. glycerol, fatty acids) and to the triglycerides transformation (e.g. trans-esterification process) and the upstream stages: on one hand, the rapeseed cultivation and oil production, on the other hand the breeding and the tallow production. In fact, as previously reported, they represent the most intensive steps in terms of energy and resources requirement. The results in terms of characterization analysis are shown in Table 3.3.

**Table 3.3** - Acrolein production from propylene partial oxidation, ReCiPe I/A - Characterization analysis. Adapted from Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

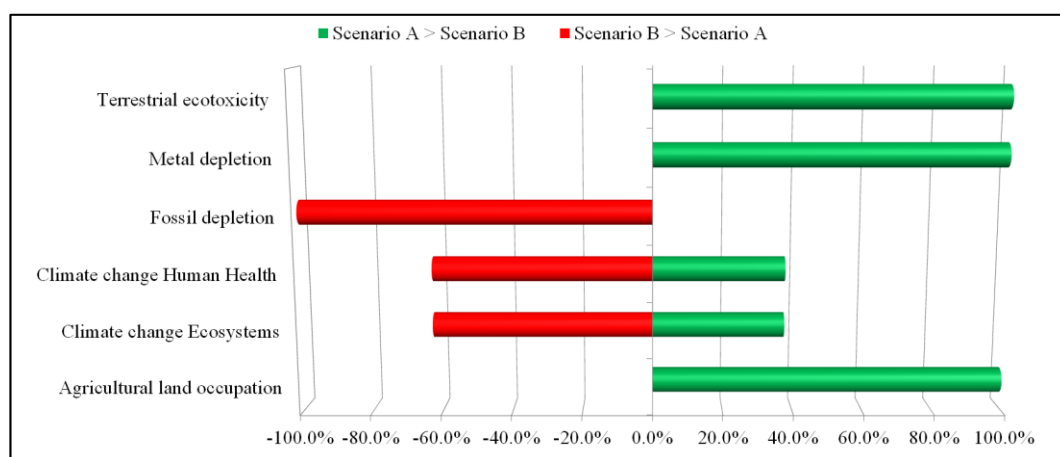
<b>Impact category</b>	<b>Unit</b>	<b>Amount</b>
<b>Total impact</b>	Pt	3.1E-01
<b>Agricultural land occupation</b>	species·yr	9.3E-11
<b>Terrestrial ecotoxicity</b>	species·yr	5.8E-12
<b>Climate change - Ecosystems</b>	species·yr	2.9E-08
<b>Climate change - Human health</b>	DALY	4.3E-06
<b>Metal depletion</b>	\$	9.9E-03
<b>Fossil fuel depletion</b>	\$	9.0E-02

However, if the comparison is made considering the global impacts achieved by each process alone, Scenario B seems to be the most environmentally sustainable one due to the benefits associated with the avoided dedicated crops usage.

- **Sensitivity analysis**

Lastly, in order to evaluate the robustness of the models created, a sensitivity analysis was carried out using the Monte Carlo statistical method. Data uncertainties were evaluated by combining the pedigree matrix developed by Weidema and Wesnaes<sup>95</sup> with the method previously reported in literature.<sup>96</sup> A lognormal statistical distribution with a 95% confidence interval was assumed; by performing an iterative calculation of 1000 simulations, both of the bio-based acrolein production scenarios were compared using ReCiPe2008 as the analysis method. The results of the sensitivity analysis are shown below, in Figure 3.17 and Table 3.4.

**Figure 3.17** - Monte Carlo analysis - comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



**Table 3.4** - Monte Carlo analysis - comparison between two bio-based acrolein scenarios, in terms of ReCiPe impact categories. Adapted from Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Impact category	A > B	B > A
Agricultural land occupation	100%	0%
Climate change - Ecosystems	38%	63%
Climate change - Human health	38%	62%
Fossil fuel depletion	0%	100%
Metal depletion	100%	0%
Terrestrial ecotoxicity	100%	0%

On the y-axis the six midpoint impact categories are reported, while the x-axis shows the frequency in terms of percentage. The frequency indicates how many times a scenario shows impacts higher than the other one for a particular impact category. Frequency equal to 100% (or -100%) means that for all the 1000 iterations the results are confirmed; on the other hand a frequency of 0% means that this situation does not

occur. Green bars stand for the case in which Scenario A attains higher environmental impacts than B; red bars, on the other hand, indicate the opposite. As can be seen, the Monte Carlo method confirms the results obtained previously in the LCIA. 100% frequency was achieved for fossil fuels and metal depletion as well as for the impact categories related to land exploitation (agricultural land occupation and terrestrial ecotoxicity). Furthermore, higher frequencies (62-63%) were achieved by both climate change categories, thus confirming results robustness.

### 3.3.5 Personal conclusions and recommendation

This work presents a life cycle assessment “from cradle to gate” for the production of 1kg of acrolein starting from glycerol generated as an industrial co-product. Two main industrial alternatives for the production of feedstock were compared: triglycerides trans-esterification and hydrolysis, which led respectively to the production of biodiesel and fatty acids as the main products. The aim of the study was to verify, from a life-cycle perspective, the environmental sustainability associated with the application of a principle of Green Chemistry, i.e. the use of renewable feedstocks,<sup>100</sup> by evaluating the possibility of using glycerol as a valuable chemical raw material instead of downgrading it for energy uses. Inventory analysis, which includes the main stages of the manufacturing chain (from source of triglycerides up to dehydration to obtain acrolein, also including the intermediate stages which lead to glycerol production and purification) was carried out using the data supplied by two companies (regarding the trans-esterification and hydrolysis processes and purification procedures) and extracted from literature (also including patents). The results show that the acrolein produced from glycerol and obtained as a co-product in biodiesel production seems to be less sustainable in terms of global impacts if compared with the hydrolysis-based scenario. However, contribution analysis indicates that the higher significance is not associated with the industrial consumptions, but with the triglycerides supply. Due to the land occupation and exploitation, the vegetable source of triglycerides seems to have higher environmental loads. Nevertheless, if rapeseed is substituted (even in part) by a marginal cultivation which does not require the use of pesticides and does not subtract space from agricultural cultivation, lower impacts could be achieved. For example, as suggested by literature,<sup>156</sup> marginal lands could be exploited for the cultivation of *Jatropha curcas* and castor beans, which however need higher quantity of freshwater.<sup>156</sup>

In addition, it should be considered that, although the cultivation phase represents the more stressful step for the environment,<sup>157</sup> it could be also influenced by many variables connected to different agricultural practices (e.g. higher or lower use of fertilizers) or different soil characteristics, typical of each geographical area.<sup>157</sup> On the other hand it is not possible to feed the entire glycerol industry using only tallow as the source of triglycerides (despite the fact that meat consumption is increasing due to the world's population growth). Moreover, this source is not without impacts, due to the significant environmental loads associated with both animal rearing and tallow production. For this reason, alternative routes should be pursued. Literature<sup>103</sup> points out the increasing attention to the use of biomass waste as a possible source for bio-based industry. This solution could be an interesting opportunity, considering that in 2012 the European production of organic waste was estimated to range between 118 and 138 million tonnes, with an estimated increase of 10% expected by 2020.<sup>158</sup> Also, this alternative could be even more advantageous for the Italian case study, thanks to its contribution to the reduction of CO<sub>2</sub> emissions: in Italy, in fact, the average percentage of organic waste not recovered (composted) amounts to around 60-70% of the total production.<sup>158</sup> Anyway, it should be considered that the use of alternative raw materials for the production of biofuels and chemicals in Europe will also be affected by EU and national fiscal incentives policies. In conclusion, this study highlights the importance of the application of LCA methodology as an assessment tool for evaluating the potential impacts associated with the industrial chemical sector. However, as commonly remembered in LCA studies, results should be considered valid only within the system boundaries concerned in the study. Further considerations regarding possible changes due to future trends could be estimated by an extension of the system boundaries to include economic and social variables also, but this would clearly go beyond the aim of this study.

### **3.3.5.1 Renewable feedstock in the domestic heating system - an LCA approach**

In addition to the assessment of the sustainability associated with the use of renewable feedstock in the chemical industry, the use of biobased resources was also evaluated in the domestic heating system sector. The study, which concerned the application of LCA methodology as a tool to address environmental load of the heating system appliances (both traditional and wood-based), was started

during the Master degree thesis and then completed in the first year of the PhD program with the publication of a manuscript in the International Journal of LCA edited by Springer.<sup>96</sup> Therefore, the following parts were extrapolated from the manuscript by permission of the editor.

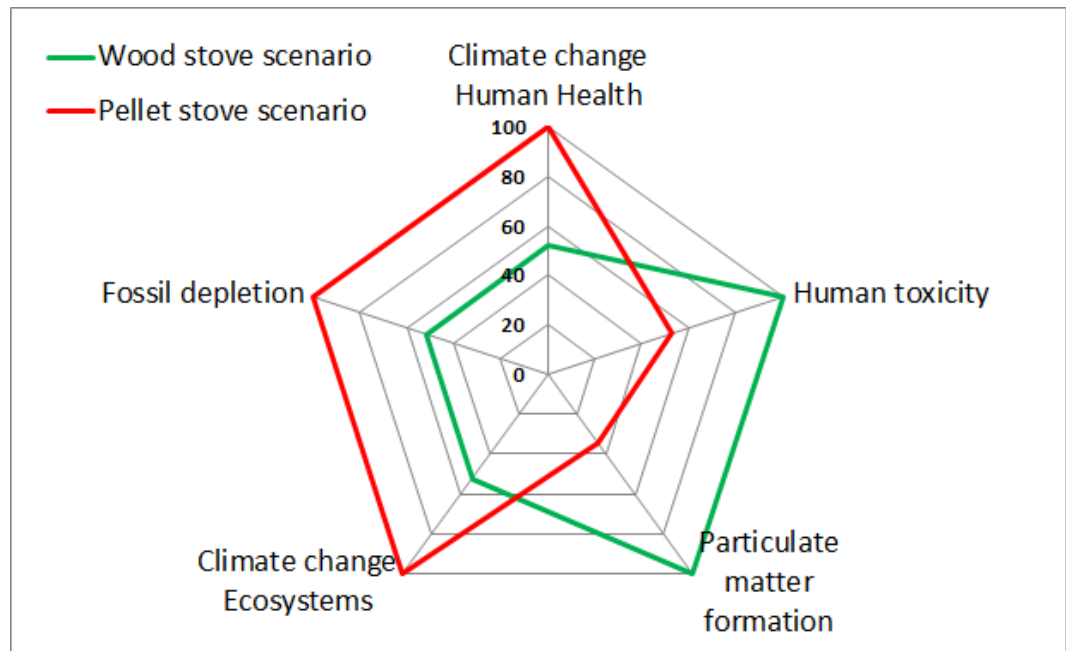
### 3.3.5.1.1 Introduction, main results and conclusions

