

Eero Martikainen

Life Cycle Assessment of Novel Bioplastics from Lignocellulosic Biorefinery

Integrated Production System of Polypropylene and
Polyethylene Furanoate

Master's thesis in International Master's Programme on Circular Economy
Supervisor: Francesco Cherubini
Co-supervisor: Otávio Cavalett
July 2022

Eero Martikainen

Life Cycle Assessment of Novel Bioplastics from Lignocellulosic Biorefinery

Integrated Production System of Polypropylene and
Polyethylene Furanoate

Master's thesis in International Master's Programme on Circular
Economy
Supervisor: Francesco Cherubini
Co-supervisor: Otávio Cavalett
July 2022

Norwegian University of Science and Technology
Faculty of Engineering
Department of Energy and Process Engineering

Abstract

This Thesis is a state-of-art study in which an integrated, raw material-efficient, biorefinery production system was designed for the combined production of bio-PP and PET. The aim was to find out how the environmental impacts of these bioplastics compare to their fossil alternatives and whether the high raw material efficiency is beneficial in terms of environmental impacts. In addition, the importance of energy sources was evaluated by modelling the environmental impacts with a system based on three different energy sources: wood chips, natural gas and coal.

The environmental assessment was based on the cradle-to-gate Life-Cycle Assessment (LCA). In the initial scenario based on wood chips as an energy source, bio-PP resulted in a GWP of 0,81 kg of CO₂ eq. and the PEF resulted in a GWP of 2,17 kg of CO₂ eq and in general the initial scenario performed well compared to scenarios based on natural gas and coal as an energy source.

The main finding of the study was that a high material-efficient biorefinery requires large amounts of energy and therefore the choice of the energy sources is a crucial factor in determining the environmental impacts related to the products. When wood chips were used, the products performed well compared to the fossil alternatives but when natural gas or coal was applied, the impacts on many categories were remarkably higher than the ones related to the fossil alternatives. The good performance of the wood chips as an energy source is based on the exclusion of biogenic GHG emissions which is an important factor to consider. The exclusion of biogenic GHG emissions on the other hand is dependent on the renewable energy status of wood combustion which is, therefore, a crucial factor in determining the environmental performance of the products and the biorefinery system as a whole.

To conclude, if wood combustion was not considered renewable energy, either another renewable energy source should be used or then the biorefinery should be designed in the conventional way in which enough sidestreams for energy production are produced to cover the energy source demand.

Preface

Writing this Thesis has been an instructive process, during which, I have acquired essential skills for modelling the environmental impacts of systems and solving complex challenges. While expanding my knowledge on biorefining and environmental impacts modelling, I have been privileged to provide new information to the scientific community. Although modelling relatively novel technologies has been anything but easy, especially due to the lack of reliable data, I am satisfied with the results. Although the results are prone to significant uncertainty, they do provide valuable insights for future work and points of improvement.

I want to thank my supervisor Francesco Cherubini and especially my co-supervisor Otávio Cavalett for sharing their knowledge and providing extensive feedback along the way. Their expertise has been truly inspirational and their effort is crucial for the quality of this Thesis.

In addition to the ones involved in the Thesis process, I want to thank everyone who has influenced my study path and shaped my skills and knowledge along the way. This thesis marks the end of eighteen years of almost continuous studies and a shift of my focus from educating myself to applying my knowledge and skills for a better future.

I am truly grateful for the opportunity to study and graduate from the International Master's Programme on Circular Economy. It has been amazing to learn from the top researchers in the field and to share ideas with highly motivated peers in all three universities: Norwegian University of Science and Technology, Leiden University and the Delft University of Technology.

Table of Contents

1	Introduction	11
1.1	Objectives	12
2	Methodology	13
2.1	Goal and Scope	13
2.2	Method and framework	13
2.3	Product system modelling and integration	14
2.3.1	Integration of the production system	14
2.3.1.1	Separation process.....	16
2.3.1.2	Propylene and Phenol production	17
2.3.1.3	Propylene polymerization	17
2.3.1.4	Production of furfural from waste sugars.....	17
2.3.1.5	Production of FDCA from furfural.....	18
2.3.1.6	Production of ethanol from cellulose	18
2.3.1.7	Production of ethylene glycol from ethanol	19
2.3.1.8	Production of HMF from cellulose.....	20
2.3.1.9	Production of FDCA from HMF	20
2.3.1.10	Production of PEF from FDCA and Ethylene Glycol	21
2.3.1.11	Combined heat & power production (CHP).....	21
2.3.2	Mass balance	24
2.3.3	Energy balance	25
2.3.4	Summary of main assumptions for the biorefinery modelling	26
2.4	Life-Cycle Inventory	27
2.4.1	Flow data	27
2.4.2	Allocation	27
2.5	Life-Cycle Impact Assessment.....	29
3	Results and Discussion	30
3.1	LCIA of bio-PP and PEF	30
3.1.1	PP environmental impacts	30
3.1.2	PEF environmental impacts.....	31
3.2	Life cycle assessment of PP and PEF	31
3.3	Contribution analysis of bio-PP and PEF.....	36
3.3.1	Bio-PP contribution analysis.....	36
3.3.2	PEF contribution analysis.....	38
3.4	Remarks and points of improvement.....	39

3.5	Limitations	40
4	Conclusions.....	41
4.1	Recommendations for future work	42
	References	44
	Appendices	51
	Appendix 1: Processes from mass balance to Simapro.....	51
	Appendix 2: Mass balance.....	52
	Appendix 3: Calculation for allocation of EG production	53
	Appendix 4: LCIA results based on the three scenarios.....	54

List of Figures

Figure 2.1: Diagram of the product system considered in this analysis	16
Figure 3.1: Comparison of climate change results for the different products analyzed in this study	33
Figure 3.2: Comparison of terrestrial ecotoxicity results for the different products analyzed in this study	34
Figure 3.3: Comparison of human toxicity results for the different products analyzed in this study	35
Figure 3.4: Comparison of fossil resource scarcity results for the different products analyzed in this study	36
Figure 3.5: Contribution analysis of bio-PP.....	37
Figure 3.6: Contribution analysis of PEF	38

List of Tables

Table 2.1: Mass and energy flows of FDCA from furfural	18
Table 2.2: Mass and energy flows of EG production	19
Table 2.3: CHP and absorption efficiencies	22
Table 2.4: Energy requirement calculations	22
Table 2.5: Additional demand for energy sources	22
Table 2.6: Emissions of H ₂ gas bypass combustion	23
Table 2.7: Emissions of off-gas combustion	23
Table 2.8: Total emissions for all scenarios	23
Table 2.9: Overall mass balance of the integrated system	24
Table 2.10: Overall energy balance of the system.....	25
Table 2.11: Power balance of the system.....	25
Table 2.12: Allocation of emissions	29
Table 3.1: LCIA of 1 kg of PP	30
Table 3.2: LCIA of 1 kg of PEF.....	31

List of Abbreviations

Bio-PP	Bio-based polypropylene
DEG	Diethylene glycol
TEG	Triethylene glycol
CHP	Combined Heat and Power
EG	Ethylene Glycol
EU	European Union
FDCA	2,5-Furandicarboxylic acid
GHG	Greenhouse Gas
GVL	gamma-Valerolactone
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LHV	Lower heating value
MEG	Monoethylene glycol
PEF	Polyethylene Furanoate
PET	Polyethylene Terephthalate
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PP	Polypropylene

1 Introduction

A major part of global chemical production is based on fossil resources. The chemical industry contributes significantly to climate change and creates various other environmental impacts. In 2012 the chemical industry was responsible for 7 % of global greenhouse gas (GHG) emissions and 20 % of the industrial GHG emissions (IEA, 2013). In other words, the chemical industry is a major contributor to climate change. Over the decades efficiencies in chemical production have been increasing improving economic performance while reducing environmental impacts (Government of Canada, 2018). As the emergence of climate change has increased and the importance of shifting from fossils has become clear, sustainable feedstocks for chemical production have become a focus area in research and development (Baldoni et al., 2021). Many companies are investing in chemical production based on other than fossil feedstocks and the development is seen to be increasing (Avantium, 2021; Spekrijse et al., 2019; UPM Biochemicals, 2022). The alternative feedstocks are mostly based on materials from the biosphere and the process of transforming these feedstocks into chemical products is called biorefining (Baldoni et al., 2021). It is stated that biorefineries are among the most potential solutions for reducing the environmental impacts of chemical production (Baldoni et al., 2021).

Plastics account for a large part of global chemical production. Almost all plastic production is based on fossil oil and therefore contributes largely to climate change (European Bioplastics e.V., 2021; Our World in Data, 2016). On the other hand, plastics as moldable and light materials are important today for example by improving energy efficiency in the mobility sector (European Commission, 2018). Because of the importance of plastics as materials, bioplastics are considered the most promising solution to decrease the environmental impacts and reliance on fossil resources, together with improved recycling efficiencies (Isikgor & Becer, 2015). The term bioplastic has several meanings from fossil-based biodegradable plastics to plastics made of bio-based raw materials (Cherubini & Strømman, 2011; van den Oever et al., 2017). In this study, the focus is on bioplastics included in the latter definition.

The production of bioplastics is expected to grow rapidly. In 2021 the global bioplastics production was 2.4 million tons and it is expected to grow to 7.6 million tons in 2026 (European Bioplastics e.V., 2021). When compared to the annual production of most common plastic types being over 350 million tons per year, bioplastics are accounting only for a small fraction of the total production (Our World in Data, 2016). On the other hand, the rapid growth in the next five years during which global bioplastic production is expected to triple, shows a strong trend based on which bioplastics might account for a significant amount of the total plastic production in the coming decades.

When considering bioplastics as a solution to fight climate change, it is important to make sure that they perform better in terms of environmental impacts than conventional products (Farzad et al., 2020). For example, utilizing food crops for chemical production competes with food production meanwhile potentially contributing to deforestation (Serrano-Ruiz et al., 2011). The standardized procedure of Life-cycle Assessment (LCA) provides a tool to model these impacts and to build an overview of the environmental performance of different products (International Organization for Standardization, 2006).

As many bioplastics such as polyethylene furanoate (PEF), are based on novel technologies, environmental assessments of many bioplastics do not exist or only the results without details have been published by the companies developing the technologies (nova-Institute, 2022). For some plastics such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA), there are several studies on the environmental impacts but for many others, the amount of studies is low (Spierling et al., 2018). In addition to some chemical products relevant for bioplastic production, LCAs can be found, but they are usually only considering climate change impacts and are limited to specific production systems (H. Kim et al., 2020; Lippits & Nieuwenhuys, 2010; Motagamwala et al., 2018). Also, many of the existing LCAs are based on food crops and the environmental assessments on second-generation biorefining based on lignocellulosic feedstocks are limited (Ganguly et al., 2021). This study contributes to filling this gap by presenting a resource-efficient biorefinery and providing an environmental assessment of bioplastics based on lignocellulosic feedstock.

As bioplastics are a vast group of polymers, a selection of them for the system design of the biorefinery and the environmental assessment was necessary. The selection was done based on a study by Martikainen (2022) on the feasibility of different bioplastics based on lignocellulosic feedstock. In the study, bio-based polypropylene (bio-PP) based on lignin and polyethylene furanoate (PEF) based on cellulose were identified as the most promising bioplastics (Martikainen, 2022). Polypropylene is a polymer with the largest global production quantities of all plastics accounting for 68 million tonnes in 2015 (Our World in Data, 2016). Bio-PP is a plastic material chemically the same as conventional polypropylene but produced from bio-based feedstock. PEF is a biobased alternative for polyethylene terephthalate (PET) commonly used for the production of plastic bottles (nova-Institute, 2022). PET had a global production of 33 million tonnes in 2015 being the sixth-largest plastic type in terms of mass. These two bioplastics, bio-PP and PEF, were selected for modelling environmental impacts based on LCA.

In this thesis, a production system of these two bioplastics, bio-PP and PEF is created and studied. The production processes are combined into an integrated system and then joint mass and energy balances are calculated. Furthermore, an LCA is performed for the two end-products: bio-PP and PEF. The system design and environmental assessment of novel technologies require several assumptions and therefore the nature of the study is explorative. In addition, the design of the biorefinery is state-of-art and made just for this study which highlights the explorative nature of the study even more. The results of this study will break the path for the environmental assessment of novel bioplastics and guide the focus of future research in the field.

1.1 Objectives

The study aims to answer the following research questions:

1. How do PEF and bio-PP from an integrated production system based on lignocellulosic feedstock perform in terms of environmental impacts?
2. How large of an impact does the choice of energy source have on the environmental impacts of the bioplastic products?
3. How does the high efficiency of raw material conversion affect the environmental impacts of the bioplastics?

2 Methodology

In this chapter, a core methodology of the study is presented. In the first subchapter, a goal and scope of the system integration and the LCA are provided. In the second subchapter, the method of LCA and the general overview of the framework are presented. The third subchapter, product system modelling and integration is the most extensive subchapter of this chapter, as the system integration was a major part of the work. In the fourth subchapter, the method for Life cycle impact assessment (LCIA) is presented more in detail and relevant modelling choices are explained. In the fifth subchapter, the method for Life Cycle Assessment is explained.

2.1 Goal and Scope

The goal of the study is to design an integrated biorefinery focused on the production of PEF and bio-PP and to compare the environmental impacts of the products to their fossil alternatives. In the design of the biorefinery, the focus is on the high material efficiency and carbon yield of products.

In the LCA, a cradle-to-gate approach is chosen as a system boundary, in which the environmental impacts are modelled for the products leaving the production system and the use phase and end-of-life are excluded. The approach is chosen due to the goals of the study and the chosen bioplastics. Bio-PP has the same chemical structure as fossil-based PP and therefore their use phase and end-of-life are the same. PEF, on the other hand, has some advantages in its lifecycle compared to fossil alternative PET but it also serves as a drop-in solution and the differences in use and end-of-life phase are decided to be left out of the study. These differences are discussed in the results.

Due to the nature of the study, the LCA is compiled as a black-box study, in which unit processes are combined into larger units. Although a black-box study doesn't allow precise contribution analysis, it simplifies modelling significantly and is necessary for such an explorative study.

The biorefinery is considered to be built in Northern Europe and the Ecoinvent 3.6 database is used for background processes. The foreground of the system includes production steps from the initial separation process of the feedstock to the final products.

To model the effect of energy choices three scenarios based on different energy sources are considered: wood chips, natural gas and coal. The results are compared between the scenarios and available PET, PEF, bio-PP and conventional PP data.

2.2 Method and framework

LCA is an ISO standardized modelling tool aiming to calculate the environmental impacts of products and systems (International Organization for Standardization, 2006). In general, the methodology contains four steps: Goal and Scope, Life-cycle Inventory, Life-cycle Impact Assessment, and Interpretation. This study follows these principles and is in the line with the standard. The modelling is done in a form of cradle to gate and focuses on the integrated production system. Focus on the production system itself means that for example values from the database are applied for harvesting of feedstock instead of modelling the process in detail.

The mass and energy balances were built on Excel spreadsheets based on data from the literature. As the data was in some cases based on lab-scale studies, several

assumptions were necessary. In modelling of LCI and LCIA Simapro software is applied together with background processes from the ecoinvent 3.6 database. Recipe 2016 - method with midpoint assessment, built into Simapro, is applied for LCIA. All the impact categories in the ReCiPe 2016 were modelled, but deeper discussion and contribution analysis were provided for the following four categories:

1. Climate change
2. Fossil resource scarcity
3. Human toxicity
4. Terrestrial ecotoxicity

2.3 Product system modelling and integration

In the study, a goal was to design a resource-efficient biorefinery in which cellulose, hemicellulose and lignin are preferred to be turned into products rather than energy through combustion. In addition, a goal was to produce at least two different bioplastics from the biorefinery system.

