Environmental footprints of bio-based products for the chemical industry

Emma Anna Roosje Zuiderveen

Institute for Biological and
Environmental Sciences

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In memory of Craig and Fiona

Voor mama, opdat ik je nog heel lang bij me mag houden.

Voor papa, omdat je in acht decennia de wereld hebt zien veranderen – van een modeontwerper die de opkomst van synthetische stoffen als belofte voor de ‘gewone man’ meemaakte, tot het verdriet van *fast fashion* in de wereld van vandaag.

The constant acceleration of production and exploitation is unsustainable — not only for the planet but also for the human soul.
Franco "Bifo" Berardi

The earth is the very quintessence of the human condition.
Hannah Arendt

Ik luister hoe de zee raast door de lege schelp.
Het lichaam gaat altijd verloren.
Andrea Koll

Paranimfen:
Dr. K. de Kleijne
A. C. Koll

Contents

1.

Introduction

1.1. Reducing environmental impacts of the petrochemical industry

The climate crisis requires from citizens, corporations, institutions and governments to rethink society and the global economy. To respond to global challenges, including limited resources and climate change, we need systemic change and widely supported mitigation and adaptation strategies (IPCC 2021). Such a societal transformation implies that we need new ways of producing and consuming that respect the (ecological) boundaries of our planet.

One of the industries that will most likely encounter major changes in the future is the petrochemical industry. This industry facilitates modern society across thousands of manufactured products that support our modern life-style, with petrochemical production at its core (Levi and Cullen 2018). Petrochemicals include methanol, ethylene, propylene, ammonia, benzene, toluene and xylene (IEA 2013). Production volumes are rapidly growing, and the petrochemical industry is expected to become the largest driver for oil consumption by 2050 (IEA 2018).

This chapter introduces the main topic of my thesis which is about how to reduce the environmental footprint of the chemical industry with a focus on bio-based products. The environmental impacts of the petrochemical industry, including several mitigation strategies, are introduced in the next section. Life Cycle Assessment (LCA), a method that can be used to evaluate the environmental impacts of (emerging) products, is explained in section 1.2. Section 1.3 addresses the scientific challenges in understanding the variability of environmental footprints of bio-based chemicals, while section 1.4 specifies the goal and outline of my thesis.

Environmental impact of the petrochemical industry

The petrochemical industry is responsible for about 4% of global anthropogenic annual greenhouse gas (GHG) emissions, even not accounting for upstream and downstream processes in the supply chain (Bauer et al. 2022). It is the largest industrial energy consumer, accounting for 14% of global oil consumption and 9% of global natural gas consumption (Meng et al. 2023), yet ranks third among industry subsectors in terms of direct CO_2 emissions. This difference is explained by the fact that 58% of the sector's energy input is not combusted but consumed as feedstock becoming embedded in the industry's products (IEA 2018). To mitigate the petrochemical industry's environmental impact, strategies focus on reducing emissions from chemicals production. Electrification and carbon capture and storage (CCS) are considered key mitigation options (IPCC 2023). These options, however, do not eliminate the industry's reliance on fossil fuels as feedstocks (Schiffer and Manthiram 2017), nor the fossil carbon that is embedded in and ultimately released from petrochemical products. Therefore, strategies including alternative feedstock, such as biomass (Figure 1.1d), are required to improve the sustainability of chemicals (Galán-Martín et al. 2021).

At EU level, the Chemicals Strategy for Sustainability identified actions to reduce environmental impacts associated with chemicals and products on the EU market (EC 2020a), and the Bioeconomy Strategy was developed aiming at maximizing contributions from a bio-economy (European Commission 2018). The Safe and Sustainable by Design (SSbD) framework has recently been developed to set criteria for chemicals to contribute to a safer and more sustainable chemical production. One of the ambitions of the SSbD is to facilitate transitions in the chemical industry towards a safe, zero pollution and resource-efficient production and consumption, addressing impact on humans, biodiversity and ecosystems from a lifecycle perspective (Caldeira et al. 2022).

Strategy 1: Alternative feedstocks

Fossil fuels, as currently used in the chemical industry as feedstock, are carbon chains, therefore requiring alternative carbon-rich feedstocks as a replacement. Currently, the three main options are: biomass (Figure 1.1d), plastics waste (Figure 1.1b) and CO_2 (Figure 1.1c).

Biomass as feedstock

Biomass can serve as carbon feedstock. Conversion yields of biomass to chemicals are typically lower than for fossil fuels due to biomass' high oxygen content (Park et al. 2018), which affects selectivity and reactivity. However, biomass offers potential carbon neutrality since CO_2 is naturally captured during growth.

Biomass feedstock is classified into first, second, and third generation biomass. First generation biomass includes edible crops, such as corn and soybeans. While conversion of first generation biomass have been in technical uplift and has commercial applications (e.g., bioethanol from sugarcane) (Jonker et al. 2019), a significant drawback is direct competition with the food system (Lambert and Wagner 2017). Other potential issues are raised regarding biodiversity loss (Hof et al. 2018), water scarcity (D'Odorico et al. 2018) and deforestation (Plevin et al. 2010). Research indicate variation in GHG footprint of bio-based chemicals (Ögmundarson et al. 2020), especially when land use changes are taken into account (Searchinger et al. 2008).

Second generation biomass encompasses a broad range of feedstocks, from dedicated lignocellulosic (i.e., woody or grassy) energy crops such as perennial grasses or willow trees to various organic waste streams and agricultural or forestry residues. While energy crops can reduce the risk of soil erosion and improve soil carbon sequestration in some cases, they can also lead to soil depletion (Harris et al. 2015). Using waste biomass or residues typically does not cause additional land use change (LUC), which therefore in most cases prevent GHG emissions from LUC (Akkari et al. 2018; Verdade et al. 2015). Most second-generation feedstock types require additional pretreatment due to their lignin content, resulting in more energy-intensive conversion processes (Jagtap et al. 2018).

Third-generation biomass involves (micro)algae, which is still in early stage of development (Sachin Powar et al. 2022). Producing algae-based products is currently energy-intensive and costly with unknown prospects for the future (Guiton et al. 2022; Sachin Powar et al. 2022)

Plastic waste as feedstock

Chemical recycling of plastic waste, turning it as feedstock for chemical production, is one strategy to mitigate environmental consequences of plastic waste. The rapid increase in global plastic production and consumption has raised concerns about ecosystem impacts (Villarrubia-Gómez et al. 2018), human health (Rochman et al. 2013), and climate change (Zheng and Suh 2019). Annually, over 400 Mt of plastic is produced, with 77% of the cumulative 8.3 million Mt becoming waste (Jambeck and Walker-Franklin 2023).

