



Norwegian University of
Science and Technology

Life Cycle Assessment of platform chemicals from fossil and lignocellulosic biomass scenarios

LCA of phenolic compounds, solvent, soft and hard plastic
precursors

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Master in Industrial Ecology

Submission date: June 2011

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MASTER THESIS. MARTIN GALLARDO*

ABSTRACT

One of the challenges of our time is the substitution of the existing fossil based economy by a green economy within the framework of sustainable development of our society. Biomass, especially from lignocelluloses, is a promising solution for the substitution of fuels, energy, chemicals and materials from fossil sources in a so called “Biorefinery”. The production of chemicals from biomass presents higher mass and carbon theoretical efficiency, and it seems an interesting alternative to provide a renewable path for globally and widely demanded platform chemicals like phenols, solvents (Acetone), soft plastic precursor (Polyethylene) and hard plastic precursor (Polypropylene).

In this report, the environmental loads associated to the production of chemicals (Phenolic compounds, Acetone, PolyHydroxyButyric Acid and Polylactic Acid) from lignocellulose biomass scenarios (Poplar and Eucalyptus) are evaluated and compared to the petrochemical equivalents. Life Cycle Assessment Methodology and the latest Global Warming Potential Indicator that accounts biogenic greenhouse gas effect related to the rotation period of the feedstock along the entire carbon cycle are used along this study.

The production of chemicals from biomass could contribute to possible reductions between 37% and 48% on greenhouse gas emissions for the functional unit when taking into account the entire carbon cycle and not only cradle to gate approach. Also, up to 80% fossil fuel can be saved while ecotoxicity indicators present much lower values for the production of chemicals from biomass. PHB seems to be the most environmentally friendly of all the chemicals from biomass, and phenolic compounds the worst. But there are some trade-offs; chemicals from biomass may increase other impact categories such Eutrophication and Acidification, but also Human toxicity, Photochemical Oxidant Formation and Particulate Matter Formation. Last but not least, water depletion is a fundamental issue involved, being substantially higher for chemicals from biomass, even when irrigation of certain wood species may not occur. Decrease of fertilizers and irrigation, new solutions for disposal, treatment and recycling of ash and gypsum, increase of yields and production, energy efficiency techniques and a cleaner electricity mix, could bring the production of chemicals from biomass to an status where they are dramatically better in all impact indicators if all the stakeholders on the life cycle of the chemicals from biomass (Agriculture and Industry sectors, research institutions, policy makers and final customers) get involved.

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14th June 2011

*"We can use our scientific knowledge to improve and beautify the earth,
Or
we can use it to poison the air, corrupt the waters, blacken the face of country
And harass our souls with load and discordant noises,
Or,
We can use to mitigate or abolish all these things."
John Burroughs (1837-1921)
American writer and naturalist*

PREFACE

Acknowledgments

This report is written as fulfilment of the Master Thesis for my MSc Degree on Industrial Engineering (Energy Technologies) for both the Norwegian University of Science and Technology (NTNU) and the University Madrid Carlos III (UC3M).

I feel really grateful to my supervisors at Industrial Ecology, Anders Hammer Strømman and Francesco Cherubini. Anders has helped me to raise the quality of the content and the presentation of my research, while Francesco has been closely working to build and correct my research. His perspective, patience and quality of the advices have been priceless. Also, I must thank Geoffrey Guest for his help in the inventory development, and my officemates Oddbjørn Dahlstrøm and Octavio Torres, for sharing their ideas about the thesis and life in general.

Also, I must remember the help received from CEPSA, S.A. It was extremely helpful and very easy to work with them, besides their vision on environmental protection has been certified as a reference in the industry for years.

Last, but not least, my deepest thanks to my girlfriend, for her love understanding and support. Having her by my side encourage me to become a better person and surpass any obstacle. I would like to make a special mention to my parents, my brother and my best friend; they were always supporting me from the distance, which I really appreciate it.

Martin Gallardo Hipólito

Trondheim, 14.6.2011

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1.1 Goal and scope definition of the study

The following study responds to a Life Cycle Assessment (LCA) regarding a set of the most important petrochemicals and its possible bio derived substitutes in the Spanish framework. The objective of this study is to understand deeper the environmental performance of such a substitution in order to provide a better insight of the processes involved, its related impacts and where potential improvements can be achieved. The functional unit is “1 unit of platform chemicals composed by 1 kilogram of phenolic compounds, 1 kilogram of solvent, 1 kilogram of soft plastic precursor and 1 kilogram of hard plastic precursor”. The Carbon Cycle follows the indications for the biogenic Global Warming Potential lately researched. For LCIA (Life Cycle Impact Assessment), ReCiPe Method was used; selecting the most relevant indicators for our results. A final discussion is held containing justifications and clarifications of the inventory development and main findings of the study, where conclusions can be extracted to help future research and policy making strategies.

1.2 Environmental sustainability goal: Green economy concept and Life Cycle Assessment (LCA)

Environmental Sustainability is set as one of the Millennium Development Goals by the United Nations (U.N, 2005). From the environmental point of view, anthropogenic causes, like burning petroleum derived fuels and products, are modifying the carbon cycle once we are releasing CO₂ rapidly to the atmosphere from carbons sequestered hundreds of millions years before; hence, some unexpected consequences can be derived of it, like a greenhouse effect on a planetary scale. This is called “Anthropogenic Climate Change”. It is widely accepted by the scientific community and most of the countries and organizations across the world, and it implies a change in the policies of those countries that agreed on the Kyoto Protocol (1997). Article 2 of The Kyoto protocol promotes sustainable forms of agriculture in light of climate change considerations, as well as, supports research on, and promotion, development and increased used of, new and renewable forms of energy, of carbon dioxide sequestration technologies and of advanced and innovative environmentally sound technologies (Kyoto Protocol, 1997).

One of the most capable approaches for the achievement of the Environmental sustainability target is the green economy concept.

“the one that results in improved human well-being and social equity, while significantly reducing environmental risks and ecological scarcities. In its simplest expression, a green economy can be thought of as one which is low

carbon, resource efficient and socially inclusive. In a green economy, growth in income and employment should be driven by public and private investments that reduce carbon emissions and pollution, enhance energy and resource efficiency, and prevent the loss of biodiversity and ecosystem services.” (UNEP Green Economy Report, 2011)

The current increasing focus on global warming makes it easy to forget holistic perspectives of environmental impacts (for example, extraction, transport and refining of petroleum account for other environmental threats for ecosystems and humans) and not only emissions related to global warming potential. While solving one type of environmental problem by changing one process, another environmental issue could arise in other one. Life Cycle Assessment (LCA) is a methodological framework that could offer this holistic focus on the environmental performance of a system and it stands as one of the most promising tools for the green economy. One example of this implication of Life Cycle Assessment on decision making bodies is the acceptance of Life Cycle Assessment from the European Union as a state-of-the-art methodology, including aspects of Life Cycle Thinking in the 6th Environmental Action Programme (European Commission, 2001; European Topic centre on sustainable consumption and Production).

But what is exactly Life Cycle Assessment (LCA)? According to the environmental management standards *ISO 14040:2006* and *ISO 14044:2006* (International Organization for Standardization) “Life Cycle Assessment is a technique [...] compiling an inventory of relevant inputs and outputs; and interpreting the results of the inventory and impact phases in relation to the objectives of the study”. It can be summarize as a tool to assess the environmental impacts of product systems and services, accounting for the emissions and resource uses during the production, distribution, use and disposal of a product (Hertwich, E.G, 2005). It emphasizes the importance of including all the phases in the life cycle of a product. The objective of an LCA study is generally to compare different technological systems with respect to their environmental performance. The importance of the LCA perspective is to obtain a holistic understanding of the environmental aspects associated with a service or product delivered from a system. (Strømman, 2008). The consequence of understanding the relationships within the entire life cycle and the environment make LCA a solid and relevant environmental tool that allows us to transcribe its implications in a clearer way for policy makers and industry leaders. For example, Mercedes-Benz is one of the industry players which are developing further the inclusion of LCA Methodology into its Life Cycle:

“To be confident with measures to improve the environmental performance of products requires the system perspective. Therefore, Life Cycle Assessment and Life Cycle Engineering are valuable tools to achieve this goal” [Finkbeiner, 2006].

1.3 Lignocelluloses biomass and biorefinery concept. Previous studies and motivation

One of the most promising resources to mitigate climate change is the use of biomass, since it is an effective way of producing a variety of fuels, energy (heat and power) and materials (from wood based elements to chemicals from biomass) decreasing CO₂-emissions (Cherubini, 2010). We can define Biomass as abbreviation given to any organic matter of recent origin (then, not fossil) which was derived from animals, plants, fungi and bacteria as a result of the conversion process photosynthesis. Just by taking a look at the European Union Directives biomass should play an important role in the future as part of the solution for a scenario without fossil derived energy and materials since biomass is abundant and accessible resource on the Earth and it can be renewable if well managed (UE Biomass Action Plan, 2005). This approach to substitute petroleum (oil and gas) products is called “biorefinery” (Cherubini, 2010; Demirbas, 2010; Kamm et al, 2006).

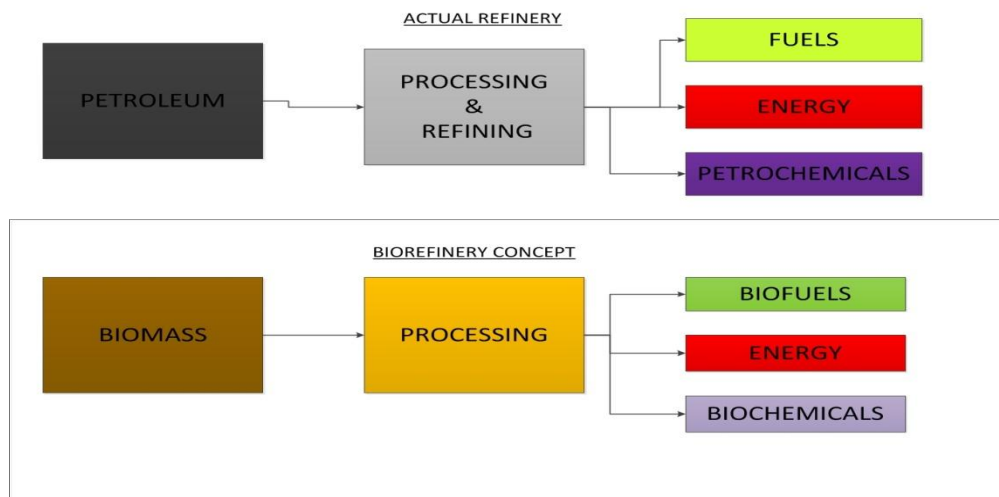


Figure 1: Oil and gas value chain versus biorefinery value chain

Although the biorefinery feedstock can be provided from different kinds of biomass, in the last years some studies have noticed the potential of lignocellulose (composed mainly by cellulose, hemicelluloses and lignin) for biorefinery purposes. (Cherubini, 2010; FitzPatrick et al, 2010 Hamelinck, 2005; Kamm et al, 2006; Michels, 2010)

“After green biomass, lignocelluloses feedstock is the most common raw material for continental biorefinery processes” (Kamm et al, 2006)

In-depth studies about crop and wood residues, short rotation wood, Poplar and Eucalyptus production and their ecological implications have been made with the intention of providing lignocellulose to the production of fuels and combined heat and power. (Cherubini, 2010; Da Costa Sousa, 2009; Guest et al, 2010; Karacic, 2005; González-García, S. et al., 2009).

Within this framework, it has been pointed out that the biochemical oriented biorefinery presents the highest theoretical efficiency in carbon and mass terms (Cherubini, F. and A. H. Strømman (2010). In my prethesis (Gallardo.M, 2010) the theoretical efficiencies of Cherubini and Strømman were compared to “state of the art” biorefineries approaches, confirming that the biochemical oriented biorefinery can be already more efficient in terms of carbon and mass balance, concluding that *“Production of Succinic Acid, Levulinic Acid, Furfural or Xylitol should be taken as real option of platform chemicals that are able to compete with petrochemicals in terms of volume and range of applications. Ethanol production, although it is the most energy efficient approach of the system studied, produces Carbon Dioxide in its fermentation process, subtracting interest to this approach. Both systems produce around 50% of a high carbon content residue from the entire feedstock, around half of it composed by lignin. This residue should be used in a very carbon efficient process, for example, synthetic diesel or production of chemicals from biomass from the phenols present in that residue”*. At that point, different common chemicals from biomass feedstock had been already identified in the previous years. (Haveren et al, 2008; Marshall and Alaimo, 2010; U.S PNNL/NREL, 2004).

It has been already research life cycle assessment of the biorefinery concept that includes a chemical oriented approach (Cherubini and Jungmeier, 2009), even out of the biorefinery concept, other environmental studies have been made about fermentation of sugars into bioplastics: PHA (Harding et al, 2007) and PLA production (Dornburg, 2006; Groot and Borén, 2010; Vink et al, 2003, Vink et al, 2010), but still they are focused on energy consumption and CO₂ mitigation, mostly carrying out CO₂ accounting starting from the CO₂ sequestration on soil.

This lack of a Full-LCA of a biochemical oriented biorefinery for the substitution of the most important petrochemicals seemed to be a relevant and interesting study for this thesis, especially after concluding in the prethesis that the chemicals from biomass has a large potential in terms of efficiency and that a complete environmental evaluation must be researched. This topic, related to lignocelluloses biomass and biorefineries LCA, satisfied the interest of the Industrial Ecology department at NTNU, where this thesis was entirely developed.

1.4 State of the art of Petrochemicals and selection of its possible substitutes from lignocelluloses biomass.

1.4.1 State of the art and selection of petrochemicals

Petroleum derived resources, like oil and gas, are essential for today’s human society, as 84 million barrels of petroleum derivatives are consumed every day (IEA, 2007). The oil and gas sector is based on well known processes of exploitation, logistics, refining and chemicals processing. Literature is extensive about it, though, it is a sector in continuous improvement to understand the geological structure, find new wells, exploit them better or increase yields.

Interesting for us is the fact that 7.8% of the total oil and gas is converted into petrochemicals. (OECD/IEA, 2005).

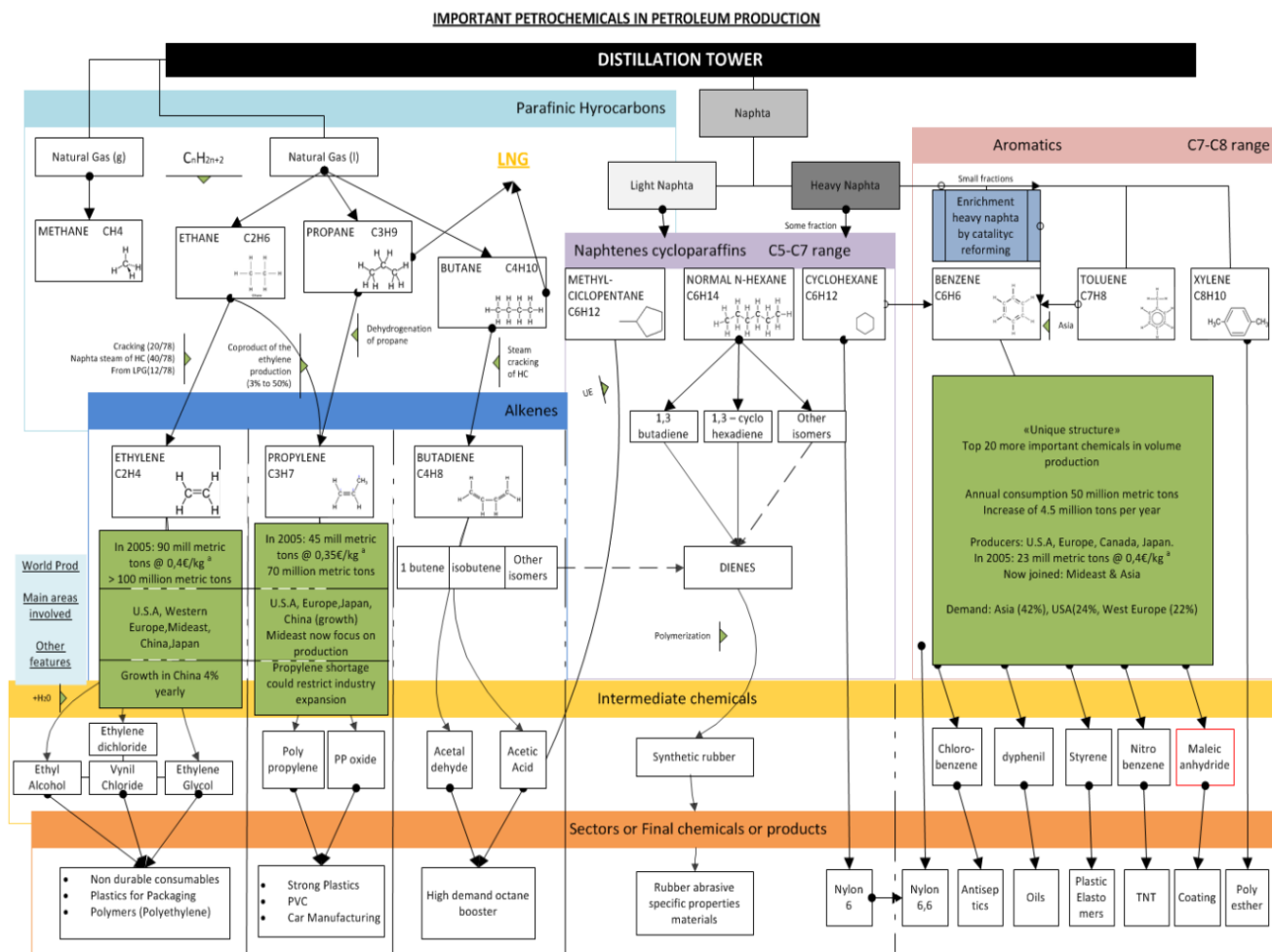


Figure 2: Schematic flow diagram of petrochemicals production from fossils. Upper part of the distillation tower. (Gallardo, M, 2010).

The Port of Rotterdam is responsible for 4-5% of the total world production of base chemicals (Haveren et al, 2007). Using their data we can estimate an annual production volume of about 250-300 million tonnes worldwide of petrochemicals. From them, Benzene, ethylene and propylene are massively used in products of our daily life (APPE).

“Global demand for ethylene exceeded 100 million metric tons per year in 2005. The largest world market for ethylene is the production of polymers, with the largest being polyethylene (PE). During 2008–2013, polyethylene will continue to be the largest consumer of ethylene, increasing to nearly 60% of total consumption and growing at a rate of 3% per year. Large growth markets include LLDPE at 4.3%, driven by substitution of LLDPE for other polyethylene in packaging. The largest single ethylene market, HDPE, with 27% of the total.”

[SRI consulting]

Meanwhile, for propylene:

“Propylene demand has historically exceeded ethylene demand and the forecast is for this to continue with a differential of about 0.5%/year. The driver is stronger growth in polypropylene compared to polyethylene. This plastic is tougher and can replace metal applications in automobiles and other consumer durables” [GLG Consulting group]. “Global consumption of Polypropylene (PP) is expected to witness healthy growth rate and cross 51 million metric tons by 2010”. [Global Industry Analysts, Inc]

The nylon industry, as main consumer of benzene, provides in its reports a complete nylon value chain report “Global benzene production touched 40.8 million tons in 2007, an increase of 3.9% over previous year” (Yarn and Fibers Benzene Report, 2011). One of their subproducts, phenol, has a significant share downstream.

“In 2008, the world-wide phenol capacity for phenol production was around 9.9 million tons, with 98.5% based on the cumene-to-phenol process. The total production in 2008 was around 8.7 million tons. [...], the largest use with around 44% was for the production of bisphenol-A, followed by phenolic resins (26%), cyclohexanone/caprolactame (12%), and others like alkylphenols (4%)”. [Weber and Weber, 2010]

In total Benzene, Propylene and Ethylene accounts for around 250 million metric tons and growing, most of the petrochemical production in the world and its possibilities as precursors are multiple and well known, for example, in the production of **Phenols**, **Polypropylene** and **High Density Polyethylene (HDPE)** respectively, which are very interesting and demanded petrochemicals. We have added **Acetone** to our study, for two main reasons, its importance as solvent in multiple processes in the industry, and for the fact of being co-product in the cumene-phenol process, although its production and consumption values are lower; around 5.5 million metric tons (SRI Consulting).

Phenols, Acetone, Polypropylene and High Density Polyethylene (HDPE) will be then our targeted petrochemicals. We had to find proper alternatives to them from lignocelluloses biomass.

1.4.2 Substituting petrochemicals with lignocelluloses biomass

1.4.2.1 Pathways of lignocelluloses biomass derivatives

There are two main ways to produce equivalent platform chemicals to those from fossil derived sources: Arriving to the same chemical structure or finding a chemical that can perform the same duties. What we want is a product that has similar properties to act as a platform chemical coming from renewable sources and present environmental advantage. In our case, acetone from

ethanol is a clear example of the first strategy, while Polylactic Acid and PHA are examples of the second one. Phenolic compounds are in between these two alternatives, since phenolic compounds contain the type phenol, but also other similar ones.

1.4.2.2 Substituting phenols by Phenolic compounds from lignin.

Phenolic resins from lignin are a potential substitute of petro derived phenols (Kamm et al. 2006). There are several methods (Effendi et al, 2008), but pyrolysis of lignin into pyrolysis oil (Basu, 2010; Gayubo et al, 2010) prior to phenols extraction seems to be an adequate approach (Brehmer et al, 2009; Cherubini and Ulgiati, 2010; Ekerdt, J. G., 2010; Pakdel et al, 1992; and Kim, 2011; Pinto, P.C.R. & Borges, E.A., 2011). Some of the advantages that present the production of phenolic compounds are the increase of mass and carbon efficiency in the biorefinery (Mass and Carbon goes to products instead of being burnt) and possible environmental advantages (González-García, 2010), but it yield low quantities (Pandey and Kim, 2011).