The bioplastics, bio-PP and PEF were selected based on a study by Martikainen (2022). In the project, the selection of bioplastics was compared utilizing multicriteria analysis focused on feasibility and economic factors. Out of all the bioplastics compared it was found that bio-PP and PEF show the highest potential for commercial-scale production (Martikainen, 2022).

The system integration was built based on the Phenol and bio-PP production presented by Liao et al. (2020). The production steps necessary for PEF production were searched from literature and added to the system. Some of the studies were based on existing commercial applications but some, especially ones related to 2,5-Furandicarboxylic acid (FDCA) production, were lab-scale studies, as commercial production is only taking off and the companies developing the technologies do not publish their process designs or data. Data availability of the PEF production steps was a major constraint and as the data availability had to be prioritized, the technologies chosen for the study do not necessarily represent the latest advances in the field.

Although data availability was prioritized, several assumptions were needed. In some cases, process data was lacking about the energy data, and in some cases solvent demand. On the other hand, some of the studies were actual process designs with published data, which provided detailed information for the LCA. Therefore, there is inconsistency in the quality and details of the data between processes. The assumptions needed for the mass- and energy balances as well as for the LCA are stated in this chapter and the most important ones are collected in a separate subsection.

2.3.1 Integration of the production system

Systemwide integration was compiled based on the idea of combining two different production routes: phenol and bio-PP presented by Liao et al. (2020) and PEF production from FDCA and ethylene glycol (EG). The joint production of phenol and bio-PP is not yet commercialized whereas PEF production is entering the phase of large-scale industrial production in the coming years. For example, Dutch research company Avantium has large ambitions for FDCA and Finnish forestry company UPM Oyj is building a biorefinery to produce ethylene glycol from lignocellulosic feedstock (Avantium, 2021; UPM

Biochemicals, 2022). On the other hand, a difference between PEF based on plans of Avantium and PEF from this study is a feedstock for FDCA production. Avantium uses mainly sugar crops whereas the FDCA in this study is produced from cellulose (nova-Institute, 2022).

The method presented by Liao et al. (2020) was chosen as the main separation process for the system. The method is based on methanol and is a so-called "lignin-first" separation process in which high purity of lignin is achieved. For high utilization of lignin, purity is crucial and therefore lignin first separation is required (Liao et al., 2020).

After the initial separation phase, lignin monomers are processed into phenols and polypropylene as presented by Liao et al. (2020). The lignin monomers go through hydroprocessing to form alkylphenols and further through dealkylation to form phenols and alkenes. In the last step phenols and propylene are separated into sellable products (Liao et al., 2020).

The wastewater stream from lignin purification contains large quantities of sugars from hemicellulose. Of these sugars, methyl-xylosides present the largest group. Furfural can be produced from methyl-xylosides as presented by Iglesias et al. (2016) and furfural is then further processed to FDCA. This addition to the production system is one of the main measures considered in this thesis to increase the industrial symbiosis of the system.

The separated cellulose is transformed into ethylene-glycol via the processes presented by Falcones et al. (2019) and Liao et al. (2020). In addition, as the FDCA production purely relying on methyl-xylosides is imbalanced with ethylene-glycol production if all the cellulose would be turned into ethylene-glycol, an additional process is added to produce HMF from cellulose based on H. Kim et al. (2020) and further FDCA from HMF based on Motagamwala et al. (2018). The system is balanced based on the principle that the production of PEF is optimised to utilize all cellulose.

The two streams consisting of carbohydrates from the process designed by Liao et al. (2020) were utilized in energy production in this study. Although the integrated process design of bio-PP and PEF results in many other waste streams containing unutilized carbon, the possibilities of these streams in energy production were not explored in this study. These streams were usually considered wastewater. If high utilization of these streams for energy production would be possible, it would likely reduce the demand for additional energy sources.

To cover the energy demand of the integrated production system, a CHP plant was included. CHP was designed to cover the heating, cooling and power demand of the system meanwhile feeding the excess electricity to the power grid. As the energy demand was found to be higher than the two side streams considered could provide, an additional energy source was required. Wood chips were considered as the initial additional energy source, but in addition, the modelling was repeated for two other scenarios: using natural gas as an additional energy source and using coal as an additional energy source. The results of LCA based on these additional scenarios were compared to the initial scenario based on wood chips.

Based on the integration principles presented above a block diagram was compiled and it is shown in figure 2.1. The diagram includes the main carbon sources from the background, the processing steps of the system, intermediate products and the main products considered in this study as well as their co-products.

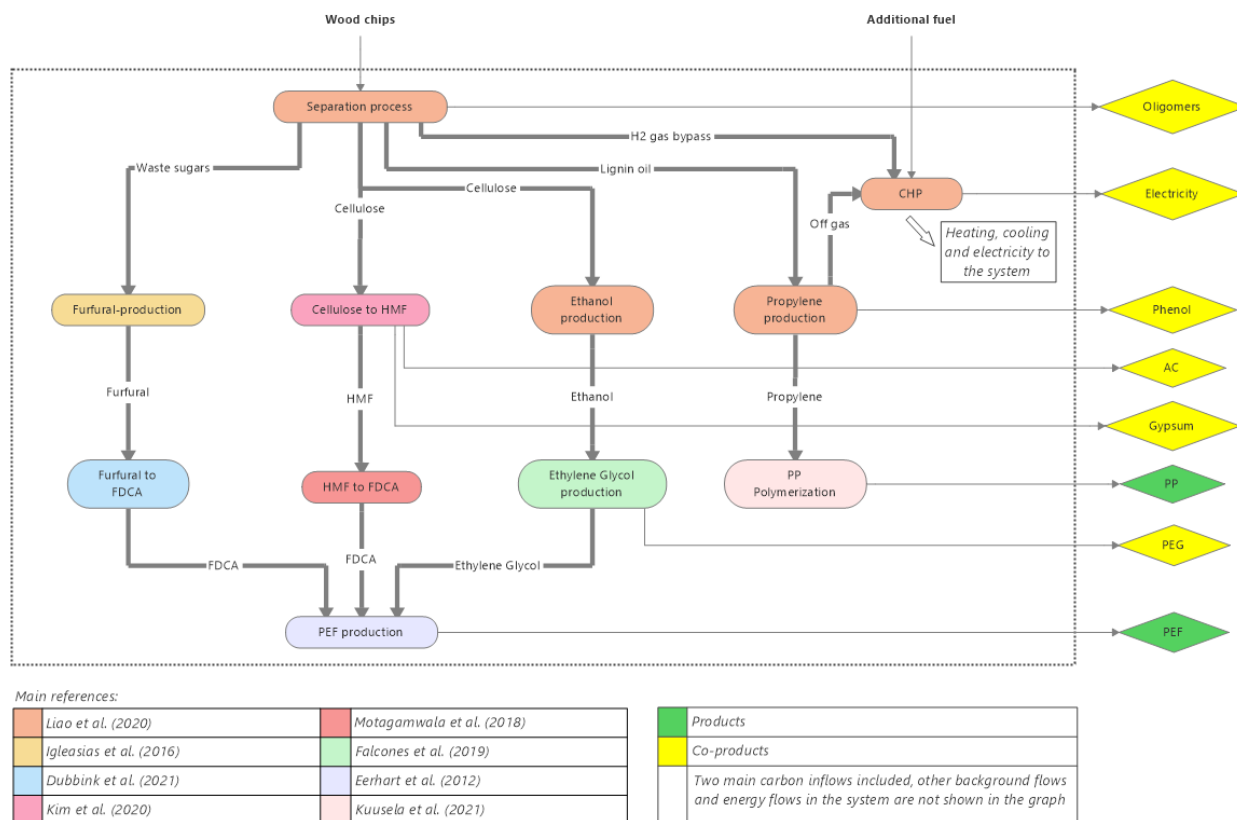


Figure 2.1: Diagram of the product system considered in this analysis

In the following subchapters, each process step is described more in detail. In addition, necessary modelling choices and assumptions are presented. At the end of Chapter 2.3. mass balances and energy balances for the whole system are presented.

2.3.1.1 Separation process

In lignocellulosic biorefineries, the first major processing step is a separation of wood components: cellulose, hemicellulose, and lignin. The conventional way is often based on the Kraft process which has been developed to maximize the yield of cellulose and its purity (Fernández-Rodríguez et al., 2019). In biorefineries aiming for high utilization of lignin, other approaches are needed. In the process presented by Liao et al. (2020) a process called Reductive Catalytic Fractioning is applied. The process is the so-called lignin first process guaranteeing high quality of lignin. Methanol is used as a solvent in the process, Ru is used as a catalyst and hydrogen is used as a reducing agent (Liao et al., 2020). The second step after the separation of crude lignin oil from cellulose is another separation process applying liquid-liquid extraction with water and dichloromethane (DCM). In this process, soluble sugars are extracted from lignin. Lignin monomers are separated from the lignin oil via liquid-liquid extraction in n-hexane (Liao et al., 2020).

Most of the values are directly used based on Liao et al. (2020). The Ru catalyst used in their process was modelled based on the generic metallic catalyst process in Ecoinvent 3.6. based on palladium. From the mass balance, only 5 % of the mass of the catalyst was considered as that was the metal concentration in the catalyst.

The wastewater stream from liquid-liquid extraction in DCM contains mainly methyl-xylosides (Liao et al., 2020). Methyl-xylosides can be turned into furfural through various process steps (Iglesias et al., 2016). Furfural on the other hand can be turned into FDCA, the main substance in the production of PEF (Dubbink et al., 2021). Although the yield of furfural from methyl-xyloside is low, approximately 10 %, this production path was included in the system due to the idea of utilizing a waste stream. In addition Dubbink et al. (2021) stated that the main constraint in production of commercial production of FDCA from furfural is the high price of furfural. It is assumed that utilizing a waste stream as feedstock for production would reduce the costs of the process. On the other hand, there is uncertainty related to the production costs of the furfural from methyl-xyloside and the purification of the furfural to fit the requirements of FDCA production.

2.3.1.2 Propylene and Phenol production

The lignin monomers, one of the intermediate products from the main separation process are further processed into propylene and phenols based directly on process design by Liao et al. (2020). The process design includes hydroprocessing of lignin monomers to alkylphenols, dealkylation to form phenols and alkenes and the final separation into phenols, propylene, off-gas and wastewater. The hydroprocessing is done in a fixed-bed reactor in presence of Ni/SO₄ catalyst and the off-gas from the initial separation containing hydrogen and methane is fed to the reactor in addition to pure hydrogen. The dealkylation is also done in a fixed-bed reactor in presence of a Z140-H catalyst. The water in the reaction is considered deionised industrial water. The final separation process includes a gas-liquid separator to separate a liquid phenol stream and a gaseous mixture of water, olefins, hydrogen, and methane. Further impurities are removed through distillation. All in all, the process design converts 107 kg of lignin monomers into 42 kg of phenol and 19 kg of propylene (Liao et al., 2020). Detailed mass and energy flow information can be found in Appendix 2.

The values from Liao et al. (2020) were used mostly directly in the LCA. The catalyst Ni was modelled based on the generic metal catalyst process in the Ecoinvent 3.6. and the catalyst Zeolite was modelled based on the zeolite powder production process in the Ecoinvent 3.6.

2.3.1.3 Propylene polymerization

After propylene production the last step to produce polypropylene is polymerization. Polymerization is a mature industrial process applied widely in plastic production and there is reliable data available. Based on Kuusela et al. (2021) polymerization of propylene requires 0.84 MJ of heat, 1.27 MJ of electricity, 3.6 kg of H₂O, and 1.02 kg of propylene for 1 kg of product (Kuusela et al., 2021). These values were used in mass and energy balances directly.

2.3.1.4 Production of furfural from waste sugars

As mentioned in section 2.3.1.1. it was found that the wastewater flow from separation processes contains mainly methyl-xyloside. Methyl-xyloside can be used as feedstock in furfural production (Iglesias et al., 2016). The yield of methyl-xylose to furfural reaction was not as good as for example the yield of propyl-xyloside and resulted in to yield of 10 % (Iglesias et al., 2016). Despite the relatively low yield, the process step was included due to the possibility of utilizing a waste stream and increasing the overall carbon efficiency of the system.

As the conversion of furfural from methyl-xylosides is only based on lab-study by Iglesias et al. (2016), detailed flow information was not available. Therefore, no information about solvents or catalysts was included. This exclusion increases the uncertainty of the results and is likely to result in overly positive results. For energy flows only the heating demand of the waste sugar stream from the temperature of the separation process (298 K) to the required reaction temperature (423K) was included. Also, for the heat capacity, the heat capacity of cellulose was used due to data availability issues regarding the heat capacity of methyl-xylosides. The waste sugar stream also includes some water, and it was assumed that the heat capacity of cellulose would present the average good enough, especially when the uncertainty of the energy requirement is already high and likely to be underestimated (D. Kim et al., 2017).

2.3.1.5 Production of FDCA from furfural

Process design for production of FDCA from furfural is presented by (Dubbink et al., 2021). In their process design, there are four main processes: oxidation of furfural to furoate salt, carboxylation of furoate salt to FDCA, recovery of FDCA by acidification, and acid/base regeneration utilizing bipolar membrane (Dubbink et al., 2021). The molar yield of furfural conversion to FDCA was 83 %, and the overall heating demand of the process was 52 MW (Dubbink et al., 2021). Detailed information about the mass and energy flows can be found in table 2.1 and Appendix 2.

Mass and energy flows	Inflow	Outflow
Furfural (kg/day)	136,41	
O2 (kg/day)	21	
Water (kg/day)	2539,01	
Ethyl acetate (kg/day)	0,11	
H2SO4 makeup (kg/day)	0,01	
CO2 (kg/day)	118	
CSCO3 makeup (kg/day)	0,01	
FDCA (kg/day)		185,92
By-product (kg/day)		42,41
Wastewater (kg/day)		2586,1
Heat (kW)	51574	
Cooling (kW)	49777	

Table 2.1: Mass and energy flows of FDCA from furfural

2.3.1.6 Production of ethanol from cellulose

The production of ethanol was based on the study of Liao et al. (2020). They proved that the pulp fraction from the separation process is suitable for bio-ethanol production despite the catalysts in the stream. Based on their design the conversion of RCF pulp resulted in a 26.8 % yield of ethanol in citrate buffer (Liao et al., 2020).

The study by Liao et al. (2020) was based on a laboratory experiment and no heat flows were calculated. Therefore, the energy requirements had to be estimated. As the experiment was based on the idea of saccharification and fermentation, the energy requirements can be estimated based on other studies applying the technology. Morales et al. (2021) presented an integrated bioethanol process design producing ethanol from glucose and xylose. As in this study, xylose is not included in the ethanol production, the

energy data had to be estimated to present ethanol production purely from cellulose (mainly glucose).

Based on Morales et al. (2021) birch wood of 128,000 kg has a theoretical potential of producing 25,774 kg of glucose and 18,459 kg of xylose. Furthermore, based on reaction equations the glucose from birch wood has a theoretical potential of producing 12,887 kg of ethanol and the xylose from birch wood has a theoretical potential of producing 11,075 kg of ethanol. Therefore, ethanol produced from glucose results in 54 % of the total ethanol potential. To simplify the energy demand estimation these theoretical values are applied. Because xylose is excluded in this study, the amount of glucose going to saccharification must increase to supply the same amount of product for co-fermentation. It is assumed that the energy demand increases in the same ratio. To form a simple estimation, the energy demand of saccharification is divided by 54 %, assuming no losses in the process. The estimation is aiming to give a scale of energy demand as the yields of the production phase are based on another study and therefore these simplifications can be tolerated. The total energy demand was estimated to be 0.42 MJ of heat per MJ of ethanol and 0.037 MJ of Power per MJ of ethanol. With ethanol's lower heating value of 27 MJ/kg, the heat demand is considered as 3.15 kWh of heat/kg of ethanol and 0.275 kWh of power/kg of ethanol (Engineering ToolBox, 2008).