Researchers highlight the environmental benefits of chemical recycling over incineration or landfill (van der Hulst et al. 2022; Vollmer et al. 2020), and can contribute to net-zero emissions in the chemical industry (Saygin and Gielen 2021). Stegmann et al. (2022) showed, for example, that using biomass as feedstock for plastic, which is then recycled over many use-cycles, can act as a carbon sink.

CO_2 as feedstock

CO_2 can serve as a feedstock. It can be captured from point sources (Carbon Capture) or via direct air capture (DAC) and further converted into chemicals (Figure 1.1c) (Huo et al. 2023). Synthesizing chemicals from CO_2 usually requires energy-intensive processes (de Kleijne et al. 2022), due to the thermodynamic stability of CO_2. Synthesis gas (a mixture of CO and H_2) can be a viable option for producing various chemicals, such as methanol (Liu et al., 2020). However, few CCU options are likely to reach net-zero emissions by 2050 (de Kleijne et al. 2022) and applying CCU across the chemical industry would require up to 55% of the projected global electricity production in 2030 (Kätelhön et al. 2019). CO_2 as feedstock can still considered to be part of a multifactorial solution in the petrochemical industry (Meng et al. 2023; Huo et al. 2023).

Strategy 2: Electrification of production processes

Chemical production requires large-amounts of energy, which is currently still 77% fossil-based (Ritchie and Rosado 2020). To decarbonize the chemical industry, production based on renewable electricity is thus required, which would involve new types of processes and reactors (Figure 1.1e) (Schiffer and Manthiram 2017). Alternative electrochemical processes are being developed to produce chemicals (Foulet et al. 2019; Sorunmu et al. 2020; Biddinger and Kenis 2023). Although some processes have been commercialized, such as electrolysis of hydrogen (Palou-Rivera and Grieco 2022) or adiponitrile for nylon production (Biddinger and Kenis 2023), most of the chemical production pathways are still traditional thermochemical routes (Saygin and Gielen 2021). Moreover, a large share of industry's energy requirements relates to heat (Lange 2021). An option to decarbonize steam process heating is to use renewable resources, such as wind and solar energy, and electric boilers or electric heating such as resistance of microwave heating (den Ouden et al. 2017). Although electric heating is already used in industry, none of the technologies have been applied in large-scale petrochemical processes (Oliveira et al. 2021).

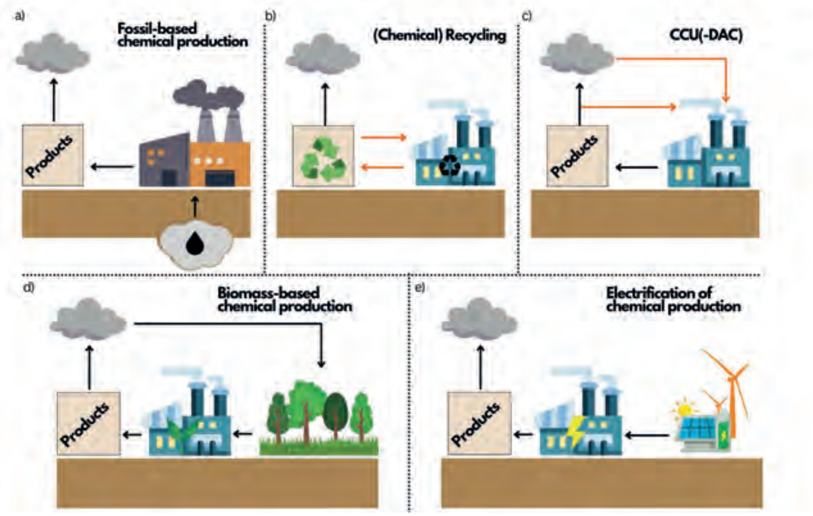

Figure 1.1: Schematic representation of petrochemical production routes via a) fossil-based production (business-as-usual), b) chemical recycling of plastics, c) Carbon Capture and Utilization (CCU) with or without Direct Air Capture (DAC), d) biomass-based production and e) production based on (renewable) electricity.

1.2. Prospective environmental assessments

Promoting the development of sustainable technologies and bio-based chemicals is not a simple undertaking (European Commission 2020a; Cucurachi et al. 2022). Together with technological development, economic feasibility and social benefits, environmental improvements are crucial and needs to be demonstrated (European Commission 2018). Life Cycle Assessment (LCA) is a method used to evaluate the environmental impacts of a product or service over its full life cycle, including the full supply chain required for its production, use and end-of-life, and analyses possible trade-offs between impacts. LCA offers the possibility of identifying environmental hotspots - especially important in early-stage processes - securing sustainability and avoiding lock-ins (Keijer et al. 2019). In the next section, the method of Life Cycle Assessment (LCA) is introduced, followed by an explanation of prospective LCA, a type of LCA that is able to assess emerging technologies.

Quantification of environmental footprints

To assess the environmental impact of a product, LCA is designed to account for the full production chain: from resource extraction to waste management (Figure 1.2). LCA allows for comparison of environmental impacts of products in terms of the same functional equivalent (Hauschild and Huijbregts, 2015). Within LCA, context is created by defining a 'goal and scope'. This involves specifying a goal and a functional unit, i.e. all inputs and outputs are referred to one unit, e.g. disposal of a PET-bottle or production of 1 kg of chemical, as well as system boundaries, and temporal and spatial scale. System boundaries can for example be formulated as 'cradle-to-gate', from resource extraction to production of, for example, plastic bottles at factory gate, or 'cradle-to-grave' which takes into account the production chain up to waste handling, e.g. plastic recycling. All relevant input and output flows during each lifecycle stage are compiled to an inventory, which are then translated into so-called 'impact scores' using an impact assessment method. There are various impact assessment methods, such as ReCiPe 2016 (Huijbregts et al. 2017) and the European Commission Environmental Footprint (EF) (Manfredi et al. 2012; EC 2021). Results can be generated at both midpoint and endpoint level. Midpoint indicators translate changes in the natural environment to specific environmental impacts, e.g. global warming, land use or eutrophication (Figure 1.2). Endpoint indicators aggregate the midpoint results into impacts on the three areas of protection: human health, natural resources and ecosystem quality, which offers a way to compare midpoint categories by their relative contributions to the endpoints but also introduces more uncertainties (Hauschild and Huijbregts 2015).