1.4.2.3 Acetone from bioethanol

Acetone from ethanol seems a logical path since ethanol fermentation, even from lignocellulose, is a well known process (Lynd, 1996; Olsson, 1994; Stenberg, 1999). There is still current research on developing more efficient processes for 2nd generation bioethanol (Hamelinck et al, 2004; Pfromm, P.H, 2008; Wingren, 2008; Zhu and Pan, 2010). A new path to acetone has been lately patented (Masuda et al, 2011).

1.4.2.4 Substituting Polypropylene by Polylactic acid.

Polypropylene could be substituted by Polylactic acid: *“Polylactic acid is a promising plastic substitute. PLA is a bio-based, biodegradable polymer with much potential as raw material for food packaging because of its mechanical properties, because its strength, PLA can be fabricated into fibres, films and rods that are fully biodegradable (lactic acid, CO₂) and compostable, having degraded within 45-60 days”* (Kamm et al, 2006). Being renewable, biodegradable and flexible to produce shapes are clear advantages. Studies have revealed also the interesting thermo-mechanical properties of the PLA (Madhavan Nampoothiri et al, 2010). On the other hand, PLA production is a costly and high energy intensive process. It is already produced from corn by Nature Works (United States) and from sugarcane by Purac (Europe/Malaysia).

1.4.2.5 Substituting Polyethylene by PHAs

PHB (Poly Hydroxy Butyric acid) is an environmental degradable (to compost) material belonging to the PHA (Poly Hydroxy Alkanoates) family. PHB, and especially P3HB, seem to deliver similar properties than those from Polyethylene. (Kamm et al, 2006). With a theoretical yield of 75% and a fermentation yield of 98%, PHB is a renewable and biodegradable alternative to petrochemicals

(European Bioplastics organization), and its main advantage is to be able to be fermented from hemicelluloses (Ramsay et al, 1995; Lopes et al, 2009) being this approach more profitable, but showing lower thermal stability and excessive brittleness upon storage (Huey, C.S., 2006). It is already commercially available from sugar cane (Biocycle, Brazil).

Considering that the substitutes can perform the same duties and sometimes surpass performance, we can conclude that the selection proposed is a reasonable approach for the substitution of petrochemicals in a biochemical oriented biorefinery in a mid-term perspective.

1.5 Structure of the report

Along Chapter II is explained the Life Cycle Methodology applied, reviewing history, background, importance and mathematical framework, followed by the definitions of LCA stages from quality standards that must be followed. The last section is dedicated to the CO₂ accounting method used in this study.

In Chapter III the Functional Unit, system boundaries, databases and other parameters of the LCA Methodology are presented. Both cases flow diagrams are compared and a review of the technologies for each case are explained with no further data, in order to make the life cycle easily understandable by the reader.

Chapter IV is the compilation of the data for the LCI (Life Cycle Inventory). We will go through each case in detail, presenting the data (inputs in terms of raw materials, energy and capital, and outputs in terms of yields and emissions) for each process and the sources utilized to build the LCI.

Results are presented in Chapter V. Impact along the life cycles for each case will give an insight on which processes have a deeper impact of different categories in the production. The main results then are shown as comparison of the environmental performance for the functional unit for all the cases presented in ten relevant indicators. Benchmarking of each product within the functional unit is also part of the results as well as a special section for energy consumption.

Last chapter, will hold the discussions including implications and further work related. With no more remarks, we just hope you enjoy the reading.

2.1 Concept and mathematical structure of LCA

2.1.1 Concept of Life Cycle Assessment

We could first cite the Norwegian philosopher and ecologist Arne Næss, who coined the concept of “deep ecology” in 1972:

“Life is fundamentally one. ... The deep ecology movement is the ecology movement which questions deeper. The adjective 'deep' stresses that we ask why and how, where others do not”

Arne Næss

His “why and how” can be related to the quite complex interrelations during the life cycle of any product...

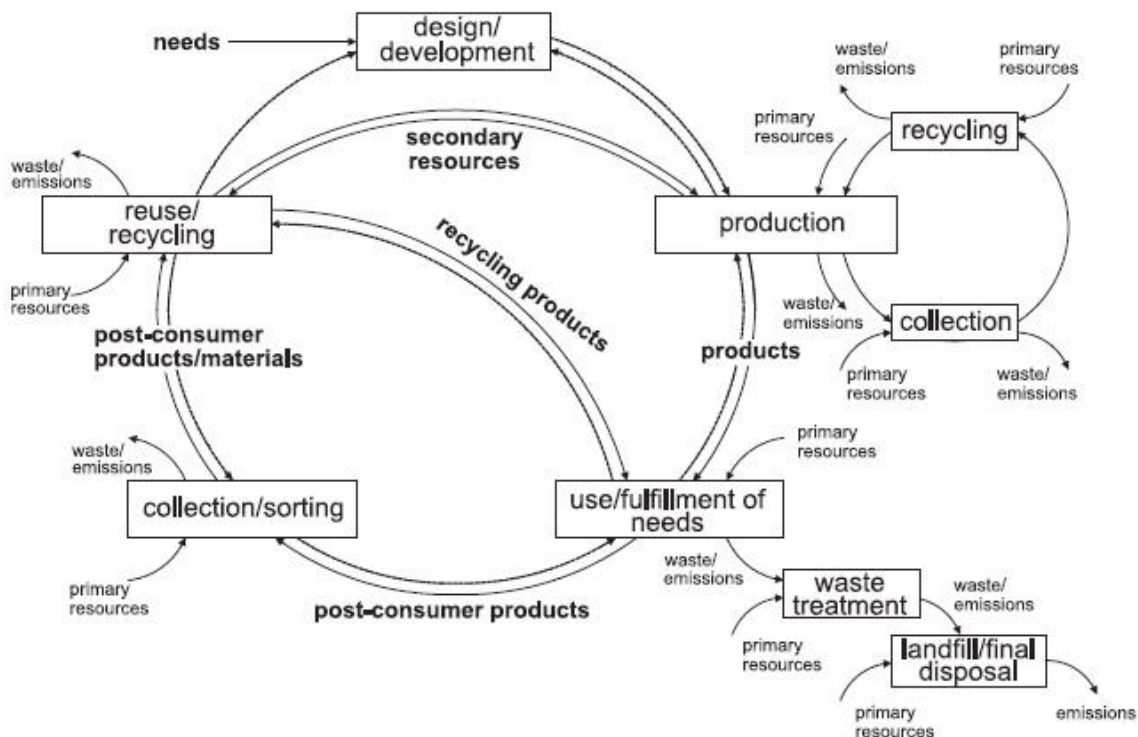


Figure 3: Schematic representation of a generic life cycle of a product.
 Full arrows represent material and energy flows, while the dashed arrows represent information flows.
 (Rebitzer et al, 2004)

...as we can see there are several inputs and outputs in each step or node. Emissions related to them are considered outputs. These emissions can be stated as direct (generated by the process which we require the functional unit) or indirect (emission generated in all the other processes as a results of the functional unit). Recycling and end-of-life scenarios also play an important role in LCA.

2.1.2 Mathematical structure

From the mathematical point of view, such complexity can be modeled in an algebraic formulation. Following the model formulation and notation developed by Nobel Laureate in economics, Wassily Leontief (Strømman, A. H. and Solli, C., 2008), and the lectures notes of the Industrial Ecology Programme at NTNU we can establish an equivalence of an LCA to a linear system with interconnected production nodes (Strømman, A.H., 2008).

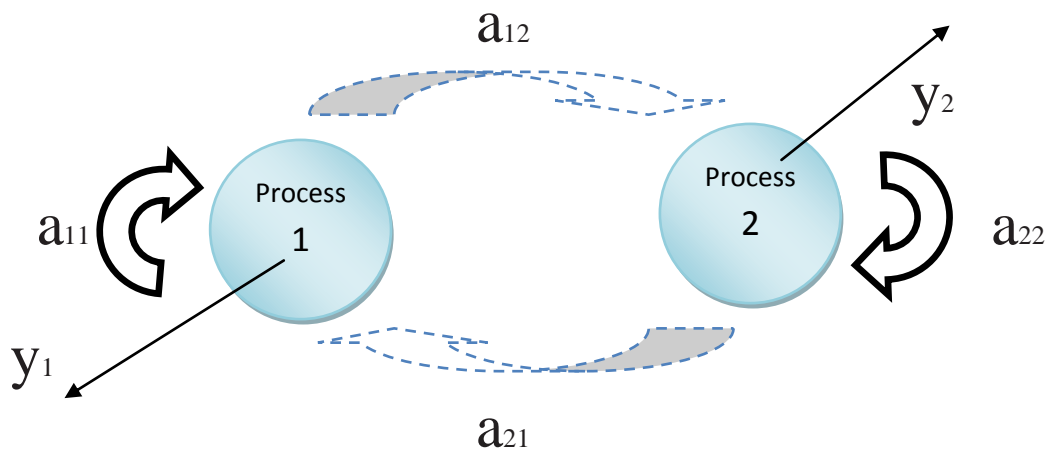


Figure 4: System with interconnected production nodes and external demands

Each node a_{ij} represents “the amount of i required per output of j process”. All these nodes define the requirement matrix A . We introduce the production vector x (which describes the production output in each node). Vector of production has to contemplate two kinds of demand, the internal demand (internal requirements of the system x_{ij}) and external demand (y), which it is the vector that at the end “pulls” the production in the system, as follows:

$$\begin{aligned}
 [x_1] &= [a_{11} \cdot x_1 + a_{12} \cdot x_2] + [y_1] \\
 [x_2] &= [a_{21} \cdot x_1 + a_{22} \cdot x_2] + [y_2] \\
 [\text{Production}] &= [\text{Internal/intermediate demand}] + [\text{External demand}]
 \end{aligned}$$

We can solve such a system by using Leontief inverse.

$$\begin{aligned}
 x &= A \cdot x + y; \\
 (I-A) \cdot x &= y; \\
 x &= (I-A)^{-1} \cdot y \quad \text{where } L = (I-A)^{-1}; \\
 x &= L \cdot y
 \end{aligned}$$

But this would only solve the production system problem.

We need to define a contribution analysis, setting up an S matrix or intensity matrix, which contains stressors produced by each process, and the vector e, total stressors due to the production level

S=

$$\begin{array}{|ccc|} \hline S_{11} & \dots & S_{1,pro} \\ \hline \dots & \dots & \\ \hline S_{str,1} & \dots & S_{str,pro} \\ \hline \end{array}$$

where $e=S \cdot x$;

The last step is to translate these stressors into emissions that can indicate in a more understandable way, the implications of those stressors. For that purpose, we define the Matrix C, or Characterization Matrix, where the stressors are identified by columns and the impact categories are identify by the rows and the vector d, or vector of impacts.

C=

$$\begin{array}{|ccc|} \hline C_{11} & \dots & C_{1,pro} \\ \hline \dots & \dots & \\ \hline C_{str,1} & \dots & C_{str,pro} \\ \hline \end{array}$$

where $d=C \cdot x$;

Now we have a very good overview of the system, and we are able to understand deeper the interconnectivity of such a system, and how its production is generating stressors, and how those stressors contributes to one or several emissions.

The review from Rebitzer and coauthors about LCA is a very spread and solid explanation of the LCA methodology (Rebitzer, G. et al., 2004). We have based the following section on his comments and indications, transcribing most of their speech.

2.2 Methodology

2.2.1 Goal and Scope definition and Inventory analysis (ISO 14041:1998)

An LCA starts with an explicit statement of the goal and scope of the study, which sets out the context of the study and explains how and to whom the results are to be communicated. This is a key step and the ISO standards require that the goal and scope of an LCA be clearly defined and consistent with the intended application. The goal and scope document therefore includes technical details that guide subsequent work:

- *Functional Unit*

It defines what precisely is being studied and quantifies the primary function/service that fulfills/delivered by the product/system, providing a reference to which the inputs and outputs can be related; basis for selecting one or more alternative products or systems that can provide

the same function(s), and by this way the functional unit enables different systems to be treated as functionally equivalent. It should be neutral to alternatives, but specific to location, quality and duration of the function.

- *System boundaries*

The flow model is typically illustrated with a flow chart that includes the activities that are going to be assessed in the relevant supply chain and gives a clear picture of the technical system boundaries.

- *Foreground and background system*

A common approach in LCA is to distinguish between the modeled system and the background data used to construct value chains upstream the system. The data found especially for a given case study is generally referred to as the foreground system, and the data used for compiling upstream value chains is referred to as the background system. It is advantageous to collect as much data as possible for the foreground system in order to obtain a reliable result. A more complete data from the foreground system will result in more precise results; hence a large fraction of impacts from the foreground system is often preferred. Collecting good data for the foreground system could, however, be difficult, and LCA databases could be used in completing the data set. This led us to put emphasis into the data quality.

- *Data quality*

The data quality can be described and assessed in different ways, and its use in the life cycle inventory is naturally reflected in the quality of the final LCA and how difficult is to manage by others. We could point out the following parameters related to the quality of the data:

Time-related coverage, geographical coverage, technology coverage and sources. Data from specific sites should be used for those unit processes that contribute the majority of the mass and energy flows in the systems being studied as determined in the sensitivity analysis. Data from specific sites should also be used for unit processes that are considered to have environmentally relevant emissions. In all studies, the following additional data quality indicators shall be taken into consideration in a level of detail depending on goal and scope definition: Precision, completeness, representativeness, consistency and reproducibility (European Environmental Issues series, 1997).

- *Life cycle inventory*

Life Cycle Inventory (LCI) analysis involves creating an inventory of flows from and to nature for a product system. Inventory flows include inputs of water, energy, and raw

materials, and releases to air, land, and water. To develop the inventory, a flow model of the technical system is constructed using data on inputs and outputs. The input and output data needed for the construction of the model are collected for all activities within the system boundary, including from the supply chain (referred to as inputs from the techno sphere). The data must be related to the functional unit defined in the goal and scope definition. Data can be presented in tables and some interpretations can be made already at this stage. The results of the inventory is an LCI which provides information about all inputs and outputs in the form of elementary flow to and from the environment from all the unit processes involved in the study.

- *Environmental databases*

Data for the background system can be found by using LCA databases. Today, LCA is used to assess all types of products and product systems and LCA analysts have collected data on a wide range of emissions and resource uses (SimaPro Pre consultants, PE International) and some institutions have found it useful to compile and link environmental data together in a database (EcoInvent). Some of the life cycle inventory databases available today are Franklin US98, Idemat 2005, Buwal250 database, ETH-ESU96 and Ecoinvent. The main database that will be used as a background system in this analysis is the Ecoinvent database. The Ecoinvent database is a continuation of the work on the ETH-ESU 96 database, and is recognized as the best quality and most complete LCA database for European purposes. The database is compiled as a joint project between several Institutions and includes process categories like energy supply, fuels, heat production, electricity generation, plastics, paper and board, basic chemicals, detergents, waste treatment services, metals, wood, building materials, transport and agricultural products etc. Ecoinvent is a recent, comprehensive and high quality LCA database that today is available in several LCA software packages.

- *Allocation methods*

The allocation methods used to partition the environmental load of a process when several products or functions share the same process. Different allocation methods can be used (energy, exergy, mass, economic ...) and it conveys quite important consequences. More literature about allocation methods can be found in (Curran, 2007; Heijungs and Guinée, 2007).

- *Assumptions and limitations*

The study must be clear in all moment about the assumptions taken and the limitations of the study.

2.2.2 Life Cycle Impact Assessment (ISO 14042:2000)

2.2.2.1 Elements

This phase of LCA is aimed at evaluating the significance of potential environmental impacts based on the LCI flow results. Classical Life Cycle Impact Assessment (LCIA) consists of the following mandatory elements:

1. *Selection of impact categories, category indicators, and characterization models;*
2. *Classification stage, where the inventory parameters are sorted and assigned to specific impact categories; and*
3. *Impact measurement; where the categorized LCI flows are characterized, using one of many possible LCIA methodologies, into common equivalence units that are then summed to provide an overall impact category total.*

In many LCAs, characterization concludes the LCIA analysis; this is also the last compulsory stage according to ISO 14044:2006. However, in addition to the above mandatory LCIA steps, other optional LCIA elements – normalization, grouping, and weighting – may be conducted depending on the goal and scope of the LCA study. In normalization, the results of the impact categories from the study are usually compared with the total impacts in the region of interest, the European Union for example. Grouping consists of sorting and possibly ranking the impact categories. During weighting, the different environmental impacts are weighted relative to each other so that they can then be summed to get a single number for the total environmental impact. ISO 14044:2006 generally advises against weighting, stating that “*weighting, shall not be used in LCA studies intended to be used in comparative assertions intended to be disclosed to the public*”. This advice is often ignored, resulting in comparisons that can reflect a high degree of subjectivity as a result of weighting. Methods have been developed for weighting the different environmental pressures or emissions and categorize them into impact indicators. This is done by taking into account environmental mechanisms and human values. In this way characterization factors allow us to convert emissions of different substances with the same type of environmental impact into equivalents. In the prevailing LCA databases the number of stressors reaches thousands, and a list that long will not be of any use to a decision maker. Different environmental stressors are therefore classified into impact categories to which they contribute. A process can have other environmental loads than just those associated with physical emissions. Land use is an example of another type of environmental stressor. Dividing into impact categories aim to simplify the complexity of hundreds of flows into a few environmental areas of interest. In this study we will be using the ReCiPe method for impact categories.

2.2.2.2 ReCiPe Method

“ReCiPe is the most recent and harmonized indicator approach available in life cycle impact assessment” (Pré Consultants). The primary objective of the ReCiPe method is to transform the long list of life cycle inventory results, into a limited number of indicator scores. These indicator scores express the relative severity on an environmental impact category. In ReCiPe we determine indicators at two levels:

Table 1: ReCiPe midpoint and endpoint indicators

Eighteen midpoint indicators <i>Relatively robust, but not easy to understand</i>	Three endpoint indicators <i>Easy to understand, but more uncertain</i>
<ul style="list-style-type: none"> • Ozone Depletion • Human toxicity • Ionising radiation • Photochemical Ozone formation • Particulate Matter formation • Climate Change • Terrestrial Ecotoxicity • Terrestrial Acidification • Agricultural land Occupation • Natural land transformation • Marine Ecotoxicity • Marine Eutrophication • Freshwater Eutrophication • Freshwater Ecotoxicity • Fossil fuel consumption • Minerals consumption • Water consumption 	<ul style="list-style-type: none"> • Damage to human health • Damage to ecosystems • Damage to resource availability

Each method (midpoint, endpoint) contains factors according to the three cultural perspectives. These perspectives represent a set of choices on issues like time or expectations that proper management or future technology development can avoid future damages:

Individualist <i>-Short term-</i>	Hierarchical <i>-Mid term-</i>	Egalitarian <i>-Long term-</i>
Optimism that technology can avoid many problems in future	Consensus model, as often encountered in scientific models, this is often considered to be the default model	Based on precautionary principle thinking

ReCiPe framework, relative to other approaches, has the broadest set of midpoint impact categories, where possible, it uses impact mechanisms that have global scope, and unlike other approaches (Eco-Indicator 99, EPS Method, LIME, and Impact 2002+) it does not include potential impacts from future

extractions in the impact assessment, but assumes such impacts have been included in the inventory analysis.

2.2.3 Life Cycle Assessment Interpretation (ISO 14043:2000)

Life Cycle Interpretation is a systematic technique to identify, quantify, check, and evaluate information from the results of the life cycle inventory and/or the life cycle impact assessment. The results from the inventory analysis and impact assessment are summarized during the interpretation phase. The outcome of the interpretation phase is a set of conclusions and recommendations for the study. According to ISO 14040:2006, the interpretation should include:

1. *Identification of significant issues based on the results of the LCI and LCIA phases of an LCA.*
2. *Evaluation of the study considering completeness, sensitivity and consistency checks.*
3. *Conclusions, limitations and recommendations.*

A key purpose of performing life cycle interpretation is to determine the level of confidence in the final results and communicate them in a fair, complete, and accurate manner. Interpreting the results of an LCA is not as simple as 3 is better than 2, therefore Alternative A is the best choice! Interpreting the results of an LCA starts with understanding the accuracy of the results, and ensuring they meet the goal of the study. This is accomplished by identifying the data elements that contribute significantly to each impact category, evaluating the sensitivity of these significant data elements, assessing the completeness and consistency of the study, and drawing conclusions and recommendations based on a clear understanding of how the LCA was conducted and the results were developed.

2.3 CO₂ emissions from biomass. Atmospheric decay and contribution to global warming

Some research has been done lately regarding carbon accounting; one of the latest advances in the topic has been the development of the Global warming potential from biogenic sources, related to the combustion of biomass. Before this contribution was neglected but new research has pointed out that the rotation period of the feedstock is an important parameter that influences the carbon cycle.

“Carbon dioxide (CO₂) emissions from biomass combustion are traditionally assumed climate neutral if the bioenergy system is carbon (C) flux neutral, i.e. the CO₂ released from biofuel combustion approximately equals the amount of CO₂ sequestered in biomass. This convention, widely adopted in life cycle assessment (LCA) studies of bioenergy systems, underestimates the climate impact of bioenergy. Besides CO₂ emissions from permanent C losses, CO₂ emissions from C flux neutral systems (that is from temporary C losses) also contribute to climate change: before being captured by biomass regrowth, CO₂ molecules spend time in the atmosphere and contribute to global warming. In

this paper, a method to estimate the climate impact of CO₂ emissions from biomass combustion is proposed. Our method uses CO₂ impulse response functions (IRF) from C cycle models in the elaboration of atmospheric decay functions for biomass derived CO₂ emissions. Their contributions to global warming are then quantified with a unit-based index, the GWPbio. Since this index is expressed as a function of the rotation period of the biomass, our results can be applied to CO₂ emissions from combustion of all the different biomass species, from annual row crops to slower growing boreal forest.”
(Cherubini et al., 2011).

This approach will be used during our study, couple with the cited LCA methodology, in the following chapters.