With the rising concerns in the more developed Countries over energy dependence on fossil fuels and the environmental hazards connected with global warming, energy policies started to trend toward renewable energy sources.<sup>159</sup> In Europe, the Directive 2009/28/EC<sup>160</sup> promotes the use of woody biomass as feed in combustion plants to produce heat or electricity, and to reduce non-renewable resource consumption. Scaling down from industrial combustion plants to residential systems, biomass feedstock provide an attractive option for domestic heating needs, where fossil fuels account for about 15% of the total energy consumed in that sector throughout Europe.<sup>159</sup> Biomass resources are more available locally, and they are commonly recognized as having better environmental implications thanks to a lower contribution to global warming, supporting the goal of achieving a Low Carbon Society.<sup>161</sup> However, the carbon balance should be carefully evaluated and different performances on the environment (e.g. land use occupation and depletion) may result whether or not energy-related implications from dedicated crop cultures are considered. Besides, there is some concern over their usage in residential heating due to the emissions of various pollutants, such as polycyclic aromatic hydrocarbons, NO<sub>x</sub>, CO, SO<sub>x</sub>, and particulate matter.<sup>162,163</sup> Both the gas emission regulations contained in EU legislation for protecting the population and the environment and technological progress have led to more efficient combustion processes and emission control, thus helping to counter the negative effects connected with residential heating systems. In any case, an intensive use of biomass stoves in highly populated urban areas, obsolete appliances, bad common practices in stove combustion and maintenance, and geographical micro-area conditions may cause a worsening of air quality and related health issues.<sup>159,163</sup> In Italy, microclimate conditions and an intense industrial activity have combined to create critical air quality conditions in urban areas of the Po Valley. In 2006, a survey conducted in Italy revealed a significant contribution to PM<sub>10</sub> from the use of biomass for residential heating;<sup>164</sup>

two years later, another study was started for the purpose of estimating in detail the amount of particulate matter formation from biomass heating appliances.<sup>163</sup> The study quantified an amount of about 84,000 tons, which is equal to 30% of total PM<sub>10</sub> emissions from all anthropic sources in the same year. On the other hand, benefits from CO<sub>2</sub> emission savings were estimated at 9 Mt or 2% of carbon dioxide emissions in the year 2005.<sup>163</sup> To prevent pollution and preserve air quality, some Italian regions have banned biomass-based heating systems not complying with certain technical specifications (e.g. Lombardy Regional Law no. 24, 2006). Although environmental monitoring is widely performed by environmental agencies in urban areas to study the burdens and repercussions of combustion processes on human health and the ecosystem, only a few studies in literature have used a life-cycle approach when focusing on wood biomass heating systems.<sup>162,165,166,167,168</sup> Indeed, such an approach would provide a concrete contribution to the search for the best option, by comparing all the material and energy flows involved in the different residential heating systems. In the study, LCA was applied to create a model for comparing the environmental impacts of two wood-based combustion systems, a wood and a pellet stove included among the Best Available Technologies (BATs) according to the definition given in the European Commission DG TREN report.<sup>169</sup> The model was used to obtain a screening analysis of the two solutions, based on literature studies and local information relevant to Lombardy Region ; this could provide a reliable basis which can be improved with further data from direct monitoring campaigns. Unlike other studies, no dedicated crops were assumed for fuel production, but only spontaneous biomass. The comparison between wood and pellet stoves was carried out in terms of thermal energy produced (1MJ). Such a functional unit was chosen in order to make the model suitable for extending system boundaries to other heating systems such as domestic boiler or advanced integrated systems (e.g. heating pump or solar panels). A cradle-to-grave approach was adopted in order to provide an overview of the whole heating systems being studied. System boundaries include the appliance manufacture (e.g. the stove, the boiler, etc.), its usage (i.e. heat generation) and its final disposal. All the inward and outward flows within the system boundaries were considered in the study, such as energy sources, material types, and waste. More details are reported in literature.<sup>96</sup> The environmental impacts resulting from the systems investigated were assessed using

the ReCiPe method for the following midpoint categories: CH and CE, HT, PMF and FD. The main results are reported below in Figure 3.18 which depicts trend in terms of midpoint (percentage): the radar chart gives a quick overall view of the environmental loads from each scenario.

**Figure 3.18** - Radar chart showing results in terms of single point (by percentage). Impact categories are at vertexes of the radar, while the lines lay in correspondence of the share gained by each scenario. Source: Cespi et al. 2014<sup>96</sup> - with kind permission of Springer Science+Business Media.



As plotted, the scores show that the wood stove produces the highest impact for HT and PMF compared to the pellet stove, while the latter presents the worst results in the CH, CE, and FD categories. Moreover, Table 3.5 summarizes the processes and substances which have the main contribution for each environmental midpoint category studied. For both scenarios the ash final disposal processes entail the highest contribution to HT: 40% to 48% from incineration and 39% to 46% from landfill disposal when considering pellet and wood stove respectively. Impacts from the incineration process include air and water emissions, auxiliary material consumption for flue gas cleaning, and the disposal of residual material such as solidified fly ash and scrubber sludge in landfill. On the other hand, landfilling is a common practice in Italy, and harmful effects may be caused by the release of heavy metals such as cadmium, zinc, manganese, and lead into groundwater basins, thus leading to potential exposure risks for humans.<sup>170</sup> The contribution analysis also revealed that the damage to human health resulting from direct emissions during the combustion phase is less than 10% (3% and 5%

for the wood and the pellet stove, respectively). The PMF midpoint has the highest contribution from the combustion phase, which seems to cause up to 60% and 88% of substance emissions reported in Table 3.5 for the pellet and the wood stove, respectively; the remaining fraction is due to the transportation and auxiliaries fuels contribution. The PMF takes into account both the direct particulate emitted by the plant and precursor substances such as NO<sub>x</sub> and SO<sub>2</sub> emissions. As known, the particulate toxicity is influenced by dimension and chemical composition of the particle. For this reason we decided to verify for each scenario which substances contribute mainly to the category. The contribution analysis results in Table 3.5 show that for the wood stove scenario the highest impacts are primarily due to the emission of fine primary particulate PM<sub>2.5</sub> (69%), and then to the secondary particulate produced by NO<sub>x</sub> and SO<sub>2</sub> (29%). PM > 2.5 μm counts for about 1%. The pellet stove scenario, on the other hand, shows that the finest particulate contributes for 43%, while a higher contribution from the secondary particulate comes from NO<sub>x</sub> (38%) and SO<sub>2</sub> (16%) emissions. The results are in line with the outcomes reported in literature studies.<sup>166,171,172</sup> Generally speaking, variables that affect PM composition, size, and effects on human health depend on the stove's combustion and pollutant removal efficiency on the one hand, and the fuel type and composition on the other. The pellet stove has the advantage of higher efficiencies, and the fuel has greater energy density, size, and moisture content, more suitable for better combustion performance. In any case, the higher quantity of secondary particulate is associated with pellet combustion, due to the nucleation, agglomeration, and condensation processes involving the NO<sub>x</sub> and SO<sub>x</sub> species. CC and FD categories are closely related, due to the CO<sub>2</sub> equivalent emission factor resulting from combustion processes. The CC midpoint entails effects at a more global scale than the other impact categories. Both scenarios show similar percentage contributions to the climate change midpoint, due to direct greenhouse gas emissions, where carbon dioxide plays the largest role, followed by nitrous oxide. In any case, although wood pellet size distribution leads to an efficient combustion,<sup>173,174</sup> the pellet stove almost doubles the CC environmental impact compared to the wood stove (Figure 3.18 and Figure 3.19); the reasons must be sought in the pelletizing phase. This process comprises several operations in which large quantities of energy are required, such as the drying, conditioning, and extrusion steps. Consequently, the fossil fuel



consumption, mainly in terms of natural gas, depends on the chemical and physical characteristics of the pellet produced; for example, moisture content of less than 10% may indicate a reduction of the drying phase and a decrease in CO<sub>2</sub> emission. However, as pointed out above, the pelletizing phase is affected by a wide range of uncertainty, mainly related to the technological systems used by plants. The percentage contribution to fossil depletion listed in Table 3.5 for the wood stove scenario shows, on the other hand, higher oil consumptions, since the Italian transportation sector is mainly road-oriented, with less than 15% of all goods transported by rail. Accordingly, the values indicate that the main environmental impacts (82%) derive from fossil fuel used to produce liquefied fuels used in the transport sector (e.g. diesel oil). In addition to the direct consumption of primary energy carriers for the biomass input treatments, the transportation process for delivering wood logs and pellet bags contribute significantly to the climate change and fossil depletion categories. In particular, repercussions are more significant when feedstock is imported from other regions or foreign countries. Overall, the transportation of wood logs covers longer distances than that of pellet bags, and the impact on the pellet stove scenario is, on average, less than 10% as resulting from the sensitivity analysis ahead described. The use of wood collected directly from the pruning of urban trees could entail potential benefits for the Italian municipalities since, generally speaking, tree prunes, when composting plants are not available, are disposed of in landfills, the worst waste treatment option of the European waste hierarchy.<sup>175</sup> Thus a way for a potential and positive exploitation of these residues might be inspired by a short chain, where cut wood is distributed/ marketed to the local community as a fuel for domestic heating (in the form of logs or pellets). In Lombardy Region wood consumption for heating purpose amounted to about 1.5 Mt in 2008,<sup>176</sup> while separate collection of MSW embodied 900 kt organic waste, including compostable fraction and wood residues, in the same year:<sup>164</sup> assuming that the wood share is one third of the total, according to some national estimations,<sup>177</sup> the short chain for feedstock supply might be up to 20%. Municipalities should organize cutting, storage, and distribution operations by reducing the negative features related to high moisture levels, usually due to short storage periods; indeed, moisture increases wood weight and the amount of pollutants emitted during the combustion phase.<sup>178</sup> Also, the distribution distance would not be long

and the pruning period, specific for each tree species, would guarantee continuous storage and distribution. As a recommendation, the study looked at the heating appliances for domestic environments modeled in accordance with the BAT. This means that the results describe some of the best contemporary performances, but these may vary from the average technological level, because the cheapest biomass-based stoves with the worst combustion and removal efficiencies may be more widespread throughout the country.<sup>176</sup>

**Table 3.5** - Process contributions to impact categories by percentage. Adapted from Cespi et al. 2014<sup>96</sup> - reproduced by permission of Springer.

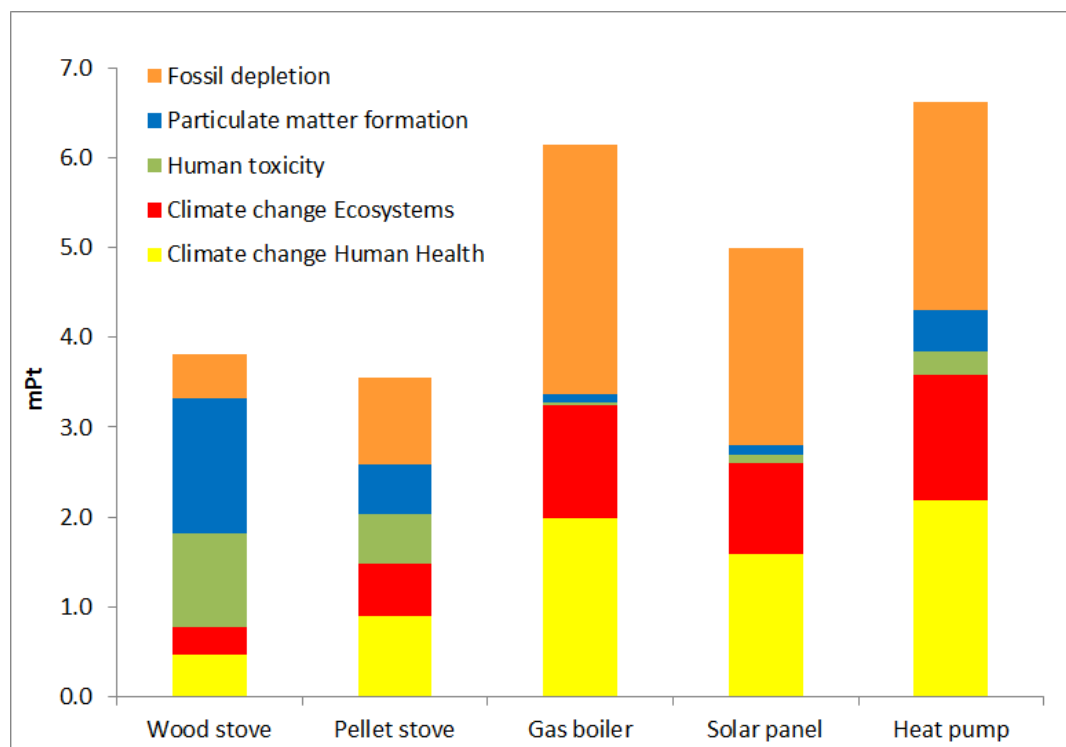
Impact categories	Wood stove	Pellet stove
<b>HT</b>	48% incinerated ash 46% landfilled ash 3% combustion process 3% other	40% incinerated ash 39% landfilled ash 5% combustion process 16% other
<b>PMF</b>	69% PM <sub>2.5</sub> 28% NO <sub>x</sub> 1% SO <sub>2</sub> 1% PM <sub>10</sub> 1% other	43% PM <sub>2.5</sub> 38% NO <sub>x</sub> 16% SO <sub>2</sub> 2% PM <sub>10</sub> 1% other
<b>CC*</b>	71% CO <sub>2</sub> 21% N <sub>2</sub> O 7% CH <sub>4</sub> 1% other	89% CO <sub>2</sub> 5% N <sub>2</sub> O 5% CH <sub>4</sub> 1% other
<b>FD</b>	82% oil production 5% coal production 4% natural gas production 9% other	29% oil production 18% coal production 49% natural gas production 4% other

\*The Climate Change category includes processes contribution to both the human health and the ecosystem damage categories.