Another way to put environmental impacts into a broader context is by performing an absolute environmental sustainability assessment (AESA). AESA quantifies whether a product, individual or sector, is sustainable in absolute terms (Figure 1.2) (Bjørn et al., 2019). The term 'absolute' refers to whether the environmental impacts stay within certain limits, thresholds or targets. Examples of these include Planetary Boundaries (PBs) or Science Based Targets (SBT 2022). The PB framework has proven to be a useful concept, offering a scientific analysis of the risk of human activities in destabilizing Earth's systems on a global scale (Rockström et al. 2009; Steffen et al. 2015). It defines nine biophysical processes fundamental to Earth system functioning to not be driven away from Holocene-like conditions, thus avoiding unacceptable environmental change. Absolute assessments can guide research and policy in their support to develop more sustainable chemical production.

Environmental assessment of emerging technologies

Prospective LCA or ex-ante LCA is a type of LCA that assesses the potential future environmental impacts of technologies that are currently in development or only just emerging. Technically, there are differences between prospective and ex-ante LCA. Where the first is more focused on exploring future scenario's (Buyle et al. 2019), the latter is more technically-oriented, upscaling emerging technologies to large-scale implementation (Cucurachi et al. 2018). However, the differences are subtle and in this thesis, the term prospective is used for both prospective and ex-ante, adopting the broadest interpretation.

Prospective LCA involves additional challenges compared to LCA. Comparison across technologies can be difficult due to the technologies being at different technical development stages. Additionally, less data is available compared to commercialized technologies, and there are issues and uncertainties regarding scaling and future large-scale deployment (Thonemann et al. 2020). Scaling involves process changes but also process synergies, such as heat integration and re-use of waste streams, and future deployment can involve numerous external developments, for example, future renewable electricity mixes (Moni et al. 2020). The maturity of technology and the scale of production can impact the LCA results of emerging technologies. To define technology maturity, Technological Readiness Levels (TRL) is a qualitative scaling method to evaluate the development stage of a technology, from TRL 1 (scientific breakthrough) to TRL 9 (commercialisation) (Gavankar et al. 2015). Previous studies have provided methodological guidance for prospective LCA (Buyle et al. 2019; Moni et al. 2020; Thonemann et al. 2020) and presented a framework to systematically estimate environmental impacts of emerging technologies by scaling from the lab to industrial level (Figure 1.2) (van der Hulst et al. 2020), using scaling laws and information on process changes (Piccinno et al. 2016), industrial learning curves and information on external developments in the larger economy.

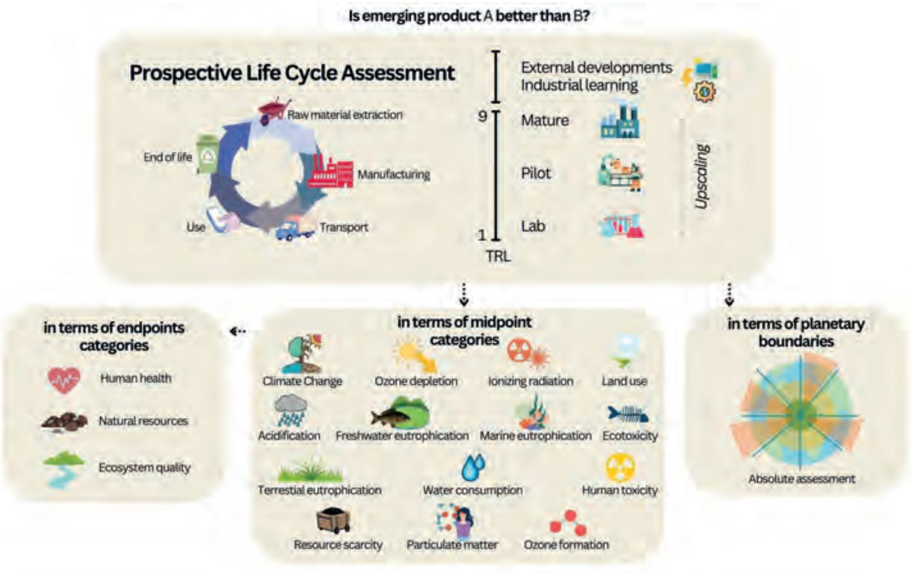

Figure 1.2: Schematic representation of the Life Cycle Assessment (LCA) method, including reference to prospective LCA and technological maturing of an emerging product in terms of the technological readiness levels (TRL) and future developments; the impacts in terms of midpoint categories (ReCiPe (Huijbregts et al. 2017)); and an absolute environmental sustainability assessment.

1.3. Scientific challenges

Moving from a fossil-based to a bio-based economy may contribute to climate change mitigation by reducing overall GHG emissions (European Commission 2017; Luhas et al. 2021; El-Chichakli et al. 2016; Maina et al. 2017; Ingrao et al. 2018). However, to assess these potential GHG benefits, as well as possible burden shifting to other environmental impacts, key aspects need to be critically evaluated, including the sustainable use of biomass and the development of clean technologies for bio-based production (European Commission 2018), which is challenging as further explained in the next section. Moreover, products based on biomass as a feedstock bring about specific extra challenges regarding their environmental assessment, and in respect to the GHG footprints these are: treatment of biogenic carbon, including accounting methods and temporal dynamics, and emissions related to land use changes (see the last section of 1.3.).

Understanding variation in environmental footprints of bio-based chemicals

New bio-based products are said to improve environmental sustainability (Global Bioeconomy Summit 2020), but research reports opposing results in environmental benefits, showing inconsistencies in coverage of environmental impacts and life cycle stages (Ögmundarson et al. 2020), and data intensity and uncertainty with emerging technologies (Tsoy et al. 2020a). Reviews on bio-plastic seem to question the claim of reduced environmental impacts (Rosenboom et al. 2022; Walker and Rothman 2020; Atiwesh et al. 2021), and studies on bio-chemicals (Ögmundarson et al. 2020; Kajaste 2014) and bio-adhesives (Arias et al. 2021; Eisen et al. 2020) show large variation between products for their climate change impacts, with both higher and lower impacts compared to fossil-based products, and trade-offs regarding land use (change) and nutrient emissions, such as eutrophication impact. Currently, the sustainability and GHG benefits of bio-based products remain a subject of debate.

While an increasing number of prospective LCA studies have been conducted on emerging bio-based products (Aryapratama and Janssen 2017; Pachón et al. 2020; Müller-Carneiro et al. 2023; Moretti et al. 2021; Saavedra del Oso et al. 2023), their results vary strongly. This variability may arise from differences in biomass feedstock, land use changes and technological processes but also from the methodological challenges in prospective LCA (Ögmundarson et al. 2020) and variations in biogenic carbon accounting practices (Guest et al. 2013a; Brandão et al. 2013). To understand if, and to what extent, emerging bio-based products have environmental benefits compared to their fossil-based equivalents, it is important to map and compare their environmental footprints. In this context, consistent procedures regarding biogenic carbon handling (Cucurachi et al. 2022), upscaling and processing features, and life cycle modeling factors, including allocation method, geographical scope, or study scope (Montazeri et al. 2016) are useful.