CHAPTER III FUNCTIONAL UNIT, SYSTEM BOUNDARIES AND CASE DESCRIPTIONS

3.1 Goal and Scope definitions, system boundaries, LCI parameters and other important information of the LCA

Table 2: LCA Summary

	Goal
Project goal	<ul style="list-style-type: none"> LCA of a set of platform chemicals from fossil and lignocelluloses sources
	Scope and definition
Functional unit	<p>“1 unit of platform chemicals”. This unit of platform chemicals is composed by:</p> <ul style="list-style-type: none"> 1 kilogram of phenol (Phenols or Phenolic compounds). 1 kilogram of solvent (Acetone). 1 kilogram of soft plastic precursor (Polyethylene or PHA). 1 kilogram of hard plastic precursor” (Polypropylene or PLA). <p>Note that this is the functional unit of our study; but due to the different natures of the systems benchmarked we will have to define other functional units (delivery or production units) to respect the idiosyncrasy of each system</p>
Comparability technologies / Products	<ul style="list-style-type: none"> Techno-economic review “vise-a-vise” in the Introduction chapter
System boundaries <i>(Figure 6)</i>	<ul style="list-style-type: none"> WTG Well To Gate for petrochemicals FTG Field To Gate for chemicals from biomass It is not include any end-of-life scenario in which the sub products of these platform chemicals are disposed, incinerate or recycled due to the wide range of sub products and the variability of assumptions, but on the other hand, a carbon cycle approach is considered when dealing with carbon accounting
Framework	<ul style="list-style-type: none"> Spain
Database	<ul style="list-style-type: none"> Wherever possible the Life Cycle Inventory includes relevant and consistent data from companies in the sector or scientific papers. For other generic inputs upstream we use the EcoInvent Database. For emissions from combustion of wood we use the GEMIS v4.5 database and IPCC factor for Dinitrogen monoxide
Allocations	<ul style="list-style-type: none"> Cumene-Phenol process is allocated according to exergy (=portion of chemical energy sources in the products) for a delivery unit of the petrochemical plant. Allocation by mass in all the rest of processes where allocation is needed. No further specific allocations
Cut-off criteria	<ul style="list-style-type: none"> No explicit cutoff criteria. All available weight information is processed
Parameters	<ul style="list-style-type: none"> ReCiPe Method was chosen for Impact Assessment, selecting ten indicators to show the main results of the functional unit: Climate Change (CC), Fossil Depletion (FD), Water Depletion (WD), Freshwater Ecotoxicity (FWE), Freshwater Eutrophication (FWEU), Human Toxicity (HT), Particulate Matter Formation (PM), Photochemical Oxidant Formation (PO), Terrestrial Acidification (TA) and Terrestrial Ecotoxicity (TE). HIERARCHICAL PERSPECTIVE Interpretation: The results were compared to the EcoInvent database for petrochemical productions, and other scientific papers and references in the discussion part.
Software	<ul style="list-style-type: none"> LCA GUI Software developed at Industrial Ecology Department of NTNU (Norwegian University of Science and Technology)
Evaluation	<ul style="list-style-type: none"> Academic supervisors (Anders Strømman and Francesco Cherubini) and Professors evaluation both at NTNU (Norwegian University of Science and Technology) and UC3M (University Madrid Carlos III) as part of the completion of Master Thesis.
Documentation	<ul style="list-style-type: none"> Final report with all parameters

3.2 Flow sheet of both scenarios

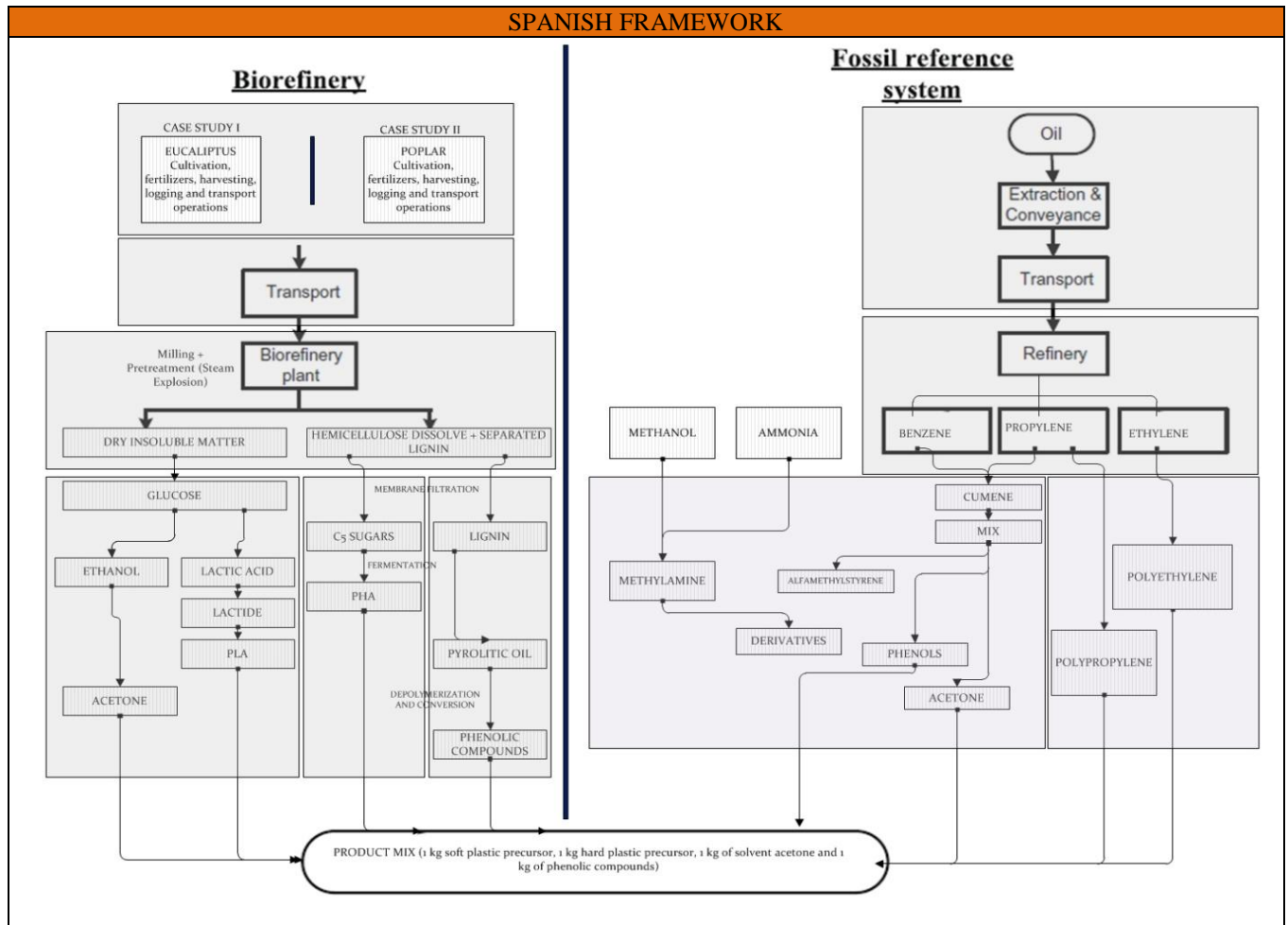


Figure 5: Functional unit, System boundaries and process description of all the scenarios.

3.3 The Biorefinery concept. Forest Operations, pulp and paper industry and biochemical processes and technology

Our study is “Cradle to Gate”, or “Forest to Gate” in this case, this means that we will track the production of chemicals from biomass from the lignocelluloses source to the end as platform chemical for diverse uses. Although, our system does not match completely the concept of biorefinery, once do not produce biofuels and the energy is for self supply, we can argue that we do produce energy coming from biofuels that we should have produce before, in this case, mainly pyrolytic oil from lignin, but also ethanol and charcoal are produced.

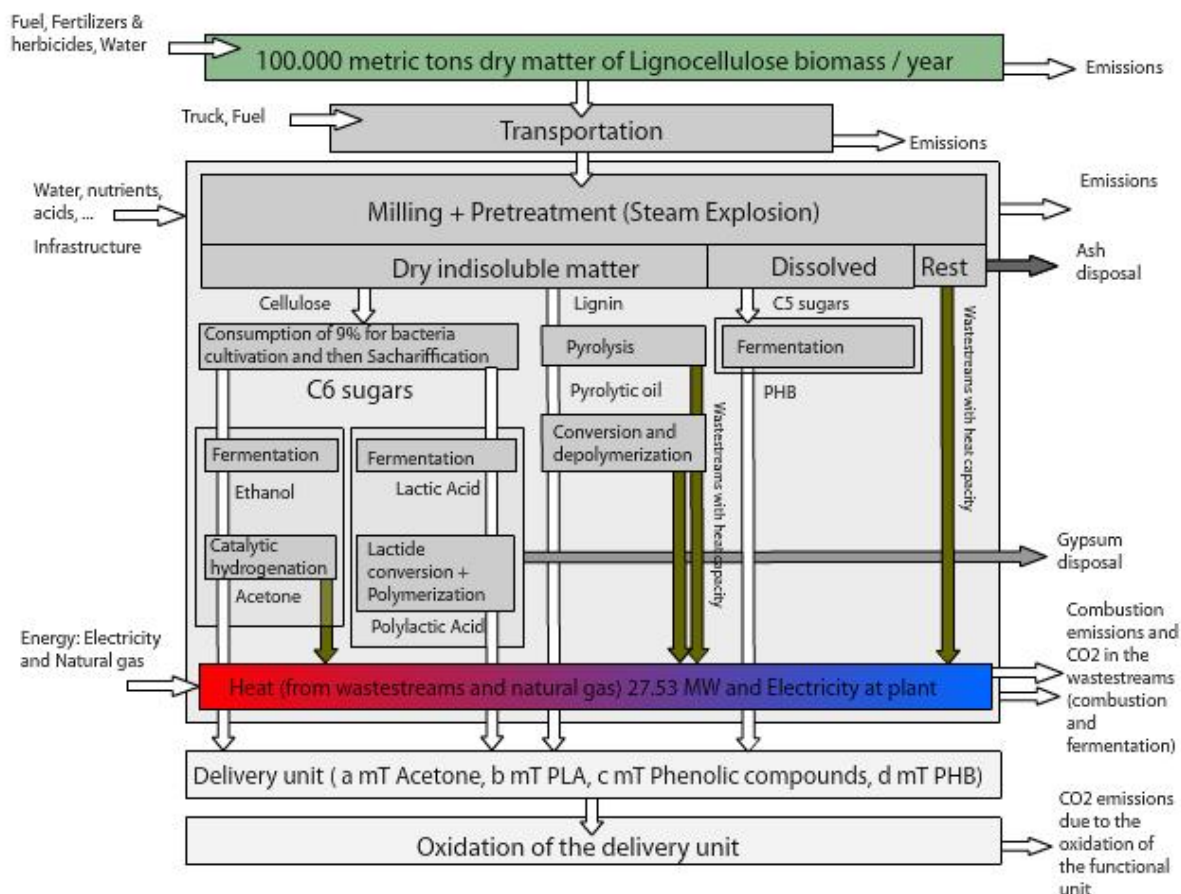


Figure 6: Detailed Life Cycle of Chemicals from biomass production.

3.3.1 Cultivation, forest operations and transport of lignocelluloses biomass

It is the main source upstream, for example, short rotation wood, softwood, hardwood or forest residues. Forest operations include plantation, fertilizing, usually irrigation, cutting, logging and transportation to the storage place. In the Spanish background the exploitation is modeled in base of several studies in the North of Spain about Forest Operations. For our cases two main lignocelluloses sources are considered: Poplar and Eucalyptus. Biomass is usually transported by high load trucks from the regional storage to the biorefinery.

3.3.2 Biorefinery step (Milling and pretreatment)

The first step is partially equivalent to a pulp and paper mill. The main goal is to split the lignocelluloses matter into cellulose, hemicellulose and lignin, the three main constituents of biomass. There are several possible pretreatments available (Da Costa Sousa, 2009):

3.3.2.1 Physical Pretreatment

Particle size reduction, hence increasing surface area, by mechanical stress.

3.3.2.2 Solvent fractionation

Differential solubilization and partitioning of various components of the plant cell wall. The most attractive are organosolv process (using organic solvents, usually alcohols

in the presence of an acidic catalyst), phosphoric acid fractionation (includes solvent extraction using phosphoric acid, acetone and water) and ionic liquids based fractionation (ionic liquids have the capability to form hydrogen bonds with cellulose at high temperature, because of the presence of anions like chloride).

3.3.2.3 Chemical pretreatment

Acidic (concentrated and dilute acid, steam explosion and liquid hot water pretreatments), alkaline (lime, ammonia fiber expansion AFEX and sodium hydroxide are utilized) and oxidative based pretreatments like alkaline wet oxidation.

3.3.2.4 Biological treatment

Non-energy intensive approach, normally using fungi that help to remove the lignin. On the other hand, residence times are much longer, which it is a serious limitation for economical development.

In our case, a chemical treatment (Steam Explosion) will be used since it is one of the most used methods in the industry, being successfully applied to several types of lignocelluloses biomass (Da Costa Sousa, 2009; Zhu, J.Y. and Pan, X.J., 2010). It operates at high temperatures (160 to 290°C) and pressure for a certain duration of time (from seconds to minutes) before the pressure is explosively released.

3.3.3 Separating outputs of the pretreatment and bacteria cultivation

Hemicellulose dissolves with some other components of wood. We assume that ash, extractives and these components get dissolved as well. A membrane filtration is able to separate the hemicellulose (mainly xylose) from that stream. *“The simplest and most suitable separation is a filter with relatively large pores on the order of 20–25 mm that retains residual corn stover solids while passing reaction products such as glucose and cellobiose to form a sugar stream for a variety of end uses. Such a simple separation is effective because cellulose remains bound to the residual solids”* (Knutsen and Davis, 2004). *“In the drum filtration stage, 90% of the suspended solids were removed. In the subsequent microfiltration stage, the remaining solids and the extractives were removed. A concentrated and purified hemicellulose solution was separated in the ultrafiltration stage. In the nanofiltration stage, purified water of fresh water quality could be produced. The proposed method was successfully operated at conditions closely resembling industrial conditions by treating a large volume of process water and running the process stages back-to-back”* (Persson, T. et al., 2010). After analyzing the results an assumption of perfect separation is taken, where we can separate all hemicelluloses from the rest of the hydrolyzate.

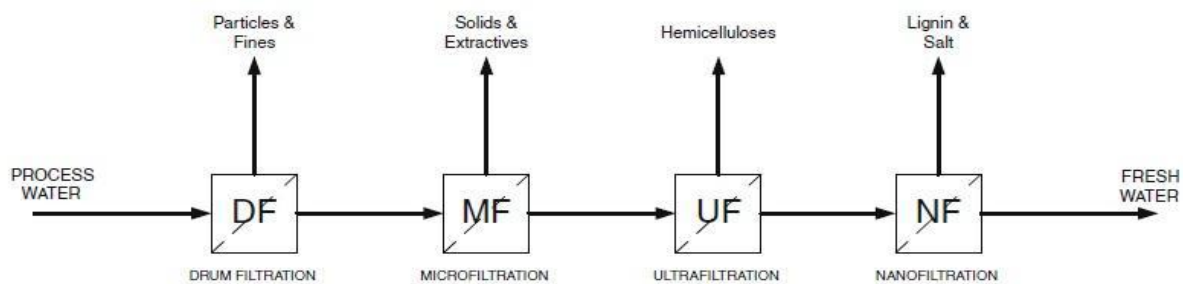


Fig. 1. A schematic illustration of the overall process.

Figure 7: Schematic illustration of a membrane filtration system for biorefinery Persson et al (2009).

The dry fraction can be washed and separated into lignin and cellulose. Part of this cellulose, around 10%, must be taken for the bacteria cultivation prior to fermentation, while the other 90% of it goes to saccharification to be converted into glucose, although this can be done in a so called “SSF” or “Simultaneous Saccharification and Fermentation”. Glucose is separated in two equal streams, one for fermentation of polylactic acid and one for ethanol prior to acetone.

3.3.4 Phenolic compounds

Lignin will be pyrolyzed into pyrolysis oil. The main difference between gasification and pyrolysis is that while in gasification we have a controlled amount of oxygen and it produces synthetic gas, pyrolysis is a process in absence of oxygen, and produces pyrolytic oil from biomass. Pyrolysis of lignin has been studied with enthusiasm lately, regarding the possibilities of upgrading the lignin into a valuable fuel (Kamm et al, 2006; Gayubo et al, 2010). More detailed and practical research has been done on pyrolysis (Basu, 2010) as well as related to lignin polymerization (Pandey, M. P., & Kim, C. S., 2011) and phenolic compounds extraction (Brehmer et al, 2009; Pinto, P.C.R. & Borges, E.A., 2011). “*Unlike the whole biomass pyrolysis oil, lignin pyrolysis oil is mainly phenolic in nature and therefore no further purification is needed if a group of compounds is to be utilized*” (Pakdel et al, 1992).

3.3.5 Acetone production

We will use the cellulose as sugar source (saccharification of cellulose into glucose) for ethanol production, which is a well-known process (Brehmer et al, 2009; Hamelinck et al, 2004; Lynd, 1996; Olsson, 1994; Pfromm, P.H, 2008; Stenberg, 1999; Wingren, 2008; Zhu and Pan, 2010). For modelling the path from ethanol to acetone we follow a catalytic hydrogenation of alcohol. Alcohol is vaporized, heated and feed in a reactor, where a catalytic hydrogenation occurs. The outflow gases (acetone, water, hydrogen and unreacted isopropyl alcohol) pass through a condenser where most of the acetone, water and alcohol condense. Final traces of alcohol and acetone are removed by a water absorbent process. This effluent is combined with the condenser outflow and distillation provides pure acetone and effluent of water and alcohol. A second distillation column is used to separate the excess water. The product of this azeótrope water and isopropyl alcohol content approximately 91% alcohols,

which is usually recycled to the reactor. Copper oxide is usually used as catalyst, and the reaction is carried out normally at 400-500°C and 4.5 bars. Yield of acetone is 98% and conversion of alcohol 85-90%.

3.3.6 Polyactic acid production

We will use the cellulose as sugar source (sacharification of cellulose into glucose) for the production of polyactic acid.

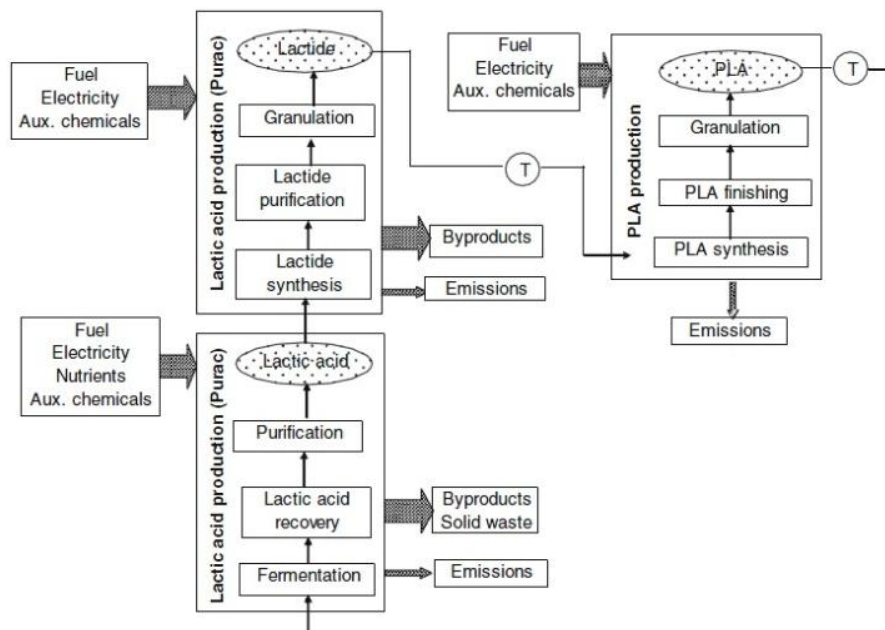
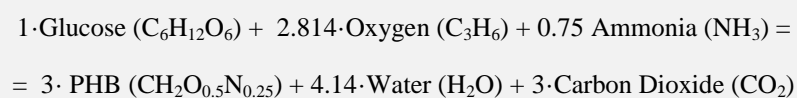


Figure 8: PLA Production (Groot and Borén, 2010)

We are interested on the fermentation process of lactic acid from sugars, which includes fermentation, lactic acid recovery and purification, and requires fuel, electricity, nutrients and auxiliary chemicals. Also, it is equally important the step from lactic acid to lactide (which includes lactide synthesis, purification, granulation and the inputs of fuel, electricity and auxiliary chemicals). Finally the step from Lactide to Polylactid acid (which includes PLA synthesis, PLA finishing and granulation, plus inputs of fuel, electricity and auxiliary chemicals).

3.3.7 PHB production

Usually glucose is used to produce PHB (Marcela, B. et al., 2005) following the route:



We will use the hemicelluloses as carbon source for Poly hydroxy butyric acid production (Ramsay et al, 1995; Lopes et al, 2009). The production includes other nutrients in the seed media (organism,

carbon source, water, nutrients and salts) and fermentation media (carbon source, water, nutrients and salts) plus enzymes in a series of steam sterilization, fermentation reactors, centrifugations and other processes like spray drying and wastewater treatment (Harding et al, 2007).

3.3.8 Revalorization of waste stream into heat for the biochemical processes

Revalorization of the waste streams is one of the main challenges of biorefineries in terms of mass, carbon and energy efficiency (Cherubini, F. and A. H. Strømman (2010); Gallardo.M, 2010). A proper use of them can lead to increase substantially the efficiency of the system. The energetic valorisation of these streams can produce heat and power to our facility, in that case, imports and combustion of fossil fuels would be decreased or even become unnecessary.

For our case, the rest of the pyrolytic oil plus all waste streams are valorised energetically and used to provide heat to the plant. The revalorization of waste streams leads to the following point about supply of heat and power in plant.

3.3.9 Heat and power at plant and combustion issues

The self-sufficient of the plant in terms of heat and power is also reviewed in this study. Our system definition as algebra matrix contemplates this issue, and as results, we will obtain an estimation of calorific value in the waste streams.