Morales et al. (2021) also provided a mass balance for their study. This mass balance is largely excluded from this LCA as the conversion of cellulose to ethanol is mainly based on Liao et al. (2020). In the process by Liao et al. (2020) a citrate buffer was used but due to lack of process design, the recyclability and therefore the need for a new buffer liquid was difficult to estimate. Citrate buffer was decided to be excluded from the study.

2.3.1.7 Production of ethylene glycol from ethanol

Process design for the production of ethylene glycol from ethanol was presented by Falcones et al. (2019). Their study intended to explore the scaling up of novel research by Lippits & Nieuwenhuys (2010) at Leiden University on the direct conversion of ethanol to ethylene glycol. Falcones et al. (2019) provided a complete mass balance which was used in this Thesis. In their design, they also did a heat integration, and the overall energy demands after heat integration were considered. The emissions were allocated between the main product, monoethyleneglycol (MEG) and a mix of MEG, diethylene glycol (DEG) and triethylene glycol (TEG), called polyethylene glycol (PEG). Mass and energy flows of Ethylene Glycol production are shown in the table 2.2. The values are directly retrieved from Falcones et al. (2019) and converted into SI units.

Mass and energy flows	Inflow	Outflow
Ethanol (kg/hr)	26446,66	
Oxygen (kg/hr)	9239,586	
CO2 (kg/hr)	2986,498	
Water (kg/hr)	97032,98	
Wastewater (kg/hr)		104396,6
MEG (kg/hr)		27925,01
MEG DEG TEG mix (kg/hr)		3989,073
Heat (kW)	218631	
Cooling (kW)	339874,5	
Power (kW)	20300	

Table 2.2: Mass and energy flows of EG production

2.3.1.8 Production of HMF from cellulose

H. Kim et al. (2020) presented a process design in which HMF is produced from cellulose and further processed into FDCA (H. Kim et al., 2020). In their design, THF/water mix (90/10) is used as a solvent with 3 wt-% of cellulose and the reaction conditions are 483 K and 68 atm. H. Kim et al. (2020) published a partial mass and energy data of their process which were used in the mass and energy balances. As their data was not complete, some of the data had to be calculated based on Motagamwala et al. (2018) who presented a process of converting HMF to FDCA. As this process was one of the main references in the study of H. Kim et al. (2020) it was assumed to be acceptable. The inflows and outflows of the system for an LCA by H. Kim et al. (2020) were given based on kg/kg of FDCA. As they did not provide the amount of the actual product (FDCA), it was assumed that the yield would be the same as in the study by Motagamwala et al. (2018). In addition, it was assumed that a stream of HMF from HMF production to FDCA production by H. Kim et al. (2020), containing already the required solvent, had 7.5 wt-% of HMF as in the study of Motagamwala et al. (2018)

The energy demand was retrieved from H. Kim et al. (2020). In their study, they presented a heat integration resulting in a significant reduction in heating and cooling demand. As this study only considers a part of their system, only the heat integration within the production of HMF to cellulose was considered. This partial heat integration reduced the heating demand by 27 % and cooling demand by 25 %. Still, a large potential for heat integration remains in this energy-intensive processing step.

2.3.1.9 Production of FDCA from HMF

The production of FDCA from HMF was presented by Motagamwala et al. (2018). In the study, they formed a production pathway from fructose to FDCA through HMF. Although the first part of the pathway, fructose to HMF is not relevant for this study due to different feedstock, the second part of the pathway including conversion of HMF to FDCA, FDCA purification and solvent recycling was suitable as a data source. Also H. Kim et al. (2020) referenced Motagamwala et al. (2018) in their process design exactly for the conversion of HMF to FDCA.

The process design by Motagamwala et al. (2018) is based on oxidation. They found out that GVL/H₂O (50/50) solvent with 7.5 wt-% of HMF proved to be the most promising and included that into their design and that design was directly applied in this LCA study. In addition, Pt/C (5 wt-%) catalyst was used in 1/30 of the mass of HMF. The design also includes flows of hydrogen and oxygen as well as wastewater (Motagamwala et al., 2018). See Appendix 2 for more detailed flow data.

Although heat integration was done for the whole process and in this study the HMF production was excluded, the energy requirements after heat integration for each process step were considered. The decision is justified based on Motagamwala et al. (2018) stating that the majority of the heat demand is related to solvent recycling and the majority of cooling demand to FDCA production and purification. The decision does create uncertainty but was necessary due to lacking data on energy requirements before heat integration per process step. The total energy demand for purified FDCA production from HMF including solvent recycling was calculated to be as follows: heating 0.22 kWh/kg of HMF, cooling 2.10 kWh/kg of HMF and electricity 0.23 kWh/kg of HMF.

In the study by Motagamwala et al. (2018) the loss of GVL solvent was replaced by the conversion of Lactic acid to GVL. Although part of the process pathway was excluded from this study, it is assumed that the GVL conversion from Lactic acid can still be included, and therefore no GVL outside the system is needed.

For the Pt/C catalyst, only 5 % of the mass was considered in the LCA. That 5 % represents the mass of platinum in the catalyst makeup and is responsible for the major part of the environmental impacts. A generic catalyst process based on palladium was used from theecoinvent 3.6. to represent the catalyst. The other substances in the catalyst were not considered in the LCA.

2.3.1.10 Production of PEF from FDCA and Ethylene Glycol

The polymerization of PEF from FDCA and Ethylene Glycol was modelled based on assumptions made by Eerhart et al. (2012). Due to lacking production data of the PEF polymerization, they used values common for polymerization of fossil alternative PET. Following that principle values for the energy demand of PET were used: 0.38 kWh of electricity and 1.75 MJ of heat are required for the production of PET (Papong et al., 2014). Although the energy demand of PEF production is expected to be lower than PET, it was assumed that the values for PET represent PEF with acceptable accuracy (Eerhart et al., 2012).

2.3.1.11 Combined heat & power production (CHP)

In process design by Liao et al. (2020) trigeneration from two side streams was modelled based on 87 % overall efficiency. In their design, the side streams were enough to cover the energy demand of their process, but in the integrated production of bio-PP and PEF, the energy demand exceeds the side stream potential. Therefore, an additional energy source is needed.

In this LCA study, three scenarios were built based on the additional energy source: the initial scenario based on wood chips and two alternative scenarios based on natural gas and coal. The choice of wood chips as the additional energy source was made based on the principle of utilizing biobased materials to large extent. On the other hand, a large number of wood chips for energy production do not come without problems. Forests in many areas are scarce or desired feedstocks and such a low degree of processing as combustion could not be seen as a feasible way to utilize that feedstock (Parshley, 2022). In addition, there are ongoing discussions in the European Union on whether the combustion of wood chips should be considered as renewable energy as it is at the moment or not (Parshley, 2022). If the combustion of wood chips for energy production was not considered renewable energy, it would affect the environmental performance as well as the economic performance of the process (Parshley, 2022).

Therefore, alternative energy sources were considered. Natural gas, with in general lower environmental impacts than coal, can be seen as a more promising option but due to the geopolitical tensions between western Europe and Russia and the impacts of the Russian attack on Ukraine on the European gas market, it was decided to model the environmental impacts also based on energy production from coal (Aurora Energy Research Ltd., 2022).

The choice of energy source affects the choice of technology. To simplify the modelling the energy production from side streams of bio-PP production was modelled based on the values of trigeneration given by Liao et al. (2020). The additional energy sources were modelled based on industry standards. For solid energy sources, wood chips and coal,

the steam turbine was chosen as a technology. The overall efficiency of 80 % was considered, of which electric efficiency was 10 % (US Department of Energy, 2017). For natural gas, a gas turbine was chosen as a technology. The overall efficiency was 70 % of which electric efficiency was 30 % (US Department of Energy, 2017). For cooling production, a co-efficient of absorption (COP) of 1.42 was considered (US Department of Energy, 2017). The values are compiled in Table 2.3.

CHP efficiency	Overall	Elec	Heat	Absorption COP
Steam turbine	0.8	0.1	0.7	1.42
Gas turbine	0.7	0.3	0.4	1.42

Table 2.3: CHP and absorption efficiencies

Although the main energy demand was related to heating and cooling, instead of electricity, combined heat and power production was considered with the assumption that excess electricity could be sold to the national power grid. CHP provides higher efficiency than for example pure heat production, which decreases the environmental impacts of the energy per unit (US Department of Energy, 2017).

The demand for energy from each additional energy source was calculated separately based on the energy demand and energy potential from side streams and the values given above. The lower heating values of the additional energy sources were retrieved from Pacific Northwest National Laboratory (2022) and the average lower heating value for H₂ gas bypass and CH₄ gas was calculated for reference. The results are shown in Table 2.4.

Energy balance	LHW (MJ/kg)	Heating (kWh)	Cooling (kWh)	Power (kWh)
Energy demand		3572,35	3771,14	435,52
Energy production		-	-	
<u>Side products</u>				
H ₂ gas bypass & CH ₄ gas	23,46	226,21	332,34	287,22
		=	=	
<u>Additonal energy sources:</u>				
Scenario Wood chips	19,55	3346,14	3438,80	823,98
Scenario Natural gas	47,13	3346,14	3438,80	4325,87
Scenario Coal	22,73	3346,14	3438,80	823,98

Table 2.4: Energy requirement calculations

Based on the energy requirement calculations, the demand for energy sources in mass and emissions related to their combustion were calculated. Emission factors were retrieved from U.S. Environmental Protection Agency (2022). The results are shown in Table 2.5.

Additional fuel demand	Mass kg	Emissions CO ₂ (kg)	CH ₄ (kg)	N ₂ O(kg)
Scenario Wood chips	1517,30	2742,92	0,21	0,11
Scenario Natural gas	1101,43	2892,03	0,05	0,01
Scenario Coal	1305,02	3743,04	0,40	0,06

Table 2.5: Additional demand for energy sources

As Liao et al. (2020) did not publish emission factors for the combustion of the two side streams, the emissions had to be estimated. The estimation was done based on stoichiometry and the principle that combustion of $C_aH_bO_c$ results in $a \cdot CO_2$ and $1/2b \cdot H_2O$ (University of Calgary, 2022). This estimation includes an assumption that the combustion reaction is complete combustion, and no other substances are formed. The emissions related to the two side streams are calculated as shown in Tables 2.6 and 2.7.

Combustion of H2 gas bypass	Chemical structure:	Molar mass (g/mol):	Mass (kg):	Amount of substance (mol)
<u>Composition of the gas</u>				
Methyl acetate	C3H6O2	74,08	72,54	979,22
Methanol	CH4O	32,04	2,81	87,57
<u>Products</u>				
Carbon dioxide	CO2	44,01	133,14	3025,23
Water	H2O	18,02	59,23	3287,92

Table 2.6: Emissions of H2 gas bypass combustion

Combustion of off-gas	Chemical structure:	Molar mass (g/mol):	Mass (kg):	Amount of substance (mol)
<u>Composition of the gas</u>				
Hydrogen	H2	2,02	8,23	4084,54
Methane	CH4	16,04	24,27	1512,69
Propylene	C2H4	42,08	0,85	20,17
Ethylene	C3H6	28,05	0,37	13,17
<u>Products</u>				
Carbon dioxide	CO2	44,01	70,09	1592,54
Water	H2O	18,02	129,52	7189,77

Table 2.7: Emissions of off-gas combustion

The overall emissions from the CHP of the integrated production system are shown in Table 2.8. The scenarios are shown separately and as the initial scenario is based on the combustion of wood chips, a distinction between fossil and biogenic emissions is done.

Total emissions	CO2 (fossil) (kg)	CO2 (biogenic) (kg)	CO2 total (kg)	CH4 (kg)	CH4 (biogenic) (kg)	N2O (kg)
Scenario Wood chips	203,22	2742,92	2946,15		0,21	0,11
Scenario Natural gas	3095,25		3095,25	0,05		0,01
Scenario Coal	3946,26		3946,26	0,40		0,06

Table 2.8: Total emissions for all scenarios

2.3.2 Mass balance

The mass balance was compiled in Excel using 1000 kg of wood chips as a base value. Based on the mass balance 18,8 kg of PP and 175,9 kg of PEF are generated. An overall mass balance is provided in Table 2.9. See Appendix 2 for division to production steps.

Overall mass-balance - Inflows and Outflows

Feedstock	Inflows	Outflows	Balance
Wood chips (Birch) (kg)	1000,00		1000,00
H2 (kg)	17,73	0,04	17,69
H2O (kg)	516,99	18,58	498,42
n-Hexane (kg)	1,01		1,01
Methanol (CH3OH) (kg)	61,14		61,14
DCM (CH2CL2) (kg)	12,60		12,60
N2 (kg)	0,63		0,63
Catalyst Ru (kg)	0,01		0,01
Catalyst Ni (kg)	0,001		0,001
Catalyst Zeolite (kg)	0,001		0,001
O2 (kg)	64,12		64,12
CO2 (kg)	13,24		13,24
H2SO4 makeup (kg)	0,0006		0,0006
Cs2CO3 makeup (kg)	0,0006		0,0006
Ethyl acetate (kg)	0,01		0,01
THF (kg)	7,98		7,98
Catalyst Pt/C (kg)	0,004		0,004
Scenario 1: Coal (kg)	1305,02		1305,02
Scenario 2: Natural gas (kg)	1101,43		1101,43
Scenario 3: Additional Wood chips (kg)	1517,30		1517,30
Emissions & waste	Inflows	Outflows	Balance
Wastewater (m3)		1,16	-1,16
Off gas N2 (kg)		0,63	-0,63
CO2 (kg)		264,08	-264,08
H2O(steam)		188,76	-188,76
Products	Inflows	Outflows	Balance
Oligomers (kg)		64,12	-64,12
Phenol (kg)		41,73	-41,73
Polypropylene (kg)		18,76	-18,76
Furfural-FDCA byprod (kg)		2,45	-2,45
Activated carbon (kg)		88,60	-88,60
Gypsum (kg)		24,36	-24,36
PEF (kg)		175,90	-175,90
Scenario 1: Electricity (kWh)		675,68	-675,68
Scenario 2: Electricity (kWh)		4177,57	-4177,57
Scenario 3: Electricity (kWh)		675,68	-675,68

Table 2.9: Overall mass balance of the integrated system

2.3.3 Energy balance

The energy balance was compiled in Excel using 1000 kg of wood chips as a base value. The total heat demand of the production system is 3572,35 kWh, coolant demand 3771,14 kWh and electricity demand 435,52 kWh.

Due to the exploratory nature of the study, no actual systemwide heat integration with heat exchangers was considered. Some of the process designs had integrated heat flows but some of them did not. If the production system was to be developed further, proper heat integration is likely to reduce its emissions and energy demand significantly.

The overall energy balance is provided below. As the choice of additional energy source affected the production of energy, the balance is calculated for all the scenarios separately. The energy balance is provided in Table 2.10. In Appendix 2 more detailed information on the energy demands of individual processing steps is available.

Energy balance	Heating (kWh)	Cooling (kWh)	Power (kWh)
Energy demand	3572,35	3771,14	435,52
Energy production			
Scenario Wood chips	3572,35	3771,14	1111,19
Scenario Natural gas	3572,35	3771,14	4613,09
Scenario Coal	3572,35	3771,14	1111,19

Table 2.10: Overall energy balance of the system

In addition, as the power production exceeds the power demand a separate power balance was calculated for all the scenarios. The excessive power is considered to be sold to the power grid as a side product. The power balance is provided in Table 2.11.

Power balance	Total power production	Total power demand	Power sold out
Scenario Wood chips	1111,19	435,52	-675,68
Scenario Natural gas	4613,09	435,52	-4177,57
Scenario Coal	1111,19	435,52	-675,68

Table 2.11: Power balance of the system

2.3.4 Summary of main assumptions for the biorefinery modelling

In this subchapter, a list of main assumptions is provided. The list is not complete as several other assumptions were needed. The assumptions not mentioned in the list below are mentioned inside the text of Chapter 2.