The comparison with the most widespread alternative technologies for domestic heating (Figure 3.19) show that the biomass stoves achieves the highest contribution to PMF and HT categories: as discussed previously, these effects result from the characteristics of biomass feedstock, and justify the current concerns over the effect of biomass fuel appliances on urban air quality. In the same two categories, among the alternatives, the third highest contribution comes from the heat pump scenario, due to the high quantity of fossil fuel used to

produce the electricity necessary for the appliance's operation; gas boiler and solar panel scenarios have negligible effects. In this sense, an improvement in heat pump effectiveness could derive from combination with a photovoltaic system that would lead to a reduction in particulate emissions as well as to positive returns in air conditioning during the summer season. The remaining midpoints indicate the highest impacts for the alternative scenarios, mainly for FD and damage to human health and ecosystem from CC. This is due to the energy-intensive production processes for high-tech materials included in those technologies. Also, while for gas boiler and solar panel scenarios sensible improvements would result from technological progress and efficiency increases, the heat pump scenario is even affected by the power production mix adopted by a country: thus if Italy would move toward renewable sources of electricity, significant benefits might result for such a scenario. Lastly, the analysis performed limited the scope to thermal heat generation only, excluding the complementary functions of systems such as power generation. A comprehensive knowledge of the issue should, however, include the energy and economic returns obtained from the systems investigated.

**Figure 3.19** - Comparison of biomass based scenarios and innovative domestic heating systems. Values are expressed in ReCiPe single scores (mPt). Source: Cespi et al. 2014<sup>96</sup> - with kind permission of Springer Science+Business Media.



Therefore, it appears that a life cycle approach can support the choice of a better domestic heating system and would promote policy initiatives on a more consistent basis. Specifically, LCA allows a thorough investigation of different environmental impact categories, which can overcome partial analyses or uncompleted evaluations: in this sense, the comparison between the scenarios of domestic heating by wood and pellet stoves can lead to different conclusions in terms of environmental benefits whether the climate change and fossil depletion impact categories are considered beside the PMF and HT. Moreover, the methodology gives the advantage to quantify every single process contribution, helping to understand which are the more critical aspects to be tackled for reducing the total burdens to the environment. Anyway, the study shows that a preference for latest-generation pellet stoves, with efficient emission control systems, and a ban on obsolete wood stoves might lead to significant improvements in the quality of air in urban areas as combustion emissions are among the most impacting causes, even though further environmental benefits would come from a reduction in the energy consumption of the pelletizing process. However, a shift toward renewable sources in power production would encourage alternative heating systems: a solar panel, combined with a gas boiler for meeting winter heating needs, seems to greatly reduce particulate matter formation and negative human toxicity effects.

## References

---

- 1 L. Jacquemin, P.-Y. Pontalier, C. Sablayrolles, *Int. J. Life Cycle Assess.*, 2012, **17**, 1028-1041.
- 2 A.A. Burgess, D.J. Brennan, *Chem. Eng. Sci.*, 2001, **56**, 2589-2604.
- 3 S.T. Gillani, J.-P. Belaud, C. Sablayrolles, M. Vignoles, J.-M. Le Lann, *Chem. Prod. Process. Model.*, 2010, **5**, 1-26.
- 4 D. Kralisch, D. Ott, D. Gericke, *Green Chem.*, 2015, **17**, 123-145.
- 5 T. Benko, P. Mizsey, *Chem. Eng.*, 2007, **51**, 19-27.
- 6 J. Chevalier, P. Rosseaux, V.R. Benoit, B. Benadda, *Chem. Eng. Sci.*, 2003, **58**, 2053-2064.
- 7 A. Scipioni, A. Mazi, M. Nicro, T. Boatto, *Waste Manag.*, 2009, **29**, 2462-2474.
- 8 N. Tangsubkul, K Parameshwaran, S. Lundie, A.G. Fane, T.D. Waite, *J. Membr. Sci.*, 2006, **284**, 214-226.
- 9 P.R.S. Da Silva, F.G. Amaral, *J. Clean. Prod.*, 2009, **17**, 1339-1350.
- 10 T.E. Norgate, S. Jahanshahi, W.J. Rankin, *J. Clean. Prod.*, 2007, **15**, 838-848.
- 11 F. Baratto, U.M. Diwekar, D. Manca, *J. Power Sources*, 2005, **139**, 2141-222.
- 12 L. Gerber, M. Gassner, F. Maréchal, *Comput. Chem. Eng.*, 2011, **35**, 1265-1280.
- 13 J. Kenthorai Raman, V. Foo Wang Ting, R. Pogaku, *Biomass Bioenerg.*, 2011, **35**, 4221-4229.
- 14 S.M. Al Salem, E. Mechleri, L.G. Papageorgiou, P. Lettieri, *Comput. Aided Chem. Eng.*, 2012, **30**, 101-106.
- 15 M. Aresta, M. Galatola, *J. Cleaner Prod.*, 1999, **7**, 181-193.
- 16 X. Domènech, J.A. Ayllon, J. Peral, J. Rieradevall, *Environ. Sci. Technol.*, 2002, **36**, 5517-5520.
- 17 M.C.B. Figueiredo de, M. Freitas Rosa de, C.M.L. Ugaya, M. Souza Filho de Sá Moreira de, A.C.C. Silva Braid da, L.F..L. Melo de, *J. Cleaner Prod.*, 2013, **35**, 130-139.
- 18 O. G. Griffiths, J. P. O'Byrne, L. Torrente-Murciano, M.D. Jones, D. Mattia, M.C. McManus, *J. Cleaner Prod.*, 2013, **42**, 180-189.
- 19 P.A. Holman, D.R. Shonnard, J.H. Holles, *Ind. Eng. Chem. Res.*, 2009, **48**, 6668-6674.
- 20 Z. Kowalski, J. Kulczycka, Z. Wzorek, *J. Cleaner Prod.*, 2007, **15**, 28-37.
- 21 P. Pérez-López, S. González-García, C. Jeffryes, S.N. Agathos, E. McHugh, D. Walsh, P. Murray, S. Moane, G. Feijoo, M.T. Moreira, *J. Cleaner Prod.*, 2014, **64**, 332-344.
- 22 J.-F. Portha, J.-N. Jaubert, S. Louret, M.-N. Pons, *Oil & Gas Science and Technology – Rev. IFP Energies nouvelles*, 2010, **65**, 793-805.
- 23 J.-F. Portha, S. Louret, M.-N. Pons, J.-N. Jaubert, *Resour. Conserv. Recy.*, 2010, **54**, 291-298.
- 24 G. Jodicke, O. Zenklusen, A. Weidenhaupt, K. Hungerbühler, *J. Cleaner Prod.*, 1999, **7**, 159-166.
- 25 P.T. Anastas, R.L. Lankey, *Green Chem.*, 2000, **2**, 289-295.

- 
- 26 A. Azapagic A, *Life cycle assessment: a tool for identification of more sustainable products and processes, handbook of green chemistry and technology*, Blackwell Science, Oxford, pp 62–85, 2002.
- 27 L.M. Gustafsson, P. Börjesson, *Int. J. Life Cycle Assess.*, 2007, **12**, 151-159.
- 28 I. Muñoz, *Int. J. Life Cycle Assess.*, 2012, **17**, 517-519.
- 29 L.M. Tufvesson, P. Tufvesson, J.M. Woodley, P. Börjesson, *Int. J. Life Cycle Assess.*, 2013, **18**, 431-444.
- 30 R.A. Urban, B.R. Bakshi, *Ind. Eng. Chem. Res.*, 2009, **48**, 8068–8082.
- 31 S. Madival, R. Auras, S.P. Singh, R. Narayan, *J. Cleaner. Prod.*, 2009, **17**, 1183–1194.
- 32 V. Dornburg, B.G. Hermann, M.K. Patel, *Environ. Sci. Technol.*, 2008, **42**, 2261–2267.
- 33 K.G. Harding, J.S. Dennis, H. von Blottnitz, S.T.L. Harrison, *J. Biotechnol.*, 2007, **130**, 57–66.
- 34 L. Shen, M.K. Patel, *J. Polym. Environ.*, 2008, **16**, 154–167.
- 35 B.G Hermann, M. Patel, *Appl. Biochem. Biotechnol.*, 2007, **136**, 361–388.
- 36 A.L. Roes, M.K. Patel, *Risk. Anal.*, 2007, **27**, 1131–1321.
- 37 A.D. Patel, K. Meesters, H. den Uil, E. de Jong, E. Worrell, L. Gerber, M. Gassner, M.K. Patel, *ChemSusChem*, 2013, **6**, 1724-1736.
- 38 P. Börjesson, L.M. Tufvesson, *J. Cleaner Prod.*, 2010, **19**, 108–120
- 39 R. Müller-Wenk, M. Brandão, *Int. J. LifeCycle Assess.*, 2010, **15**, 172–182.
- 40 F. Cherubini, *Renew Energ.*, 2010, **35**, 1565–1573.
- 41 F. Cherubini, N.D. Birg, A. Cowie, G. Jungmeier, B. Schlamadinger, S. Woess-Gallasch, *Resour. Conserv.*, 2009, **53**, 434–447.
- 42 L. Gerber, M. Gassner, F. Maréchal, *Comput. Chem. Eng.*, 2011, **35**, 1265-1280.
- 43 H. Kim, S. Kim, B.E. Dale, *Environ. Sci. Technol.*, 2009, **43**, 961–967.
- 44 J.H. Kløverpris, K. Baltzer, P.H. Nielsen, *Int. J. Life Cycle Assess.*, 2010, **15**, 90–103.
- 45 D. Zilberman, G. Hochman, D. Rajagopal D., *Indirect land use: one consideration too many in biofuel regulation. Agricultural and Resource Economics Update*, University of California, 2010.
- 46 F. Cherubini, G. Jungmeier, , 2010, **15**, 53–66.
- 47 F. Cherubini, S. Ulgiati, *Appl. Energy*, 2010, **87**, 47–57.
- 48 G. Wernet, S. Conradt, H.P. Isenring, C. Jiménez-González, K. Hungerbühler, *Int. J. Life Cycle Assess.*, 2010, **15**, 294–303.
- 49 G. Van der Vorst, J. Dewulf, W. Aelterman, W.B. De, L.H. Van, *Environ. Sci. Technol.*, 2011, **45**, 3040–3046.
- 50 G. Van der Vorst, W. Aelterman, W.B. De, B. Heirman, L.H. Van, J. Dewulf, *Green Chem.*, 2013, **15**, 744–748.
- 51 D. Ott., D. Kralisch, I. Denčić, V. Hessel, Y. Laribi, P.D. Perrichon, C. Berguerand, L. Kiwi-Minsker, P. Loeb, *ChemSusChem*, 2014, **12**, 3521-3533.
- 52 C. Jiménez-González, R. Overcash, *Green Chem.*, 2014, **16**, 3392-3400.