Combined Heat and Power seems like a good alternative in our case, since our facility is demanding both source of energy. Anyway, after some analysis of the results, we observed that the assumption of combined heat and power could not be taken, and there was not even enough energy in the waste stream for self-supplying heat. Considering that the heat demand in plant is high and the electricity efficiency in combined heat and power is low we did not include the electricity (Combined heat and power equipment and operation) inside the system boundaries, hence, the national grid will satisfy our needs of electricity and natural gas if needed.

On the other hand, we will combust the residues in waste streams in a boiler for generating heat. The emissions and factor applied in this process will be explained further in the Life cycle inventory in the next chapter.

3.4 Oil and gas operations and petrochemical processes and technology

3.4.1 Oil and gas extraction, exploitation and transportation

The first difference we can find regarding exploitation is the location of the well, onshore or offshore. This radically changes the concept of exploiting and has a consequence on the impacts that we generate by its exploitation, for example, drilling, construction of facilities or transporting by pipeline or by boat carriers. Location also regarding the country of exploitation, since the properties of the oil differs in term of composition and quality. And in last term, the company methods can also become important regarding yields or environmental protection. In the Spanish background the extraction occurs in North of Africa, mainly Argelia, and then, transportation by pipeline (oil) and carrier (LNG) to Huelva, in the south of Spain, where the refinery and petrochemical facilities of the petrochemical company CEPSA, S.A. are located.

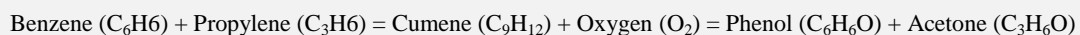
3.4.2 The refinery

When the crude oil arrives to the refinery is heated in the distillation tower and cracked into different hydrocarbon chains. The upper part of the distillation tower, containing the products with lower density (Naphtha and gas phase) is shown in the figure 2 in the Introduction section. From heavy naphtha we can extract aromatic components, so called BTX (Benzene, Toluene and Xylene) which contains usually between seven and eight carbon molecules. The gas phase provides ethane and propane, from where we can arrive to ethylene (process such cracking, naphtha steam of hydrocarbons or from LPG) and propylene (dehydrogenation of propane) respectively.

The company which owned these facilities is CEPSA, S.A. Although ethylene is not produced in this refinery (the refinery gas is burned in flare to produce energy); we consider that it would be feasible to integrate into it.

3.4.3 Petrochemical Plant. The cumene-phenol process

The cumene phenol process or Hock process is an industrial process for developing phenol and acetone from benzene and propylene. The term stems from cumene (isopropyl benzene), the intermediate material during the process. It was invented by Heinrich Hock in 1944. This process converts two relatively cheap starting materials, benzene and propylene, into more valuable ones, phenol and acetone. Other reactants required are oxygen from air and small amounts of radical initiator. Cumene also is converted into cumene hydroxiperoxide prior to become Phenol and Acetone.



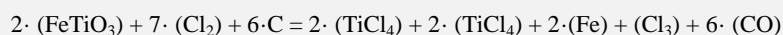
hours results in a 97% conversion of ethylene. A considerable amount of heat is liberated from the polymerization of ethylene as the reaction is exothermic. Heat is generally removed by cooling unreacted ethylene gas coming off the top of the reactor and recycling the cool gas back to the reactor.” (University of Washington).

3.4.5 Polypropylene process

Similarly to the polymerization of ethylene, polymerization of propylene uses a reactor in which the propylene and the catalyst produce polypropylene. The catalyst used are Ziegler-Natta Catalyst, usually based on Titanium (TiCl₄) or Magnesium (MgCl₂), that are activated with special co catalyst containing organo aluminium compound such as Al (C₂H₅). The two most important technological characteristics of all supported catalyst are high productivity and high a high fraction of the crystalline isotactic polymer they produce at 70-80°C under standard polymerization conditions.

3.4.6 Catalyst production

As we have seen, various catalysts (catalyst and co catalyst) are needed in the production of polyethylene and polypropylene. The preparation of Titanium tetrachloride from Titanium oxides TiCl₄ is formed by passing chlorine over a mixture of coke and Titanium dioxide at 800°C. The source of Titanium dioxide is ilmenite, which can contain a 42% of Titanium dioxide in mass. The chemical formula would be as follows:



The catalysts needed are produced in the petrochemical plant of Tarragona (Spain) that belongs to the company BASF.

3.5 CO₂ along the entire Carbon Cycle for biochemical and petrochemical Scenarios

A “Cradle to Gate” approach seemed to be unequal to the scenarios, being quite favorable to the petrochemicals since most of their carbon remains from the feedstock into the products of the functional unit. This meant that we were taking into account most of the carbon for chemicals from biomass before gate and few of the carbon for petrochemicals till the same point, leaving apart external CO₂ emissions related to the production process. We need to compare the entire carbon cycle without compromising our system boundaries for the reasons stated before. We will use the method already exposed (Cherubini et al., 2011) to evaluate the greenhouse gas effect of the biogenic CO₂, considering that oxidation of all biogenic C takes place within one year after the harvesting of the feedstock. A further discussion can be found in the last chapter.

CHAPTER IV LCI: LIFE CYCLE INVENTORY: CASES, PROCESSES AND INVENTORIES

4.1 Chemicals from biomass: Basic and specific data of the Life Cycle Inventory

4.1.1 Poplar

Composition of Poplar (44.70 % Cellulose, 18.55 % Hemicellulose, 26.44 % Lignin, rest made of ash, derivatives and other components). A reference value of 1% of biomass input converted to ash when combusted and sent to a sanitary landfill is taken (Guest, 2010), assumed to be filtered from hydrolizate in pretreatment effluent and rectified to 0.9 % to be coherent with our pretreatment and wastewater assumptions. Heating value is assumed to be similar than softwood, 19.3MJ/kg (Cherubini and Strømman, 2010). Data about energy usage, herbicides and fertilizing for 1 kg of poplar produced is taken from scientific literature (Fan, J. et al., 2011). Although its background is United States, we consider this study to be valuable for our interest. Amount of N and P in each herbicide and fertilizer were calculated through their molecular weight, and emissions were modeled using IPCC factors *“Direct soil emissions of N as N₂O, at 1% of synthetic N application (mean value); Volatilization of N as NH₃, at a rate of 10% of total N of synthetic N application. One percent of N in NH₃ is then converted to N₂O; Leaching to groundwater as nitrate (30% of total N applied); 0.75% of it is converted to N₂O; The resulting effect is that 1.325% of N in synthetic fertilizer is emitted as N in N₂O; this corresponds to an emission of 0.042 g N₂O per g N fertilizer”* (IPCC, 2006). *“A default value of 10 g CH₄/kgN for the emission of CH₄ from agricultural land is reasonable for most circumstances and results in a relatively small contribution to life cycle GHG emissions of the bioenergy chain”* (Delucchi and Lipman 2003).

Though Phosphate is quite difficult cycle to understand (Gonzalez-Garcia, S. et al., 2009), the United States Department of Agriculture already alerted in 2003 (Anon, 2003) about overfertilization of soil via phosphates, and the eutrophication issues derivated. Only a portion is taken from the soil imbibed in the crop, being this overstock prone to surface and subsurface runoff. Values seem to underestimate this influence. Anyway, to be consistent within our study we will use the same emission factor for P than in the Eucalyptus case, 0.024 kgP_{emission} / kg P_{fertilizer} (Gonzalez-Garcia, S. et al., 2009).

No values for water consumption in the poplar cultivation were given in the study. However the water needed for growing a Populus SRF crop is lower than the consumption of other irrigated crops, as corn, that can compete for the same lands in the Mediterranean area (Sevigne, E. et al., 2011); hence, we will consider that the poplar population can manage without more water than the received from the annual precipitation.

4.1.2 Eucalyptus

Composition of Eucalyptus (49.5% Cellulose, 27.71 % Hemicellulose, 13.07% Lignin, rest made of ash, derivatives and other components with heating value between 18.6 and 19.3MJ/kg, being this last value taken into account) (Cherubini and Strømman, 2010). Other data from Eucalyptus (dry density of eucalyptus 549 kg/m³ and annual production), and forest operations (fuel consumption, herbicides and fertilizers application and emission factors) in Spain were used (Gonzalez-Garcia, S. et al., 2009). Emission factor to surface water of 0.024 kgP / kgP was used as for Poplar. Another study from the same author gives the fertilizers consumption per kg of kraft pulp from Eucalyptus (González-García, S. et al., 2009). Utilizing the cellulose content of the Eucalyptus for our study, and under the supposition that the kraft pulp can be considered equivalent to cellulose, we can arrive to the material and energy inputs needs per kg dry biomass of Eucalyptus.

We compared the energy consumption of these studies with other studies from the same (González-García, S. et al., 2009) and other author (Miranda, I., 2001). Both of them showed a total energy input of this phase of around 1MJ per kg of dry biomass (Eucalyptus).

Table 3

Inputs (raw materials, energy and capital) and emissions from forest operations per kg of lignocellulosic materials. Poplar and Eucalyptus cases.

Material and Energy inputs	Poplar, at regional storage, kg	Eucalyptus, at regional storage, kg	Output as Emissions	Poplar	Eucalyptus
Raw Materials			Direct emissions and waste		
Water, kg	0	32.7	Methane, biogenic/ air/ low population density	2,57E-05	6.45E-06
Glyphosate,kg	0.0000092	0.0008	Nitrogen oxides/ air/ high population density	0	1.16E-06
Single Superphosphate, kg	0.00156	0	Dinitrogen monoxide/ air/ unspecified	2,57E-05	1.16E-05
Thomas meal, P ₂ O ₅ , kg	0.00226	0	Ammonia/ air/ low population density	0,000257	3.99E-05
[thio]-carbamate compounds, kg	0.0000146	0	Phosphate/ water/ ground-, long-term	2,5E-05	2.72E-05
Ammonium Nitrate, Phosphate, as N, kg	0.00257	0.012	Glyphosate/ soil/ agricultural	0	0.00014
Energy inputs			Nitrate/ water/ ground-, long-term	0,000772	0
Diesel, kg	0.00353	0.023	Wood, unspecified, standing/ resource/ biotic	0.0018	0.0018
			Occupation, forest, intensive, normal/ resource/ land	3.19	3.19

Wood as biotic resource is included and the occupation of forest intensive was calculated from the density and annual productivity (11.3 m³/ha) for Eucalyptus, and it was also applied for Poplar. Note that the yields listed through the processes are linked to the poplar case since variations due to the feedstock composition may occur.

4.1.3 Transportation

In theecoinvent report about biomass for the bioethanol from wood chips distillery case we find that “Wood chips are transported to the distillery from nearby forest areas over an average distance of 70 km, of which 5km are done by tractor and trailer and 65km by 28t lorry” (EcoInvent. Biomass Report). Transport is modeled then as “Transportation service. High load trucks. 28tn lorry” from Ecoinvent database with a value of a 0.130 tkm (tons per kilometer), which is 1 kg delivered 65 km and trip back (130km) of the lorry.

4.1.4 Pretreatment

The process we use is: “*Spruce 2-10mm wood chips. 5 minutes at 215°C, SO₂=3% in two steps: Step I 2 minutes at 190°C; SO₂=3% and step II 5 min at 210°C SO₂=0%. L/W*” (Zhu, J.Y. & Pan, X.J., 2010). The “Liquid to solid ratio” is 1, which means that we need 3% in the liquid fraction, which it is the same as the solid. Heat consumption is 1.79 MJ and electricity consumption is 0.18MJ. Sulphur dioxide was supposed not to be recycled in each round of operation.

Regarding the yield, it is considered that all cellulose, hemicellulose and lignin are obtained separately as output, and all the rest components of wood are separated in this phase, for example, using a membrane filtration of the dissolved components (hemicellulose). Production is set as 100000 metric tons per year for 30 years in a pulp and paper plant.

Table 4

Inputs (raw materials, energy and capital) and emissions from forest operations per kg of dry lignocellulosic biomass. Poplar and Eucalyptus cases.

Material and Energy inputs	Biorefinery 1st step, kg
Raw Materials	
Lignocellulose, at plant, kg	1
Water, kg	0.42
sulphur dioxide, liquid, at plant/ RER/ kg	0.03
Transport, tkm	0.13
Disposals, ash from paper prod. sludge, 0% water, to residual material landfill/ CH/ kg	0.009
Energy inputs	
of which, heat MJ	1.797
of which, electricity MJ	0.18
Capital	
pulp plant/ RER/ unit	3.3E-10

4.1.5 Bacteria Cultivation

As mention in the cases, 9% of the cellulose is consumed in bacteria cultivation, which is subtracted from the available cellulose downstream. That cellulose is converted into glucose with 90% efficiency. Glucose is divided into two equal flows, one for the ethanol-acetone process, and the other one for the Hemicellulose-PHB process.

4.1.6 From lignin to Phenolic compounds

For the production of phenolic it has been estimated 75% pyrolysis oil from lignin, a mix of different chemical compounds having an average phenol content of 32.3%, which can be recovered at an efficiency of 50% (Cherubini, F. & Jungmeier, G., 2009). For the energy input from lignin to aromatics, we follow the estimations of Brehner and coauthors (Brehner et al, 2009). We had to convert their values due to the fact that the conversion rate of their study was 18.5%, while we were using 12.18%, and they were referred to lignin input, but not output. Data only includes requirements inputs from lignin and energy, being 16.22 MJ of heat and 0.59 MJ of electricity per kg of phenol. No capital or other materials considered for the process or the pyrolysis equipment. No waste during the process which is consistent with our mass balance, which gives the waste stream a calorific value for self supply of heat.

Table 5
Inputs (raw materials, energy and capital) for the production of 1 kg of phenols in plant

Material and Energy inputs	Phenols, kg
Raw Materials	
Lignin, unit (0,264kg)	8.21
Energy inputs	
of which, heat MJ	16.22
of which, electricity MJ	0.59

4.1.7 From glucose to acetone

For acetone we need to produce ethanol (96%). Also Brehner and coauthors when replacing petrochemicals study the process from fermentation sugars to ethanol, giving C6 sugars (glucose) and C5 sugars (xylose) conversion rate (%) for standard and recent system, and the electric and thermal energy required (Brehner et al, 2009). We have converted their values to fit our study where sugars fermentate into CO₂ (48%) and ethanol (52%), with a yield of 85% and energy consumption of 11.74 MJ of heat and 1.04 MJ of electricity. No wastewater treatment considered as main outputs are water and carbon dioxide. No water consumption is given in the study, though Kansas State estimates —2.85 gallons of water per gallon of ethanol, produced assuming zero liquid discharge and otherwise current industrial practice data (Pfromm, P.H., 2008). Therefore, water consumption is estimated on 15.39kg/kg ethanol. For modeling the path from ethanol to acetone we have used the U.S Patent number US 21011/0015445 published on January 20, 2011 and registered by Masuda and coauthors,

in which they present a technique for producing acetone in a high yield from hydrated ethanol derived from biomass, without requiring a large amount of energy: —*Hydrated ethanol derived from biomass is heated to a reaction temperature of 400°C or higher in the presence of a Zr-Fe catalyst, thereby producing acetone* (Masuda et al, 2011). The value of water was calculated by using the solution composition and ethanol recovery rates. The energy consumption was calculated by the energy required to bring the solution to the operation point and estimating no residual energy recovered, finally being estimated on 6.21 MJ of heat. Due to the efficiency of the process an amount of 0.43 kg/kg acetone of waste streams is produced, of which 0.142kg is CO₂ and 0.286kg is ethanol. Ethanol is not recycled and it is sent to the waste stream to provide heat for the process.

For the capital, we can use ethanol plant infrastructure that includes transformation and occupation of land, materials, energy uses, emissions and dismantling from EcoInvent database, which has an annual production of 90000 tons of ethanol along 20 years. We can adjust this value for our ethanol plant, which has a production of 8090 metric tons of ethanol (density 0.789 kg/l) along 30 years.

Table 6
Inputs (raw materials, energy and capital) for the production of 1 kg of ethanol and acetone in plant

Material and Energy inputs	Ethanol, kg	Acetone, kg
Raw Materials		
Glucose, kg	2.47	0
Ethanol, kg	0	1.43
Water, kg	15.39	4.57
Energy inputs		
of which, heat MJ	11.74	6.21
of which, electricity MJ	1.04	0
Capital		
ethanol fermentation plant/ CH/ unit	4.12E-09	

4.1.8 From Glucose to PLA

For the production of Polylactic acid from Glucose we use the values of energy consumption given of a commercial plant (Vink et al, 2003) that we split into 85% Thermal energy and 15% Electricity, following other studies (Dornburg et al, 2006; Groot and Borén, 2010; Gruber and O’Brien, 2002). Finally an energy consumption of 12.66 MJ of heat and 2.23 MJ of electricity per kg of lactic acid, and 10.88 MJ of heat and 1.92 MJ of electricity per kg of Polylactic acid is estimated. Waste streams and energy consumptions related to other operations and supplies are not taken into account. Water is estimated from the graphs in the study to be around 30 kg per kg of Polylactid acid. 1 kg of dry gypsum is generated per kg of PLA (Dornburg et al, 2006), which is disposed to sanitary landfill. Capital is modeled as a fermentation plant, considering a production of 7616 metric tons per year along 30 years.

Table 7

Inputs (raw materials, energy and capital) for the production of 1 kg of lactic acid and Polylactic acid in plant

Material and Energy inputs	Lactic acid, kg	Polylactic acid, kg
Raw Materials		
Glucose, kg	1.37	0
Lactic acid, kg	0	1.75
Water, kg	0	30
disposal, gypsum, 19.4% water, to sanitary landfill/ CH/ kg	0	1.24
Energy inputs		
of which, heat MJ	12.66	10.88
of which, electricity MJ	2.23	1.92
Capital		
ethanol fermentation plant/ CH/ unit	4.38E-09	

4.1.9 From Hemicelluloses to PHB

Fermentation process of sugars into PHB was modeled following the study of Harding and coauthors. We have used their table “*Mass and energy values for PHB production used in the LCA study*” as data source (Harding et al, 2007) where Energy consumption is 14.8 MJ of heat and 3.94 MJ of electricity per kg of PHB., and match it with Ecoinvent processes.

Table 8

Inputs (raw materials, energy and capital) and emissions for the production of 1 kg of PHB in plant

Material and Energy inputs	PHB, kg	Output as Emissions	PHB, kg
Raw Materials		Direct emissions and waste	
Hemicellulose, unit (0,186kg)	9.022	Carbon dioxide, fossil/ air/ unspecified	0.0024
Water	65.2	Sulfur dioxide/ air/ unspecified	0.000012
zinc monosulphate, ZnSO4.H2O	0.00116	Ethyne/ air/ unspecified	0.0000012
sodium sulphate, from natural sources	0.003	Phosphate/ water/ river	0.0000048
magnesium sulphate	0.0209	COD, Chemical Oxygen Demand/ water/ unspecified	0.8
Ammonium Sulphate, as N	0.0148	Water, cooling, unspecified natural origin/ resource/ in water	13.1
Hydrogen peroxide, 50% in H2O	0.529		
sulphuric acid, liquid	0.03		
phosphoric acid, industrial grade, 85% in H2O	0.0081		
propylene glycol, liquid	0.000005		
Energy inputs			
of which, heat MJ	14.8		
of which, electricity MJ	3.942		
Capital			
ethanol fermentation plant/ CH/ unit	4.49E-09		

Regarding the production of enzymes, an LCA carried out by Novozymes presents some data about emissions linked to the production of their enzymes (Nielsen, P.H. et al, 2006). We have match these values to insert them in our study, despite the amount of enzymes could be neglectable. Again, capital is modeled as a fermentation plant, considering a production of 7420 metric tons per year along 30 years.

4.1.10 Valorization of the waste streams into available heat at plant

In our study we try to assume the proper energetic values of each waste stream, in dry basis, so we could technically use this energy for our processes. These needs of heat and electricity are symbolized as the following processes: “of which, heat” and “of which, electricity”. They were included in our algebraic model so the results will be able to show how much energy we have available, and how much energy we need, split into heat and electricity. This is very useful to know if we can satisfy our needs with the waste streams. Values given for the different waste streams are:

Table 9
Energy content of the waste streams

Process	Amount	Content	Valorized	Comments
Pretreatment	10.3% of initial dry biomass	Extractives and others (19.3MJ/kg) Ash disposed (9%, 0.9% of initial dry biomass)	17.37 MJ/kg	
Pyrolysis	25% lignin pyrolyzed	80% charcoal (31.8MJ/kg), 20% gas (9.2MJ/kg)	27.28 MJ/kg	(Pakdel et al, 1992)
Ethanol from glucose	55.8 % glucose processed	78.8% CO ₂ (48/55.8), bacteria cells, others	---	No taken into account bacteria calorific value
Phenolic compounds	83.75% of the pyrolysis oil	Pyrolysis oil not transformed into phenolic compounds	22.5 MJ/kg	(Pakdel et al, 1992)
Acetone	0.26 kg per kg acetone produced	Ethanol	27.3 MJ/kg	Ethanol not converted is burned for heat.
Fermentations of Lactic acid, Polylactic acid and PHB	---	Mainly fermentation residues and gypsum (Calcium Sulphate)	---	Not found source which supports this practice, hence we do not assign a calorific value

The energy balance results that 7.77 MJ/kg dry biomass and 4.92 MJ/kg dry biomass input are available for the case of Poplar and Eucalyptus respectively. Meanwhile, our process requires 7.24MJ of heat and 1.1 MJ of electricity per kg dry biomass input for the case of Poplar, and 7.93 MJ of heat and 1.26MJ of electricity for the case of Eucalyptus. This means that for the case of the poplar we could theoretically cover the demand of heat in plant as we have supposed, but technically we should achieve efficiency in the boiler of around 93%, and we have modeled our boiler (For burning charcoal

and pyrolysis oil) with an efficiency of 85% following the indications of the study of green electricity production based on bio-oil co firing in a natural gas fired power station when burning this mix (Biomass Technology Group, The Netherlands). Eucalyptus cannot even cover this demand theoretically due to its lower lignin content. We will then need to supply heat from natural gas (grid) at the facility to match our needs.