Furfural production from methyl-xylosides	It is assumed that the production of furfural is possible also as an industrial process as presented by Iglesias et al. (2016). Also as no data is available, solvents are not considered and as energy demands only the heating of the waste sugar stream to needed reaction conditions is considered. It is likely to be an underestimation. Also, it is considered that the separation of the furfural can be done feasibly, either by separating first the methyl-xylosides from other sugars and then separating furfural or by feeding all the sugars to the reactor and separating furfural from the mix. In other words, the separation of furfural is not considered in this study.
The energy demand for ethanol production	As the pulp from the separation process contains some solvents and catalysts, the yield presented by Liao et al. (2020) was considered. As their study was only a laboratory experiment, the energy demand of ethanol production had to be estimated based on other studies. Morales et al. (2021) presented a process design to produce ethanol from cellulose and hemicellulose. The energy requirement from their design was used after modification to present this system better.
PEF production energy demand	As energy demand for PEF production was not available, energy demand for PET was used instead based on Papong et al. (2014). It was assumed that the energy requirements of PET production represent PEF production well enough.
GVL solvent formation in FDCA production	It was assumed that although only part of the process presented by Motagamwala et al. (2018) is included in this study, the GVL solvent required in the process can be produced inside the system as they presented.

2.4 Life-Cycle Inventory

2.4.1 Flow data

The lifecycle inventory (LCI) was built based on the data shown in mass- and energy balances (see Appendix 2). The data for background processes was retrieved from the ecoinvent 3.6 database as well as the data for environmental flows such as emissions and wastewater. As defined in the Goal and Scope of the study, values relevant to the Nordic location were applied when available otherwise European or global data were used. See Appendix 1 for a complete list of the chosen background processes.

2.4.2 Allocation

Allocation is a method used for dividing environmental impacts for multiple products of a function. Based on the ISO standard on LCA, the allocation should be avoided either by dividing the unit process into sub-processes or by expanding the products system to take into account functions related to the coproducts (International Organization for Standardization, 2006). When the former two are not options and allocation cannot be avoided, partitioning should be applied (International Organization for Standardization, 2006). In partitioning the emissions and all the raw materials and impacts related to them are divided between products based on a chosen metric such as mass, energy content or economic value of the products (International Organization for Standardization, 2006).

Due to the complexity of the system, the division into sub-processes or the system expansion was not feasible and therefore partitioning was applied. Several partitioning methods were considered, but because of many intermediate products without economic value and products consisting of energy and material, the partitioning based on energy content was chosen. Energy content is a common partitioning factor in biorefining and is preferred rather than mass allocation, as it takes into account both material and energy products which would not be the case with partitioning based on mass (Cherubini et al., 2011). On the other hand, allocation based on energy content might be inconsistent and not logical for products which are not used for their energy content and have low energy content (Cherubini et al., 2011). For example, no impacts are allocated for a co-product of HMF production, gypsum, as it is inert material without notable energy content. In this study, the partitioning based on energy content was done by applying lower heating values (LHV) of the products and intermediate products. Some of the mass flows are mixes of several substances and the LHVs had to be calculated or estimated.

Allocation was used in the following processes:

1. Separation process
Allocation was done between Cellulose, Lignin monomers, H₂ gas bypass and Oligomers. Waste sugars from the process are considered waste and therefore no emissions are allocated to them. The lower heating values for cellulose and lignin monomers were retrieved from D. Kim et al. (2017). In addition, due to the difficulty of finding a value for phenolic oligomers, the lower heating value of lignin was applied for phenolic oligomers. For H₂ gas bypass, it was assumed that the value for the main substance, methyl

acetate, represents the intermediate product well enough. The value was retrieved from PubChem (2022).

2. Propylene & Phenol production

Allocation was done between Phenol, Propylene and off-gas (used in CHP). For phenol, the lower heating value was retrieved from Cox (2009). For propylene, the lower heating value was retrieved from Liquisearch (2022). For the off-gas, consisting of hydrogen and methane, the lower heating value was calculated based on the fraction of the substances from Liao et al. (2020) and their lower heating values retrieved from Essom CO. (2022)

3. HMF production

Allocation was done between HMF and activated carbon. The lower heating value of HMF was retrieved from Nilges & Schröder (2013) and the lower heating value of activated carbon was retrieved from Chen et al. (2012)

4. Ethylene glycol production

Allocation was done between monoethylene glycol and a side stream including a mixture of polyethylene glycols. A detailed explanation, calculation and data sources of the lower heating value of the co-product are provided in Appendix 3.

5. CHP

Allocation was done between heat, coolant, and electricity and it is based on their values in the energy balance.

The details of the allocation are shown in Table 2.12.

Separation process	LHV (MJ/kg)	Mass (kg)	Total energy content (MJ)	Allocation (%)
Cellulose	16,5	653,02	10774,82	65 %
Lignin monomers	20,4	107,00	2493,10	15 %
H2 gas bypass	21,5	88,52	1903,09	12 %
Phenolic oligomers	20,4	64,12	1308,12	8 %

Propylene & Phenol production	LHW (MJ/kg)	Mass (kg)	Total energy content (MJ)	Allocation (%)
Phenol	32,47	41,73	1354,97	31 %
Propylene	45,80	19,13	876,23	20 %
Off gas	65,41	33,72	2205,61	50 %

Ethylene Glycol production	LHW (MJ/kg)	Mass (kg)	Total energy content (MJ)	Allocation (%)
MEG	14925,13	59,95	894707,50	84 %
PEG	19487,28	8,56	166875,62	16 %

Cellulose to HMF	LHW (MJ/kg)	Mass (kg)	Total energy content (MJ)	Allocation (%)
HMF	22,04	124,72	2749,32	60 %
Activated carbon	20,69	88,60	1833,57	40 %

CHP (Scenario wood chips)	Total energy content (kWh)	Allocation (%)
Heat	3572,35	42 %
Coolant	3771,14	45 %
Electricity	1111,19	13 %

CHP (Scenario natural gas)	Total energy content (kWh)	Allocation (%)
Heat	3572,35	30 %
Coolant	3771,14	31 %
Electricity	4613,09	39 %

CHP (Scenario coal)	Total energy content (kWh)	Allocation (%)
Heat	3572,35	42 %
Coolant	3771,14	45 %
Electricity	1111,19	13 %

Table 2.12: Allocation of emissions

2.5 Life-Cycle Impact Assessment

For life-cycle impact assessment (LCIA) ReCiPe 2016 Midpoint -method was applied based on the hierarchical scenario. In the LCIA the inventory of emissions, such as CO₂, are translated into impacts such as climate change with a metric of global warming potential in 100 years (GWP100).

Life-cycle impacts were calculated for both main products with a functional unit of 1 kg of product (PP or PEF). As stated earlier, the impacts were also calculated for two additional scenarios: natural gas as an additional energy source and coal as an additional energy source.

The LCIA was provided for all impact categories of ReCiPe 2016, but a closer look and contribution analysis was provided for the following four categories: climate change, fossil resource scarcity, human toxicity and terrestrial ecotoxicity. Human toxicity is aggregated category of two impact categories in ReCiPe 2016, non-carcinogenic human toxicity and carcinogenic human toxicity.

3 Results and Discussion

In this chapter, the results of LCA are shown and interpreted. The chapter is divided into three subchapters. In the first subchapter, the general LCIA results for both bio-PP and PEF are provided. The second subchapter consists of an overview of the LCA results, a comparison of the scenarios based on different energy sources for energy production and a comparison to reference values from the literature. The third subchapter consists of the contribution analysis for the initial scenario based on wood chips as an energy source. The fourth subchapter consists of general remarks and points of improvement and in the last subchapter, the key limitations are discussed. In general, the discussion of the results is blended into the chapter.

3.1 LCIA of bio-PP and PEF

In this subchapter, the results of the lifecycle impact assessment are provided for both plastic products. The results include all impact categories of the ReCiPe 2016 for the initial scenario in which wood chips are used as the additional energy source for energy production.

3.1.1 PP environmental impacts

The environmental impacts per category for 1 kg of polypropylene from biomass produced in the integrated system are shown in Table 3.1.

Indicator	Unit	Total
Global warming	kg CO ₂ eq	8,10E-01
Stratospheric ozone depletion	kg CFC11 eq	3,13E-06
Ionizing radiation	kBq Co-60 eq	3,10E-02
Ozone formation, Human health	kg NO _x eq	3,67E-03
Fine particulate matter formation	kg PM _{2.5} eq	7,39E-03
Ozone formation, Terrestrial ecosystems	kg NO _x eq	3,80E-03
Terrestrial acidification	kg SO ₂ eq	2,48E-02
Freshwater eutrophication	kg P eq	1,18E-03
Marine eutrophication	kg N eq	4,41E-05
Terrestrial ecotoxicity	kg 1,4-DCB	2,22E+00
Freshwater ecotoxicity	kg 1,4-DCB	9,44E-02
Marine ecotoxicity	kg 1,4-DCB	1,21E-01
Human carcinogenic toxicity	kg 1,4-DCB	3,43E-02
Human non-carcinogenic toxicity	kg 1,4-DCB	3,36E+00
Land use	m ² a crop eq	2,81E+00
Mineral resource scarcity	kg Cu eq	2,79E-02
Fossil resource scarcity	kg oil eq	5,28E-01
Water consumption	m ³	6,99E-03

Table 13.1: LCIA of 1 kg of PP

3.1.2 PEF environmental impacts

The environmental impacts per category for 1 kg of PEF from biomass produced in the integrated system are shown in Table 3.2.

Indicator	Unit	Total
Global warming	kg CO ₂ eq	2,17E+00
Stratospheric ozone depletion	kg CFC11 eq	8,03E-06
Ionizing radiation	kBq Co-60 eq	1,69E-01
Ozone formation, Human health	kg NO _x eq	4,33E-03
Fine particulate matter formation	kg PM _{2.5} eq	4,19E-03
Ozone formation, Terrestrial ecosystems	kg NO _x eq	4,51E-03
Terrestrial acidification	kg SO ₂ eq	1,28E-02
Freshwater eutrophication	kg P eq	1,96E-03
Marine eutrophication	kg N eq	2,35E-04
Terrestrial ecotoxicity	kg 1,4-DCB	4,04E+00
Freshwater ecotoxicity	kg 1,4-DCB	7,94E-02
Marine ecotoxicity	kg 1,4-DCB	1,01E-01
Human carcinogenic toxicity	kg 1,4-DCB	5,07E-02
Human non-carcinogenic toxicity	kg 1,4-DCB	2,18E+00
Land use	m ² a crop eq	7,15E+00
Mineral resource scarcity	kg Cu eq	1,31E-02
Fossil resource scarcity	kg oil eq	5,87E-01
Water consumption	m ³	3,71E-02

Table 14 LCIA of 1 kg of PEF

3.2 Life cycle assessment of bio-PP and PEF

The results of the four chosen impact categories were compared between the initial scenario based on the combustion of wood chips for energy supply for the biorefinery and the alternative scenarios based on natural gas and coal as energy sources. The difference between the scenarios shows that the choice of the energy source is a major factor in the environmental impacts of the products from the integrated production system. A list of impacts on all categories in ReCiPe 2016 for all the scenarios is provided in Appendix 4.

In terms of climate change, the initial scenario based on wood chips as an additional energy source has the lowest impact. The scenario in which natural gas is used as an additional energy source has a 138 % higher impact on climate change in the case of bio-PP and a 312 % higher impact on climate change in the case of PEF compared to the initial scenario. The scenario based on coal combustion resulted in a 307 % higher impact on climate change in the case of bio-PP and a 695 % higher impact on climate change in the case of PEF compared to the initial scenario.

Based on PlasticEurope (2014) the climate change impact of conventional polypropylene is 1,63 kg of CO₂ eq with a scope of cradle-to-gate. Liao et al. (2020) calculated a GWP of 0,469 kg of CO₂ -eq for propylene in their study. This value is used as a reference value when estimating a reference value for biobased propylene. When comparing to the results of the study by Liao et al. (2020) and considering that the end product of this LCA is polypropylene instead of propylene and the carbon footprint includes also the impacts of polymerization, it can be stated that the initial scenario based on wood chips as an

energy source results to higher impacts than in the study by (Liao et al., 2020) but to significantly lower impacts than baseline scenario of the conventional propylene. The scenario based on natural gas results in approximately 30 % higher impacts than conventional propylene whereas the scenario based on coal results in over 100 % higher emissions than conventional propylene.

Based on CPME (2017) the climate change impact of PET, the fossil-based alternative for PEF, is 2,19 kg of CO₂ eq. Although PET and PEF are not chemically the same, they can be used for the same functions and both suit the same production system. Avantium has published a cradle-to-grave LCA study based on a PEF bottle executed by nova-Institute (2022). As the scope of this study was cradle to gate, the LCA from Avantium does not provide completely comparable results as the use phase and end-of-life phase are included. On the other hand, good quality LCA studies on this novel bioplastic were not available and therefore values from their study were considered for PEF to form a bio reference value for comparison (nova-Institute, 2022).

The PEF from the integrated production system performed almost equally as the conventional PP in terms of impacts on climate change and performed better compared to the bio reference value and the scenarios based on other additional energy source scenarios. On the other hand, when comparing to the fossil baseline it must be noted that the polymers (PET and PEF) are different on a chemical level and that PEF has some advantages which are expected to reduce the impacts on cradle to grave assessment (nova-Institute, 2022). Therefore it can be stated that the performance of PEF from the integrated biorefinery is better than PETs. In addition, with the bio reference value based on nova-Institute (2022), it must be considered that the scope of the studies was different. On the other hand, the production process of PEF from the integrated production system was not optimised and therefore it is likely that the impacts would be reduced to even lower values. The PEF from the integrated system resulted in 50 % lower impacts on climate change than PEF based on the Avantium study and 1 % lower impacts than the conventional PET. When compared to the two alternative energy source scenarios, the initial scenario performed well resulting in more than 75 % lower impacts than the scenario based on natural gas and 85 % lower impacts than the scenario based on coal.

A good performance of the initial scenario in which wood chips are used as an energy source is mostly related to the exclusion of the biogenic carbon from GHG emissions. In chapter 2.3.1.11. the scenario was calculated to have an almost equal amount of CO₂ emissions as the alternative scenario based on natural gas as an energy source and higher levels of CH₄ emissions. Although the exclusion of biogenic carbon is a standard approach in LCA studies, it can be discussed whether it provides fair results. Within the geographical boundary of the study, it can be assumed that the forest harvested as feedstock will grow back. On the other hand, from harvesting until the forest is fully grown, the biogenic carbon in the atmosphere contributes to climate change (Parshley, 2022). In the future biogenic carbon might be included as a contributor to the environmental impacts by standard in one way or another, as for example in European Union (EU) there is an ongoing discussion whether wood combustion for energy production shouldn't be considered as renewable energy as it is today (Parshley, 2022). If the bioenergy from primary (un-processed) biomass were excluded, and if the sidestreams of biorefineries were not excluded from the list of renewable energy as discussed by Parshley (2022), the raw material-efficient biorefinery as designed in this study would not make sense. It would be better to have enough sidestreams from the

biorefining to cover the energy demand than combust wood chips, as the former would be considered renewable energy and the latter not.

All in all, it can be stated that the products from integrated biorefinery perform well when the initial scenario is considered with the exclusion of the GHG emissions based on biogenic carbon. Without the exclusion or when other energy sources are applied, both products perform worse than the fossil-based alternatives or the bio alternatives chosen as references. The impacts on climate change are shown in the Figure 3.1.