- 
- 53 A. Bruggink, P. Nossin, *Assessment of bio-based pharmaceuticals—the cephalixin case, in the book renewables-based technology—sustainability assessment*, Wiley, West Sussex, pp 315–330, 2006.
- 54 C. Jiménez-González, A.D. Curzons, D.J.C. Constable, V.L. Cunningham, *Int. J. Life Cycle Assess.*, 2004, **9**, 114–121
- 55 C. Ponder, M. Overcash, *Sci. Total Environ.*, 2010, **408**, 1331–1337.
- 56 P. Blowers, M. Titus, *Environ. Prog.*, 2004, **23**, 284–290.
- 57 U. Krtschil, V. Hessel, P. Loeb, D. Reinhard, S. Huebschmann, D. Kralisch, *Chem. Eng. J.*, 2011, **167**, 510–518.
- 58 A. Stark, S. Huebschmann, M. Sellin, D. Kralisch, R. Trotzki, B. Ondruschka, *Chem. Eng. Technol.*, 2009, **32**, 1730–1738.
- 59 S. Kressirer, D. Kralisch, A. Stark, U. Krtschil, V. Hessel, *Environ. Sci. Technol.*, 2013, **47**, 5362–5371.
- 60 C. Capello, G. Wernet, J. Sutter, S. Hellweg, K. Hungerbühler, *Int. J. Life Cycle Assess.*, 2009, **14**, 467–479.
- 61 C. Capello, U. Fischer, K. Hungerbühler, *ChemSusChem*, 2007, **9**, 111–127.
- 62 Y. Zhang, B.R. Bakshi, E.S. Demessie, *Environ. Sci. Technol.*, 2008, **42**, 1724–1730.
- 63 O.G. Griffiths, J.P. O’Byrne, L. Torrente-Murciano, M.D. Jones, D. Mattia, M.C. McManus, *J. Cleaner. Prod.*, 2013, **42**, 180–189.
- 64 A. Ancil, C.W. Babbitt, R.P. Rafaele, B.J. Landi, *Environ. Sci. Technol.*, 2011, **45**, 2353–2359.
- 65 T. Walser, E. Demou, D.J. Lang, S. Hellweg, *Environ. Sci. Technol.*, **45**, 4570–4578.
- 66 C. Jiménez-González, D.J.C. Constable, *Green Chemistry and Engineering: A Practical Design Approach*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011.
- 67 D. Cespi, F. Passarini, E. Neri, I. Vassura, L. Ciacci, F. Cavani, *J. Clean. Prod.*, 2014, **69**, 17–25.
- 68 Sustainable Chemistry (SusChem), [www.suschem.org](http://www.suschem.org). Accessed 9 January 2014.
- 69 F. Cavani, *J. Chem. Technol. Biot.*, 2010, **85**, 1175–1183.
- 70 J. F. Brazdil, *Acrylonitrile*, Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2012, DOI: 10.1002/14356007.a01\_177.pub3.
- 71 S. Garmston, *Acrylonitrile and derivatives –World Supply/Demand Report 2009*, PCI Acrylonitrile Ltd. [www.pci-acrylo.com](http://www.pci-acrylo.com) Accessed 9 January 2014.
- 72 P.W. Langvardt, *Acrylonitrile*, Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, DOI: 10.1002/14356007.a01\_177.pub2
- 73 J.F. Brazdil, *Top. Catal.*, 2006, **38**, 289–294.
- 74 Chemsystems, [www.chemsystems.com/about/cs/news/items/PERP0910\\_2\\_Acrylonitrile.cfm](http://www.chemsystems.com/about/cs/news/items/PERP0910_2_Acrylonitrile.cfm). Accessed 9 January 2014.
- 75 The Dow Chemical Company (Dow), [www.dow.com/investors/pdfs/presentations/USGC\\_101211.pdf](http://www.dow.com/investors/pdfs/presentations/USGC_101211.pdf). Accessed 9 January 2014.
- 76 F. Cavani, J.H. Teles, *ChemSusChem*, 2009, **2**, 508–534.

- 
- 77 F. Cavani, *Catal. Today*, 2010, **157**, 8-15.
- 78 M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs and R. van Zelm, *ReCiPe 2008 - A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level, First edition (version 1.07)*, Ministry of Housing, Spatial Planning and the Environment (VROM), Netherlands, 2012.
- 79 A. Chauvel, G. Lefebvre, *Petrochemical processes, Vol. 2 Major oxygenated, chlorinated and nitrated derivatives*, ISBN2710805618, 9782710805618 Institut français du pétrole publications Edition Technip, France, 1989.
- 80 F. Cavani, G. Centi, P. Marion, *Catalytic Ammoxidation of Hydrocarbons on Mixed Oxides, in Metal Oxide Catalysis* (eds S. D. Jackson and J. S. J. Hargreaves), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009.
- 81 R. K. Grasselli, *Top. Catal.*, 2002, **21**, 79-88.
- 82 R.K. Grasselli, *Catal. Today*, 2005, **99**, 23-31.
- 83 Ecoinvent Centre (formerly Swiss Centre for Life Cycle Inventories): Ecoinvent 2.2 Database 2009.
- 84 Plastics Europe, 2005. Eco-profiles of the European Plastics Industry - Propylene. Published Online on [www.plasticseurope.org/plasticssustainability/eco-profiles/browse-by-list.aspx](http://www.plasticseurope.org/plasticssustainability/eco-profiles/browse-by-list.aspx). Accessed 9 January 2014.
- 85 S.D. Raseev, *Thermal and Catalytic Processes in Petroleum Refining, Cap. 7. Industrial Catalytic Cracking*, Marcel Dekker Inc., New York, United States of America, 2003.
- 86 IPPC - Integrated Pollution Prevention and Control, *Reference document on best available techniques in the large volume organic chemical industry*, 2003, Published Online on [www.epa.ie/downloads/advice/brefs/name,14517,en.html](http://www.epa.ie/downloads/advice/brefs/name,14517,en.html). Accessed 9 January 2014.
- 87 Friedrich, M., S., Seely, M., J., Suresh, D., D., European Patent 0 437 056 A2 1991. Assigned to the Standard Oil Company, OH, USA.
- 88 T. Nemecek, T. Kägi, Life Cycle Inventories of Agricultural Production Systems, Ecoinvent Database report No. 15. Zürich and Dübendorf, CH, 2007.
- 89 X. Domènech, J.A. Ayllon, J. Peral, J. Rieradevall, *Environ. Sci. Technol.*, 2002, **36**, 5517-5520.
- 90 A. Pavone, R.H. Schwaar, *PEP Review No. 88-2-4 Acrylonitrile from propane by new BP/SOHIO patented process*, SRI INTERNATIONAL, Menlo Park, California, 1989.
- 91 European Fertilizer Manufacturers' Association, EFMA, 2000. Production of ammonia. Best available techniques for pollution prevention and control in the European fertilizer industries. Booklet N°1. Brussels, Belgium.
- 92 M. Appl, *Ammonia, 3 - Production Plants*, Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, DOI:10.1002/14356007.o02\_o12.
- 93 M. Buchert, D. Schüler, D. Bleher, (Öko-Institut e.V., Freiburg Germany), *Sustainable Innovation and Technology Transfer Industrial Sector Studies - Critical metals for future sustainable*



---

*technologies and their recycling potential*, 2009, United Nations Environment Programme (UNEP) & United Nations University.

- 94 T.E. Graedel, R. Barr, C. Chandler, T. Chase, J. Choi, L. Christoffersen, E. Friedlander, C. Henly, C. Jun, N.T. Nassar, D. Schechner, S. Warren, M. Yang, C. Zhu, *Environ. Sci. Technol.*, 2012, **46**, 1063-1070.
- 95 B.P. Weidema, M. Wesnaes, *J. Cleaner Prod.*, 1996, **4**, 167-174.
- 96 D. Cespi, F. Passarini, L. Ciacci, I. Vassura, V. Castellani, E. Collina, A. Piazzalunga, L. Morselli, *Int. J. LCA*, 2014, **19**, 89-99.
- 97 M.A. Curran, *Curr. Opt. Chem. Eng.*, 2013, **3**, 273-277.
- 98 <http://www.aidic.it/cisap6/>
- 99 D. Cespi, F. Passarini, F. Cavani, E. Neri, I. Vassura, *CET*, 2014, **36**, 169-174.
- 100 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
- 101 D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chieriegato, J.-L. Dubois, F. Cavani, *Green Chem.*, 2015, **17**, 343 - 355.
- 102 F. W. Lichtenthaler, *Carbohydrates as Organic Raw Materials*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010, DOI: 10.1002/14356007.n05\_n07.
- 103 R. Sheldon, *Green Chem.*, 2014, **16**, 950-963.
- 104 C. F. M Pestana, A. C. O. Guerra, G. B. Ferreira, C. C. Turci, C. J. A. Mota, *J. Braz. Chem. Soc.*, 2013, **24**, 100-105.
- 105 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Eur. J. Lipid Sci. Technol.*, 2009, **111**, 788-799.
- 106 B. Katryniok, S. Paul, M. Capron, F. Dumeignil, *ChemSusChem*, 2009, **2**, 719-730.
- 107 A. Behr, J. Eilting, K. Irawadi, J. Lechinski and F. Lindner, *Green Chem.*, 2008, **10**, 13-30.
- 108 L. Tao, B. Yan, Y. Liang and B. Xu, *Green Chem.*, 2013, **15**, 696-705.
- 109 M. Ayoub, A. Z. Abdullah, *Renew. Sust. Energ. Rev.*, 2012, **16**, 2671-2686.
- 110 C. Zhou, J. N. Beltramini, Y. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527-549.
- 111 J. A. Kenar, *Lipid Technology*, 2007, **19**, 249-253.
- 112 J. A. Posada, L. E. Rincón, C. A. Cardona, *Bioresource Technol.*, 2012, **111**, 282-293.
- 113 B. Katryniok, S. Paul, V. Bellière-Baca, P. Rey, F. Dumeignil, *Green Chem.*, 2010, **12**, 2079-2098.
- 114 *US. Pat.*, 8 686 195 B2, 2014.
- 115 *US. Pat.*, 8 378 136 B2, 2013.
- 116 *US. Pat.*, 8 252 960 B2, 2012.