How the available power is allocated among the different process is worth to mention, although a simple approach has been taken. Per kg dry biomass input:

Heat available = Gross Energy available * Efficiency;

Self-sufficiency factor = Heat available / Heat needed;

This ratio is applied to each process, for example, if the ratio is 0.9, a 10% of the heat needs for each processes come from natural gas combustion. Therefore, we will have two heat processes:

- Heat from waste streams (self-supply)
- Heat from outside (natural gas from the grid): EcoInvent database

Although this has more influence in the most energy intensive processes, it makes sense from the physic point of view, since we expect to have a mix source of heat to distribute along all the plant.

Our system handles 100000 tons/year, at a rate of 8000h/y working hours, gives us 12500 kg/h, which is the feed rate. We have to provide energy for the worst case, Eucalyptus, which needs 7.93MJ of heat/kg dry biomass. Multiplying by the feed rate we get 9115 MJ/hour or 27.53 MW. Components of the boiler for pyrolysis oil would be: 1 component / (total useful energy in lifetime) per useful energy unit. It is considered 30 years as operation and capital time as in the previous processes. A scaling factor of 0.7 was applied as effect of the high level of energy production.

Values of emissions per MJ followed the Combined Heat and Power study at NTNU (Guest, 2010) for “*Heat from waste streams (self-supply)*”, which used the GEMIS v4.5 database process: “*Small scale CHP: ‘woodgas-aCFB-wood-wastes-A ½-ICE-cogen 1 MW – 2010/gas’*”. Methane emission factor has a very small contribution to the overall greenhouse gas impact (despite the characterization factor is much higher) and it will be neglected since we are considering the whole carbon cycle as CO₂ for the climate change indicator, on the other hand, carbon monoxide is included since it has a important contribution on other indicators such human toxicity.

Table 10

Inputs (raw materials, energy and capital) and emissions for the production of 1 MJ of heat from waste streams at plant

Material and Energy inputs	Heat from waste streams (self-supply), MJ	Output as Emissions	Heat from waste streams (self-supply), MJ
Raw Materials		Direct emissions and waste	
Wastestream for energy recovery, kg	0.71	Sulfur dioxide/ air/ high population density	0.00000018
Energy inputs		Particulates, > 10 um/ air/ high population density	0.00000625
of which, electricity MJ	0.0111	Carbon monoxide, biogenic/ air/ high population density	0.00012389
Capital		NMVOC, non-methane volatile organic compounds, unspecified origin/ air/ high population density	1.2389E-05
cogen unit 1MWe, common components for heat+electricity/ RER/ unit	4.40E-10	Nitrogen oxides/ air/ high population density	9.2222E-05
cogen unit 1MWe, components for heat only/ RER/ unit	4.40E-10	Dinitrogen monoxide/ air/ high population density	0.0001

4.1.11 Modeling the Electricity mix in Spain

The last step is modeling the electricity mix of Spain using the report by the Spanish Electric Network “Red Eléctrica Española” for the year 2009 (REE, Annual Report 2009).

Table 11

Share of the electricity mix in Spain, and its contribution for 1 MJ electricity from the grid at plant

Energy mix in Spain	Share of the electricity mix in %	Of which Electricity, MJ
electricity, natural gas, at combined cycle plant, best technology/ RER/ kWh	29	0.08
electricity, oil, at power plant/ ES/ kWh	1	0.0027
electricity, hydropower, at power plant/ ES/ kWh	10,6	0.029
electricity, hard coal, at power plant/ ES/ kWh	12	0.033
electricity, nuclear, at power plant/ UCTE/ kWh	19	0.052
electricity, at wind power plant/ RER/ kWh	13,8	0.038
electricity, production mix photovoltaic, at plant/ ES/ kWh	2,6	0.0072
electricity, production mix ES/ ES/ kWh	12	0.033
Electricity Mix Spain 2009, kWh	100	0.277

4.2 Carbon Cycle in biomass scenarios

Once the rotation period has been defined we obtain the Global Warming Potential for it following the FIRF factor for CO₂eq in 100 years horizon, which is 0.08. Per 1 kg of dry biomass, which is our starting point for the delivery unit, we have 0.494 kg of C. All of this carbon will be combusted or

oxidized within one year from the harvest of the lignocellulose biomass. The combustion/oxidation of this carbon follows the formula:

$$1 \text{ C} + \text{O}_2 = 1 \text{ CO}_2$$

Molar weight of Carbon (C) = 12 gr/mol
Molar weight of Molecular Oxygen (O₂) = 2 · 16 gr/mol = 32 gr/mol
Molar weight of Carbon Dioxide (CO₂) = 12 gr/mol + 2 · 16 gr/mol = 44 gr/mol

$$0.494 \text{ (kg C)} \cdot (44 \text{ gr/mol}) / 12 \text{ (gr/mol)} = 1.81 \text{ kg CO}_2 \text{ per kg dry biomass}$$

Due to the delay on uptake by biomass growth according to GWPbio:

1.81 kg CO ₂ per kg dry biomass · 0.08 kg CO ₂ eq/kg CO ₂ = 0.145 kgCO₂eq per kg dry biomass.				
Combustion/Oxidation	Products	Carbon content	Amount	kg CO ₂ eq
Products	PLA (C ₃ H ₆ O ₃) 90g/mol	0.4	0.0761kg	0.0089
	PHA (C ₄ H ₈ O ₃) 104 gr/mol	0.4615	0.742kg	0.01
	Acetone (C ₃ H ₆ O) 58 gr/mol	0.62	0.566kg	0.01
	Phenol (C ₈ H ₈ O ₃) 152 gr/mol	0.63	0.322kg	0.0059
Waste streams (rest)		0.50	0.76kg	0.1096
TOTAL			1	0.145

Per kg of waste streams (not taking into account bacteria cultivation, around 5%) the value is 0.15521, and for MJ of waste streams combusted (though some of this CO₂ belongs to fermentation processes) it is 0.0166.

We proceeded analogously for the Eucalyptus Case.

4.3 Petrochemicals: Basic and specific data of the Life Cycle Inventory

4.3.1 Extraction, exploitation and transportation of oil and gas

For the extraction, exploitation and transportation of the crude oil “crude oil, from Algeria, kg” we use the process from EcoInvent database “crude oil, production RAF, at long distance transport /RER/ kg” which takes into account all these phases from North of Africa to Europe for crude oil, in average values. For natural gas, we define the process “liquefied petroleum gas, from Algeria /kg”, which is a series of the ecoinvent processes “natural gas, at production/ NG/ kg” which is natural gas from Nigeria and considered equivalent, with a density value of 2.02 kg/Nm³, and “transport, liquefied natural gas, freight ship /OCE/ tkm”, with a distance of 1100 km and 30 years of operation with the annual imports of natural gas constant.

4.3.2 Refinery La Rábida. Production of ethene, propylene and benzene

La Rábida (Huelva, Spain) refinery map and processes details can be found publicly available in the website of CEPSA, S.A. Also, the data about general inputs and outputs of the refinery for the year 2009 and the environmental certificate (ISO 14:000 series). More details about the facility were

given very kindly for this study by the contact Carlos Manuel Delgado Chaparro through phone meetings. More specific data for the benzene and propylene production per year, like mass and energetic consumptions for benzene and propylene were provided by the plant engineer. The total inputs (crude, gas, energy...) to produce one kilogram of benzene and propylene can be found in the tables below. The electricity is modelled as normal refinery mix of electricity from Ecoinvent database.

Table 12
Inputs (raw materials, energy and capital) and emissions from operation of the refinery

Material and Energy inputs	BENZENE, kg	PROPYLENE, kg	Output as Emissions	CEPSA S.A Refinery La Rábida, per kg of benzene or propylene
Raw Materials			Direct emissions and waste	
Crude Oil, kg	1	1	Carbon dioxide, fossil/ air/ unspecified	0.000267
Liquefied Natural Gas, kg	0.2618	0.2618	Sulfur dioxide/ air/ unspecified	0.00085
Water, kg	0.83	0.83	Nitrogen oxides/ air/ unspecified	0.0026
Energy inputs			VOC, volatile organic compounds, unspecified origin/water/ ocean	0.00002
Heavy Fuel Oil, kg	0.1767	0.065	Phenol/ air/ unspecified	4.48E-05
Electricity, kWh	0.127	0.2744	TOC, Total Organic Carbon/ water/ unspecified	0.010275
Steam, MJ	2.4	2.26	Suspended solids, unspecified/ water/ ocean	0.00791
Hard Coal Supply Mix, kg	0	0.475	Oils, unspecified/ soil/ industrial	0.001835
Capital			Nitrogen/ water/ river	0.003955
refinery/ RER/ unit	1.51E-10	3.02E-10	Phosphorus/ water/ unspecified	0.000489
Comments	221144 mT/year. 30 years	110274 mT/ year. 30 years.	COD, Chemical Oxygen Demand/ water/ unspecified	0.024382
			Hydrocarbons, unspecified/ water/ unspecified	0.00053
			Ammonium, ion/ water/ unspecified	0.002936

Also, Data gathered includes very small quantities of other substances:

- Catalogued as dangerous: Acid drainage, Solid and terrain polluted. That was model as a process: disposal, refinery sludge, 89.5% water, to sanitary landfill. Being the value of all sum together equals to 0.000670593 per kg of product in the refinery.

- Inert residues: Mud from effluents, mud from raw water, non useful metals, urban inert materials, isolation materials, fluorescents tubes and Hg bulbs, clean plastics and others.
- Urban and others: Organic urban waste, construction waste, ink cartridges, normal batteries, light packages, electrical/electronic waste.

For the capital 1 unit of “refinery/ RER/ unit” (takes into account facility, land use and dismantling) from EcoInvent database was selected divided by the annual production volume of each chemical along 30 years as we can see in the table above.

Regarding emissions, values reported for the activity given by ton of output of any product in the refinery were taken and included in the inventory. Other data, for example, the refinery industrial area occupation is 240 ha, it is not included in the inventory since the capital already takes it into account, though less accurate, we do not want to fall into any double counting.

Since ethylene is not produced in this plant, it was decided to use as background the EcoInvent database. But it is supposed that its production occurs in the same refinery. This approach was accurate enough as we will be able to see in the results and discussion part.

4.3.3 Petrochemical plant Palos de la Frontera. Phenols and Acetone.

The Petrochemical Plant of Palos de la Frontera (Huelva, Spain), owned also by CEPSA, S.A, it is only three kilometres from the Refinery of Palos de la Frontera, and benzene and propylene are sent by pipeline as the company confirmed. Impacts linked to the construction, operation and disposal of this pipeline will be neglected. For the phenol and acetone yields, as we could not have access to them in the Petrochemical Plant of Palos, it was used literature based on case studies from the sector (Meyers et al, 2005), exactly the “The Polimeri Europa Cumene-Phenol Processes”. As we discuss when presenting the case, the production of acetone and phenol is one unit of production, hence, we have to deal with an allocation issue. The decision taken was to use an exergy allocation (in the exergy content of the products); reasons can be found more explicitly in the discussion part.

We need to add that the allocation was performed to all the petrochemical plant, since we had inputs (raw materials and energy) and outputs (products and emissions) for the entire plant per year. In the following table we can see the main data (light green) with products production per year in kg, in share by mass, in share by total output (1.69kg output per kg phenol output, which was used as delivery unit) and chemical exergy in MJ of exergy by kg product (element), noting that dimethylacetamine, the major derivative of methylamine, was assumed to have the same chemical exergy as methylamine, this assumption that not make difference practically, since dymethylacetamide has around 1% of importance in terms of unit of production. The calculations, the last three columns in darker green, gives us the allocation factor we should apply and the share of MJ of exergy in the

unit of production (1.69kg of delivery unit: 1 kg of phenol, 0.625 kg acetone, 0.0291 kg alfa-metilstyrene, 0.027kg methylamine and 0.011 kg of dimethylacetamide).

Table 13
Exergy allocation in the petrochemical plant

Products	Data				Calculations		
	Production in mT/year	Share in Mass	Mass in delivery unit, kg	Chemical exergy Mjex/kg	Exergy Production Mjex/year	Allocation factor	MJ ex/delivery unit
Alfa-methylstyrene	12134	0.017	0.0291	5040.0	61155360	0.03	146.7
Phenol	416893	0.591	1	3128.6	1304291439	0.70	3128.6
Acetone	260848	0.370	0.625	1788.5	466526648	0.25	1119.1
Methylamine	11237	0.016	0.027	1717.0	19293929	0.01	46.3
Dimethylacetamide	4632	0.007	0.011	1717.0	7953144	0.00	19.1
Total	705744	1	1.69	2634.41	1859220520	1.00	4459.7
					Average exergy MJ of products	MJ ex/delivery unit (1.69kg)	
					2634.41	4459.7	

All the inputs in terms of raw materials, energy and capital, and emissions as outputs, are related to the unit of production in the petrochemical plant of Palos (1.69kg), which is 4459.7 MJ of exergy in petrochemical products.

Table 14
Inputs (raw materials, energy and capital) and emissions from operation of the petrochemical plant (MJ) of exergy/delivery unit

Material and Energy inputs	OPERATION PETROCHEMICAL PALOS, MJex/ unit mix	Output as Emissions	OPERATION PETROCHEMICAL PALOS, MJex/ unit mix
Raw Materials		Direct emissions and waste	
Water, kg	0.001278	Carbon dioxide, fossil/ air/ unspecified	6.28E-08
Zeolite, powder, kg	7.52E-09	Sulfur dioxide/ air/ unspecified	4.48E-09
Disposal, Zeolite, kg	7.52E-09	Nitrogen oxides/ air/ unspecified	1.3E-07
Disposal, wood untreated, kg	6.32E-07	VOC, volatile organic compounds, unspecified origin/water/ ocean	1.08E-07
Waste paper, sorted, kg	1.92E-05	Phenol/ air/ unspecified	4.48E-11
Methanol, kg	1.45	TOC, Total Organic Carbon/ water/ unspecified	1.95E-08
Ammonia, kg	0.39	Suspended solids, unspecified/ water/ ocean	3.21E-08
Energy inputs		Oils, unspecified/ soil/ industrial	3.59E-10

Electricity, kWh	8.4E-05
Heat, Natural Gas	0.002955
Capital	
chemical plant, organics/ RER/ unit	1.79287E-14
Comments	1.89E+09 MJex/year. 30 years.

In the energy inputs is convenient to note that the module called “*natural gas, burned in boiler atm. low-NOx condensing non-modulating >100kW*” from EcoInvent database includes “*fuel input from low pressure (CH) network, infrastructure (boiler), emissions, and electricity needed for operation. The module uses the average net efficiency for the type of boiler (estimated from literature). The heat distribution is not included*”.

Also, data gathered includes very small quantities of other substances:

- Catalogued as dangerous: Acid drainage, Solid and terrain polluted. That was model as a process: disposal, refinery sludge, 89.5% water, to sanitary landfill. Being the value of all equal to 0.000206621 per MJ ex/unit mix in the Petrochemical.
- Inert residues: Mud from effluents, mud from raw water, non useful metals, urban inert material, Isolation materials, Fluorescents tubes and Hg bulbs, clean plastics, others.
- Urban and others: Organic urban waste, construction waste, ink cartridges, normal batteries, light packages, electrical/electronic waste.

Regarding capital, 1 unit of “chemical plant, organics /RER/ unit” from EcoInvent database was selected (this process includes land use, buildings, facilities and dismantling of an average chemical plant) divided by the annual MJ of exergy produced in the plant along 30 years as we can see in the table above.

Regarding emissions, values reported for the activity given by ton of output of any product in the refinery were converted to MJ of exergy in each unit mix or delivery unit (1.63 kg). Apart of the reported emissions in air and water bodies, the petrochemical industrial area occupation is 65.8 ha, but we have considered the capital from EcoInvent database for a organic chemical plant.

4.3.4 Polyethylene and Polypropylene Production

We use the data provided for consumption of Raw materials and Utilities for “Borstar LLDPE and HDPE Technology” and “Borstar Polypropylene Technology” Case Studies respectively (Meyers et al, 2005).

Table 15

Consumptions for ethylene, propylene and catalysts per kg of polyethylene and polypropylene

Material and Energy inputs	HDPE Polyethylene, kg	Polypropylene, kg
Raw Materials		
Ethylene, kg	1.01	0.1002
Propylene, kg		0.9018
Ziegler Natta catalyst, kg	0.00008	0.000015
Ziegler Natta cocatalyst, kg	0	0.000215
Disposal, catalyst, kg	0	0.000215
Water, kg		0.1
Hydrogen, kg	0.0003	0.0001
Propane, kg	0.01	0
Energy inputs		
Electricity, kWh	0.5	0.16
Steam, MJ	0.2	0.17
Capital		
chemical plant, organics/ RER/ unit	3.57E-10	3.02E-10
Comments	93424.82 mT/ year. 30 years.	110274 mT/ year. 30 years.

4.3.5 Catalyst modelling

A catalyst productivity of 30kg product/gr catalyst based on Basell technology is used; this is 1/30000 kg catalyst/kg product. BASF sent for this thesis a package of information about its catalyst products through the Global business director of Polyolefin catalyst, Apala Mukherje. This information was regarding the quality of the products more than the process of preparation itself, but it was valid to assume that the “Business to Business” purchase is from Tarragona facility of BASF, so we have accounted an estimation of 1000 km from both facilities (2000km return trip) utilizing a heavy transport lorry. The process used from EcoInvent database was “transport, lorry >16t, fleet average/ RER/ tkm”.

Modelling the catalyst production is complicated due to the fact that it is a long process. We have included the needs of raw materials upstream (EcoInvent dabatase processes) from the chemical path shown in the previous chapter, but not intermediate processes and their related energy consumptions.

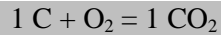
Table 16

Catalyst production

Material and Energy inputs	Process	Amount
Hydrochloric Acid, 30% in H2O, kg	ZIEGLER-NATTA CATALYST, kg	0.71
Ilmenite, 54% Titanium dioxide, kg	ZIEGLER-NATTA CATALYST, kg	0.5731
Ethylene, kg	TEAL COCATALYST, kg	0.736
Aluminium primary, kg	TEAL COCATALYST, kg	0.236
Hydrogen Liquid, kg	TEAL COCATALYST, kg	0.000005262

4.4 Carbon Cycle in the Petrochemical scenario

There are 0.84 kg of C per 1 kg of crude oil, 0.82 per kg C of VGO (Vacuum gas oil) and 0.8571 per kg of ethene gas (multineer refining characteristic brochure). In our case we remember that VGO is supposed to be equivalent to Natural gas. All of this carbon will be combusted or oxidized within one year from the extraction of the oil and gas. The combustion/oxidation of this carbon follows the formula:



Molar weight of Carbon (C) = 12 gr/mol

Molar weight of Molecular Oxygen (O₂) = 2 · 16 gr/mol = 32 gr/mol

Molar weight of Carbon Dioxide (CO₂) = 12 gr/mol + 2 · 16 gr/mol = 44 gr/mol

0.84 kg C · 44 gr/mol / 12 gr/mol = 3.08 kg CO₂ per kg crude oil.

0.82 kg C · 44 gr/mol / 12 gr/mol = 3.00 kg CO₂ per kg vacuum gas oil.

0.857 kg C · 44 gr/mol / 12 gr/mol = 3.14 kg CO₂ per kg ethene gas.

2.31 kg of crude oil · 3.08 kg CO₂ per kg crude oil = 7.24 kg CO₂eq

0.612 kg of VGO · 3.00 kg CO₂ per kg VGO = 1.84 kg CO₂ eq

1.11 kg ethene gas. = 3.48 kgCO₂eq

Total = 12.58kgCO₂eq

Chapter V

Analysis and Results

5.1. Environmental Impact Assessment of life cycle stages

Prior to the main results for the Functional unit, relevance of the different life cycle stages for petrochemical and biochemical scenarios is shown. This will give us an insight of which steps of the production of a delivery unit (Production unit) are more important and hold most of the impacts for all indicators. This results will let us understand deeper the system regarding the production of a functional unit.

5.1.1. Chemicals from biomass

Over the cradle to gate study, the lifecycle inventory calculations indicate, for example, that for most impact categories the pretreatment phase is a critical process of the production of chemicals from biomass, since it deals with the initial input in the biorefinery. But using structural path analysis methodology we can note down that those impacts are related to the assumption of capital, more in detail, copper extraction, use and disposal in the facility.

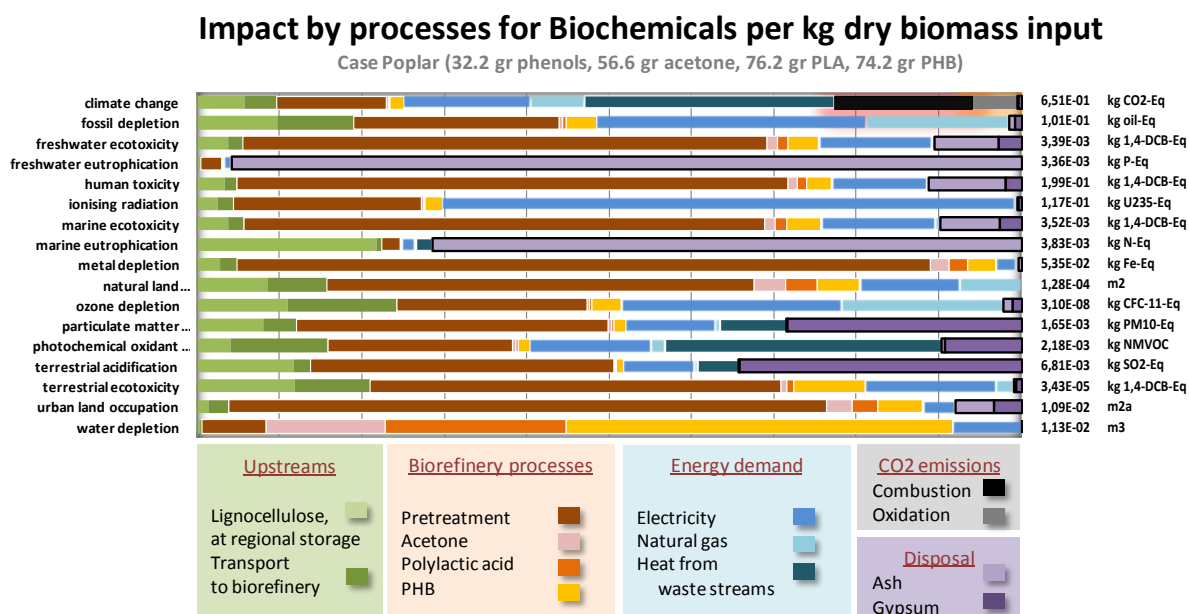


Figure 10: Impacts for the delivery unit of chemicals from biomass (Poplar Case) from field to gate including CO₂ emissions along the entire carbon cycle.