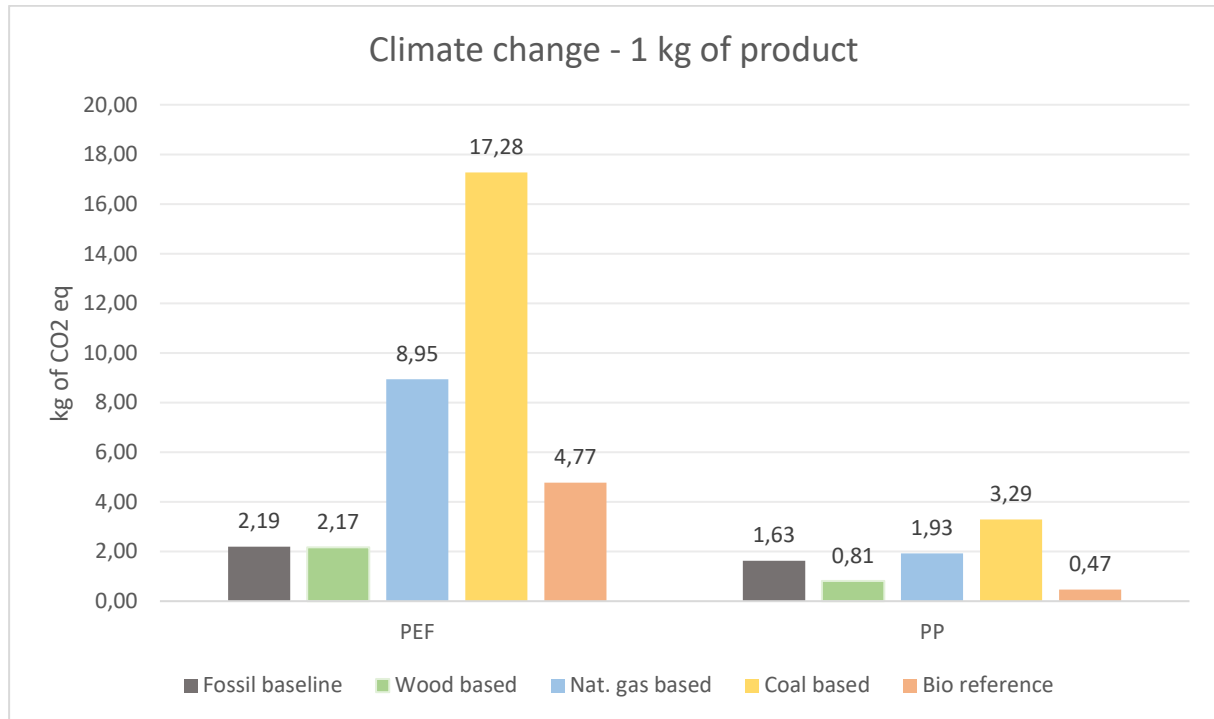


Figure 3.1: Comparison of climate change results for the different products analyzed in this study

For other considered environmental impact categories comparable values were difficult to find in the literature. For the alternative scenarios, the impacts on all categories in ReCiPe 2016 were calculated and the results are provided in Appendix 4. For the three impact categories, a deeper discussion and contribution analysis are provided below.

In the case of terrestrial ecotoxicity, the percentual differences between the initial scenario and the additional scenarios for both products were smaller than with climate change. What is to be noted is that despite the small difference, the products from the initial scenario based on wood chips as an energy source performed worse than the products from the alternative scenarios. With bio-PP, the scenario based on natural gas resulted in a 4 % lower impact and the scenario based on coal resulted in a 2 % lower impact than the initial scenario. With PEF the scenario based on natural gas resulted in a 12 % lower impact and the scenario based on coal resulted in a 7 % lower impact than the initial scenario. The differences in impacts are related to the energy sources as they

were the only differences between the scenarios. The impacts on terrestrial ecotoxicity are shown in Figure 3.2.

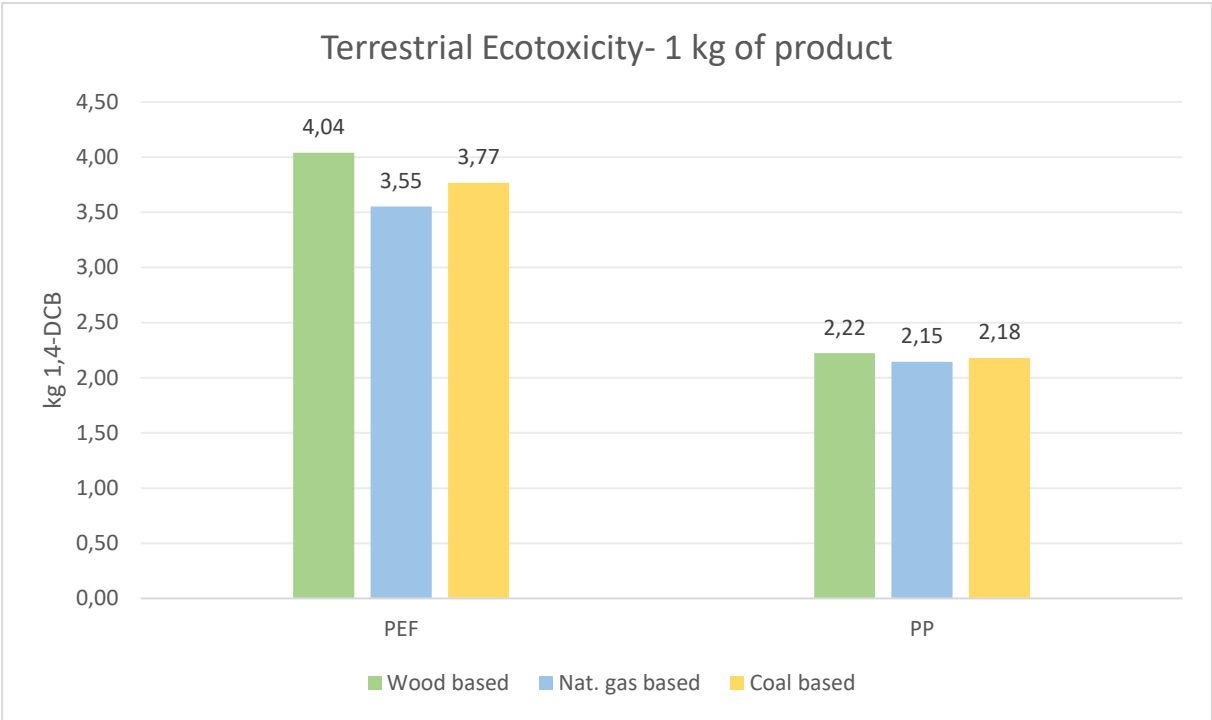


Figure 2.2: Comparison of terrestrial ecotoxicity results for the different products analyzed in this study

With human toxicity, the initial scenario and scenario based on natural gas as an energy source resulted close to the same results for both products whereas the scenario based on coal as an energy source resulted in significantly higher impacts. With bio-PP, the scenario based on natural gas as an energy source resulted in 1 % lower impacts whereas the scenario based on coal as an energy source resulted in 17 % higher impacts than the initial scenario. With PEF the scenario based on natural gas as an energy source resulted in 7 % lower impacts whereas the scenario based on coal as an energy source resulted in 157 % higher impacts than the initial scenario. As the only difference between the scenarios is the energy source, the large effect of coal combustion on human toxicity is highlighted in the environmental impacts of PEF. The impacts on human toxicity are shown in Table 3.3.

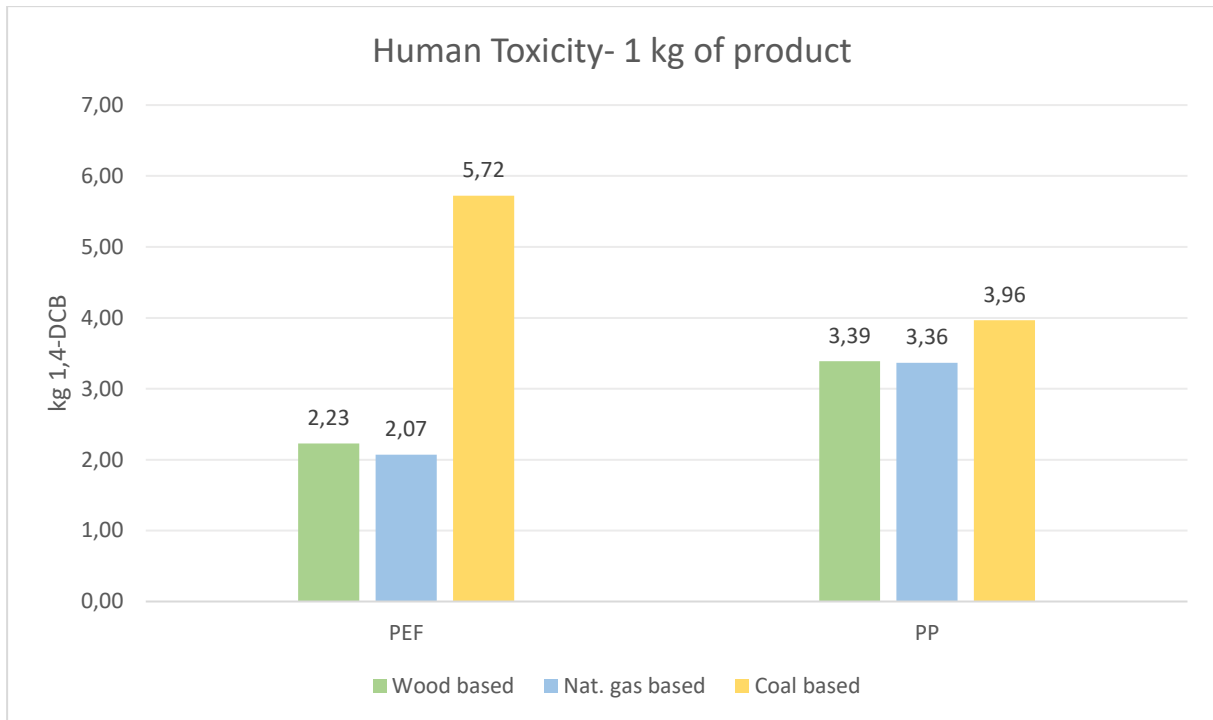


Figure 3.3: Comparison of human toxicity results for the different products analyzed in this study

In the case of fossil resource scarcity, there are major differences between the initial scenario and the alternative scenarios. With bio-PP, the scenario based on natural gas as an energy source resulted in 84 % higher impacts and the scenario based on coal as an energy source resulted in 91 % higher impacts than the initial scenario. With PEF the differences were even more significant. The scenario based on natural gas as an energy source resulted in 458 % higher impacts and the scenario based on coal as an energy source resulted in 499 % higher impacts than the initial scenario. These results are expected and highlight the importance of avoiding fossil-based energy sources to reduce the impacts on fossil resource scarcity. The impacts on fossil resource scarcity are shown in Table 3.4.

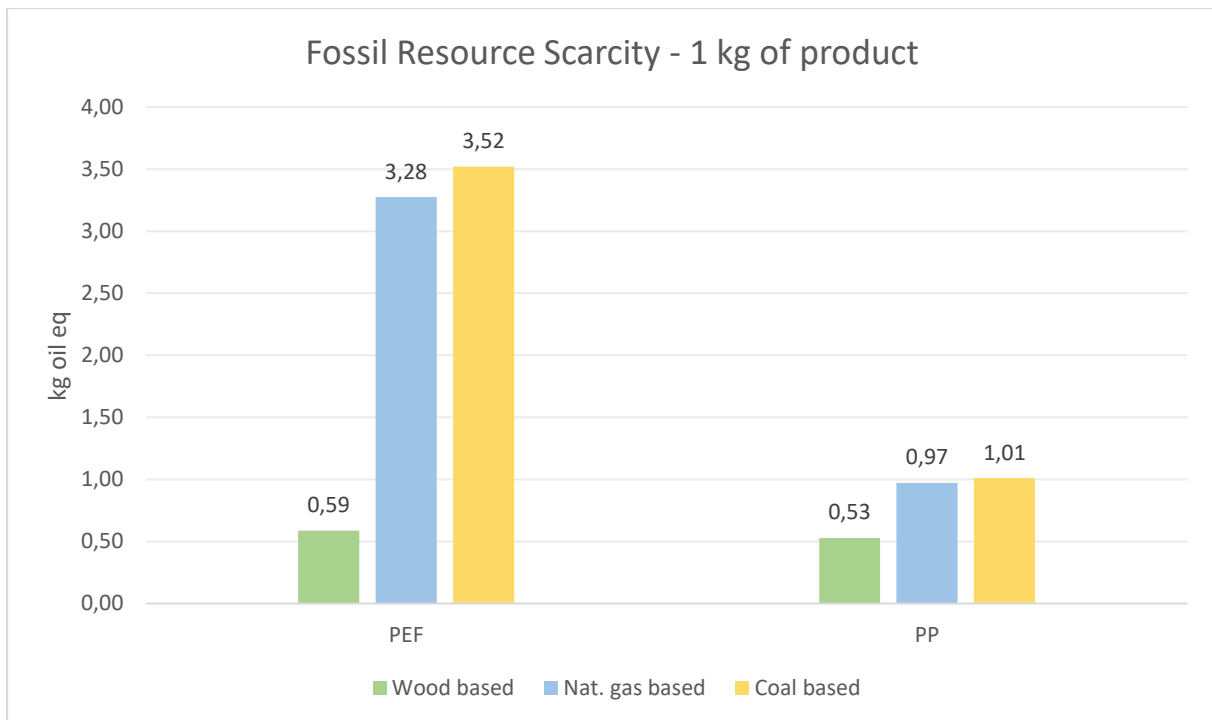


Figure 3.4: Comparison of fossil resource scarcity results for the different products analyzed in this study

Although with human terrestrial ecotoxicity the initial scenario based on energy supply from wood chips performed the worst and with human toxicity, the scenario based on natural gas performed slightly better, it can be concluded that the initial scenario provides the most promising results based on the four impact categories. This conclusion is emphasized by the large differences in the other two categories, climate change and fossil resource scarcity.

3.3 Contribution analysis of bio-PP and PEF

Contribution analysis was performed for both bioplastics in four impact categories: climate change, fossil resource scarcity, human toxicity (combination of carcinogenic and non-carcinogenic human toxicity) and terrestrial ecotoxicity. The processes consist of both foreground processes as well as background processes.

3.3.1 Bio-PP contribution analysis

The major processes of bio-PP production contributing to the selected impact categories are shown in Figure 3.5.