- 
- 117 A. Chierigato, M.D. Soriano, F. Basile, G. Liosi, S. Zamora, P. Concepción, F. Cavani and J. M. López Nieto, *Appl. Catal. B-Environ.* 2014, **150-151**, 37-46.
- 118 A. Chierigato, F. Basile, P. Concepción, S. Guidetti, G. Liosi, M.D. Soriano, C. Trevisanut, F. Cavani and J. M. López Nieto, *Catal. Today*, 2012, **197**, 58-65.
- 119 M.D. Soriano, P. Concepción, J. M. López Nieto, F. Cavani, S. Guidetti and C. Trevisanut, *Green Chem.*, 2011, **13**, 2954.
- 120 L. Liu, X.P. Ye, J.J. Bozell, *ChemSusChem*, 2012, **5**, 1162-1180.
- 121 PRé Consultants, SimaPro7, PhD version 7.3.3, Amersfoort, The Netherlands, 2013.
- 122 IPCC - Intergovernmental Panel on Climate Change, *Climate Change 2007. Fourth Assessment Report. The Physical Science Basis*, Cambridge University Press, United Kingdom, 2007.
- 123 *US. Pat.*, 2013-053595 A1, 2013.
- 124 *US. Pat.*, 8 143 454 B2, 2012.
- 125 *US. Pat.*, 8 198 477 B2, 2012.
- 126 L. Shen, H. Yin, A. Wang, X. Lu, C. Zang, F. Chen, Y. Wang, H. Chen, *J. Ind. Eng. Chem.*, 2014, **20**, 759-766.
- 127 Chem Systems - Process Evaluation/Research Planning (PERP program), *Acrylic Acid 08/09-3*, 2010.
- 128 *US. Pat.*, 8 212 070 B2, 2012.
- 129 P.A. Holman, D.R. Shonnard, J.H. Holles, *Ind. Eng. Chem. Res.*, 2009, **48**, 6668-6674.
- 130 G. Knothe, J. Van Gerpen, J. Krahl, *The Biodiesel Handbook*, AOCS Press, United States of America, 2005.
- 131 *Belgian Pat.*, 422 877, 1937.
- 132 I. B. Banković-Ilčić, O. S. Stamenković, V. B. Veljković, *Renew. Sust. Energ. Rev.*, 2012, **16**, 3621-3647.
- 133 A. Demirbas, *Energ. Convers. Manage.*, 2009, **50**, 14-34.
- 134 M. Balat, *Energ. Convers. Manage.*, 2011, **52**, 1479-1492.
- 135 A. Karmakar, S. Karmakar and S. Mukherjee, *Bioresource Technol.*, 2010, **101**, 7201-7210.
- 136 M. Pagliaro, M. Rossi, *The Future of Glycerol - New Usages for a Versatile Raw Material*, RCS Publishing, Cambridge, UK, 2008.
- 137 R. Christoph, B. Schmidt, U. Steinberner, W. Dilla, R. Karinen, *Glycerol*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, DOI: 10.1002/14356007.a12\_477.pub2.
- 138 H. A. van Kalker, A. L. Blom, F. P. J. T. Rutjes, M. A. J. Huijbregts, *Green Chem.*, 2013, **15**, 1255-1263.

- 
- 139 Food and Agricultural Organization of the United Nations, FAO, *Biofuels and the sustainability challenge: A global assessment of sustainability issues, trends and policies for biofuels and related feedstocks*, 2013, <http://www.fao.org/docrep/017/i3126e/i3126e.pdf>, (accessed August 2014).
- 140 M. T. Firisia, I. Van Duren, A. Voinov, *Energ. Effic.*, 2014, **7**, 79-95.
- 141 D. Kralisch, C. Staffel, D. Ott, S. Bensaid, G. Saracco, P. Bellantoni and P. Loeb, *Green Chem.*, 2013, **15**, 463-477.
- 142 BP, *Statistical Review of World Energy*, 2013, [http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical\\_review\\_of\\_world\\_energy\\_2013.pdf](http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical_review_of_world_energy_2013.pdf), (accessed August 2014).
- 143 EIA - International Energy Statistics, *Independent Statistics & Analysis - U.S. Energy Information Administration*, <http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=79&pid=81&aid=1&cid=regions.&syid=2007&eyid=2011&unit=TBD> (accessed August 2014).
- 144 M.D. Bohon, B.A. Metzger, W.P. Linak, C.J. King, W.L. Roberts, *Proceedings of the Combustion Institute*, 2011, **33**, 2717-2724.
- 145 EBB - European Biodiesel Board, *Statistics - The EU biodiesel industry 2011*, <http://www.ebb-eu.org/stats.php> (accessed November 2014).
- 146 D. J. Anneken, S. Both, R. Christoph, G. Fieg, U. Steinberner, A. Westfechtel, *Fatty Acids*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, DOI: 10.1002/14356007.a10\_245.pub2.
- 147 Council Regulation (EC) 1069/2009 of 21 October 2009 laying down health rules as regards animal by-products and derived products not intended for human consumption and repealing Regulation (EC) No 1774/2002 (Animal by-products Regulation) OJ L 300/1.
- 148 P.H. Nielsen, A.M. Nielsen, B.P. Weidema, R. Dalgaard, N. Halberg, *LCA food data base*, 2003.
- 149 Gov.uk, Ecofys, *Tallow review: a report on the current animal market*, 2012, [www.gov.uk/government/uploads/system/uploads/attachment\\_data/file/144447/tallowreview.pdf](http://www.gov.uk/government/uploads/system/uploads/attachment_data/file/144447/tallowreview.pdf) (accessed August 2014).
- 150 W. Hahn, *USDA Economic Research Service calculations based on Bureau of Labor Statistics and USDA Agricultural Marketing Service Data 2013*, <http://www.ers.usda.gov/data-products/meat-price-spreads.aspx> (accessed August 2014).
- 151 D. Arntz, A. Fischer, M. Höpp, S. Jacobi, J. Sauer, T. Ohara, T. Sato, N. Shimizu, H. Schwind, *Acrolein and Methacrolein*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, DOI: 10.1002/14356007.a01\_149.pub2.
- 152 Chem Systems - Process Evaluation/Research Planning (PERP program), *Epichlorohydrine 99/00S11*, 2000.
- 153 *EU. Pat.*, 1 005 908 A2, 2000.
- 154 *US Pat.*, 8 530 697 B2, 2013.
- 155 *US Pat.*, 0 171 685 A1, 2014.

- 
- 156 S. Liang, M. Xu, T. Zhang, *Bioresource Technol.*, 2013, **129**, 72-77.
- 157 J. Malça, A. Coelho, F. Freire, *Appl. Energ.*, 2014, **114**, 837-844.
- 158 ISPRA - Istituto Superiore per la Protezione e la Ricerca Ambientale, *Urban waste report - edition 2013*, <http://www.isprambiente.gov.it/> (accessed August 2014).
- 159 V. K. Verma, S. Bram, J. De Ruyck, *Biomass Bioenerg.*, 2009, **33**, 1393-1402
- 160 Directive 2009/28/EC of the European Parliament and of the council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. OJ L 140, 5.6.2009, pp. 16-62.
- 161 R. Madlener, M. Koller, *Energ. Policy*, 2007, **35**, 6021-6035.
- 162 C. Solli, M. Reenaas, A. H. Strømman, E.G. Hertwich, *Int. J. Life Cycle Assess.*, 2009, **14**, 517-528.
- 163 APAT-ARPA Lombardia , Stima dei consumi di legna da ardere per riscaldamento ed uso domestico in Italia, 2008 <http://www.isprambiente.gov.it/contentfiles/00004100/4156-stima-dei-consumi-di-legna-da-ardere.pdf>. Accessed 7 September 2012.
- 164 Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) Rapporti <http://www.isprambiente.gov.it/it/pubblicazioni/rapporti.html>. Accessed 7 September 2012
- 165 A. Roedl, *Int. J. Life Cycle Assess.*, 2010, **15**, 567-578.
- 166 S. Caserini, S. Livio, M. Giuliano, M. Grosso, L. Rigamonti, *Biomass and Bioenerg.*, 2010, **34**, 474-482.
- 167 A. Bonoli, *Applicazione di una metodologia LCA (Life Cycle Assessment) per una valutazione costi/benefici di carattere ambientale nell'impiego di biomasse per la produzione energetica nell'Appennino tosco emiliano*, 2007, [http://www.centrocisa.it/ricerche/archivioB/allegati/MEB\\_LCA.pdf](http://www.centrocisa.it/ricerche/archivioB/allegati/MEB_LCA.pdf) Accessed 7 September 2012
- 168 G. Bidini, F. Cotana, C. Buratti, G. Fantozzi, M. Barbanera, *Analisi del ciclo di vita del pellet da srf attraverso misure dirette dei consumi energetici*, 2006, <http://www.crbnet.it/File/Pubblicazioni/pdf/1290.pdf> Accessed 7 September 2012.
- 169 European Commission - DG TREN, *Preparatory Studies for Eco-design Requirements of EuPs(II), Lot 15- Solid fuel small combustions installations- Task 5: Base Cases*, 2009, <http://www.ecosolidfuel.org/>. Accessed 7 September 2012.
- 170 CTI Energia e Ambiente, TCVVV S.p.A., FIER, CFAV, KOBA s.r.l., Università Politecnica delle Marche, VTT Energy, Regione Lombardia (2004), *BIOCEN Gestione e valorizzazione delle ceneri di combustione nella filiera Legno-Energia*, 2004, [www.cti2000.it/solidi.htm](http://www.cti2000.it/solidi.htm), Accessed 7 September 2012.
- 171 AIEL, *La combustione del legno- fattori di emissione e quadro normativo*, [http://www.aiel.cia.it/easy.php?COD\\_PAG=997](http://www.aiel.cia.it/easy.php?COD_PAG=997), Accessed 7 September 2012.
- 172 L.S. Båfuer, B. Leckner, C. Tullin, M. Bernten, *Biomass and Bioenerg.*, 2011, **35**, 3648 - 3655.
- 173 F. Fiedler, *Renew. Sust. Energ. Rev.*, 2004, **8**, 201-221.

- 
- 174 W. Heschel, L. Rweyemamu, T. Scheibner, B. Meyer, *Fuel Process. Technol.*, 1999, **61**, 223-242.
- 175 Directive 2008/98/EC of the European Parliament and of the council of 19 November 2008 on waste and repealing certain Directives. OJ L 312, 22.11.2008, pp. 3-30.
- 176 C. Pastorello, P. Dilara, *Estimation of residential wood combustion in the Lombardy Region*, European Commission-JRC (Joint Research Centre), 2010.  
[http://ita.arpalombardia.it/ita/qaria/pdf/Full\\_IX\\_Report-final.pdf.%20](http://ita.arpalombardia.it/ita/qaria/pdf/Full_IX_Report-final.pdf.%20) Accessed 7 September 2012.
- 177 Osservatorio Nazionale sui Rifiuti - ONR, *Programma e Rapporto dell'Osservatorio - PRO2 Rapporto 2008, Rome, Italy*, 2009,  
[http://www.minambiente.it/export/sites/default/archivio/notizie/programma\\_convegno\\_rifiuti.pdf](http://www.minambiente.it/export/sites/default/archivio/notizie/programma_convegno_rifiuti.pdf)  
Accessed 19 March 2013.
- 178 T. Nord-Larsen, A. Bergstend, O. Farver, N. Heding, *Biomass and Bioenerg.*, 2011, **35**, 2993-2998.