Cultivation, forest operations and transportation show a moderate contribution to most of the impacts except agricultural land occupation and eutrophication. Phenols are not presented in the graphic because there were model just attending their energy needs, which are represented stand alone. Electricity is an important contributor to several impact categories, especially taking into account that the energy needs in the facility are mainly heat. Import and combustion of natural gas to cover the rest of the heat is not very prominent in the poplar case, since all the heat demand is almost covered, but

still we can appreciate a significant impact on fossil and ozone depletion. Disposal of ash filtrated from the sludge has a tremendous impact on freshwater and marine eutrophication, while disposal of gypsum from polylactic acid production contributes significantly to particulate matter formation and acidification. Pyrolytic oil and phenol production are not present since their impacts are just associated with energy consumption.

For the Climate Change Indicator we can observe that the carbon content in the feedstock (CO₂ combustion and CO₂ oxidation) only accounts for an overall 20% of the global CO₂eq along the entire process (16.84% for combustion and 5.4% for use). The share of this contribution can change substantially due to the GWP factor used when assuming other rotation period, for example, one year rotation period would reduce these values almost to zero, while more than the assumed 20 years horizon would increase substantially the contribution for combustion and oxidation stages. 30.2% the overall GHG effect is due to dinitrogen monoxide formation in the combustion of waste streams.

Freshwater ecotoxicity indicator is formed by disposal of sulfidic tailing from the building demolition (31.99%), pulp plant dismantling (14.81%) and disposal of lignite/coal mining from coal extraction (13.53%/12.91%). Eutrophication indicators as commented are a consequence of ash disposal (>70%) on both cases. Human toxicity is a product of the disposal of sulfidic tailings for the building demolition (46.24%), lignite+coal in the electricity mix (10.14% + 9.6%) and ash disposal (9.2%). Similar behavior presents marine ecotoxicity indicator. Particulate matter formation is a sum of the impact provoked by disposal of gypsum (28%), production of sulphur dioxide for steam explosion (17%), heat from waste streams (8.12%), burning of hard coal in the electricity mix (8.09%). Meanwhile, Heat from waste streams and wood transportation are main contributors of photochemical oxidant formation, 33.45% and 9.8% respectively, followed by coal in the electric mix (9.2%). Terrestrial acidification indicator is a sum of the disposal of gypsum (34%), and production of sulphur dioxide (20.7%), being the third in importance phosphorus in soil (9.2%). Terrestrial ecotoxicity has as main contributor drilling waste due to gas production (18%), followed by disposal of wood (12.09%). We could also comment that the urban land occupation indicator is covered by biorefinery facility for pretreatment, equivalent to a pulp plant (63.44%), and all fermentation processes equivalents to a ethanol fermentation plant (8.5%), being the third component landfill (2.9%).

In the Eucalyptus Case we can appreciate that the lignocellulosic production has much more importance than before in the life cycle. This is due to our fertilizing and irrigation assumptions. The second thing we can observe is the increase of impact on diverse categories of the natural gas combustion. This is logical since Eucalyptus has lower lignin content; therefore less available energy in the waste streams.

Impact by processes for Biochemicals per kg dry biomass input

Case Eucalyptus (15.92 gr phenols, 62.7 gr acetone, 84.3 gr PLA, 110.8 gr PHB)

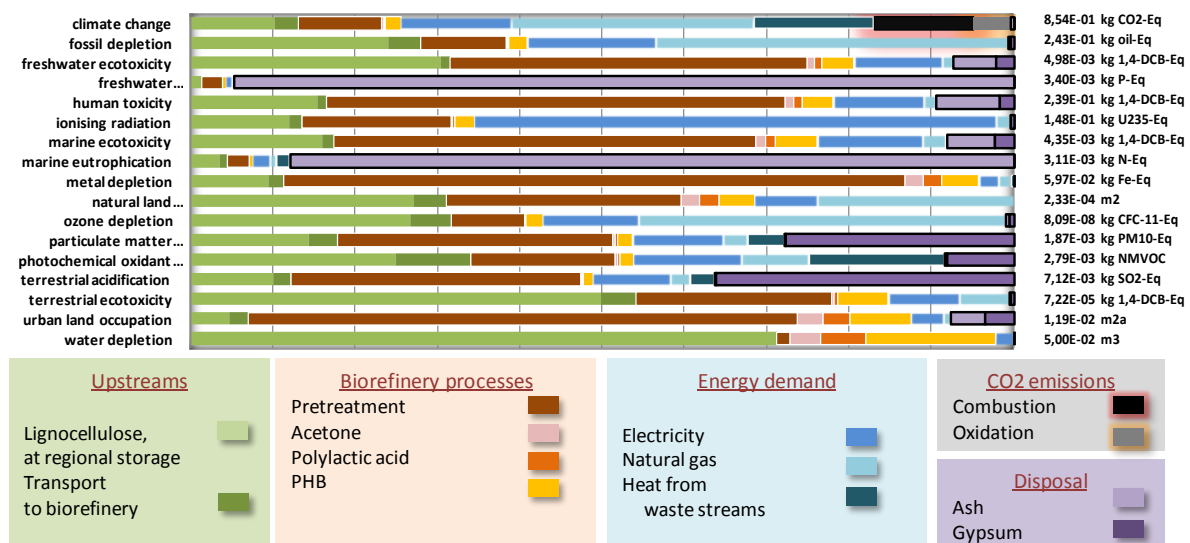


Figure 11: Impacts for the delivery unit of chemicals from biomass (Eucalyptus Case) from field to gate including CO₂ emissions along the entire carbon cycle.

After changing feedstock, Climate change contributions are mainly combustion of waste streams (12% CO₂ and 14.57% CO₂eq from other emissions, mainly Dinitrogen monoxide), natural gas combustion (24%), coal in the electricity mix (6.2%) and oxidation of the chemicals from biomass within one year (4.5%). Freshwater ecotoxicity indicator is formed by disposal of sulfidic tailing from the building demolition (23.79%), glyphosate fertilizer (19.11%) and disposal of lignite mining from coal extraction (14.14%). Eutrophication indicators as commented are a consequence of ash disposal, being fertilizers responsible for only 1.6% on marine eutrophication. Human toxicity is again a product of the disposal of sulfidic tailings for the building demolition (42%), lignite and coal in the electricity mix (12.9% + 9.8%) and ash disposal (7.7%). Similar behavior presents marine ecotoxicity indicator. Particulate matter formation is a sum of the impact provoked by disposal of gypsum (27.4%), production of sulphur dioxide for steam explosion (15%), hard coal in the production mix (8.3%) and fertilizers (6.8%). Heat from waste streams only accounts 4.5% here and particulate matter from the transport of wood 2.8%. Meanwhile, Heat from waste streams and fertilizers are main contributors of photochemical oxidant formation, 26.53% and 14.2% respectively, followed by coal in the electric mix (8.4%). Terrestrial acidification indicator is a sum of the disposal of gypsum (36%), and production of sulphur dioxide (19.8%), again, the third in importance is coal in the electric mix. Terrestrial ecotoxicity has as main contributor, glyphosate (24%), drilling waste due to gas production (21.4%) and disposal of ash as important factor (7.5%).

5.1.2. Petrochemicals

The relevance of each life cycle stage depends on the particular environmental impact being considered, for example, that for greenhouse gases emissions, the oxidation of the petro derived products within one year accounts for approximately 60% of the emissions, the remain 40% is due to exploitation and transport of petroleum products (oil and gas) with a 10% of share, refining around 15%, petrochemicals processes around 15% and the rest on others (disposal to municipal waste 7.2%). Meanwhile import of petroleum products is evidently the main contributor to fossil depletion, being the rest related to the combustion process for heat and electricity in plant. The values of direct emissions in the refinery and petrochemical plant are main contributors for eutrophication and ecotoxicity of water bodies (freshwater and ocean).

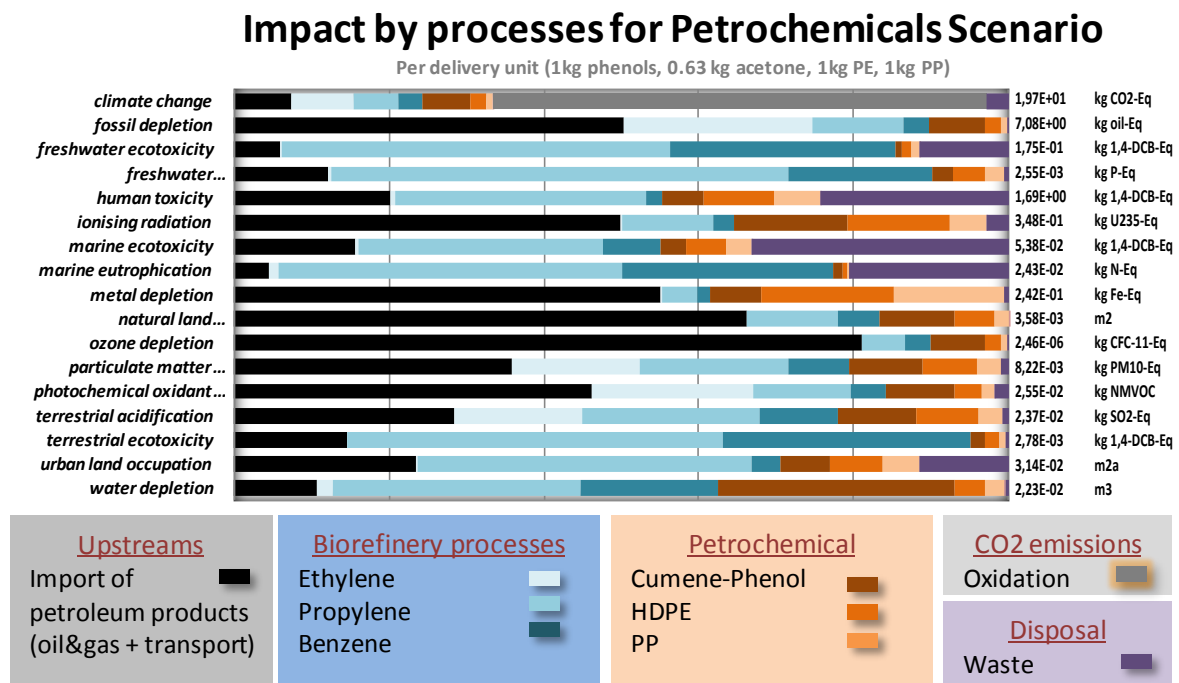


Figure 12: Impacts for the delivery unit from well to gate, including CO₂ emissions along the entire carbon cycle.

Catalysts impact are neglectable since its yield it's very high. Ozone depletion due to the imports of petroleum products is linked to the use of fire extinguishing equipment (containing BrCl3/Halon 131) onshore and offshore and the metal depletion is linked to the construction of infrastructures, mainly stainless steel and electrical wires in facilities and the disposal measured of heavy mud and heavy metal drainage in plant.

5.2. Main results: Benchmarking of the different scenarios for the functional unit

In the table we can find the results of our study for the functional unit for ten different indicators, sorted in the table in four categories:

- Climate change and Fossil depletion
- Water bodies and water depletion
- Human toxicity and air emissions
- Terrestrial impacts

Table 17
Result of the environmental profile of the functional unit for ten different impact categories

Impact category	Unit	Petro chemicals	Chemicals from biomass from Poplar	Chemicals from biomass from Eucalyptus
Climate change	kg CO ₂ -Eq	7.62E+00	1.06E+01	1.30E+01
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	2.14E+01	1.12E+01	1.36E+01
Fossil depletion	kg oil-Eq	8.21E+00	1.75E+00	3.96E+00
Water depletion	m ³	2.40E-02	1.63E-01	8.76E-01
Freshwater ecotoxicity	kg 1,4-DCB-Eq	1.92E-01	6.25E-02	9.04E-02
Freshwater eutrophication	kg P-Eq	2.68E-03	6.55E-02	6.62E-02
Human toxicity	kg 1,4-DCB-Eq	1.67E+00	3.70E+00	4.33E+00
Particulate matter formation	kg PM10-Eq	8.13E-03	2.79E-02	2.88E-02
Photochemical oxidant formation	kg NMVOC	2.87E-02	3.75E-02	4.61E-02
Terrestrial acidification	kg SO ₂ -Eq	2.50E-02	1.14E-01	1.05E-01
Terrestrial ecotoxicity	kg 1,4-DCB-Eq	3.12E-03	6.22E-04	1.31E-03

Across the different scenarios the emissions to the environment of greenhouse gases are about 7.62 kgCO₂eq for the petrochemicals and in the range [10.0-12.8] kgCO₂eq for chemicals from biomass. When tracking the complete carbon cycle, emissions come 21.42 kgCO₂eq for petrochemicals and in

the range [11.1-13.4] kgCO₂eq for chemicals from biomass. An extended and precise discussion on this issue is held in the last chapter. For fossil depletion, once we do not use crude oil or natural gas as feedstock in the chemicals from biomass scenarios, it is between 50% to 80% lower; although biomass scenarios consume fossil fuels along the life cycle, for example, diesel in the forest operation and transport of biomass, electricity mix and natural gas (especially Eucalyptus since its lignin content is lower and there is less energy available in its case) to supply the rest of the heat not satisfied by waste streams. Water depletion is 24 litres for the petrochemicals, and around 163 litres and 875 litres for Poplar and Eucalyptus respectively, being this big difference due to the assumption that Poplar is not irrigated during its growth. While petrochemicals impact on the water bodies is double for ecotoxicity, results for eutrophication are much lower (disposal of ash in chemicals from biomass). Also, chemicals from biomass perform worse in Human Toxicity Potential, Photochemical Oxidation formation and Particulate matter formation. Last but not least, we can mention the impacts on ground. Acidification due to the production of chemicals from biomass is almost triple for both poplar and eucalyptus; the terrestrial ecotoxicity is significantly lower, around 80% for poplar and 60% for eucalyptus. In the figure below these values are normalized and compared to the highest value of each scenario.

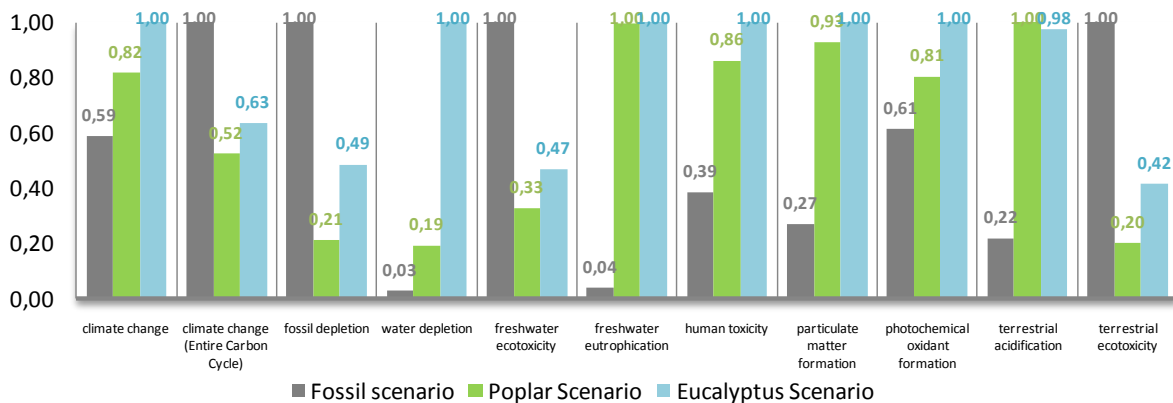


Figure 13: Normalized impact in ten relevant indicators for the different scenarios

5.3. Benchmarking of products within the functional unit

The previous results have shown the environmental performance of the different scenarios. Some common results when benchmarking the different products of the functional unit are:

- Similar environmental profile than the functional unit. Only soft plastics precursors show significant variations.
- Eutrophication is much higher on chemicals from biomass for all products and both cases due to the ash disposal.

Results are presented following this structure: Relevant numbers on Climate change indicators and other relevant category indicators for the product, table with the results, chart with the difference in environmental performance that the product shows compared to 1 kg of Functional Unit (values inside the red circle are more environmentally friendly than average for each indicator) and comments on this relationship.

5.3.1. Phenolic compounds

The production of phenolic compounds shows a clear structure of impacts for petrochemicals. CO₂ emissions are 2.41 kgCO₂eq for petrochemicals, 3.19 kgCO₂eq for Poplar Case (33% higher) and 4.01 kgCO₂eq (66% higher) but when taking into account the entire carbon cycle emissions become 5.8 kgCO₂eq for petrochemicals, 3.38 kgCO₂eq for Poplar Case (42% lower) and 4.19 kgCO₂eq (28% lower). Fossil depletion decreases 74% for poplar but only 39% for Eucalyptus due to natural gas combustion. Water depletion in phenols from Eucalyptus (333 litres) is the biggest from all the products due to low yield and irrigation, but from poplar is the lowest of all (higher yield with no water consumption in the process itself). Also Terrestrial Acidification indicator doubles its impact for the phenol production.

Table 18
Result of the LCA study for Phenols in ten different impact categories

Impact category	Unit	Petro chemicals	Chemicals from biomass from Poplar	Chemicals from biomass from Eucalyptus
Climate change	kg CO ₂ -Eq	2.41E+00	3.19E+00	4.01E+00
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	5.80E+00	3.38E+00	4.19E+00
Fossil depletion	kg oil-Eq	2.22E+00	5.71E-01	1.35E+00
Water depletion	m ³	9.35E-03	1.09E-02	3.34E-01
Freshwater ecotoxicity	kg 1,4-DCB-Eq	6.76E-02	2.51E-02	3.76E-02
Freshwater eutrophication	kg P-Eq	7.40E-04	3.05E-02	3.05E-02
Human toxicity	kg 1,4-DCB-Eq	5.55E-01	1.53E+00	1.80E+00
Particulate matter formation	kg PM10-Eq	2.14E-03	8.65E-03	9.72E-03
Photochemical oxidant formation	kg NMVOC	8.36E-03	1.20E-02	1.67E-02
Terrestrial acidification	kg SO ₂ -Eq	6.63E-03	3.46E-02	3.36E-02
Terrestrial ecotoxicity	kg 1,4-DCB-Eq	1.02E-03	2.40E-04	5.42E-04

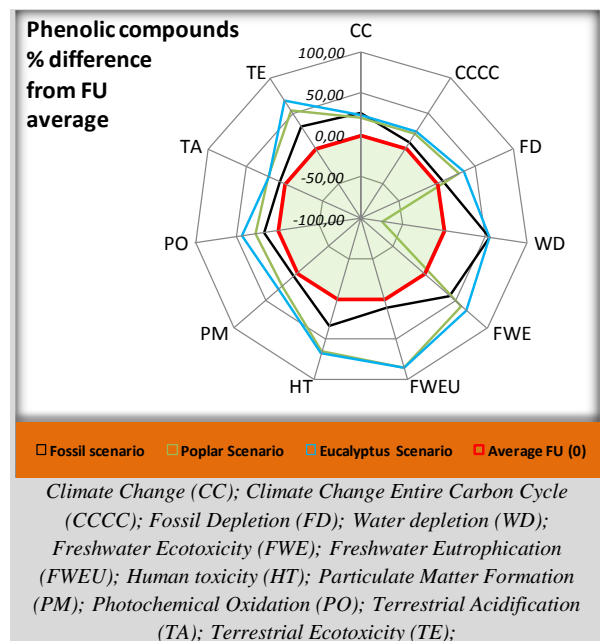


Figure 14: % Difference of phenolic compounds from Functional unit average

Phenol production is the most pollutant chemical of all by the results obtained, being 22% in average for all impact indicators more pollutant than Petrochemicals average, 30% worse than Poplar average and 47% worse than Eucalyptus average. In the case of the petrochemicals is due to the lower efficiency and higher impacts of the cumene-phenol process and in the case of chemicals from biomass in due to the low yield of phenolic compounds.

5.3.2. Solvent (Acetone)

The comparison of chemicals from biomass and petrochemicals follows the same pattern as the functional unit, but with lower values than average; there are no strange behaviours when comparing both environmental profiles. Climate change Impact is 1.83 kgCO₂eq of CO₂ emissions for petrochemicals, 2.42 kgCO₂eq for Poplar Case and 2.99 kgCO₂eq, but when taking into account the entire carbon cycle: 5.27 kgCO₂eq for petrochemicals, 2.6 kgCO₂eq for Poplar Case (51% reduction) and 3.17 kgCO₂eq for Eucalyptus (40% reduction).