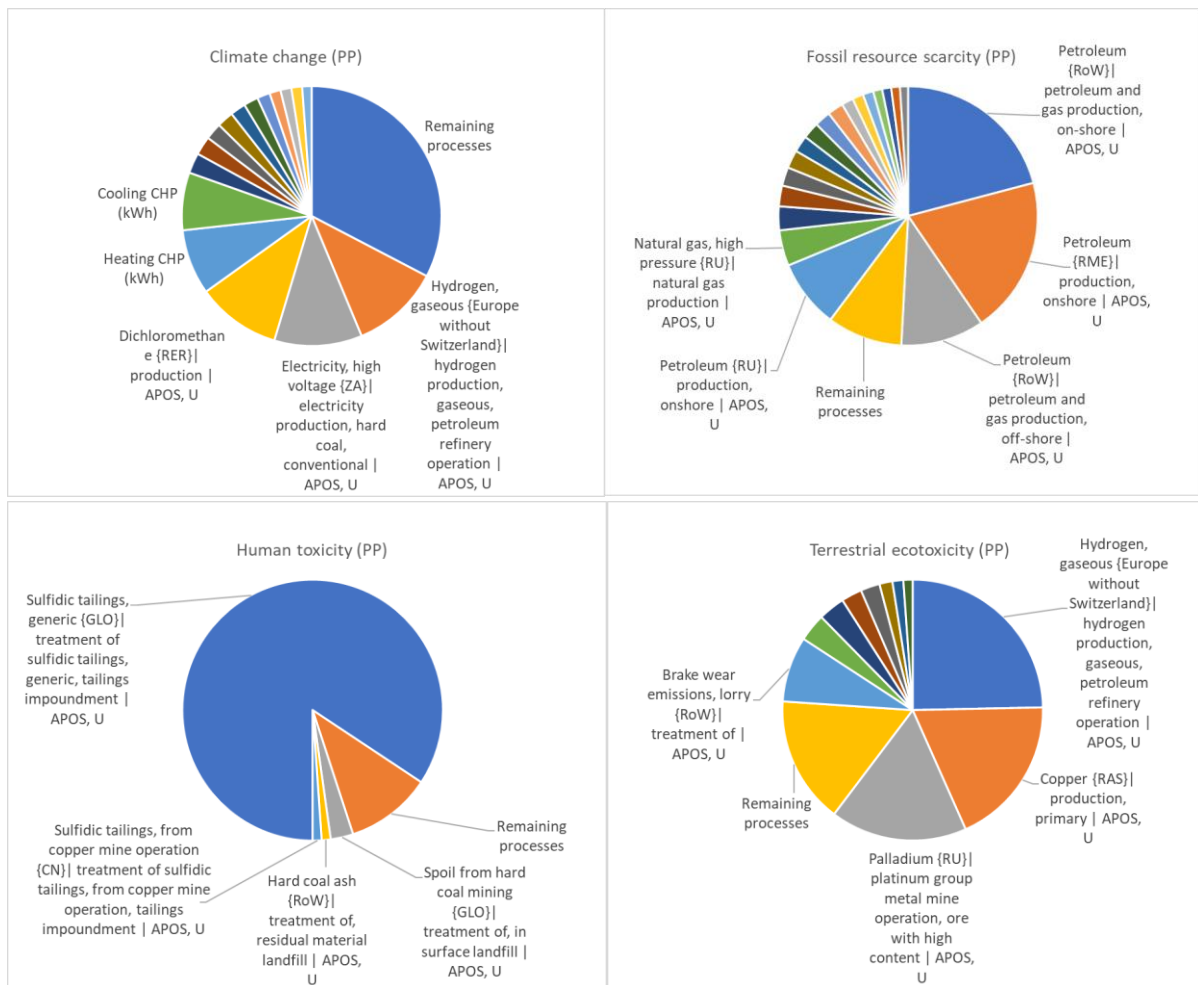


Figure 3.5: Contribution analysis of bio-PP

For impact on climate change, hydrogen production was the largest single contributor in bio-PP production. Hydrogen usage is related to reductive catalytic fractioning and hydrogenation processes. The second-largest contributor was electricity usage mainly related to the production of metal catalysts. The third-largest contributor was dichloromethane production used in reductive catalytic fractioning followed by cooling and heating production for the integrated production system.

For fossil resource scarcity the major contributors were mostly petroleum production processes related to the production of the raw materials of the integrated production system. The processes are background processes and linked to several raw materials. The only major contributor with a direct link to the modelled system was natural gas.

For human toxicity, the major contributors are related to mining operations of minerals for metal catalysts. From the mining operations, sulfidic tailings contribute over 80 % of the total human toxicity. Other notable contributors are related to hard coal production and combustion. Although in the initial scenario hard coal is not used as an energy source in the production system, it is used in the background processes for example for electricity production for raw materials. In other words, the impacts related to hard coal are a result of several background processes.

For terrestrial ecotoxicity, the largest contributor resulting in almost 25 % of the total impact was hydrogen production. Hydrogen is used in various processes in the system from reductive catalytic fractionation to hydrogenation processes. The second-largest contributor was copper production and the second-largest palladium mine operation. Both of these are related to metal catalyst production. Although palladium is not used in the production system, it is presented in the contribution analysis because a general metal catalyst process was chosen from the ecoinvent 3.6 to represent the catalysts used in the system, and that general catalyst process is based on palladium production. The fourth-largest contributor was break wear from lorry transport related to transportation of goods in the background system.

3.3.2 PEF contribution analysis

The major processes contributing to the four impact categories are shown in Figure 3.6.

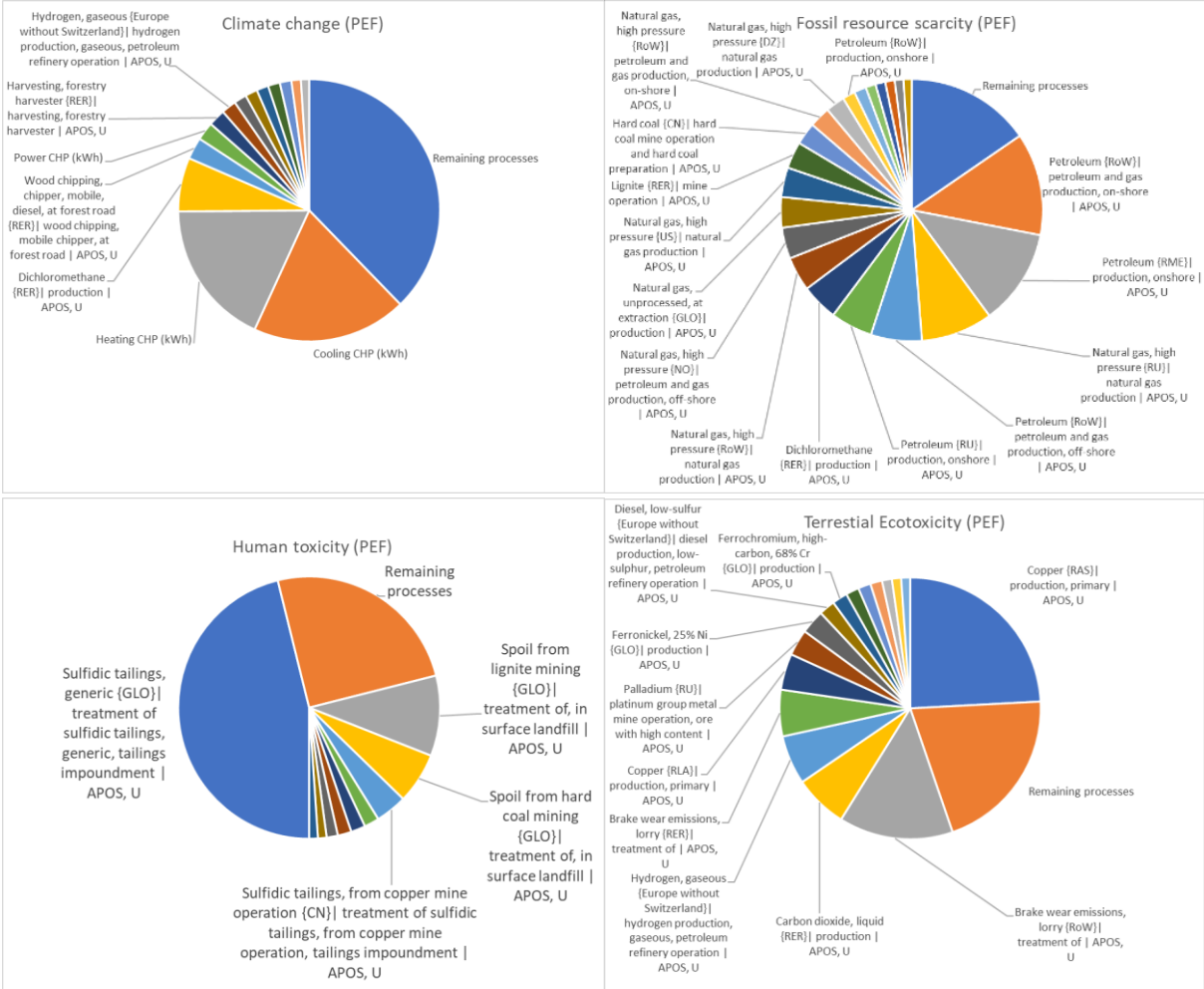


Figure 3.6: Contribution analysis of PEF

For impact on climate change of PEF, the energy production within the integrated production system is a major contributor. Cooling and heating are the two single largest contributors contributing roughly 30 % of the total impact on climate change. Power is the fifth-largest contributor to the impact of climate change. Dichloromethane related to the separation process is the third-largest contributor followed by wood chipping. In addition harvesting and hydrogen production contributed significantly to the impact on climate change. The most energy-consuming foreground process was the production of

HMF from cellulose followed by the production of ethylene glycol from ethanol. This is due to the low solvent/cellulose ratio in HMF resulting in high energy demand and high temperature requirements in ethylene glycol production.

For fossil resource scarcity the impacts are divided for various contributing processes. Most of these are related to petroleum production and natural gas production related to the production of the raw materials of the system but also dichloromethane production related to the separation process and lignite mine operation related to electricity production for the production of raw materials in the background have a significant contribution to the impacts on fossil resource scarcity.

For human toxicity, activities related to mining are contributing to most of the impacts. General sulfidic tailings and sulfidic tailings from copper mining contributed to about half of the total impact, followed by spoil treatment from lignite and hard coal mining operations. These operations are mostly related to the production of fossil fuels used in the background for energy production for raw materials of the system and mining for metallic compounds for the metal catalysts used in the production system.

For terrestrial ecotoxicity, the main contributor is a background process of copper production contributing to almost 25 % of the total impact. Copper production is related to the production of the catalyst used in the production system. It is followed by two different brake wear processes from lorry transport related to the production of raw materials used in the production system and the production of carbon dioxide and hydrogen used directly in the production system, more specifically hydrogen in the separation process and propylene production, and carbon dioxide in FDCA production from furfural. Four different processes related to metallic compound production are also presented as well as diesel production. The palladium production represented as one of the main contributors to the impacts on terrestrial ecotoxicity is related to the modelling choices of metallic catalysts. As no exact processes for the metal catalyst of this study were not found, a generic metal catalyst background process from Ecoinvent 3.6 was applied and the generic catalyst process is based on palladium catalyst.

3.4 Remarks and points of improvement

Industrial symbiosis provides a notable possibility for reducing the environmental impacts of the integrated production system. Producing some of the chemicals necessary for reaction within the system could reduce environmental impacts. Hydrogen in the modelling is based on purchased hydrogen from the European market. An alternative way to cover the demand would be to use the excess power production for the electrolysis of water to produce hydrogen. At the same time, oxygen demand could be covered. Hydrogen is a significant contributor to the impacts on climate change in the case of bio-PP and terrestrial ecotoxicity in the case of both products, lower impact hydrogen would reduce notably the impacts on these categories.

In addition, the solvent in the main separation process, methanol, could be produced from cellulose feedstock (Wang et al., 2022). Although that would reduce the conversion of wood feedstock into the target products, the methanol based on renewable feedstock could reduce the environmental impacts. The utilization of the industrial symbiosis would reduce the dependence of the refinery on external chemical suppliers, and reduce the risks in supply-chain and price fluctuation. Also, lower voltage connection lines to the power grid would be needed if the electricity would be used within the plant reducing

investment demand on power infrastructure and reducing the limitations on refinery location.

3.5 Limitations

As with all research, also this study has several limitations. Most of the limitations are related to the explorative nature of the study, modelling choices and scope of the study. These limitations are discussed more in detail in this subchapter.

First, the study is explorative by nature with several assumptions creating uncertainty. Most of the data were collected from literature based on laboratory-scale experiments or more detailed process designs without existing commercial applications. Some of the processes included in the integrated production system were based on cutting-edge technology which limits the usage of the results to different production pathways of the same plastics. In addition, several assumptions were necessary, and the results are dependent on them. On the other hand, the results do give an idea of how promising the production of the two bioplastics, bio-PP and PEF is, and on which aspects the research should focus on when developing the production pathways.

Second, although partial heat integration on some production steps was considered, no systemwide heat integration was included, there is a potential for reduction in overall energy requirements. Therefore, environmental impacts modelled may be higher than from actual commercial applications. On the other hand, for some of the production steps it was necessary to exclude some mass- and energy flows due to data availability issues, which is prone to decrease the modelled environmental aspects. Therefore there is a relatively high level of uncertainty in the results, and it would be necessary to model the environmental impacts of the integrated production system after a thorough process design.

Third, the geographic boundary of northern Europe limits the usability of the results in other areas. It can be expected that the results do give an idea of the range of results in other areas too, but for example, a change of feedstock might affect the results significantly. Therefore, the modelling should be performed separately for different areas with different biosphere and forest management.

Finally, in the study, no economic aspects were considered. The study focused purely on modelling environmental aspects and no insights into economic feasibility were provided. Therefore, no conclusions on the general feasibility of the production system can be given.

4 Conclusions

In this study, an integrated production system of two bioplastics, bio-PP and PEF, was compiled and the environmental impacts of these two products were modelled. The goal was to find out how large environmental impacts these products have, how the choice of energy source in energy production affects their environmental impacts and how the integrated production system performs compared to other studies of these bioplastics and their fossil alternatives.

The modelling was performed on three different scenarios based on the energy supply options choice. In the initial scenario, the energy demand was fulfilled with the combustion of wood chips, in the first alternative scenario the energy demand was fulfilled with the combustion of natural gas and in the second alternative scenario, the energy demand was fulfilled with the combustion of the coal. The initial scenario resulted in the GWP of 2,17 kg of CO₂ eq. for PEF and 0,81 kg of CO₂ eq. for bio-PP, terrestrial ecotoxicity potential of 4,04 kg of 1,4-DCB eq. for PEF and 2,22 kg of 1,4-DCB eq. for bio-PP, human toxicity potential of 2,23 kg of 1,4-DCB eq. for PEF and 3,39 kg of 1,4-DCB eq. for bio-PP and 2,22 kg of 1,4-DCB eq. for bio-PP and fossil resource scarcity potential of 0,59 kg of oil eq. for PEF and 0,53 kg of oil eq. for bio-PP.

The choice of the energy source for energy production had a remarkable effect on environmental impacts. The initial scenario in which wood chips were used as an additional energy source had the lowest environmental impacts on most of the impact categories, and the scenario based on coal as an additional energy source had the highest impacts, especially on climate change. In the scenario based on coal, bio-PP had four times higher impacts on climate change and PEF eight times higher impacts on climate change than in the scenario based on wood chips. The impacts on climate change in the scenario based on natural gas were in between the two other scenarios for both plastic products. With terrestrial ecotoxicity, the initial scenario performed slightly worse than the alternative scenarios although the differences were not large. With human toxicity scenario based on natural gas resulted in slightly lower impacts than the initial scenario while the scenario based on coal had significantly higher impacts. With fossil resource scarcity the differences between the initial scenario and the alternative scenarios were naturally high, as the alternative scenarios were based on fossil energy sources and therefore resulted in high impacts on the category.

The difference between the scenarios is in line with the general understanding of emissions related to the combustion of different energy sources. Coal in general has large GHG emissions compared to for example natural gas. The combustion of wood chips does create a significant amount of GHG emissions, but as they have a biogenic origin, they are not counted in the carbon footprint. The exclusion of the biogenic carbon is the main reason for the good performance of the initial scenario compared to the scenario based on coal and the scenario based on natural gas. All in all, it can be concluded that out of the three scenarios modelled, the biorefinery based on wood chips as an additional energy source results in the lowest overall environmental impacts although the impacts on some categories were slightly higher than the impacts from other scenarios.

When the impacts on climate change potential from this LCA study were compared to literature it was seen that the products performed well in general. It must be remembered that several assumptions do create uncertainty and the results might be too

optimistic. On the other hand, no systemwide heat integration was performed and as a large part of the impacts on climate change was related to energy production, the impacts are likely to reduce in the proper process design phase. When considering bio-PP, the impacts were higher than in the bio reference but significantly lower than in the fossil baseline scenario. When considering PEF, the product of the integrated production system resulted in close to the same impacts as the fossil baseline and 50 % lower impacts than the bio reference. On the other hand, the comparison to the bio reference is overly-optimistic as the bio reference was based on an LCA study on a different scope, but it is expected that the PEF from the integrated production system outperforms the other bio-reference even with the same scope.