## 4. Conclusions of the study

### 4.1 Main results and personal considerations about the approach

The activity carried out during the PhD program in Chemistry at the University of Bologna results in line with the professional figure of an industrial chemist, who should be able to analyze different scientific and technological solutions verifying which is the most suitable from an industrial point of view. Moreover, considering the background on environmental chemistry is always useful make an evaluation of the most sustainable option too. For this reason, the work done during the three-years program can be summarized as the intention to better understand all the fundamentals mechanisms of a general LCA methodology in order to develop a standardized approach applicable to the industrial chemistry sector and to implement the actual reference database. Indeed, there is a lack of standardization for the application of the methodology to the chemical industry, preventing the scientific community to follow a common approach. In addition, the lack of literature data which describe in detail the chemical production processes is also relevant. In fact, although some general information are reported in encyclopedias (e.g. Ullmann, Kirk-Othmer) usually they are not enough to complete a full LCI of a chemical product. Detailed description of industrial syntheses are reported in the Process Economics Program (PEP)<sup>1</sup> and Process Economics and Research Planning (PERP)<sup>2</sup> reviews. However, these reports are much expensive and ordinarily not accessible to the researchers in public institutions. Moreover, although several efforts were made during last years by the Ecoinvent<sup>3</sup> community to increase the reliability of its product and to fill the data gap, the development of a database dedicated only to the chemical substances seems necessary. As well known, the research in the chemical field never stops and it results in a huge number of new substances and methodologies developed each year. Therefore, it is appropriate to suppose that this category requires a continuous upgrade of the information guaranteed just by the joint efforts of the industries and research institutions. In general, data sharing is very difficult, due to corporate know-how (this is the reason of the high price to get the access to the reports mentioned above), thus the usage of proxy data to fill the inventories is still common. . However, if the goal of the LCA practitioners is to pursue target of sustainability reaching also an economic benefit, a deeper collaboration between several corporations is mandatory in order to develop and release a standard approach which can be apply also by the small

enterprises to enforce the concept of sustainable development. For this reason, the mission of our work can be also interpreted as the intention to improve the existing database making these information available to the researchers involved in the LCA application to GC and GE. The reduction in the production steps and the use of renewable feedstock were taken into account selecting two syntheses with higher relevance from industrial point of view: the acrylonitrile and the acrolein productions. In both cases results revealed the importance to consider the sustainability claimed by the application of GC and GE principles from a life cycle perspective confirming what already stated by literature<sup>4</sup> *"the main strengths of the life cycle inventory analysis are the holistic approach and the structured procedure for the goal definition, data investigation and systems comparison. The method considers more environmental impacts than other common methods such as environmental risk assessment. Thus, it fits in well with the detailed and systematic comparison of products that cause completely different environmental impacts along the different life cycle phases"*.

Moreover, some common aspects emerged from the several case studies. First the identification of a general approach to search and collect data useful to fill the inventories, which includes both the type of information and the way in which they can be obtained: more consolidated literature sources. Then the selection of the appropriate analysis methods, which fit with the goals of the study and the audience selected. Midpoint oriented approaches are recommended (e.g. ReCiPe), as well as the single issues (e.g. IPCC). Another well established method could be the CED evaluation, which represents a clear and fast way to address potential impacts all over the life cycle, studying all the energy flows involved. Furthermore, other more technical aspects emerged such as the importance of catalyst and the resources exploitation. Catalytic systems are fundamental to drive the reactions and their efficacy often affects the overall sustainability of the entire chemical process, as in the case of acrylonitrile production. Nevertheless, the direct impacts associated with the usage of metal are not easy to quantify and often seem negligible. This is mainly due to the absence of information concerning the production and regeneration stages (included in the corporate know-how) as well as the site-specific data regarding the ore availability. Last but not least, the resources usage to develop alternative pathways is a critical aspect, which should be carefully analyzed. The production of chemical, as well as of fuels, from biomass is still a debated argument. The scaling-up process from a laboratory to industrial scale is not always such convenient in particular as regarding the biomass

cultivation phase. Often the most diffused crops require higher amount of energy and resources during the entire production chain, without giving significant contributions if compared with the traditional fossil route.

However, the sole application of the LCA is not enough to assess the achievement of the three targets of sustainability which also include the social and the economic spheres. Therefore, a combination with other different tools complementary to LCA seems necessary. The combined use of LCA, LCC and SLCA can be a satisfactory example on how to express the sustainable development in its three dimensions. The investigation of the chemical sector by the use of a life cycle perspective together with some economic tools represents an already established approach and few examples can be found in the peer-review literature,<sup>5,6</sup> as well as the application of the risk assessment principles as a supporting information for a common LCA.<sup>7,8,9</sup>

## 4.2 Future developments

As stated above, there are multiple possibilities to assess the sustainability among the wide sector of industrial chemistry. For this reason the research started with the PhD program does not stop with the dissertation defense but it is intended to continue during the post-doc years.

The purpose is to investigate other case studies which cover different field from the applied chemistry up to the pharmaceutical sector, as well as the nanoparticles and the bio-based industry.

The overall idea is to extend the sustainability analysis to its three dimensions including the assessment of the social and the economic parts too by the application of methods already published in literature or developed by companies. An example could be the SEEBalance® approach developed by BASF.<sup>10,11</sup> Also called the *tri-objective sustainability analysis*, it is able to combine LCA with the cost and social impacts assessment of a product or process in order to make evaluation of the overall sustainability reached by the company.<sup>12</sup>

The usage of combined approaches is strictly recommended especially in the case of industrial productions, when decision making is mainly driven by the economic feasibility and social acceptance.

However, although the evaluation of the industrial sector will constitute the main purpose of our studies, the intention is to extend the targets of our future works to other aspects such as the prevention and valorization of natural resources (e.g. water,



land, etc.) and the assessment of the waste management systems. Both themes can be intended as an integrated part of the background of an industrial chemist involved in environmental issues, moreover they can be studied taking into account different situations which depend on the country under investigation. Therefore, in our opinion, a more comprehensive awareness of what sustainability means is possible just through the application of a site-specific analysis which takes into account the country availabilities and needs in terms of people, natural and economic resources.

## References

---

- 1 HIS - Process Economics Program (PEP), <http://chemical.ihs.com/PEP/yearbook.htm>, (accessed February 2015).
- 2 Nexant - Process Economics and Research Planning (PERP), <http://thinking.nexant.com/program/process-evaluationresearch-planning>, (accessed February 2015).
- 3 Ecoinvent Centre - formerly Swiss Centre for Life Cycle Inventories.
- 4 J. Dewulf, H. Van Langenhove, *Renewable-Based Technologies - Sustainability Assessment*, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2006.
- 5 Y. Kawauchi, M. Rausand, *Reliab. Eng. Syst. Safe*, 2002, **75**, 379-388.
- 6 M.A. Morales-Mora, E. Rosa-Dominguez, N. Suppen-Reynaga, S.A. Martinez-Delgadillo, *Process Saf. Environ.*, 2012, 90, 27-37.
- 7 C. Askham, A.L. Gade, O.J. Hanssen, *J. Clean. Prod.*, 2013, 51, 196-204.
- 8 E. Demou, S. Hellweg, K. Hungerbühler, *J. Clean. Prod.*, 2011, 19, 1339-1346.
- 9 M. Herrchen, W. Klein, *Pure Appl. Chem.*, 2000, 72, 1247-1252.
- 10 P. Saling, *Karlsruher Schriften zur Geographie und Ökologie*, 2007, vol. 22, pp. 1-115.
- 11 D. Kolsch, P. Saling, A. Kicherer, A. Grosse-Sommer, I. Schmidt, *Int. J. Sustainable Dev.*, 2008, 11, 1-23.
- 12 D. Kralisch, D. Ott, D. Gericke, *Green Chem.*, 2015, **17**, 123-145.

## Annex A

### Tables

**Table 3.1-** Inventory analysis for propene ammoxidation scenario. Source: Cespi et al. 2014<sup>67</sup> - reproduced by permission of Elsevier.

Processes	Unit	Scenario
		SOHIO
Feed molar ratio C <sub>3</sub> \NH <sub>3</sub> \air\inert\H <sub>2</sub> O	-	1.0\1.1\2.0\-\-
Catalyst in silica (50wt%)	-	K <sub>0.15</sub> Cs <sub>0.05</sub> Ni <sub>4.0</sub> Co <sub>0.5</sub> Mg <sub>2.5</sub> Fe <sub>2.0</sub> Bi <sub>0.5</sub> W <sub>0.5</sub> Mo <sub>12</sub> O <sub>x</sub>
Catalyst amount	g	1.0
ACN selectivity	%	83.0
ACN yield	%	81.0
Propylene conversion	%	98.0
Propylene input	kg	0.86
Propylene burned (99.9% efficiency)	kg	0.02
Propylene in air (0.01%)	kg	1.72E-05
Ammonia input	kg	0.39
Neutralized ammonia (80% of unreacted)	kg	0.04
Oxidized ammonia (20% of unreacted)	kg	0.01
Sulfuric acid input	kg	0.12
Ammonium sulfate	kg	0.16
Heat recovered	kJ	3.26E+03
Electricity recovered	kWh	2.81E-01
Natural gas avoided	m <sup>3</sup>	0.02

**Table 3.2-** Inventory analysis for propane ammoxidation scenarios. Source: Cespi et al. 2014<sup>67</sup> - reproduced by permission of Elsevier.

Processes	Unit	Scenarios			
		[1] AKCC	[2] MCC	[3] BP Poor	[4] BP Rich
Feed molar ratio $C_3NH_3$ \air\inert\H <sub>2</sub> O	-	1.0\1.2\3.0\14.8\-	1\1.5\15\-\-	1\2\1.5\5.7\3	5\1\2.8\-\1
Catalyst in silica (50wt%)	-	Mo <sub>1,0</sub> V <sub>0,33</sub> Nb <sub>0,11</sub> Te <sub>0,22</sub> O <sub>x</sub>	Mo <sub>1,0</sub> V <sub>0,3</sub> Nb <sub>0,12</sub> Te <sub>0,23</sub> O <sub>x</sub>	V Sb <sub>5</sub> W <sub>0,5</sub> Te <sub>0,5</sub> Sn <sub>0,5</sub> O <sub>x</sub>	V Sb <sub>1,4</sub> Sn <sub>0,2</sub> Ti <sub>0,2</sub> O <sub>x</sub>
Catalyst amount	g	1.7	1.7	1.7	1.7
ACN selectivity	%	65.5	65.5	56.7	61.9
ACN yield	%	59.0	59.6	39.0	8.9
Propane conversion	%	90.0	91.0	68.8	14.5
Propane input	kg	1.41	1.39	2.13	9.26
Propane burned (99.9% efficiency)	kg	0.14	0.12	0.66	7.91
Propane in air (0.01%)	kg	1.41E-04	1.25E-04	6.65E-04	7.92E-03
Ammonia input	kg	0.65	0.81	1.65	0.71
Neutralized ammonia (80% of unreacted)	kg	0.13	0.25	0.86	0.16
Oxidized ammonia (20% of unreacted)	kg	0.03	0.06	0.22	0.04
Sulfuric acid input	kg	0.38	0.73	2.49	0.45
Ammonium sulfate	kg	0.50	0.99	3.35	0.61
Heat recovered	kJ	5.79E+03	5.71E+03	6.00E+03	3.18E+03
Electricity recovered	kWh	0.50	0.49	0.52	0.27
Natural gas avoided	m <sup>3</sup>	0.18	0.16	0.86	10.22

[1] ASAHI KASEI CHEMICAL CORPORATION US PAT 6,143,916

[2] MITSUBISHI CHEMICAL CORPORATION EU PAT 529,853

[3] BP POOR US PAT 4,788,317

[4] BP RICH US PAT 5,094,989

**Table 3.3-** Impact assessment results for each category considered. Source: Cespi et al. 2014<sup>67</sup> - reproduced by permission of Elsevier.