Table 19
Result of the LCA study for Acetone in ten different impact categories

Impact category	Unit	Petro chemicals	Chemicals from biomass from Poplar	Chemicals from biomass from Eucalyptus
Climate change	kg CO ₂ -Eq	1.83E+00	2.42E+00	2.99E+00
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	5.27E+00	2.60E+00	3.17E+00
Fossil depletion	kg oil-Eq	2.03E+00	3.59E-01	8.96E-01
Water depletion	m ³	7.61E-03	4.60E-02	1.91E-01
Freshwater ecotoxicity	kg 1,4-DCB-Eq	6.17E-02	1.34E-02	1.95E-02
Freshwater eutrophication	kg P-Eq	7.32E-04	1.47E-02	1.47E-02
Human toxicity	kg 1,4-DCB-Eq	4.28E-01	8.07E-01	9.40E-01
Particulate matter formation	kg PM10-Eq	2.01E-03	4.78E-03	5.25E-03
Photochemical oxidant formation	kg NMVOC	6.65E-03	7.88E-03	9.85E-03
Terrestrial acidification	kg SO ₂ -Eq	6.29E-03	1.83E-02	1.78E-02
Terrestrial ecotoxicity	kg 1,4-DCB-Eq	1.02E-03	1.29E-04	2.81E-04

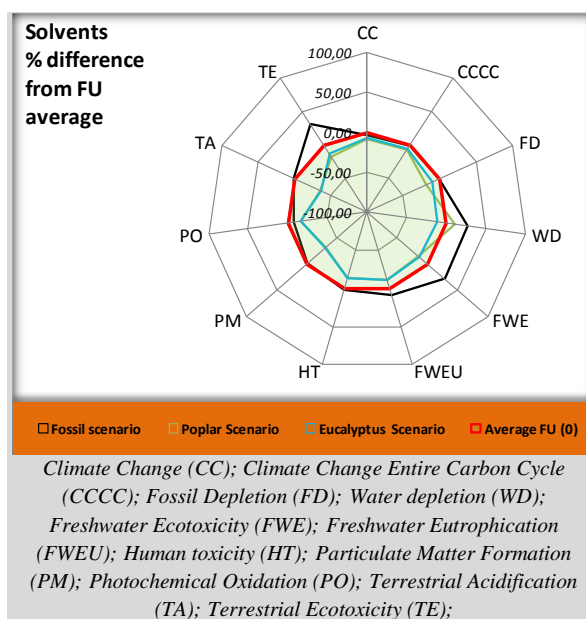


Figure 15: % Difference of solvents from Functional unit average

Acetone from poplar is only worse than the average production in terms of water consumption (not for the Eucalyptus). Acetone from cumene-phenol processes is around 30% worse than the petrochemical functional unit average in ecotoxicity (freshwater and terrestrial), and water depletion (26%).

5.3.3. Soft plastic precursor (Polyethylene and PHB)

PHB presents the best alternative to climate change mitigation with 1.79 kgCO₂eq of CO₂ emissions for petrochemicals, 1.94 kgCO₂eq for Poplar Case and 2.31 kgCO₂eq for Eucalyptus Case, and when taking into account the entire carbon cycle: 4.96 kgCO₂eq for petrochemicals, 2.03 kgCO₂eq for Poplar Case (60% reduction) and 2.44 kgCO₂eq for Eucalyptus (51% reduction). The reason of the smaller difference between Poplar and Eucalyptus Cases, even advantage of the last one on water and terrestrial ecotoxicity, is the higher hemicellulose content of Eucalyptus (higher yield), which compensate partially the lack of energy in its case. On the other hand, it is the only one that presents a higher terrestrial and water ecotoxicity than petrochemicals due to the high load on nutrients for fermentation, also double human toxicity.

Table 20
Result of the LCA study for Soft Plastic precursor in ten different impact categories

Impact category	Unit	Petro chemicals	Chemicals from biomass from Poplar	Chemicals from biomass from Eucalyptus
Climate change	kg CO ₂ -Eq	1.79E+00	1.94E+00	2.31E+00
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	4.96E+00	2.08E+00	2.44E+00
Fossil depletion	kg oil-Eq	1.71E+00	3.65E-01	7.07E-01
Water depletion	m ³	1.30E-03	7.77E-02	1.76E-01
Freshwater ecotoxicity	kg 1.4-DCB-Eq	2.81E-03	1.10E-02	1.49E-02
Freshwater eutrophication	kg P-Eq	1.16E-04	9.49E-03	9.51E-03
Human toxicity	kg 1.4-DCB-Eq	1.59E-01	6.30E-01	7.15E-01
Particulate matter formation	kg PM10-Eq	1.83E-03	3.77E-03	4.06E-03
Photochemical oxidant formation	kg NMVOC	5.77E-03	6.22E-03	7.47E-03
Terrestrial acidification	kg SO ₂ -Eq	5.45E-03	1.39E-02	1.35E-02
Terrestrial ecotoxicity	kg 1.4-DCB-Eq	5.33E-05	1.33E-04	2.29E-04

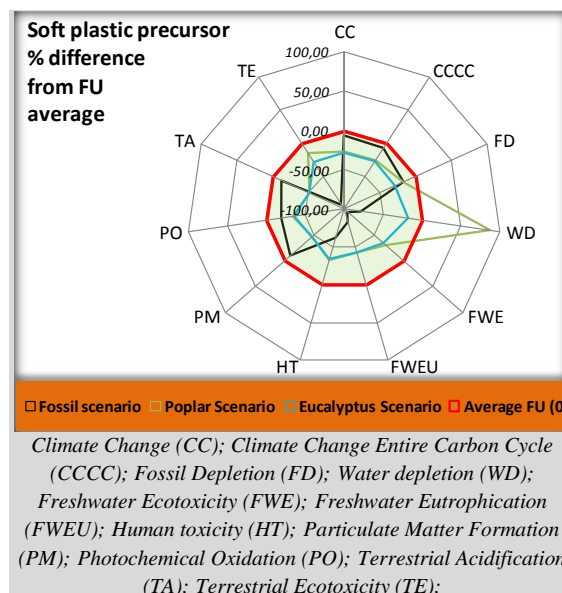


Figure 16: % Difference of soft plastic precursor from Functional unit average

Polyethylene, since comes from natural gas and has a straight polymerization, presents therefore lower impacts. PHB, besides the high load of nutrients and process water, it is also the most environmentally friendly biochemical of the functional unit.

5.3.4. Hard plastic precursor (Polypropylene and PLA)

The comparison of chemicals from biomass and petrochemicals follows the same pattern as acetone, since both come from cellulose. The more demanding processes of Lactic Acid fermentation and Polylactic acid production make PLA significantly worse than acetone. Climate change indicator is 1.59 kgCO₂eq for petrochemicals, 3.04 kgCO₂eq for Poplar Case and 3.65 kgCO₂eq for Eucalyptus Case, and when taking into account the entire carbon cycle: 5.39 kgCO₂eq for petrochemicals, 3.16 kgCO₂eq for Poplar Case (42% reduction) and 3.77 kgCO₂eq for Eucalyptus (31% reduction). Ecotoxicity values (water and terrestrial) of Polylactic acid production are the lowest compared to petrochemicals, but it is much worse on terrestrial acidification, particulate matter formation and photochemical oxidation.

Table 21
Result of the LCA study for Hard Plastic precursor in ten different impact categories

Impact category	Unit	Petro chemicals	Chemicals from biomass from Poplar	Chemicals from biomass from Eucalyptus
Climate change	kg CO ₂ -Eq	1.59E+00	3.04E+00	3.65E+00
Climate change (including entire carbon cycle)	kg CO ₂ -Eq	5.39E+00	3.16E+00	3.77E+00
Fossil depletion	kg oil-Eq	2.25E+00	4.63E-01	1.03E+00
Water depletion	m ³	5.77E-03	4.15E-02	1.57E-01
Freshwater ecotoxicity	kg 1.4-DCB-Eq	6.01E-02	1.33E-02	1.79E-02
Freshwater eutrophication	kg P-Eq	1.09E-03	1.11E-02	1.11E-02
Human toxicity	kg 1.4-DCB-Eq	5.27E-01	7.50E-01	8.53E-01
Particulate matter formation	kg PM10-Eq	2.15E-03	1.08E-02	1.11E-02
Photochemical oxidant formation	kg NMVOC	7.93E-03	1.16E-02	1.28E-02
Terrestrial acidification	kg SO ₂ -Eq	6.59E-03	4.75E-02	4.70E-02

Terrestrial ecotoxicity	kg 1.4-DCB-Eq	1.02E-03	1.24E-04	2.44E-04
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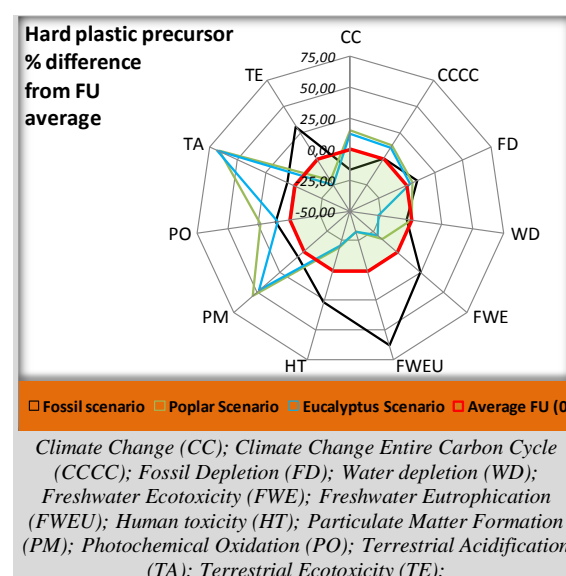


Figure 17: % Difference of hard plastic precursor from Functional unit average

Hard plastics precursors are probably the most interesting environmental profile of all. Polypropylene is more pollutant than the functional unit of petrochemicals in terms of ecotoxicity (water and terrestrial), human toxicity and freshwater eutrophication, but better on climate change than average, and on average for climate change along the entire carbon cycle. Polylactic acid is worse than the average of chemicals from biomass on climate change due to high energy consumption and on terrestrial acidification, photochemical oxidation and particulate matter formation due to the effect of the disposal of gypsum as we could see in the first results of this chapter.

5.4. Disaggregated results for CO₂

Understanding the composition of the CO₂ emissions is very important in this study, and gives us a chance to really appreciate the differences between different Life Cycle scenarios. The following diagram disaggregates the results of CO₂ to show the contribution of each component of the functional unit to the total Climate change Indicator.

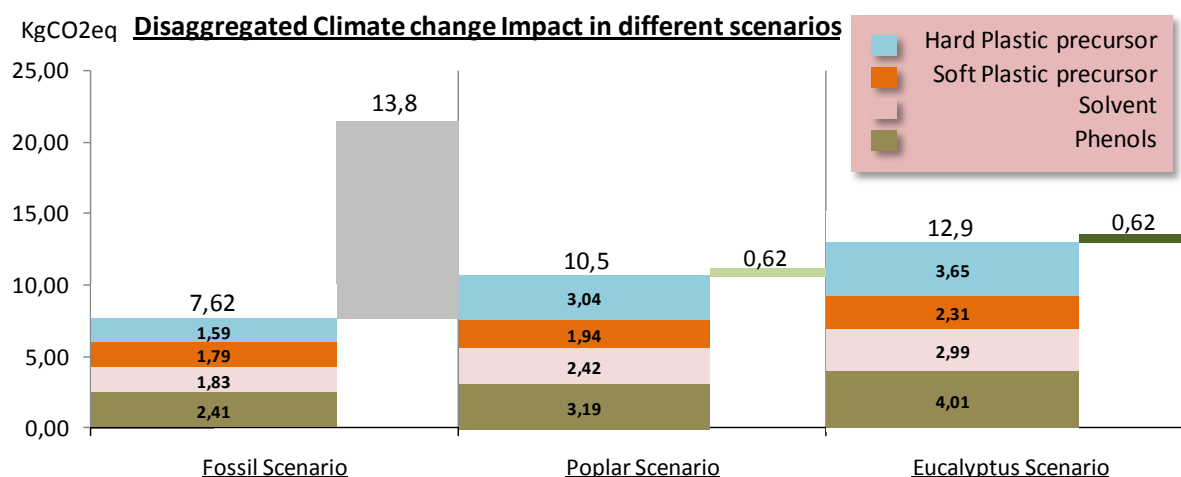


Figure 18: CO₂eq emissions for each component of the functional unit from cradle to gate (left column of each scenario) and from gate to grave (right column of each scenario)

The greenhouse gases emissions from the petrochemicals occurs substantially in the oxidation of the products since the yields are very high and most of the carbon from the feedstock goes to the products. Chemicals from biomass scenarios work the other way around. The greenhouse gas effect of biogenic source is much lower than petrochemicals. For the Poplar scenario, the CO₂eq is associated mainly to emissions from processes (78% of the total GHG emissions); being this 22% of CO₂eq distributed as 16.8% in combustion of waste streams and 5.42 % in oxidation (which is equivalent to the 0.62 kg CO₂ eq shown in the picture).

5.5. Potential improvements in the environmental profile of chemicals from biomass

In order to have more detailed information for our discussion part it seems interesting to develop a sensitivity analysis of the effect of possible improvement approaches. With the previous results of this chapter we can come up with different alternatives:

- **Scaling up:** Construction and dismantling of the pulp plant as one of the biggest contributors to some categories. Increasing the capacity of the plant up to 400000 metric tons per year, to achieve the production level of actual pulp plant production it is a challenge easily achievable, although it requires a strong investment.

- Increase of Energy Efficiency: Most of the processes are relatively new technology; decreasing energy demand on those processes seems to be a normal consequence of experience and scaling up in short term.
- Cleaner electricity: Purchasing of cleaner electricity (hydropower or wind power) in the energy market could be an option to decreasing emissions at plant. A selection of wind power is made.
- Short rotation crops: Short rotation lignocellulosic biomass, collected between one and three years of cultivation could reduce the global warming potential of combustion and oxidation of biogenic CO₂ effect almost to zero. On the other hand, other environmental impacts of a shorter rotation period are not considered here, like change in the feedstock composition or increase on the use of fertilizer and irrigation.

Reductions of environmental impacts in % for different improvement

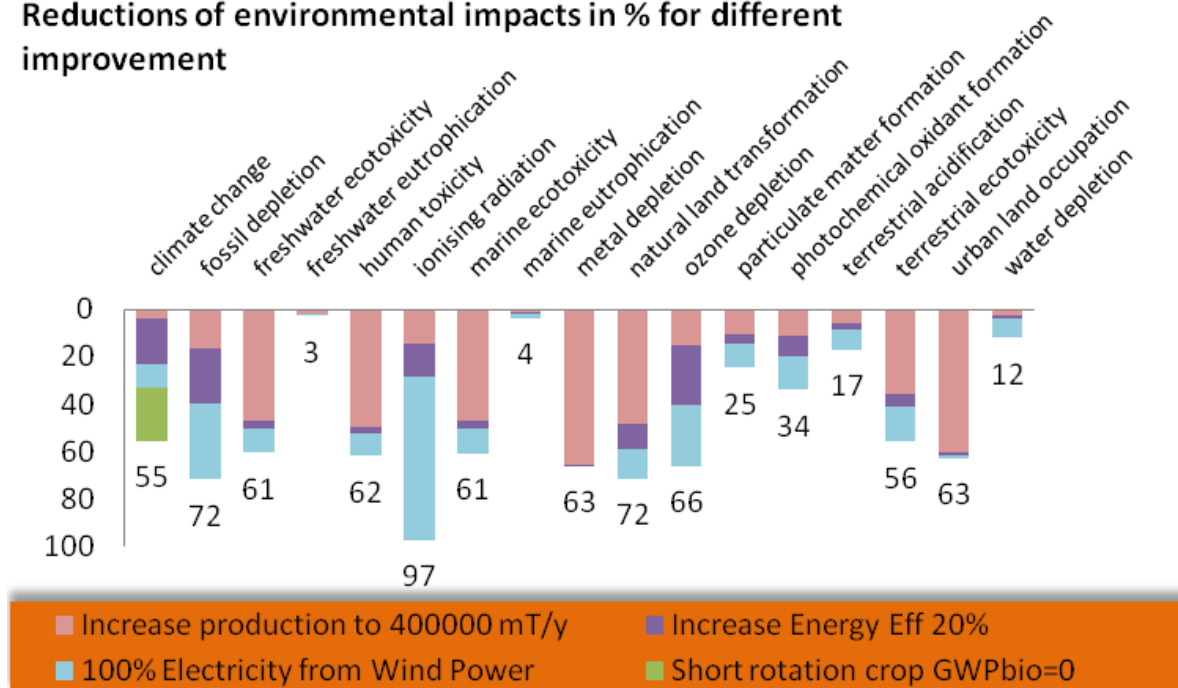


Figure 19: Response of the Impact indicators to possible mitigation approaches (Poplar Case):
Scaling up, Energy efficiency, Cleaner electricity and shorter rotation period.

Some of the results show that the construction and dismantling importance of the pulp plant on the environmental profile of chemicals from biomass are important, and scaling up to achieve the actual level of pulp and paper industry with chemicals from biomass could provide an environmental benefit in some important categories, like freshwater, marine and terrestrial ecotoxicity (47%, 47% and 36% reduction respectively), human toxicity (50% reduction), metal depletion (66% reduction) and of course natural land transformation (48%) and urban land occupation (61%).

Increasing energy efficiency on 20% would let us run our system without combustion from natural gas; this conveys an important reduction on climate change (19%) and fossil and ozone depletion (24% and 25% respectively).

Electricity from Wind power has a potential to decrease climate change (10%) and fossil and ozone depletion (32% and 26% respectively). It is the only one which present an environmental drawback, although insignificant, of an increase of metal depletion (3%).

Last but not least, the effect of a short rotation lignocellulose source could decrease the climate change indicator up to 22%, which is an additional advantage over petrochemicals of around 11%, although other environmental drawbacks of such a substitution are not considered in this study.

As we can see, some Impact indicators didn't suffer relevant modifications. Decrease on eutrophication potential must involved the process of ash disposal, also, Particulate matter formation, Photochemical oxidant formation and Terrestrial acidification could substantially decrease with a treatment of the gypsum from polylactic acid production or a cleaner combustion of waste streams. Water depletion could be reduced by water treatment and recycling at plant for pretreatment and fermentation processes and less irrigation in the case of Eucalyptus.

CHAPTER VI

DISCUSSION AND CONCLUSION

6.1 Objective completion

The goal of this study was to compare the Environmental Impacts of a set of platform chemicals (phenol compounds, solvent, soft and hard plastic precursor) from fossil derived sources and lignocellulosic biomass using Life Cycle Assessment Methodology and including the Global Warming Potential factor for biogenic oxidation. This objective has been compiled. There are, however, some uncertainties in the analysis, and there will be discussed in the following sections. Also, to check the robustness of the study performed, a comparison of the most relevant indicators is made when possible with scientific literature. In section 6.3 there will be a discussion of further studies that would be interesting to be taken in order to improve results or explore the capabilities, efficiency and limits of the system boundaries. In addition, implications of the study are discussed to provide a summary of the main findings which can be used by policy makers and industry leaders.

6.2 Main findings

The results of the comparison revealed that the biochemical system achieves a reduction between 37% and 48% on greenhouse gas emissions for the functional unit when taking into account the entire carbon cycle. Contribution to the climate change indicator from petrochemicals are 21.42 kgCO₂eq (of which 7.62 kgCO₂eq from well to gate), 11.1 kgCO₂eq for chemicals from biomass from Poplar (of which 10 kgCO₂eq from field to gate) and 13.4 kgCO₂eq from Eucalyptus (of which 12.8 kgCO₂eq from field to gate). Production of chemicals from biomass presents higher CO₂eq emissions, but products, co products and waste containing carbon from both fossil (higher carbon content) and biomass usually oxidize or combust not later than after one year of use, and this contribution, usually neglected, is fundamental to understand the beneficial effect of biomass derived products on climate change mitigation, which is also linked to the rotation period of the feedstock and the composition of the lignocellulose biomass.

Chemicals from biomass production reduces fossil depletion between 50% and 80% since we do not use fossil resources as feedstock, just to provide its part in the electricity mix of Spain and the rest of the heat demand that the waste stream is not able to cover, important when our feedstock has low lignin content. Other improvements are visible in the indicators related to ecotoxicity (freshwater and terrestrial ecotoxicity) but the production of chemicals from biomass also involves some trade-offs.

Freshwater Eutrophication and Acidification potential Impacts of the chemicals from biomass are significantly higher than the petrochemical equivalents, mainly due to the disposal of filtered ash from pretreatment and gypsum from Polylactic acid. Water depletion is a function of irrigation procedures, but the Poplar Case (no irrigation) already spends around 140 liters of water more than the

petrochemical equivalents in production processes. Human Toxicity, Particulate Matter and Photochemical Oxidant formation also present worse values than petrochemicals.

After disaggregating the functional unit into the different chemicals for benchmarking, we have found that the phenol production both from fossil and biomass is the most pollutant one, while soft plastic precursor (Polyethylene and PHB) present better environmental performance. Despite the environmental drawbacks of the biochemical production, a set of mitigation approaches like scaling up to the actual production of pulp and paper industry, increasing energy efficiency 20%, purchasing all the electricity from wind power and a shorter rotation period could decrease at least 50% the environmental impacts on 10 out of 16 Impact Indicators, including Climate Change, Fossil and Ozone depletion and Human toxicity and Ecotoxicity (Marine, freshwater and terrestrial) potential.

6.3 Quality and robustness

6.3.1 Internal

6.3.1.1 System boundaries, limitations and parameters

For the petrochemicals, a further development up stream could have increased accuracy of the results, especially regarding impacts on the exploitation and transport of crude oil and gas, but we consider that EcoInvent is enough representation of those processes. Boundaries were increased when including catalyst production, since the ones utilized in polymerization of ethylene and propylene were not present in the database, the quality of this data is evaluated later.

The decision of having a “Well to Gate” study is regarding the numerous derivatives of the functional unit. Possibilities of operating life and disposal seem infinite, and we were interested on the impact to arrive to the most demanded platform chemicals in the market. We solved this issue tracking the carbon to the grave, better said, oxidation of these derivatives in one year horizon, which is discussed in the section 6.3.1.3.

Respect to chemicals from biomass, system boundaries could have been expanded to transform phenol compounds into phenols, but literature confirmed that phenol compounds can perform well in board panels. The rest of the products in the functional unit were contrasted substitutes of the petrochemicals and no further modifications were required. The biomass cultivation, fertilization and forest operations were included into the foreground system once we wanted to develop two different lignocellulosic sources (Poplar and Eucalyptus) and there were solid literature about the topic.