Biogenic carbon accounting and land-use change emissions

Biogenic carbon accounting

For biogenic carbon, i.e., carbon obtained from grown biomass, there is a balance between carbon sequestration during biomass growth on one hand, and carbon emissions at the end of life on the other. Yet, this does not automatically mean that the use of biogenic carbon has no climate change effects (Cherubini et al. 2011, 2016; Liu et al. 2017). Biogenic carbon can be temporarily stored in living and dead biomass, in products or as landfill waste, and duration depends on the scenario assessed (Liu et al. 2017). In general, to account for biogenic flows during impact assessment, on one end the '0/0'-approach can be applied, which does not include any biogenic carbon flows during impact assessment, and on the other end, the '-1/+1'-approach, characterizing biogenic flows the same way as we do with fossil CO_2 emissions (Cucurachi et al. 2022). To account for temporary storage, there are methods 'in-between' 0 and 1 that calculate the Global Warming Potential (GWP) of CO_2 emission related to biomass, and several studies provided GWP_{bio} factors for different scenarios (Cherubini et al. 2011; Pingoud et al. 2012).

However, in literature an '-1/0'-approach is often also found, which assigns credits for carbon uptake in biomass while not considering its release, i.e. excluding the end-of-life stage, resulting in negative emissions (Weiss et al. 2012; Scown 2022). Although this approach can be useful to highlight the potential benefits of bio-based products compared to fossil-based counterfactual in 'cradle-to-gate' studies, it can lead to misleading conclusions, as the implicit assumption here is that carbon is indefinitely stored. This is particularly relevant for both fossil-based chemicals with a large carbon content, for which a large share of their climate change impact is related to the embodied carbon released at the end of life. End-of-life emissions are, however, often not included in petrochemical GHG emissions reporting (Carus et al. 2020; IEA 2020), which can lead to opposing conclusions. For this purpose, the use of consistent accounting methods and clear reporting are helpful.

Land use change

Land use changes can contribute to the overall GHG footprint of bio-based products by carbon stock losses due to removing of original vegetation (Fargione et al. 2008; Searchinger et al. 2008) or the lost capacity of natural vegetation to sequester CO_2 (Righelato and Spracklen 2007). Even if existing cropland is used to produce biomass for materials production, indirect land use changes can still occur, as overall increase in demand for crops and biomass can lead to land use changes elsewhere (Wicke et al. 2011; Gerssen-Gondelach et al. 2017). GHG emissions resulting from land use changes can significantly impact the net emissions of bio-based products, or even outweigh the GHG savings (Searchinger et al. 2008; Nong et al. 2020).

Global analyses including explicit land use change models have been performed, but have primarily focused on bio-energy (Daioglou et al. 2017) and bio-energy with carbon capture and storage (Hanssen et al. 2020). These studies have shown that GHG emissions associated with biomass production are highly dependent on land-cover types (Daioglou et al. 2017), land-use history and the management of original vegetation (Hanssen et al. 2020). Global assessment of specific bio-based petrochemical industry end-products, such as plastics, have been carried out, some of which do include LUC emissions (Stegmann et al. 2022; Zheng and Suh 2019), while others do not (e.g., Meys et al., 2021). The increasing demand for biomass to achieve a carbon-neutral plastic industry could lead to deforestation, but the associated emissions have not been quantified yet (Meys et al. 2021). Zheng and Suh (2019) have shown that biomass can contribute to GHG mitigation in plastics, while generically accounting for LUC emissions, yet highlighted the limitations of their study concerning the land-use implications of a large-scale transition to bio-based plastics. Application of biomass-based feedstocks across the whole petrochemical industry can result in larger CO_2 reduction potentials through biomass routes compared to CCU routes (Gabrielli et al. 2020), and biomass-to-methanol production on a global scale can reduce climate change, ocean acidification and biodiversity loss, compared to fossil-based production (Galán-Martín et al. 2021). Yet, these studies have not included LUC emissions. Therefore, the global climate change mitigation potential of replacing fossil-based carbon by biomass resources in petrochemicals, while fully accounting for land use-change emissions, remains to be assessed.

1.4. Aim & Outline

Decarbonizing the chemical industry is a key requirement to achieve net-zero emission targets and to reduce (global) environmental impacts. Strategies to make the chemical industry more sustainable relate to, among others, the use of biomass feedstock and developing cleaner technologies. However, the environmental sustainability of bio-based chemicals requires further investigation, specifically regarding (1) the environmental consequences of emerging technologies in a future, more technological developed stage, and (2) the environmental consequences of replacing fossil feedstocks by bio-based resources.

The main aim of this thesis is to quantify the environmental footprints of emerging bio-based products for the chemical industry compared to their fossil counterfactuals.

I thereby focus on two research questions:

- *How can the environmental impacts of early-stage chemical processes that produce bio-based products be assessed and compared to their fossil counterparts?*
- *What are the environmental consequences of replacing fossil- by bio-based products in the chemical industry?*

The first question is methodology focused, while the latter focusses on the actual evaluation of the environmental impacts of bio-based chemicals. Both research questions are addressed in parallel throughout Chapters 2 to 5. The chapters cover different choices with regard to (i) type of environmental assessment, (ii) chemicals addressed, (iii) feedstock type, (iv) technological development level of the production processes, and (v) temporal and spatial context, as further summarized in Table 1.1. This table also shows for each chapter: (a) its methodological innovation, connecting to the first research question, and (b) the environmental impacts assessed, relating to the second research question.

Chapter 2 assesses the environmental consequences of replacing fossil- by bio-resources by systematically comparing the environmental impacts of 98 emerging bio-based materials compared to their fossil counterparts, reported in 130 studies.

Chapter 3 analyzes the environmental impact and hotspots of an electrochemical process at an early developmental stage to produce the bio-plastic polyethylene-furanoate (PEF) compared to its equivalent fossil-based plastic.

Chapter 4 looks at the wider environmental impacts, including absolute sustainability assessments, of an early stage fast pyrolysis technology to produce the chemicals benzene, toluene and xylene (BTX) from biomass and mixed plastic waste at a projected commercial scale (2024) and for a future industrial situation (2050), compared to fossil-based BTX.

Chapter 5 comprehensively assesses the life cycle GHG emissions of bio-based production of six main petrochemicals, including spatially explicit LUC emissions, also determining the global climate change mitigation potentials of bio-based compared to fossil-based production in the petrochemical industry.

Table 1.1: Overview of focus area and analysis of each chapter, including decisions in temporal, spatial and technological context.