Impact Categories	Unit	SOHIO	AKCC	MCC	BP poor	BP rich
Climate change on human health	DALYs	3.05E-06	3.69E-06	4.12E-06	6.72E-06	7.67E-06
Climate change on ecosystems	species·yr	1.73E-08	2.09E-08	2.33E-08	3.80E-08	4.35E-08
Metal depletion	\$	8.93E-03	5.37E-03	5.37E-03	3.74E-03	4.78E-03
Fossil fuel depletion	\$	2.40E-01	3.15E-01	3.37E-01	4.98E-01	5.11E-01

## Equations

$$\sum_{i=1}^n \dot{m}_i^{(e)} \cdot \tilde{C}p_i^{(e)} \cdot (T^{(e)} - T^{(SR)}) - \sum_{i=1}^n \dot{m}_i^{(u)} \cdot \tilde{C}p_i^{(u)} \cdot (T^{(u)} - T^{(SR)}) - \dot{Q}_r + \dot{Q}_s = 0$$

$\dot{m}_i$  = moles of each substance input (e) and output(u) of the system;

$\tilde{C}p_i$  = heat capacity of each substance input (e) and output(u) of the system;

$T$  = temperature input (e) and output(u) of the system;

$T^{(SR)}$  = temperature of reference state(0°C)

3.4

$$\dot{Q}_r = \dot{m}_{C_3} \cdot \Delta_r \tilde{H}$$

$\dot{m}_{C_3}$  = moles of propeneor prapanereacted;

$\Delta_r \tilde{H}$  = heat of reaction.

3.5

$$\dot{Q}_s = \dot{m}_{H_2O} \cdot \tilde{C}p_{H_2O} \cdot (T_{H_2O}^{(u)} - T_{H_2O}^{(e)})$$

$\dot{m}_{H_2O}$  = moles of water in coils;

$\tilde{C}p_{H_2O}$  = heat capacity of water in coils;

$T_{H_2O}$  = temperature of water input (e) and output(u) the coils.

3.6

98

## Annex B

### Tables

**Table 3.4** - LCI Glycerol dehydration to acrolein. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Input	Process name input	Amount	Unit
Input	Water, cooling, unspecified natural origin/kg *	2.6E06	kg
	Water, process, unspecified natural origin/ kg *	5.2E03	kg
	Chemicals organic, at plant/GLO U **	1.2E-02	kg
	Argon *	2.5E+00	kg
	Chemical plant, organics/RER/I U **	4.0E-10	p
	Transport, freight, rail/RER U **	5.2E-01	tkm
	Transport, lorry >16t, fleet average/RER U **	8.6E-02	tkm
	Steam, for chemical processes, at plant/RER U *	5.4E+00	kg
	Steam, for chemical processes, at plant/RER U ***	3.7E+00	kg
	Natural gas, burned in industrial furnace > 100kW/ RER U *	1.2E+00	MJ
	Electricity, medium voltage, production FR, at grid/FR U *	3.7E-01	kWh
	Silicon *	3.8E-06	kg
	Tungsten *	3.0E-04	kg
	Titanium dioxide, production mix, at plant/RER U *	3.0E-04	kg
Air emissions	Carbon dioxide, fossil *	6.3E-01	kg
	Heat, waste **	6.8E+02	kJ
Avoided processes	Heat, unspecific, in chemical plant/RER U *	3.4E+02	kJ
	Electricity, production mix IT/IT U *	2.9E-02	kWh

\* Calculated on the basis of mass balance and data furnished by patent (*US. Pat.*, 0 053 595 A1, 2013)

or internal report (Chem Systems – Process Evaluation/Research Planning (PERP program), *Acrylic Acid 08/09-3*, 2010.)

\*\* Collected from Ecoinvent database.

\*\*\* Collected from literature (P.A. Holman, D.R. Shonnard, J.H. Holles, *Ind. Eng. Chem. Res.*, 2009, **48**, 6668-6674).

**Table 3.5 - LCI Scenario A: Acrolein from glycerol produced as a by-product of triglycerides trans-esterification. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.**

	Process name input	Amount	Unit
<b>Input</b>			
<i>Cultivation phase</i>	Rape seed conventional, at farm/DE U *	3.3E+01	kg
<i>Oil production</i>			
<u>Inputs</u>	Heat, natural gas, at industrial furnace >100kW/RER U *	2.3E+01	MJ
	Transport, freight, rail/RER U *	7.4E-02	tkm
	Transport, lorry >16t, fleet average/RER U *	1.2E-02	tkm
	Transport, lorry 3.5-16t, fleet average/RER U *	3.3E+00	tkm
	Oil mill/CH/I U *	1.1E-08	p
	Bentonite, at processing/DE U *	7.6E-02	kg
	Hexane, at plant/RER U *	3.7E-02	kg
	Phosphoric acid, industrial grade, 85% in H <sub>2</sub> O, at plant/RER U *	1.2E-02	kg
	Electricity, medium voltage, production UCTE, at grid/UCTE U *	1.4E+00	kWh
<u>Outputs &amp; Waste</u>	Carbon dioxide, biogenic *	3.9E+01	kg
	Heat, waste *	1.6E+01	MJ
	Hexane *	3.6E-02	kg
	Treatment, sewage, from residence, to wastewater treatment, class 2/CH U *	8.8E-05	m <sup>3</sup>
<i>Triglycerides trans-esterification</i>			
	Nitrogen, in air *	5.9E-02	kg
	Methanol, at regional storage/CH U *	1.7E+00	kg
	Sodium methoxide, at plant/GLO U *	2.9E-01	kg
	Hydrochloric acid, 30% in H <sub>2</sub> O, at plant/RER U *	2.2E-01	kg
	Sodium hydroxide, 50% in H <sub>2</sub> O, production mix, at plant/RER U *	6.3E-02	kg
	Compressed air, average generation, <30kW, 10 bar gauge, at compressor/RER U *	1.2E-01	Nm <sup>3</sup>
	Steam, for chemical processes, at plant/RER U *	6.2E+00	kg
	Electricity, medium voltage, at grid/IT U *	3.6E-01	kWh
	Crude glycerol 84% <sup>**i</sup>	2.1E+00	kg
	Biodiesel <sup>**ii</sup>	1.7E+01	kg
<i>Glycerol refining (84%→100%)</i>			
	Nitrogen, in air *	9.5E-02	kg
	Sodium hydroxide, 50% in H <sub>2</sub> O, production mix, at plant/RER U *	3.0E-03	kg
	Compressed air, average generation, <30kW, 10 bar gauge, at compressor/RER U *	7.6E-02	Nm <sup>3</sup>
	Steam, for chemical processes, at plant/RER U *	3.3E+00	kg
	Natural gas, burned in power plant/IT U *	1.0E+00	kWh
	Electricity, medium voltage, at grid/IT U *	1.4E-01	kWh
<b>Avoided products</b>	Diesel, at refinery/RER U *	1.7E+01	kg

\* Calculated on the basis of mass balance and data furnished by Spiga BD Srl.

\*\* Calculated on the basis of mass balance.

<sup>i</sup> Not included in the inventory, yield conversion into acrolein is 100%.

<sup>ii</sup> This flow was included in the inventory indirectly (see “Avoided products” field).

**Table 3.6 - LCI Scenario B: Acrolein from glycerol produced as a by-product of triglycerides hydrolysis.** Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

	Process name input	Amount	Unit
<b>Input</b>			
<i>Breeding phase</i>	Beef (farm type 23) *	2.3E+00	kg
<i>Tallow production</i>	Tallow, at plant/CH U *	2.3E+01	kg
<i>Hydrolysis process</i>	Water, process, unspecified natural origin/kg *	1.4E+01	kg
	Compressed air, average generation, >30kW, 7 bar gauge, at compressor/RER U *	1.8E-02	Nm <sup>3</sup>
	Steam, for chemical processes, at plant/RER U *	5.9E+00	kg
	Electricity, medium voltage, at grid/IT U *	4.6E-01	kWh
	Crude glycerol 20% **,i	2.1E+00	kg
<i>Glycerol refining (20%→99.5%)</i>	Crude fatty acids *, ii	2.0E+01	kg
	Water, cooling, unspecified natural origin/m <sup>3</sup> *	5.0E-01	m <sup>3</sup>
	Compressed air, optimized generation, >30kW, 7 bar gauge, at compressor/RER U *	8.5E+00	Nm <sup>3</sup>
	Steam, for chemical processes, at plant/RER U *	7.0E+00	Kg
	Electricity, medium voltage, at grid/IT U *	9.4E-02	kWh
<i>Fatty acids refining</i>	Water, cooling, unspecified natural origin/m <sup>3</sup> *	1.2E+00	m <sup>3</sup>
	Compressed air, optimized generation, >30kW, 7 bar gauge, at compressor/RER U *	1.2E-01	Nm <sup>3</sup>
	Steam, for chemical processes, at plant/RER U *	1.9E+01	kg
	Electricity, medium voltage, at grid/IT U *	6.2E-01	kWh
<b>Avoided products</b>	Rape oil, at oil mill/RER U *	2.1E+01	kg

\* Calculated on the basis of mass balance and data furnished by SO.G.I.S. SpA.

\*\* Calculated on the basis of mass balance.

<sup>ii</sup> Not included in the inventory, yield conversion into acrolein is 100%.

<sup>ii</sup> This flow was included in the inventory indirectly (see “Avoided products” field).



**Table 3.7** - LCI Acrolein production from propylene oxidation. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

	Process name input	Amount	Unit
<b>Input</b>	Water, cooling, unspecified natural origin/kg *	2.7E-05	kg
	Water, process, unspecified natural origin/ kg *	1.7E-04	kg
	Steam, for chemical processes, at plant/RER U *	6.0E-03	kg
	Natural gas, burned in industrial furnace > 100kW/ RER U *	7.0E+00	MJ
	Electricity, medium voltage, production FR, at grid/FR U *	1.6E+00	kWh
	Propylene, at plant/RER U *	9.9E-01	kg
	Chemical plant, organics/RER/I U **	4.0E-10	p
	Transport, freight, rail/RER U **	5.2E-01	tkm
	Transport, lorry >16t, fleet average/RER U **	8.6E-02	tkm
	Molybdenum ***	3.5E-04	kg
	Iron ***	4.1E-05	kg
	Bismuth ***	5.1E-05	kg
	Cobalt ***	1.3E-04	kg
	Potassium ***	9.6E-07	kg
	Silicon ***	1.3E-05	kg
<b>Air emissions</b>	Carbon dioxide, fossil *	7.8E-01	kg
<b>Avoided processes</b>	Heat, unspecific, in chemical plant/RER U *	1.9E+03	kJ
	Electricity, production mix IT/IT U *	1.7E-01	kWh