Out of the different production steps to produce PEF the one with the most significant impact on GHG emissions was the production of HMF, which is in line with the literature. The low cellulose/solvent ratio and high temperature differences between unit processes create a large heating and cooling demand. In fact, the production of HMF contributes to over two-thirds of the total energy demand of the integrated biorefinery. Another process with a significant contribution to GHG emissions was the production of ethylene glycol from ethanol. As with HMF production, large temperature differences combined with high mass flows result in high heating and cooling demand. The high energy demand for HMF production makes to question whether the production route can even be considered promising or if new production pathways should be developed.

From the contribution analysis, it is seen that energy supply is the major contributor to climate change impacts in all scenarios and with both plastic products. Only in the initial scenario in which wood chips are used as an additional energy source, the production of chemicals exceeds the contribution of energy production. When natural gas or coal is used as an additional energy source, the other contributors than energy production remain minor. As the choice of energy source affects significantly the environmental impacts of both bioplastics, and there is an ongoing discussion in the European Union on whether bioenergy will be excluded from the list of renewable energy, it can be concluded that the bio-PP and PEF from the integrated production system perform well in terms of environmental impacts compared to their alternatives as long as the combustion of wood chips is considered renewable energy and biogenic carbon is excluded from the GHG emissions.

The results of this explorative study provide valuable information for future research. The results highlight the importance of the renewable energy status of wood combustion for highly efficient biorefineries meanwhile pointing out the most significant factors in the impacts of bio-PP and PEF from an integrated production system such as the usage of metal catalysts. In addition, the results generate another set of reference values for comparison in other studies.

4.1 Recommendations for future work

To decrease the uncertainty of the results and increase the overall presentation of possible commercial applications, a systemwide process design and heat integration should be applied. In addition, the large number of side-streams in this study counted as wastewater provides the potential to create new products or raw materials for energy production. By studying the potential of these raw materials, it could be possible to reduce the overall environmental impacts of the system. Also, the usage of green hydrogen could create a potential to reduce environmental impacts. To avoid overly

positive results, future studies involving the impact of biogenic carbon emissions until the full regrowth of forest should be considered.

To improve the environmental performance of the integrated production system, the focus should be targeted on the most energy-intensive processes of the system. Other pathways to produce HMF should be explored to reduce the energy demand or pathways based on other intermediate chemicals to produce FDCA should be developed.

The main addition of this study for industrial symbiosis is related to the production of furfural from methyl-xylosides. Research should focus on improving the yield of the methyl-xylosides to furfural -conversion as well as modelling the separation of furfural from the other products and energy requirements of the process step.

For policymakers, it can be stated that biorefining based on renewable energy does create a large potential for replacing fossil-based chemicals. The energy production for biorefining remains a crucial factor in environmental impacts and without renewable energy, the environmental impacts could be even higher than the impacts related to conventional fossil-based products. As the forest is a main feedstock for the biorefinery, sustainable forest management plays a crucial role in environmental impacts.

References

- Aurora Energy Research Ltd. (2022). *Impact of Russia-Ukraine war on European gas markets*. https://globalinghub.com/wp-content/uploads/2022/03/EuropeanGas_RussiaUkraine.pdf
- Avantium. (2021, December 9). *Avantium takes a positive Final Investment Decision on the construction of its FDCA Flagship Plant*. <https://www.avantium.com/investor-relations/avantium-takes-a-positive-final-investment-decision-on-the-construction-of-its-fdca-flagship-plant/>
- Baldoni, E., Reumerman, P., Parisi, C., Platt, R., Gonzalez Hermoso, H., Vikla, K., Vos, J., & M'Barek, R. (2021). *Chemical and material driven biorefineries in the EU and beyond: Database and dashboard visualisation*. Publications Office. <https://data.europa.eu/doi/10.2760/8932>
- Cameo Chemicals. (1999a). *Diethylene Glycol*. <https://cameochemicals.noaa.gov/chris/EGL.pdf>
- Cameo Chemicals. (1999b). *Ethylene Glycol*. <https://cameochemicals.noaa.gov/chris/EGL.pdf>
- Cameo Chemicals. (1999c). *Triethylene Glycol*. <https://cameochemicals.noaa.gov/chris/EGL.pdf>
- Chen, W.-S., Lin, C.-W., Chang, F.-C., Lee, W.-J., & Wu, J.-L. (2012). Utilization of spent activated carbon to enhance the combustion efficiency of organic sludge derived fuel. *Bioresource Technology*, 113, 73–77. <https://doi.org/10.1016/j.biortech.2011.12.026>
- Cherubini, F., & Strømman, A. H. (2011). Chemicals from lignocellulosic biomass: Opportunities, perspectives, and potential of biorefinery systems. *Biofuels, Bioproducts and Biorefining*, 5(5), 548–561. <https://doi.org/10.1002/bbb.297>
- Cherubini, F., Strømman, A. H., & Ulgiati, S. (2011). Influence of allocation methods on the environmental performance of biorefinery products—A case study. *Resources*,

- Conservation and Recycling*, 55(11), 1070–1077.
<https://doi.org/10.1016/j.resconrec.2011.06.001>
- Cox, J. D. (2009). The heats of combustion of phenol and the three cresols. *National Chemical Laboratory, D.S.I.R., Teddington, Middlesex, U.K.*, 4.
- CPME. (2017). *An Eco-profile and Environmental Product Declaration of the PET Manufacturers in Europe—Polyethylene Terephthalate (PET) (Bottle Grade)*.
<https://plasticseurope.org/sustainability/circularity/life-cycle-thinking/eco-profiles-set/>
- Dubbink, G., Geverink, T., Haar, B., Koets, H., Kumar, A., van den Berg, H., van der Ham, A., & Lange, J.-P. (2021). Furfural to FDCA: systematic process design and techno-economic evaluation. *Biofuels, Bioproducts and Biorefining*.
<https://doi.org/10.1002/bbb.2204>
- Eerhart, A. J. J. E., Faaij, A. P. C., & Patel, M. K. (2012). Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy & Environmental Science*, 5(4), 6407. <https://doi.org/10.1039/c2ee02480b>
- Engineering ToolBox. (2008). *Fossil and Alternative Fuels—Energy Content*.
https://www.engineeringtoolbox.com/fossil-fuels-energy-content-d_1298.html
- Engineering ToolBox. (2010). *Water—Heat of Vaporization vs. Temperature*.
https://www.engineeringtoolbox.com/water-properties-d_1573.html
- Essom CO. (2022). *Heating values of hydrogen and fuels*.
- European Bioplastics e.V. (2021). Bioplastics market data. *European Bioplastics e.V.*
<https://www.european-bioplastics.org/market/>
- European Commission. (2018). *Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions—A European Strategy for Plastics in a Circular Economy*.
<https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1516265440535&uri=COM:2018:28:FIN>
- Falcones, I., Golden, S., & Kowalchuk, M. (2019). *Green Glycol: A Novel 2-Step Process*. 684.

- Farzad, S., Mandegari, M., & Görgens, J. F. (2020). 10—Life cycle assessment of lignocellulosic biorefineries. In E. X. Ferreira Filho, L. R. de Souza Moreira, E. de A. Ximenes, & C. S. Farinas (Eds.), *Recent Advances in Bioconversion of Lignocellulose to Biofuels and Value-Added Chemicals within the Biorefinery Concept* (pp. 259–277). Elsevier. <https://doi.org/10.1016/B978-0-12-818223-9.00010-2>
- Fernández-Rodríguez, J., Erdocia, X., Hernández-Ramos, F., González Alriols, M., & Labidi, J. (2019). *Separation of Functional Molecules in Food by Membrane Technology*. Academic Press. <https://doi.org/10.1016/B978-0-12-815056-6.00007-3>
- Ganguly, P., Sarkhel, R., & Das, P. (2021). 2 - The second- and third-generation biofuel technologies: Comparative perspectives. In S. Dutta & C. Mustansar Hussain (Eds.), *Sustainable Fuel Technologies Handbook* (pp. 29–50). Academic Press. <https://doi.org/10.1016/B978-0-12-822989-7.00002-0>
- Government of Canada. (2018, February 27). 3. *Greenhouse Gas Emissions from the Plastics Processing Industry*. Natural Resources Canada. <https://www.nrcan.gc.ca/energy/efficiency/industry/technical-info/benchmarking/plastics/5211>
- IEA. (2013). *Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes*. 60.
- Iglesias, J., Melero, J. A., Morales, G., Paniagua, M., & Hernández, B. (2016). Dehydration of Xylose to Furfural in Alcohol Media in the Presence of Solid Acid Catalysts. *ChemCatChem*, 8(12), 2089–2099. <https://doi.org/10.1002/cctc.201600292>
- International Organization for Standardization. (2006). *ISO 14040:2006*. <https://www.iso.org/obp/ui/#iso:std:iso:14040:ed-2:v1:en>
- Isikgor, F. H., & Becer, C. R. (2015). Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polymer Chemistry*, 6(25), 4497–4559. <https://doi.org/10.1039/C5PY00263J>

- Kim, D., Park, K. Y., & Yoshikawa, K. (2017). Conversion of Municipal Solid Wastes into Biochar through Hydrothermal Carbonization. In W.-J. Huang (Ed.), *Engineering Applications of Biochar*. InTech. <https://doi.org/10.5772/intechopen.68221>
- Kim, H., Lee, S., & Won, W. (2020). Economical process for the co-production of renewable polymers and value-added chemicals from lignocellulosic biomass. *Journal of Cleaner Production*, 276, 124237. <https://doi.org/10.1016/j.jclepro.2020.124237>
- Kuusela, K., Uusitalo, V., Ahola, J., & Levänen, J. (2021). The transformation of plastics production from net positive greenhouse gas emissions to net negative: An environmental sustainability assessment of CO₂-based polypropylene. *Journal of CO₂ Utilization*, 52, 101672. <https://doi.org/10.1016/j.jcou.2021.101672>
- Liao, Y., Koelewijn, S.-F., Van den Bossche, G., Van Aelst, J., Van den Bosch, S., Renders, T., Navare, K., Nicolai, T., Van Aelst, K., Maesen, M., Matsushima, H., Thevelein, J. M., Van Acker, K., Lagrain, B., Verboekend, D., & Sels, B. F. (2020). A sustainable wood biorefinery for low-carbon footprint chemicals production. *Science*, 367(6484), 1385–1390. <https://doi.org/10.1126/science.aau1567>
- Lippits, M. J., & Nieuwenhuys, B. E. (2010). Direct Conversion of Ethanol into Ethylene Oxide on Gold Based Catalysts. *Journal of Catalysis*. <https://doi.org/10.1016/j.jcat.2010.06.011>
- Liquisearch. (2022). *Heat of Combustion—Lower Heating Value For Some Organic Compounds (at 15.4°C)*. https://www.liquisearch.com/heat_of_combustion/lower_heating_value_for_some_organic_compounds_at_154%C2%B0c
- Martikainen, E. (2022). *Novel bioplastics from lignocellulosic biorefinery systems—Industrial Ecology project*.
- Morales, M., Arvesen, A., & Cherubini, F. (2021). Integrated process simulation for bioethanol production: Effects of varying lignocellulosic feedstocks on technical performance. *Bioresource Technology*, 328, 124833. <https://doi.org/10.1016/j.biortech.2021.124833>

Motagamwala, A. H., Won, W., Sener, C., Alonso, D. M., Maravelias, C. T., & Dumesic, J. A. (2018). Toward biomass-derived renewable plastics: Production of 2,5-furandicarboxylic acid from fructose. *Science Advances*, 4(1), eaap9722. <https://doi.org/10.1126/sciadv.aap9722>

Nilges, P., & Schröder, U. (2013). Electrochemistry for biofuel generation: Production of furans by electrocatalytic hydrogenation of furfurals. *Energy & Environmental Science*, 6(10), 2925–2931. <https://doi.org/10.1039/C3EE41857J>

nova-Institute. (2022). *PEF bottles – a sustainable packaging material ISO Certified LCA of Avantium’s PEF products*.

Our World in Data. (2016). *Primary plastic production by polymer type*. <https://ourworldindata.org/grapher/plastic-production-polymer>

Pacific Northwest National Laboratory. (2022). *Lower and Higher Heating Values of Fuels*. <https://h2tools.org/hyarc/calculator-tools/lower-and-higher-heating-values-fuels>

Papong, S., Malakul, P., Trungkavashirakun, R., Wenunun, P., Chom-in, T., Nithitanakul, M., & Sarobol, E. (2014). Comparative assessment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective. *Journal of Cleaner Production*, 65, 539–550. <https://doi.org/10.1016/j.jclepro.2013.09.030>

Parshley, L. (2022, May 17). Europe Rethinks Its Reliance on Burning Wood for Electricity. *The New York Times*. <https://www.nytimes.com/2022/05/17/climate/eu-burning-wood-electricity.html>

PlasticEurope. (2014). *Eco-profiles and Environmental Product Declarations of the European Plastics Manufacturers—Polypropylene (PP)*. <https://plasticseurope.org/sustainability/circularity/life-cycle-thinking/eco-profiles-set/>

PubChem. (2022). *Methyl acetate—Hazardous Substances Data Bank (HSDB): 95*. <https://pubchem.ncbi.nlm.nih.gov/source/hsdb/95#section=Critical-Temperature-%26-Pressure>

PubChem. (2022). *Water*. <https://pubchem.ncbi.nlm.nih.gov/compound/962>

- Serrano-Ruiz, J. C., Luque, R., & Sepúlveda-Escribano, A. (2011). Transformations of biomass-derived platform molecules: From high added-value chemicals to fuels via aqueous-phase processing. *Chemical Society Reviews*, 40(11), 5266. <https://doi.org/10.1039/c1cs15131b>
- Spekreijse, J., Lammens, T., Parisi, C., Ronzon, T., & Vis, M. (2019). *Insights into the European market for bio-based chemicals*. 162.
- Spierling, S., Knüpfper, E., Behnsen, H., Mudersbach, M., Krieg, H., Springer, S., Albrecht, S., Herrmann, C., & Endres, H.-J. (2018). Bio-based plastics—A review of environmental, social and economic impact assessments. *Journal of Cleaner Production*, 185, 476–491. <https://doi.org/10.1016/j.jclepro.2018.03.014>
- University of Calgary. (2022, September 27). *Hydrocarbon combustion—Energy Education*. https://energyeducation.ca/encyclopedia/Hydrocarbon_combustion
- UPM Biochemicals. (2022). *Building a state-of-the-art biorefinery in Leuna*. UPM Biochemicals | UPM Biochemicals. <https://www.upmbiochemicals.com/>
- US Department of Energy. (2017). *Combined Heat and Power Technology Fact Sheet Series—Absorption Chillers for CHP Systems*. <https://www.energy.gov/eere/amo/downloads/absorption-chillers-chp-systems-doe-chp-technology-fact-sheet-series-fact-sheet>
- US Department of Energy. (2017). *Combined Heat and Power Technology Fact Sheet Series—Overview of CHP Technologies*. 4.
- U.S. Environmental Protection Agency. (2022). *Emission Factors for Greenhouse Gas Inventories*. https://www.epa.gov/system/files/documents/2022-04/ghg_emission_factors_hub.pdf
- van den Oever, M., Molenveld, K., van der Zee, M., & Bos, H. (2017). Bio-based and biodegradable plastics – Facts and Figures. *Wageningen Food & Biobased Research*. <http://dx.doi.org/10.18174/408350>
- Wang, Z., Xia, S., Wang, C., Cui, C., Kang, S., Zheng, A., Zeng, K., & Zhao, Z. (2022). Sustainable production of methanol from one-pot catalytic conversion of cellulose

over non-precious copper-based catalysts. *Fuel*, 322, 123882.