	Chapter 2	**Chapter 3**	**Chapter 4**	**Chapter 5**
Bio-based products	Various	Polyethylenefuranoate (PEF)	Benzene, toluene, xylene	Methanol, ethylene, propylene, benzene, toluene, xylene
Technology	Various	Electrochemical process	Catalytic fast pyrolysis	Fermentation, gasification, catalytic conversion, dimerization & metathesis, fast pyrolysis, Fischer-Tropsch, naphtha cracking, methanol-to-olefins, methanol-to-aromatics
Methodological innovation	Systematic comparison of 98 emerging bio-based products reported in 130 studies	Prospective assessment (< TRL 3: proof of concept established) based on detailed process design	Combining insights of various sustainability methods: prospective LCA, absolute sustainability assessment, and resource use perspective	Systematic, spatial explicit modelling of land-use change emissions
Environmental impacts assessed	14 midpoint impact categories	5 midpoint impact categories	3 endpoint- and 17 midpoint impact categories, 9 planetary boundaries	Global warming
TRL	TRL 1-8	TRL 2-4	TRL 6-9	TRL 6-9
Feedstock	1st, 2nd and 3rd generation biomass	1st and 2nd generation biomass	2nd generation biomass and plastic waste	1st and 2nd generation biomass
Number of bio-based products	98	1	3	6
Temporal context	Current	2021, 2030 & 2050 (i.e. external development: renewable electricity mix)	2024 & 2050 (i.e. technology maturing & external developments)	2024
Spatial context	Generic	The Netherlands	Europe	Global

2.

The potential of emerging bio-based products to reduce environmental impacts

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2.1. Abstract

The current debate on the sustainability of bio-based products questions the environmental benefits of replacing fossil- by bio-resources. Here, we analyze the environmental trade-offs of 98 emerging bio-based materials compared to their fossil counterparts, reported in 130 studies. Although greenhouse gas life cycle emissions for emerging bio-based products are on average 45% lower (37-52%; 95% confidence interval), we found a large variation between individual bio-based products with none of them reaching net-zero emissions. Grouped in product categories, reductions in greenhouse gas emissions ranged from to 19% (-52-35%) for bio-adhesives to 73% (54-84%) for bio-refinery products. In terms of other environmental impacts, we found statistical evidence for an increase in eutrophication (369%; 163-737%), indicating that environmental trade-offs should not be overlooked. Our findings imply that the environmental sustainability of bio-based products should be evaluated on an individual product basis and that more radical product developments are required to reach climate-neutral targets.

2.2. Introduction

Many countries worldwide stimulate the development of the bio-based economy to mitigate climate change and to lower their dependency on fossil-based resources (Global Bioeconomy Summit 2020). At the European level, the Bio-Economy Strategy (European Commission 2018) was developed to guide Europe towards a sustainable bio-based economy, which was reinforced in the European Green Deal for achieving climate neutrality by 2050 (European Commission 2019). New bio-based products may improve environmental sustainability compared to their fossil counterparts (Global Bioeconomy Summit 2020). A comprehensive meta-analysis on the environmental consequences of bio-based products compared to their fossil counterparts has, however, not been performed yet. More specific reviews are mainly in the domain of bio-plastics and question the claim of reduced environmental impacts (Rosenboom et al. 2022; Walker and Rothman 2020; Atiwesh et al. 2021). Other reviews on bio-chemical (Ögmundarson et al. 2020; Kajaste 2014) and bio-adhesives (Arias et al. 2021; Eisen et al. 2020) show large variation between products for their climate change impacts and trade-offs regarding land use (change) and nutrient emissions.

Ensuring that bio-based products contribute to a sustainable economy requires comprehensive environmental assessments at an early stage of their development, considering the entire value chain, from feedstock sourcing and manufacturing, to the use phase and finally disposal. Prospective life cycle assessment (LCA) provides a method that can be applied to emerging products and technologies, i.e., with a technological readiness level (TRL) below 9, modelled to a future, more mature stage (Thonemann et al. 2020). TRLs range from 1 to 9, from scientific breakthrough via lab development and pilot-phase, to a fully developed commercialized phase (TRL = 9) (Moni et al. 2020). While an increasing number of prospective LCA studies has been carried out on emerging bio-based products (Aryapratama and Janssen 2017; Pachón et al. 2020; Gonzalez-Garcia et al. 2018; Moretti et al. 2021; Piccinno et al. 2018; Zuiderveen et al. 2021), their results vary strongly – not only due to differences in biomass feedstock and technology, but also due to the methodological challenges of prospective LCA (Ögmundarson et al. 2020) and differences in biogenic carbon accounting (Guest et al. 2013b; Brandão et al. 2013).

Here, we systematically compare the environmental footprints of 98 emerging bio-based products to their fossil-based counterparts reported in 130 prospective LCA studies. The analysis includes greenhouse gas (GHG) footprints as well as other environmental impacts (non-renewable energy-use, acidification, eutrophication, ozone depletion and photochemical ozone formation). To allow intercomparison of environmental footprints, the system boundaries and biogenic carbon accounting are harmonized across studies. Environmental footprints are interpreted via response ratios (RR), which are defined as the natural-logarithm of the environmental impacts of the emerging bio-based product (X_B) divided by its fossil counterpart (X_F): RR = $\ln(X_B/X_F)$. The response ratios have a positive value (RR > 0) when the impact of the bio-based product is larger compared to its fossil-based counterpart, and a negative value (RR < 0) when the impact of the bio-based material is smaller. We determine average response ratios for each environmental impact using random-effects models to account for non-independence in data, i.e., accounting for multiple footprints from the same study and/or representing the same product. We also break down the analysis to evaluate systematic differences between i) product category, ii) feedstock category and iii) TRL. We quantify environmental trade-offs by studying differences in GHG, eutrophication, acidification, energy use, ozone depletion, and photochemical ozone formation footprints of bio-based products relative to their fossil-based counterparts. In the supplementary materials more details can be found on the main results and other environmental footprints.

2.3. Results

Greenhouse gas footprints

The predicted mean of the bio-based products' prospective GHG footprints are found to be 45% lower compared to their fossil-based counterparts (95% confidence interval (CI): -52 to -37%). Yet, the GHG footprints of emerging bio-based products vary widely compared to their fossil counterparts, ranging from a 294% (95% CI: 114% to 624%) higher footprint for lignin bio-adhesives to a 94% (n = 1) lower footprint for wood fiber bio-composites compared to their fossil counterpart, as indicated in Figure 2.1. Although, the majority of the bio-based products – 80 in 98 – show on average lower GHG footprints compared to their fossil counterparts, no product reaches net-zero GHG emissions. This suggests that most bio-based products thus reduce GHG emissions if they replace their fossil-based counterparts, but bio-based solutions are no guarantee for emission reduction and could in few cases in fact lead to higher GHG emissions.