Regarding location, Spain was considered to be representative scenario for substitution of petrochemicals. Spain, as large importer of crude oil for its economy, it is highly dependent from fossil based resources. On the other hand, Spanish agriculture sector has been traditionally important

for the economy. The amount of agriculture residues from different crops is a potential source of lignocellulosic material for the production of chemicals from biomass in Spain.

6.3.1.2 Data quality and assumptions

6.3.1.2.1 Petrochemicals

All the data from the refinery and petrochemical cumene-phenol process has been collected directly from the petrochemical company who owned those facilities. That includes annual production, plant layout, inputs per processes and outputs in terms of air, ground and water bodies. The environmental certificate of the company was very useful for this study, where data was accessible, well explained and accurate. When some more specific data was missing, direct phone meetings were held to gather the details, for example, if the pipeline from the refinery to the petrochemical plant was longer than 10 km. This data should all be reliable. For the polyethylene EcoInvent database was used and for the polyethylene and polypropylene, company case studies from Borstar found in the literature (Meyers et al. 2005) were used, being this a relevant and up-to-date reference. Catalyst assumptions were at the end not relevant, since the catalyst yield was extremely high. In any case, a comparison between our study and other source was done to increase robustness and detect possible mistakes of the Life Cycle Inventory.

Checking the veracity of the energy consumption values for our refinery; we contrasted them with the International Energy Agency (OECD/IEA, 2009). “*Best Available techniques*” would require 0.1 MJ/kg of electricity and 2 MJ/kg of steam per kg of Benzene and Propylene respectively. Our values for electricity are 0.127 kWh (0.45MJ) for Benzene and 0.2744kWh (0.98MJ) for propylene, and for steam are 2.4 MJ for Benzene and 2.26MJ for Propylene, plus heat provided by heavy fuel oil (estimated 42.6 MJ/kg), which give us 7.52 MJ for Benzene and 2.76MJ for Propylene, which also uses 13.91MJ from hard coal (calorific value estimated 29.3MJ/kg). As we can observe our values are higher, which is normal when comparing against the best available techniques, but the steam consumption is very close, and the electricity for Benzene is comparable.

For the cumene phenol process, we should at least require 0.6 MJ/kg of electricity and 9.1 MJ/kg of steam per kg of phenols and for acetone 0.6 MJ/kg of electricity and 9.1 MJ/kg of steam per kg using best available techniques (OECD/IEA, 2009). Multiplying the exergetic value of the phenol by the energy consumption by MJ of exergy it requires 0.2628 kWh (0.946 MJ of electricity) and 9.24MJ heat, basically steam. Acetone production requires 0.15 kWh (0.541 MJ of electricity) and 5.28MJ of heat, basically steam. Values for phenols are really close to the best available techniques, and the difference why acetone is lower is due to the allocation method.

High Density Polyethylene (HDPE) requires at least of 0.9 MJ/kg of electricity and 1 MJ/kg of steam per kg; meanwhile, Polypropylene requires at least 0.9 MJ/kg of electricity and 0.1 MJ/kg of steam per kg of product (OECD/IEA, 2009). Using our reference we would require 1.8MJ of electricity and 0.2 MJ of steam for HPDE Polyethylene and 0.576 MJ of electricity and 0.17 MJ of steam for Polypropylene. Values differ but keep in the same range. Plastics Europe gives a water usage for propylene production (excluding cooling water) of 4.78 kg but since it is not related to any concrete technology is not taken into account for our study.

In the following chart we have compared the environmental profile (d vector) of our petrochemicals (left bar in each category) than the same amount from the EcoInvent database (right bar in each category):

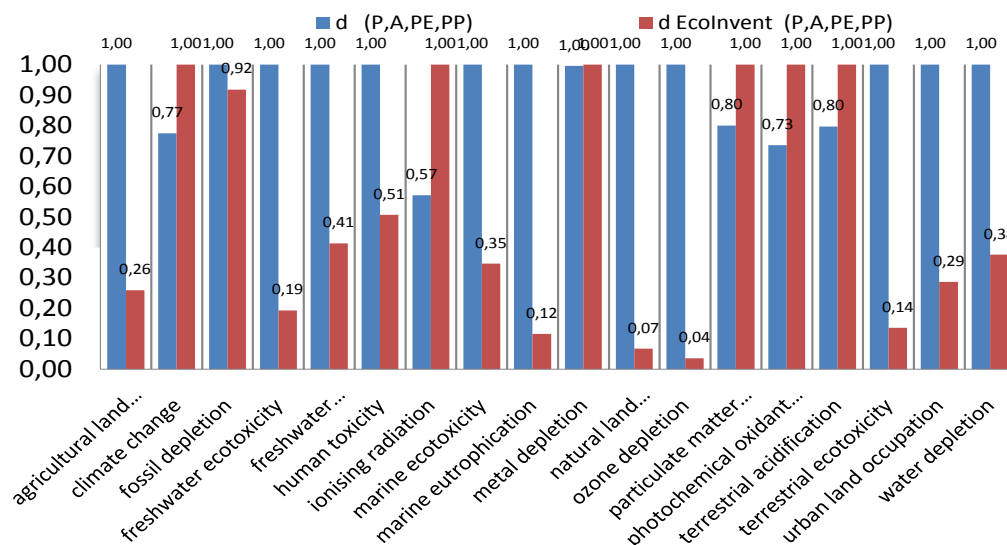


Figure 20: Environmental performance of the functional unit of petrochemicals from this study and EcoInvent database.

Values for Climate change, fossil depletion and air-related emissions like particulate matter formation or photochemical oxidation are very similar to the ones EcoInvent database propose, but slightly lower. This can be related to the increase of efficiency in the plants compared to the values from EcoInvent for petrochemicals, where all publishing years are between 1999 and 2001. Metal depletion, once is related to capital modeling confirms that our approach is valid for the functional unit, although our values for phenol were lower, while for polyethylene and polypropylene higher. The important differences found on the rest of the indicators are related to the system boundaries of both studies. In our study precise data about inputs of raw material and energy, emissions and all kind of waste were included. EcoInvent LCI for phenols estimate emissions to air and water based on mass balance, as well as energy demand and infrastructure of the plant while does not include solid waste, pointing out that process data was based on stoichiometric calculations of few literature sources and the energy demand on approximation from large chemical plant. EcoInvent values for Polyethylene and Polypropylene are taken from PlasticsEurope, where recyclable waste, air consumed, unspecific metal

emission to air and to water, mercaptan emission to air, unspecific CFC/HCFC emission to air and dioxin to water were not included.

From our point of view it is considered that our data quality satisfies the requirements of our problem, showing impact of other categories that could have been hidden in case of not developing a proper foreground system.

6.3.1.2.2 Chemicals from biomass

Regarding biochemical production, gathering of data was more complicated. First of all, because it is an incipient technology, still under development, and the scenarios formulated do not exist in real life. Hence, we had to build a LCI phase by phase. Data and assumptions prone to discussion in the Life Cycle Inventory are justified here.

- Cultivation, fertilizing and forest operations: Scientific papers support the lower irrigation of Poplar, without giving a concrete value. No irrigation was assumed, which also allowed us to quantify the effect of the irrigation from the best to the worse case.
- Pretreatment: *“The dilute acid and acid-catalyzed steam pretreatment can be performed without the recovery of acid because of the low cost of sulphuric acid. However, substantial amounts of alkaline chemicals are required to neutralize the pretreatment hydrolyzate. In addition, the salt produced from the neutralization needs to be properly disposed of”* (Da Costa Sousa et al, 2009). No recovery of acid applied, but alkaline chemicals needed to neutralize the hydrolyzate were neglected, this could lead to lower emissions on the pretreatment stage. Comparing our study with the EcoInvent process of ethanol from wood where it stated that the respective consumption of electricity and heat per ton of chips over the stage of pre hydrolysis amount to 13.5 kWh and 987 MJ of heat (EcoInvent. Bioenergy Summary Report), which is 0.0486MJ of electricity (27% of our value) and 0.987MJ of heat (54.9% of our value). Also, EcoInvent database capital for a pulp plant includes land-use, buildings, streets within the mill area, machineries and energy production as well as dismantling/disposal of the whole infrastructure, for 400000 metric tons year over 50 years horizon. We adjusted this value for our 30 years horizon and 100000 metric tons per year for a pulp plant. This means that the capital for our case has 6.6 times more impact in our Life Cycle. Although 30 year’s assumption is more suitable to these times where technology change rapidly and it is the same as petrochemical time horizon, 100000 metric tons per year is lower than a normal volume of production for a biorefinery, for example, Borregaard Biorefinery in Norway (Borregaard LCA Report).

- Glucose to PLA: Data from scientific paper based on commercial plant in operation. Energy consumption related to facilities and wastewater was not taken into account. Some questions arise from that study, like the share of energy source (How much heat and how much electricity consumes the process). *“The largest part of energy use in the facility is steam, because lactic acid is purified with vacuum distillation and steam is used for the heating of the fermentation reactor”* (Gruber and O’Brien, 2002). Dornburg and coauthors estimate this disaggregation as 95% heat and 5% electricity (Dornburg et al, 2006). The study of Purac production in Malaysia gives kgCO₂ emissions per unit of process due to electricity and heat in MJ (Groot and Borén, 2010). We can track these emissions assuming 1.3 kg of steam per kg of CO₂ and 2.6 MJ/kg steam, and 1.44 kg CO₂ per electric MJ, obtaining a share of 84.6 % heat and 15.3% electricity. This confirms the split favorable to heat consumption. Therefore, a final assumption of 85% Thermal energy and 15% Electricity was taken for this process.
- Ethanol to acetone: Data from scientific paper for ethanol production. Acetone heat needs are estimated roughly based on the calorific value of the solution. No wastewater treatment considered as main outputs are water and carbon dioxide. Those studies do not refer to the purity of the ethanol produced, hence, and overestimation could be done in this area since ethanol (96%) is enough for our ethanol-acetone process.
- Water: No water is recycled in our approach. Also no wastewater treatment has been applied, but the emissions on water of each process have been taken into account.
- Waste streams combustion: Database of emissions from wood waste incineration. No accurate or specific data about pyrolytic oil combustion was found. The accuracy of the environmental profile of the biorefinery depends on the values of these emissions. The Biomass Technology Group estimates an efficiency of 70% for co firing bio-oil and natural gas within a natural gas power station (Biomass Technology Group, The Netherlands), but we will keep 85% efficiency since our boiler is made for charcoal and pyrolytic oil.
- Carbon dioxide as direct output of the chemical processes (Ethanol and PHB fermentation and acetone production) is taken into account in the waste stream carbon content for the CO₂ accounting.

Even though there are some uncertainties in the analysis in important processes, we consider that the assumptions taken can be considered fairly representatives for giving some implications about the impact contribution from the different stages of both scenarios.

6.3.1.3 Dealing with CO₂

CO₂ accounting issues deserves a special section since our methodology for CO₂ accounting differs from other studies does not take into account the biogenic contribution of biomass oxidation. Since most of the carbon from the petroleum feedstock remains in the products, it makes sense that the carbon dioxide emission when the products, whatever petro derived product is, is oxidized, indistinctly how it is oxidized, releases most of its carbons as CO₂. For the case of chemicals from biomass we have “oxidized” most of the carbons in the feedstock (around 70%) in fermentation processes or combustion to provide heat for the facility, and the others will be oxidized after its use. The time horizon for oxidation of products, both fossil and bio based were considered one year. Having as reference Polylactic acid (*Groot and Borén, 2010*), the time frame of CO₂ emission to atmosphere would suit this assumption for the case of incineration (<1month), anaerobic digestion (<1month) and composting (>6month), when landfill (>10years) or recycling scenarios 2-10 years) and were not considered in our study.

Table 4 End of life options of PLAs

PLA destination	CO2 emission based on sorting, cleaning, collection, transport	Process related CO2 emission	Carbon retention	Timeframe of CO2 emission to atmosphere
PLA recycling to PLA via lactic acid	High	High	High	10 years
PLA recycling to lactic acid derivatives	High	Moderate	High	2 years
Mechanical recycling	Moderate	Low	High	5 years
Composting	Low	Low	Moderate	>6 months up to years
Anaerobic digestion	Low	Low	Low (energy value)	<1 month
Incineration	Low	Low	Low (energy value)	<1 month
Landfill	Low	High, in case of CH4 emission	Low	>10 years

Figure 21: End of life options of Poly Lactic acid. (Groot and Borén, 2010)

On the other hand, some of these plastics (and its carbon) could be incinerated generating other kind of emissions apart of CO₂ that are harmful, and not taken into account whereas all the possible emissions of the combustion of waste streams are accounted for chemicals from biomass and oxidation of some of the bio based products releases just water and CO₂ (PLA and PHB compost processes). These assumptions seemed to be enough representatives for our scenarios.

6.3.2 External

6.3.2.1 Comparison of CO2 values with other sources

Following the carbon cycle, first to the ocean, and in a twenty years horizon back (rotation period used was 20 years, a sustainable forest management practice which provide high yield in long term and not exhaust the soil) to the biomass feedstock, this CO₂ will contribute to a greenhouse effect in the atmosphere during its time on it. In order to ensure the reliability of our study we have compared our values for soft and hard plastics precursor with previous literature.

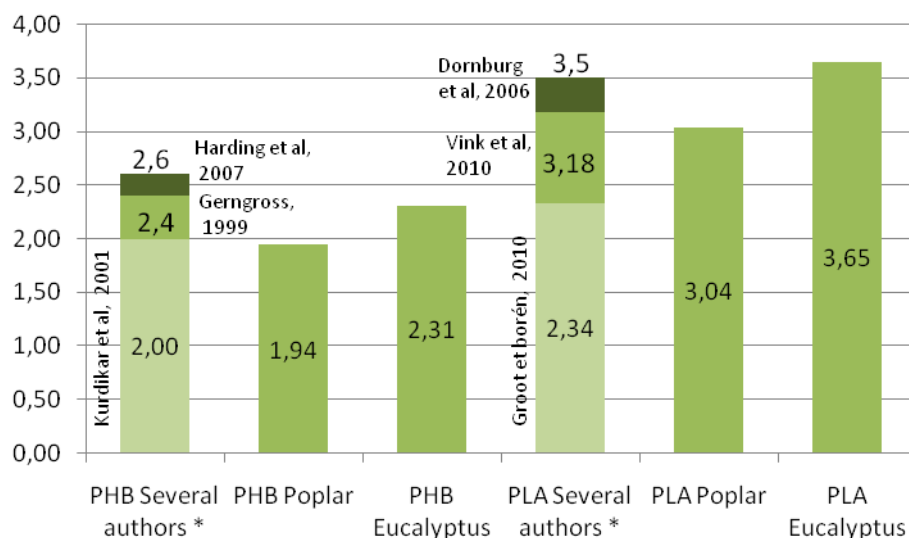


Figure 22: GHG emissions of soft and plastic precursor. Cradle to Gate.

Nature Works study of PLA was reviewed by the authors in 2010 (Vink et al, 2010), disaggregating more the results of their previous scientific paper (Vink et al, 2003). They estimates that the GHG emissions for processes are 3.18 kgCO₂eq / kgPLA (Corn production 0.37 kgCO₂eq (11.6%), 0.36 kgCO₂eq Dextrose, 1.53 kgCO₂eq lactic acid and 0.92 kgCO₂eq polymer), only 2 kgCO₂eq / kgPLA with CO₂ sequestration. In our case we have values ranging from 3.04 to 3.65 and kgCO₂ without counting sequestration but Cradle To Gate (between 5-10% of this value is due to the feedstock from lignocellulose, logically a bit lower than the value of 11.6% of the corn production impact). The minimum process CO₂ emissions of PHB are is 2.34 kgCO₂eq / kg polymer (Groot and Borén, 2010), while for short rotation wood it seems a much higher value, around 3.5 kgCO₂eq / kg polymer than from wheat straw, around 1.5 kgCO₂eq / kg polymer (Dornburg et al, 2006).

It is confirmed the trend that PHA production has lower impacts than PLA production (Kurdikar, 2001; Gerngross Harding et al, 2007), being our results very close to previous research. Values for phenols and acetone from renewable sources were not found. An initial estimation is to compare the values for vanillin (phenolic compound) and ethanol from the biorefinery Borregaard in Norway (Borregaards LCA) with our phenolic compounds and acetone respectively. Vanillin shows a GHG emission impact of 1.13 kgCO₂eq / kg, while our phenols are much higher, 3.19 kgCO₂eq / kg phenols for Poplar and 4.01 kgCO₂eq / kg phenols for Eucalyptus. Ethanol has a climate change impact of 0.335 kgCO₂eq / kg ethanol, while our acetone ranges from 2.24 and 2.99 kgCO₂eq / kg phenols. Such a difference can be a consequence of allocation methods in the studies compared or overestimation of heat and electricity demand in our cases. Our yield is also very low and possible synergies among processes, like heat recovery, were not considered.

6.3.2.2 Comparison of energy consumption values with other sources

In order to ensure the reliability of our study we have compared our energy consumption values with other studies for the same functional unit.

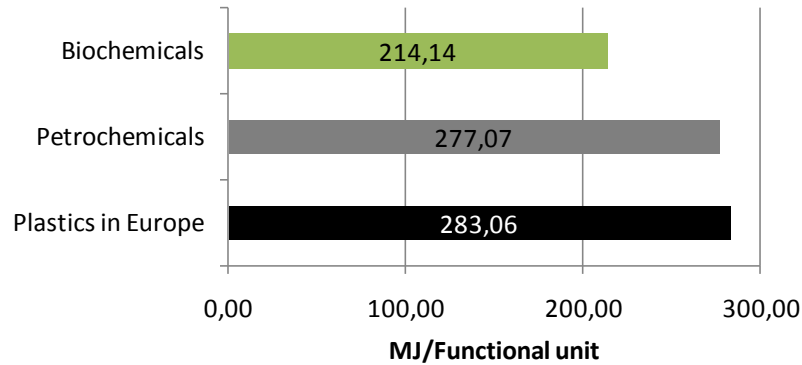


Figure 23: Energy consumption of the functional unit (MJ)

Our study estimates that the energy consumption of chemicals from biomass is 214.14 MJ/Functional unit, 77% of that consumed by petrochemicals (277.07 MJ/Functional unit), being consistent with the values given for PLA, where 54MJ/kg were required to produce PLA from corn, that being compared to the 73.37 MJ/kg needed for the production of Polypropylene (Plastics in Europe) gives us a ratio of 73.5%, which is very similar than ours. It is very important to note down that this energy includes the energy in the feedstock, being the one of the oil (around 45 MJ/kg) much higher than biomass (around 20 MJ/kg). This is an important point; per functional unit, chemicals from biomass require more process energy than petrochemicals.

6.4 Implications

The biorefinery concept is an extensive field of study; it gathers forest management, transportation and logistics, biological and chemical processes industrial economics, environmental issues and energy supply, as well as being present in the environmental agenda of most developed countries. Implications in terms of future research and recommendations for the industry and policy making are then, quite broad.

For the scientific community a more detailed research on the Nitrogen and Phosphorus life cycle must be an area of interest. Authors suggest different values so these implications may have been underestimated. New combustion technologies of pyrolytic oil and charcoal, as well as waste streams must be researched, accompanied by environmental studies. A further study of the implications of the end-of-life cycle is needed. Recycling rates for phenol and acetone were not taken into consideration, while bioplastics (PLA, PHB) are mainly biodegradable (Carbon Dioxide + Water). A Techno-economic performance of the multiple output approach presented could be consider, since the facility can adapt to different kind of lignocellulosic biomass, and can prioritize the production of some of the

products. The possibility of using some of the infrastructure for multiple processes could be interesting.

When arriving to industrial processes, new pretreatment technologies could reduce cost and environmental impacts. Also, substitution of bacteria fermentation by enzymes could increase production levels and decrease the CO₂ emissions in the production phase, although the climate change along the entire carbon cycle would be same (time horizon of combustion/compostage is less than one year). Gypsum is the main waste of Polylactic acid production, recycling of gypsum for substituting mined gypsum could be interesting from the economic and environmental point of view. At the same time, ash land filling must be re think. 1% of the production is land filled ash, with non neglectable environmental impacts. Efficiency of the systems should be evaluated as potential economic and environmental improvement, as well as integration of renewable energies in the production like wind for the production of electricity in plant (which is low compared to the heat consumption). Solar concentration tubes for the production of steam (which is highly demanded) could be a possible approach especially in southern countries like Spain. In terms of scaling up, investment should not be scarce; arriving to the same production volume of actual pulp and paper (or reconversion of these ones) would reduce substantially the environmental impact per kg of chemicals from biomass.

Decision and Policy making bodies cannot neglect that the biorefinery concept (bioenergy, biofuels, and chemicals from biomass/biomaterials) is one of the anchors of the new green economy, and lignocellulosic biomass must be one of the sources to fuel it. But further implications of the technology related to social, environmental and economic burdens should be understood. Achieving better environmental performance before moving forward at the same time as keeping high incentives and sector attractiveness should be the main objectives. In the light of this, subsidizing product might not be very efficient, whereas research support, awarding environmentally friendly practices, innovation and breakthrough technologies, promoting start-ups and regulating the waste management of chemicals from biomass production should be used as possible actuation guidelines.

Last, but not least, we must highlight the role of forest management. Reduction of fertilizing, proper rotation periods and recollection efficiency must be achieved for a long term sustainability of the lignocellulosic biomass. Governments tend to subtract priority from agriculture and silviculture departments, but including this issue in their agenda could bring potential benefits from the environmental point of view and sustainability of the sector.

6.5 Conclusions

The environmental profile of chemicals from biomass could contribute to climate change mitigation, fossil independence and a decrease on toxicity potential on ecosystems. Decrease of fertilizers and irrigation, increase of yields, new solutions for disposal, treatment and recycling of ash and gypsum and development of the approaches exposed to mitigate the other environmental drawbacks of its profile, such energy efficiency techniques or cleaner electricity, could bring the production of chemicals from biomass to an status where they are dramatically better in all impact indicators if all the stakeholders on the life cycle of the chemicals from biomass (Agriculture and Industry sectors, research institutions, policy makers and final customers) get involved.

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