<https://doi.org/10.1016/j.fuel.2022.123882>

Appendices

Appendix 1: Processes from mass balance to Simapro

Mass-balance - Simapro/Ecoinvent 3.6 - Processes		
PRODUCTS FROM BACKGROUND		
Mass-balance	Simapro/Ecoinvent 3.6	Unit
CO2 (kg)	Carbon dioxide, liquid {RER} production APOS, U	kg
DCM (CH2CL2) (kg)	Dichloromethane {RER} production APOS, U	kg
Ethyl acetate	Ethyl acetate {RER} production APOS, U	kg
n-Hexane (kg)	Hexane {GLO} market for APOS, U	kg
H2 (kg)	Hydrogen, gaseous {Europe without Switzerland} hydrogen production, gaseous, petroleum refinery operation APOS, U	kg
Methanol (CH3OH) (kg)	Methanol {GLO} production APOS, U	kg
N2 (kg)	Nitrogen, liquid {RER} air separation, cryogenic APOS, U	kg
O2 (kg)	Oxygen, liquid {RER} air separation, cryogenic APOS, U	kg
H2SO4 makeup (kg)	Sulfuric acid {RER} production APOS, U	kg
THF (kg)	Tetrahydrofuran {RER} production APOS, U	kg
H2O (kg)	Water, deionised {Europe without Switzerland} water production, deionised APOS, U	kg
Wood chips (Birch) (kg)	Wood chips, wet, measured as dry mass {SE} hardwood forestry, birch, sustainable forest management APOS, U	kg
Cs2CO3 makeup (kg)	Chemical, inorganic {GLO} production APOS, U	kg
Catalyst Ru (kg)	Metal catalyst for catalytic converter {GLO} palladium to generic market for metal catalyst for catalytic converter APOS, U	kg
Catalyst Ni (kg)	Metal catalyst for catalytic converter {GLO} palladium to generic market for metal catalyst for catalytic converter APOS, U	kg
Enzyme	Enzymes {RER} enzymes production APOS, U	kg
NaOH	Sodium hydroxide, without water, in 50% solution state {RoW} chlor-alkali electrolysis, mercury cell APOS, U	kg
NaSO4	Sodium sulfate, anhydrite {RER} sodium sulfate production, from natural sources APOS, U	kg
NH4Cl	Ammonium chloride {GLO} production APOS, U	kg
Catalyst Pt/C (kg)	Metal catalyst for catalytic converter {GLO} palladium to generic market for metal catalyst for catalytic converter APOS, U	kg
Catalyst Zeolite (kg)	Zeolite, powder {RER} production APOS, U	kg
In addition in Scenario Natural gas:		
Natural gas (kg)	Natural gas, high pressure {NO} petroleum and gas production, off-shore APOS, U	kg
In addition in Scenario Coal:		
Coal (kg)	Hard coal {Europe, without Russia and Turkey} hard coal mine operation and hard coal preparation APOS, U	kg
WASTE TO THE BACKGROUND		
Wastewater (m3)	Wastewater from vegetable oil refinery {GLO} treatment of APOS, U	m3
PRODUCTS FROM FOREGROUND		
Mass-balance	Simapro	Unit
Activated carbon (kg)	Activated carbon	kg
Cellulose (kg)	Cellulose	kg
Cooling (kWh)	Cooling CHP (kWh)	kWh
Ethylene glycol (kg)	Ethylene glycol	kg
FDCA (furfural) (kg)	FDCA (furfural)	kg
FDCA (HMF) (kg)	FDCA (HMF)	kg
Furfural (kg)	Furfural	kg
Furfural-FDCA byproduct	Furfural-FDCA byproduct	kg
Gypsum (kg)	Gypsum	kg
Heating (kWh)	Heating CHP (kWh)	kWh
HMF (kg)	HMF	kg
Lignin monomers (kg)	Lignin monomers	kg
Off gas (kg)	Off gas	kg
PEF (kg)	PEF	kg
Phenol (kg)	Phenol	kg
Phenolic oligomers (kg)	Phenolic oligomers	kg
Polypropylene (kg)	Polypropylene	kg
Power (kWh)	Power CHP (kWh)	kWh
Propylene (kg)	Propylene	kg
Sugars from PP (kg)	Sugars from PP	kg
PEG (kg)	PEG	kg

Appendix 2: Mass balance

MASS BALANCE - INTEGRATED PRODUCTION OF BIO-PP AND PEF FROM BIRCH CHIPS																								
Production phase:	Separation process		Propylene production		PP polymerization		Cellulose to Ethanol		EG from Ethanol		Cellulose to HMF		HMF to FDCA		Methyl Xylose to Furfural		Furfural to FDCA		PEF production		CHP	Balance		
Source of data:	Liao et al. 2020		Liao et al. 2020		Kuusela et al. 2021		Liao et al. 2020		Falcones et al. 2019		Kim et al. 2020		Motagamwala et al. 2018		Iglesias et al. 2016		Dubbink et al. 2021		Eerhart et al. 2012		Liao et al. 2020	+ consumption		
Process conditions:	T: 298 K						T: 323 K, 298 K.		T: 513 K		T: 483 K P: 68 atm		T: 383 K P: 40 atm		T: 423 K				T: 303 K			- production		
Intermediate products	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow				
Lignin monomers (kg)		107,00	107,00																				0,00	
Cellulose (kg)		653,02					211,84				441,18												0,00	
Sugars from PP (kg)		190,52													190,52								0,00	
HMF (kg)											124,72	124,72											0,00	
FDCA (Furfural) (kg)								56,77	56,77									10,76	10,76				0,00	
Ethanol (kg)																							0,00	
FDCA (HMF) (kg)													139,97							139,97			0,00	
Ethylene glycol (kg)										59,95										59,95			0,00	
Furfural (kg)														7,90	7,90								0,00	
Propylene (kg)				19,13	19,13																		0,00	
Off gas (kg)				33,72																		33,72	0,00	
H2 gas bypass (kg)		88,52	10,36																			78,15	0,00	
Waste sugars (kg)																							0,00	
Power (kWh)	6,42		20,74		6,62		15,51		43,58		247,10		28,71							66,84		287,22	148,30	
Cooling (kWh)	191,82		150,41						729,61		2368,16		262,00					69,15				332,34	3438,80	
Heating (kWh)	141,59		164,80		4,38		177,51		469,33		2198,48		27,516		9,26		71,64			307,83		226,21	3346,14	
Products & co-products	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow				
Oligomers (kg)		64,12																					-64,12	
Phenol (kg)				41,73																			-41,73	
Polypropylene (kg)						18,76																	-18,76	
Furfural-FDCA byprod (kg)																		2,45					-2,45	
Activated carbon (kg)												88,60											-88,60	
PEG											8,56													
Gypsum (kg)												24,36											-24,36	
PEF (kg)																				175,90			-175,90	
Feedstock	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow				
Wood chips (Birch) (kg)	1000,00																						1000,00	
H2 (kg)	10,14		7,58											0,04									17,69	
H2O (kg)	26,34	18,58	14,31		67,52				208,30					53,57				146,96					498,42	
n-Hexane (kg)	1,01																						1,01	
Methanol (CH3OH) (kg)	61,14																						61,14	
DCM (CH2CL2) (kg)	12,60																						12,60	
N2 (kg)	0,63																						0,63	
Catalyst Ru (kg)	0,00923																						0,00923	
Catalyst Ni (kg)			0,00114																				0,00114	
Catalyst Zeolite (kg)			0,00138																				0,00138	
O2 (kg)								19,83					43,07					1,22					64,12	
CO2 (kg)								6,41										6,83					13,24	
H2SO4 makeup (kg)																		0,0006					0,00058	
Cs2CO3 makeup (kg)																		0,0006					0,00	
Ethyl acetate (kg)																		0,01					0,01	
THF (kg)											7,98												7,98	
Enzyme							1,51																	
NaOH							1,80																	
NaSO4							4,72																	
NH4Cl							1,83																	
Catalyst Pt/C (kg)													0,00416										0,00416	
Emissions & waste	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow				
Wastewater (m3)				0,05		0,07				0,16				0,22										-1,16
Off gas N2 (kg)		0,63																					-0,63	
CO2 (kg)										60,86													203,22	-264,08
H2O(steam)																							188,76	-188,76

Appendix 3: Calculation for allocation of EG production

The energy content of monoethylene glycol side product, polyethylene glycol, had to be calculated and the calculation is described in this Appendix. The polyethylene glycol consists of a mix of MEG, DEG and TEG and a lower heating value had to be calculated for all of them had to be calculated separately and then an average heating value was calculated based on mass fractions. In the calculations, first was calculated how much many grams of water are formed per gram of products. Then the amount of water was multiplied by the water's latent heat of vaporization and the product was subtracted from the higher heating values from the literature.

Values:

Water molar mass: 18.02 g/mol (PubChem, 2022)

Water heat of vaporization: 2256 kJ/kg (Engineering ToolBox, 2010)

MEG molar mass: 62.07 g/mol (Cameo Chemicals, 1999b)

MEG higher heating value: 16890 kJ/kg (Cameo Chemicals, 1999b)

DEG molar mass: 106.12 g/mol (Cameo Chemicals, 1999a)

DEG higher heating value: 22370 kJ/kg (Cameo Chemicals, 1999a)

TEG molar mass: 150.17 g/mol (Cameo Chemicals, 1999c)

TEG higher heating value: 23700 kJ/kg (Cameo Chemicals, 1999c)

Stoichiometric reaction formula: $C_aH_bO_c \rightarrow a \cdot CO_2$ and $1/2b \cdot H_2O$ (University of Calgary, 2022)

Calculation of LHV of MEG:

Reaction formula (oxygen not included): $HOCH_2CH_2OH \rightarrow 2 CO_2 + 3 H_2O$

62.07 g of MEG $\rightarrow 3 \cdot 18.02$ g of H₂O

54.06 g / 62.07 g H₂O/MEG = 0,870952151

LHV = HHV - (Heat of Vaporization (water) * 0.870952151) = 16890 kJ/kg - 1965 kJ/kg
= 14925,13 kJ / kg

Calculation of LHV of DEG:

Reaction formula (oxygen not included): $(HOCH_2CH_2)_2O \rightarrow 4 CO_2 + 5 H_2O$

106.12 g of DEG $\rightarrow 5 \cdot 18.02$ g of H₂O

90.1 g of H₂O / 106.12 g of DEG $\rightarrow 0,849038824$

LHV = HHV - (Heat of Vaporization (water) * 0.849038824) = 22370 kJ/kg - 1915 kJ/kg
= 20454,57 kJ / kg

Calculation of LHV of TEG:

Reaction formula (oxygen not included): $C_6H_{14}O_4 \rightarrow 6 CO_2 + 7 H_2O$

150.17 g of TEG $\rightarrow 7 \cdot 18.02$ of H₂O

126.14 g of H₂O / 150.17 g of TEG $\rightarrow 0,839981354$

LHV = HHV - (Heat of Vaporization (water) * 0.839981354) = 23700 kJ/kg - 1895 kJ/kg
= 21805,00 kJ / kg

Composition of the PEG	wt-%	Heating value kJ / kg of total product
MEG	22,50 %	3358,15
DEG	57,00 %	11659,10
TEG	20,50 %	4470,03
sum		19487,28

Appendix 4: LCIA results based on the three scenarios

Impact category	PEF based on wood chips	PEF based on natural gas	Nat. gas / wood	PEF based on coal	Coal / wood
Global warming kg CO2 eq	2,17E+00	8,95E+00	412 %	1,73E+01	795 %
Stratospheric ozone depletion kg CFC11 eq	8,03E-06	3,80E-06	47 %	6,12E-06	76 %
Ionizing radiation kBq Co-60 eq	1,69E-01	1,66E-01	99 %	2,14E-01	127 %
Ozone formation, Human health kg NOx eq	4,33E-03	4,41E-03	102 %	4,13E-03	95 %
Fine particulate matter formation kg PM2.5 eq	4,19E-03	3,84E-03	92 %	4,23E-03	101 %
Ozone formation, Terrestrial ecosystems kg NOx eq	4,51E-03	4,56E-03	101 %	4,26E-03	94 %
Terrestrial acidification kg SO2 eq	1,28E-02	1,16E-02	90 %	1,30E-02	101 %
Freshwater eutrophication kg P eq	1,96E-03	1,92E-03	98 %	3,62E-03	185 %
Marine eutrophication kg N eq	2,35E-04	2,30E-04	98 %	3,40E-04	144 %
Terrestrial ecotoxicity kg 1,4-DCB	4,04E+00	3,55E+00	88 %	3,77E+00	93 %
Freshwater ecotoxicity kg 1,4-DCB	7,94E-02	7,52E-02	95 %	1,56E-01	196 %
Marine ecotoxicity kg 1,4-DCB	1,01E-01	1,14E-01	113 %	2,07E-01	204 %
Human carcinogenic toxicity kg 1,4-DCB	5,07E-02	5,31E-02	105 %	2,16E-01	426 %
Human non-carcinogenic toxicity kg 1,4-DCB	2,18E+00	2,02E+00	93 %	5,51E+00	253 %
Land use m2a crop eq	7,15E+00	3,76E+00	53 %	4,24E+00	59 %
Mineral resource scarcity kg Cu eq	1,31E-02	1,19E-02	91 %	1,33E-02	101 %
Fossil resource scarcity kg oil eq	5,87E-01	3,28E+00	558 %	3,52E+00	599 %
Water consumption m3	3,71E-02	3,79E-02	102 %	4,02E-02	108 %

Impact category	PP based on wood chips	PP based on natural gas	Nat. gas / wood	PP based on coal	Coal / wood
Global warming kg CO2 eq	8,10E-01	1,93E+00	238 %	3,29E+00	407 %
Stratospheric ozone depletion kg CFC11 eq	3,13E-06	2,43E-06	78 %	2,81E-06	90 %
Ionizing radiation kBq Co-60 eq	3,10E-02	3,06E-02	99 %	3,84E-02	124 %
Ozone formation, Human health kg NOx eq	3,67E-03	3,68E-03	100 %	3,64E-03	99 %
Fine particulate matter formation kg PM2.5 eq	7,39E-03	7,33E-03	99 %	7,40E-03	100 %
Ozone formation, Terrestrial ecosystems kg NOx eq	3,80E-03	3,81E-03	100 %	3,76E-03	99 %
Terrestrial acidification kg SO2 eq	2,48E-02	2,46E-02	99 %	2,48E-02	100 %
Freshwater eutrophication kg P eq	1,18E-03	1,17E-03	99 %	1,45E-03	123 %
Marine eutrophication kg N eq	4,41E-05	4,32E-05	98 %	6,13E-05	139 %
Terrestrial ecotoxicity kg 1,4-DCB	2,22E+00	2,15E+00	96 %	2,18E+00	98 %
Freshwater ecotoxicity kg 1,4-DCB	9,44E-02	9,37E-02	99 %	1,07E-01	113 %
Marine ecotoxicity kg 1,4-DCB	1,21E-01	1,23E-01	102 %	1,38E-01	114 %
Human carcinogenic toxicity kg 1,4-DCB	3,43E-02	3,47E-02	101 %	6,14E-02	179 %
Human non-carcinogenic toxicity kg 1,4-DCB	3,36E+00	3,33E+00	99 %	3,90E+00	116 %
Land use m2a crop eq	2,81E+00	2,25E+00	80 %	2,33E+00	83 %
Mineral resource scarcity kg Cu eq	2,79E-02	2,77E-02	99 %	2,79E-02	100 %
Fossil resource scarcity kg oil eq	5,28E-01	9,72E-01	184 %	1,01E+00	191 %
Water consumption m3	6,99E-03	7,12E-03	102 %	7,50E-03	107 %