When considering replacement of primary chemicals with bio-based alternatives in the chemical industry as a whole, significant GHG emission reduction may be achieved. The primary petrochemicals butadiene and ethylene are responsible for 34% of the primary chemical industry's GHG emissions (Galán-Martín et al. 2021). Replacing these with bio-based alternatives, which both have an arithmetic average reduction potential of 57% (95% CI: -71 to -37% for butadiene (n = 6), 95% CI: -73 to -32% for ethylene (n = 14)), could globally save up to 19% of the total GHG emissions from primary chemical production (Cespi et al. 2016; Ren et al. 2006). The replacement of plastics, the most known petrochemical end product group, shows an average reduction potential of 38% (95% CI: -50 to -24%), which would result in saving 1.3% of the total global GHG emissions annually (Zheng and Suh 2019) (Supplementary Table S2.4). To achieve larger reductions of GHG emissions, increasing recycling rates, as well as electricity mixes dominated by renewable energy and electrification of the processes are crucial strategies that would not only benefit plastics (Zheng and Suh 2019; Meys et al. 2020), but also all other types of products, both bio- and fossil-based.

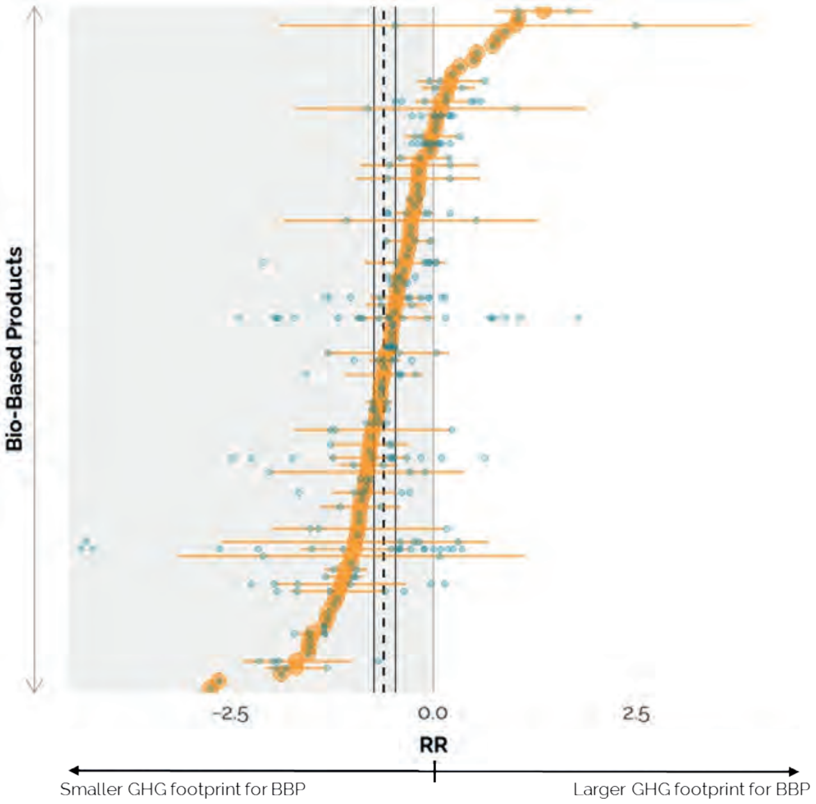

Figure 2.1: Scatterplot displaying all the response ratios as blue dots of the GHG footprints of bio-based products compared to their fossil counterparts, per bio-based product. Encircled orange dots represent arithmetic average RRs per bio-based product with corresponding 95% CI as opaque orange error-bars. There is no 95% CI for bio-based products with n = 1. Black dashed line at RR = -0.60 is the predicted mean RR based on a random-effects model including product type and study as random effects, accompanied by two black lines as overall 95% CI: -0.74, -0.47. In the grey area the GHG footprints of the bio-based products are lower than their fossil counterparts, with a grey line at RR = 0 representing no difference in GHG footprint. See Supplementary Table S2.3 for details.

Product category

The mean response ratio of bio-refinery products, bio-chemicals, bio-composites, bio-adhesives and bio-polymers are significantly different from zero, meaning the GHG footprints are lower compared to their fossil alternatives. Nevertheless, product category did not significantly explain variation in RRs (omnibus F: 2.13, p-value: 0.07). Still, the large reduction potential of bio-refinery products is particularly promising, for which an average reduction of 73% (95% CI: -54 to -84%, Figure 2.2a, n = 19) was found. Bio-refineries produce multiple products in an integrated way, valorizing different parts of biomass feedstock and waste, and can therefore significantly lower the environmental footprint per product (Moncada et al. 2016).

The differences between the bio-product categories of bio-polymers, bio-chemicals, bio-composites, bio-fibers and bio-adhesives, were relatively small. Nonetheless, the category of bio-adhesives (n = 13) stands out with the upper end of its confidence interval above zero. This result can be explained by the large influence of a single microalgae-based product that has a GHG footprint 12 times larger than its fossil counterpart due to high energy requirements of micro-algae cultivation and harvest (Guiton et al. 2022).

Biomass feedstock category

The type of biomass feedstock used did not significantly influence the RRs and the differences between the feedstock categories were relatively small (except for 3rd generation feedstock but n = 4), as shown in Figure 2.2b (omnibus F: 1.53 p-value: 0.19). Although bio-based products from agricultural and forestry residues are on the lowest end, higher GHG emission reductions were expected for second generation feedstock compared to first generation biomass (Escobar and Laibach 2021). However, there is a wide variety in second generation biomass pretreatments, and some are significantly more intensive, e.g. in steam consumption or chemical use, compared to first generation biomass treatments (Bello et al. 2021).

GHG emissions from land use change (LUC) can typically contribute a large share of the overall GHG footprint of bio-based products (Akkari et al. 2018) and bio-fuels (Hanssen et al. 2020; Akkari et al. 2018; Harper et al. 2018). Yet, in our analysis, only 13% of the studies included GHG emissions from LUC in their GHG footprint, and these did not necessarily result in systematically higher GHG footprints (Supplementary Figure S2.6). The different methods used to arrive at LUC-related GHG emissions as well as the different types of original land that was transformed, makes it difficult to find a systematic effect. GHG emissions from LUC are highly variable, but can play a big role, specifically when deforestation is considered (Khoo et al. 2016b). Future assessment of bio-based products should therefore include LUC-related GHG emissions, yet, currently, this is hindered by lack of a harmonized and standardized methodology (Ita-Nagy et al. 2020).