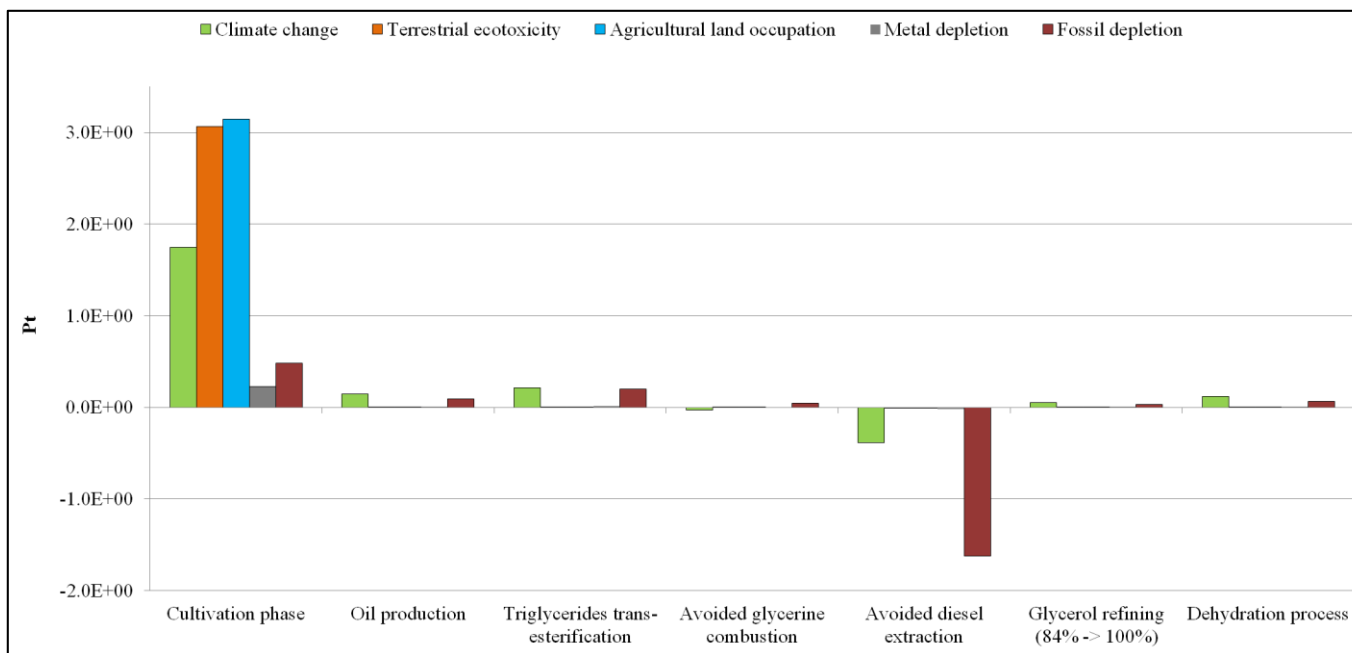
\* Calculated on the basis of mass balance and internal report

(Chem Systems – Process Evaluation/Research Planning (PERP program), *Epichlorohydrine 99/00S11*, 2000.)

\*\* Collected from Ecoinvent database.

\*\*\* Calculated on the basis of mass balance and data furnished by patent (*EU. Pat.*, 1 005 908 A2, 2000).

**Figure 3.1** - Contribution analysis Scenario A - acrolein produced from glycerol obtained as a co-product of triglyceride trans-esterification (ReCiPe 2008 I/A, Single score). Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



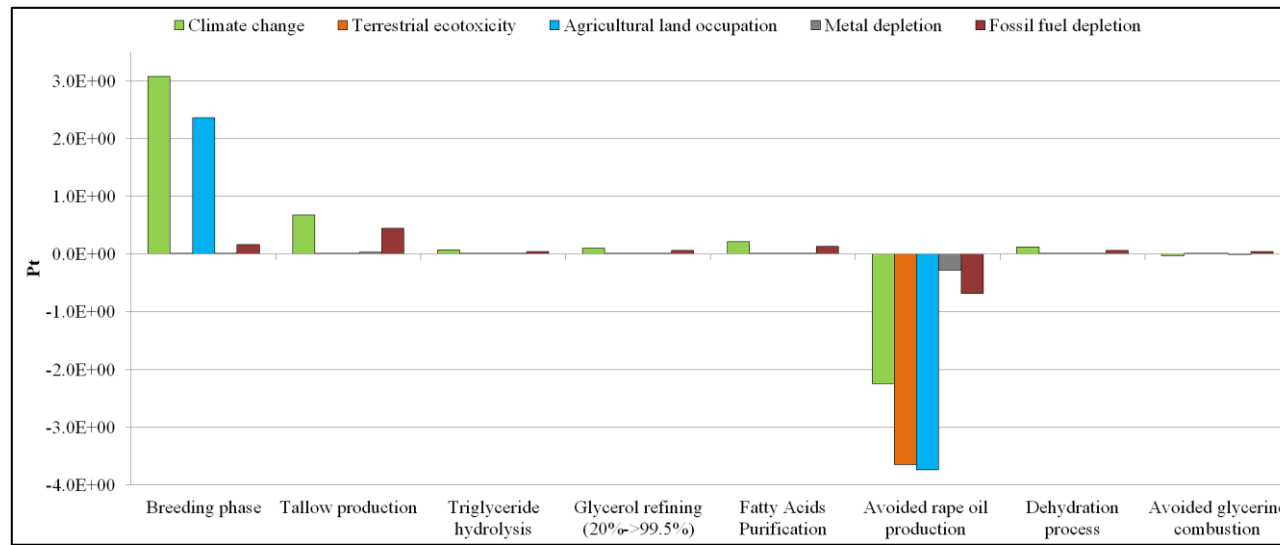
**Table 3.8** - . Contribution analysis Scenario A - Acrolein produced by glycerol obtain as a co-product of triglycerides trans-esterification (ReCiPe 2008 I/A, Single score). Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Impact category	Unit	Total	Cultivation phase	Oil production	Triglycerides trans-esterification	Avoided glycerine combustion	Avoided diesel extraction	Glycerol refining (84%→100%)	Dehydration process
Agricultural land occupation	species·yr	1.5E-06	1.5E-06	1.2E-10	2.1E-10	4.2E-11	-1.4E-10	6.5E-12	7.1E-11
Terrestrial ecotoxicity	species·yr	1.4E-06	1.4E-06	4.5E-11	7.9E-11	2.8E-11	-7.0E-10	1.3E-11	3.1E-11
Climate change Ecosystems	species·yr	3.7E-07	3.5E-07	2.9E-08	4.2E-08	-6.3E-09	-7.7E-08	9.8E-09	2.4E-08
Climate change Human Health	DALY	5.6E-05	5.2E-05	4.4E-06	6.4E-06	-9.5E-07	-1.2E-05	1.5E-06	3.6E-06
Fossil fuel depletion	\$	-4.6E-01	3.2E-01	6.2E-02	1.3E-01	3.0E-02	-1.1E+00	2.1E-02	4.2E-02
Metal depletion	\$	1.6E-01	1.5E-01	6.6E-03	1.1E-02	-6.1E-04	-1.4E-02	8.8E-04	4.7E-03

**Table 3.9** - Scenario A: percentage contribution of each life cycle stage in terms of Impacts and Avoided impacts. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Impact category	Cultivation phase	Oil production	Triglycerides trans-esterification	Avoided glycerine combustion	Avoided diesel extraction	Glycerol refining (84% -> 100%)	Dehydration process
<i>Impacts</i>							
Climate Change	77	6	9	-	-	2	5
Terrestrial ecotoxicity	100	0	0	0	-	0	0
Agricultural land occupation	100	0	0	0	-	0	0
Metal depletion	87	4	6	-	-	0	3
Fossil fuel depletion	53	10	22	5	-	3	7
<i>Avoided impacts</i>							
Climate Change	-	-	-	8	92	-	-
Terrestrial ecotoxicity	-	-	-	-	100	-	-
Agricultural land occupation	-	-	-	-	100	-	-
Metal depletion	-	-	-	4	96	-	-
Fossil fuel depletion	-	-	-	-	100	-	-

**Figure 3.2** - Contribution analysis Scenario b - acrolein produced from glycerol obtained as a co-product of triglyceride hydrolysis (ReCiPe 2008 I/A, Single score).  
 Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.



**Table 3.10** - Contribution analysis Scenario B – Acrolein produced by glycerol obtain as a co-product of hydrolysis (ReCiPe 2008 I/A, Characterization analysis). Source: Cespi et al. 2015<sup>101</sup> – reproduced by permission of The Royal Society of Chemistry.

Impact category	Unit	Total	Breeding phase	Tallow production	Triglyceride hydrolysis	Glycerol refining (20%→99.5%)	Fatty Acids purification	Avoided rape oil production	Dehydration process	Avoided glycerine combustion
Agricultural land occupation	species·yr	-6.4E-07	1.1E-06	5.4E-10	1.2E-11	5.8E-11	2.4E-11	-1.7E-06	7.1E-11	4.2E-11
Terrestrial ecotoxicity	species·yr	-1.7E-06	1.2E-11	8.0E-11	2.2E-11	3.3E-11	6.5E-11	-1.7E-06	3.1E-11	2.8E-11
Climate change Ecosystems	species·yr	3.9E-07	6.1E-07	1.3E-07	1.4E-08	2.0E-08	4.2E-08	-4.5E-07	2.4E-08	-6.3E-09
Climate change Human Health	DALY	5.9E-05	9.2E-05	2.0E-05	2.2E-06	3.0E-06	6.3E-06	-6.7E-05	3.6E-06	-9.5E-07
Fossil fuel depletion	\$	1.8E-01	1.1E-01	2.9E-01	3.1E-02	4.1E-02	9.0E-02	-4.5E-01	4.2E-02	3.0E-02
Metal depletion	\$	-1.5E-01	9.7E-04	2.4E-02	5.8E-04	3.6E-03	1.6E-03	-1.8E-01	4.7E-03	-6.1E-04

**Table 3.11** - Scenario B: percentage contribution of each life cycle stage in terms of Impacts and Avoided impacts. Source: Cespi et al. 2015<sup>101</sup> – reproduced by permission of The Royal Society of Chemistry.

Impact category	Breeding phase	Tallow production	Triglyceride hydrolysis	Glycerol refining (20%→99.5%)	Fatty Acids Purification	Avoided rape oil production	Dehydration process	Avoided glycerine combustion
<i>Impacts</i>								
Climate Change	72	16	2	2	5	-	3	-
Terrestrial ecotoxicity	4	29	8	12	24	-	12	10
Agricultural land occupation	100	0	0	0	0	-	0	0
Metal depletion	3	68	2	10	4	-	13	-
Fossil fuel depletion	17	46	5	6	14	-	7	5
<i>Avoided impacts</i>								
Climate Change	-	-	-	-	-	99	-	1
Terrestrial ecotoxicity	-	-	-	-	-	100	-	-
Agricultural land occupation	-	-	-	-	-	100	-	-
Metal depletion	-	-	-	-	-	100	-	0
Fossil fuel depletion	-	-	-	-	-	100	-	-

**Table 3.12** - Typical analyses of various types of glycerol produced at different industrial sites by triglycerides trans-esterification (extrapolated from *US Pat.*, 8 530 697 B2, 2013). Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Site	Diester Industries		
	Robbe	Saipol	Marl (RFA)
<b>Production (kt/year)</b>	10	25	15
<b>Glycerol (wt %)</b>	65	93	85
<b>Water (wt %)</b>	31	4	10
<b>NGOM* (wt %)</b>	1	1	0.5
<b>Ash (wt %)</b>	3 (Na <sub>2</sub> SO <sub>4</sub> )	2.5 (NaCl)	4.5 (NaCl)
<b>Methanol (wt %)</b>	0.3	0.2	< 0.01

**Table 3.13** - LCIA using crude instead of purified glycerol. Source: Cespi et al. 2015<sup>101</sup> - reproduced by permission of The Royal Society of Chemistry.

Analysis method	Impact category	Unit	Scenario A	Scenario B
ReCiPe2008	Total Impact	Pt	8.5E+00	-4.0E+00
	Agricultural land occupation	species·yr	1.5E-06	-6.4E-07
	Terrestrial ecotoxicity	species·yr	1.4E-06	-1.7E-06
	Climate change Ecosystems	species·yr	3.6E-07	3.8E-07
	Climate change Human Health	DALY	5.4E-05	5.6E-05
	Fossil fuel depletion	\$	-4.8E-01	1.5E-01
	Metal depletion	\$	1.6E-01	-1.5E-01