Technology readiness level

Environmental footprints of emerging bio-based products are typically up scaled from the lab- or pilot-scale to a commercial stage. In the studies included in our review, the four main upscaling methods were via process simulation data (43% of the total number of data points), followed by adapted data from patents and reports (13%) or from similar processes that operate at large-scale (11%) and linear extrapolation of data (10%). We directly used the up scaled information in our analysis. We found that the starting TRL did not significantly influence the predicted GHG footprint of a technology, as the differences between the TRL groups were small and proved not significant (Figure 2.2c; omnibus F: 2.26, p-value: 0.11). We should note, however, that predictions from lower TRLs that upscale to a TRL 9 should preferably involve a combination of process changes, size scaling and process synergies (van der Hulst et al. 2020). Although 91% of the studies up-scaled to commercial scale, based on production output or size, only 52% of them include one or more types of process synergies, such as heat integration, recovery of solvents, energy recovery from waste treatment or recycling of (waste) streams. Regardless of the original TRL, upscaling to a commercial stage can be more comprehensively assessed compared to the current state of the art.

Environmental trade-offs

We found that emerging bio-based products have on average 37% lower (95% CI: -56 to -10%) lower non-renewable energy use (NREU) compared to their fossil counterparts, as shown in Figure 2.3. In contrast, eutrophication impacts were on average 369% higher (95% CI: 163 to 737%) for bio-based products compared to their fossil counterparts. For the impact of acidification, ozone depletion and photochemical ozone formation, the bio-based products and their fossil alternatives were not significantly different from their fossil counterparts with a mean increase of 41% (95% CI: -9 to 119%), and mean reduction of 28% (95% CI: -73 to 88%) and 16% (95% CI: -57 to 63%) respectively.

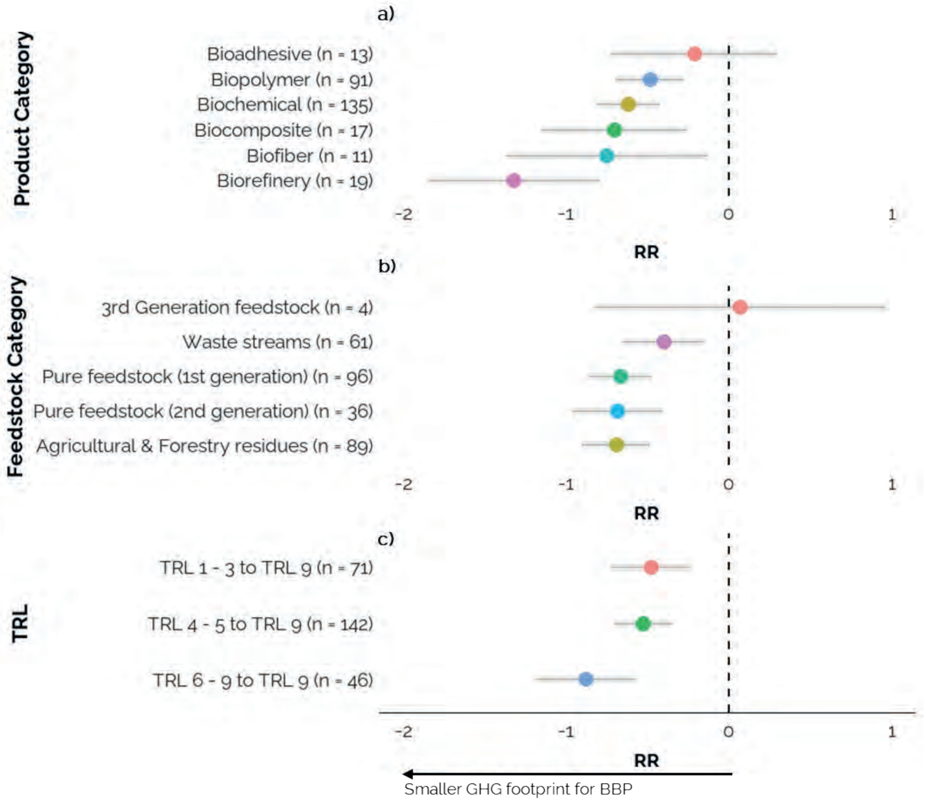

Figure 2.2: Change in GHG footprint response ratios (RR) in relation to key parameters: (a) product category, (b) feedstock category and (c) TRL category, meaning the TRL from where the study up scales to a TRL 9. n gives the number of response ratios. Grey bars indicate 95% confidence intervals. Dashed black line at RR=0 indicates no difference in GHG footprint between bio-based product and its fossil-based alternatives. In (a), bio-refinery products refers to bio-chemicals produced in an integrated bio-refinery producing multiple products and energy. For the results in (c), the thirteen studies that did not model all the way up to a TRL 9 (but to a lower TRL, e.g. TRL 7) were excluded from the analysis. Plots show the predicted mean RR and 95% CI (error-bars) from single mixed-effects models. The predictions translated to percentages per category (in a,b, and c) can be found in Supplementary Table S2.5.

Hence, for bio-based products to be more environmentally sustainable, total impacts should be minimized and burden shifting needs to be avoided, which mainly relates to the cultivation of biomass. Running linear mixed-effect models on the relationship between the RR of acidification and eutrophication impacts and feedstock categories, second generation feedstock did not seem to hold benefits over first generation feedstock (Supplementary Figure S2.7). Second generation biomass may nevertheless hold benefits over first generation biomass in terms of food competition and biodiversity loss (Harvey and Pilgrim 2011; de Jong et al. 2020).

Exploring the relationship between the eutrophication and acidification impact and the product categories indicates a strong trade-off with climate change for all bio-based products. Only bio-refinery products showed a decrease of 99% (95% CI: - 100 to -94%) for acidification impacts compared to its fossil alternatives (Supplementary Figure S2.6), though these results are relatively uncertain, due to the low number of bio-refinery data points (n =4). In general, eutrophication and acidification are highly influenced by the use of (synthetic) fertilizers (Cherubini and Strømman 2011). Therefore, the use of more precise fertilization techniques, renewable fertilizers and sustainable agricultural practices are important to mitigate these impacts (European Commission 2020b).

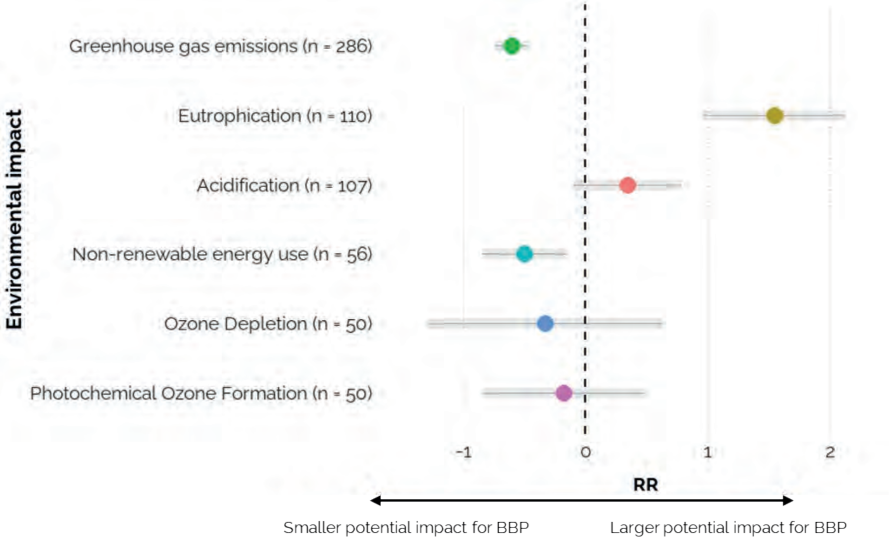

Figure 2.3: Plot showing predicted mean and 95% CI of GHG, eutrophication, acidification, NREU, ozone depletion and photochemical ozone formation impacts. In percentages, on average the GHG footprint is reduced with 45% (95% CI: -52 to -37%), eutrophication is increased with 369% (95% CI: 163 to 737%), acidification is increased with 41% (95% CI: -9 to 119%), NREU is reduced with 39% (95% CI: -57 to -14%), ozone depletion is reduced with 28% (95% CI: -73 to 88%) and photochemical ozone formation is reduced with 16% (95% CI: -57 to 63%). A plot with the arithmetic averages and 95% CIs can be found in Supplementary Figure S2.9. A plot with an overview of all environmental impacts with n≤30 and the predicted mean and 95% CI of the RRs across product types and studies can be found in Supplementary Figure S2.10.

2.4. Discussion

To be able to combine the studies in a coherent statistical modeling format, we harmonized system boundaries, functional unit, end-of-life treatment and biogenic carbon accounting across all prospective LCAs. There are different ways of considering biogenic CO_2, depending on the goal and scope of the study (Cucurachi et al. 2022). Most studies (83%) initially applied cradle-to-gate system boundaries, as chemical products are often intermediates applied in diverse downstream uses and therefore their end-of-life is unknown. For a consistent comparison across studies, we assumed that both biogenic and fossil carbon embodied in the products would eventually end up in the atmosphere, extending the system boundaries to cradle-to-grave by an incineration scenario based on the chemical structure of the product. We found that a large share of the products' climate change impact relates to the embodied carbon in the product that is released again at the product's end-of-life. Our end-of-life assumption that all products are incinerated may, however, overestimate the GHG emissions of both bio-based and fossil-based products that are currently recycled or biodegradable products that are converted into biogas, bio-energy or compost (Ögmundarson et al. 2020; Rosenboom et al. 2022). Moreover, the release of the embodied carbon can be abated by increasing the recycling rate (Meng et al. 2023; Stegmann et al. 2022). We acknowledge that assessments of product design should ultimately integrate recycling, re-use or remanufacturing (Keijer et al. 2019). A closer collaboration between environmental and circularity assessments (Rufí-Salís et al. 2021; Lokesh et al. 2020) (e.g. the Material Circularity Indicator (MCI) (EMF and Granta 2019)) which are yet to be standardized (Rufí-Salís et al. 2021), might be useful in this respect.

We found no indication that the starting TRL of a technology introduces systematic bias in the assessments. We were, however, not able to fully standardize the technology development predictions across the studies included, such as to what extent waste streams were recycled or heat integrated. To better understand the environmental impact of products at an early stage of development, clear upscaling guidelines involving different levels of technological development are required (Adrianto et al. 2021). For instance, three distinctive steps in technological development can be specified, i.e. size scaling, process changes and process synergies (van der Hulst et al. 2020), which could then be assisted by for example expert views, simulation software and upscaling frameworks (e.g. from Piccinno et al. (2016)). Additionally, a comprehensive prospective LCA would require temporal alignment of both the emerging technology and the fossil baseline product when compared at a future point in time, and should consider changes in the background system (Adrianto et al. 2021). A standardized framework for prospective LCA might also benefit from clear TRL definitions. For this reason, there is first a need to develop per technology type specific TRL guidelines, which would make assessments much more comparable. Our study identified, for example, a broad application of fermentation-based technologies (55% of RRs), which will involve different (future) developments compared to thermochemical catalytic processes or integrated bio-refineries.

The actual potential of bio-based products to reduce environmental impacts depends on scale and structure of the global bio-economy, which cannot be fully understood unless technology advancements are evaluated and, as crucial, the land-use change related emissions, which are typically not included in environmental assessment of bio-products, forming a crucial knowledge gap. Improved assessment of LUC related GHG emissions are also necessary to better understand the suggested advantages of second generation biomass (either dedicated crops or residues) over first generation biomass. Furthermore, only a limited number of studies included impacts on land use, water use and ecotoxicity from pesticide use. Yet, the studies reporting land- and water use indicate an increased impact for bio-based products (Supplementary Figure S2.10). These categories also contribute to impacts on biodiversity. For example, agricultural cultivation can have a serious impact on biodiversity, e.g. converting natural habitat for palm oil cultivation leads to reductions in local wildlife populations and species richness (Verdade et al. 2015). Further research on all of these impacts is crucial to understand the sustainability of bio-based products.

Comparing prospective LCAs of emerging bio-based products to their fossil-based counterparts reveals a significant potential for the bio-economy to reduce GHG emissions. However, the large variability in GHG benefits and burdens of bio-based products compared to their fossil alternatives, with none of the products reaching net-zero emissions, asks for nuanced conclusions when designing and evaluating the sustainability of individual bio-based products. In the end, a combination of mitigation options like biomass utilization, increasing recycling rate and low carbon electrification of the industry, alongside reducing product demand (Bachmann et al 2023; Meng et al 2023; Moncada et al. 2016) will be required to reach net-zero emissions in the chemical and plastic industry.

2.5. Methods

This section explains the data extraction process including search strategy, the screening and inclusion of prospective LCA studies and the framework developed to collect and harmonize data. The statistical analysis section describes the response ratio and the linear random- and mixed-effects models.

Data extraction process

Search strategy. We searched for literature in Scopus and Web of Science (March 2023) using the search string: TI=((lca) OR (life AND cycle AND assessment) OR (life AND cycle AND analysis) OR (environmental AND assessment) OR (environmental

AND life AND cycle) OR (carbon AND footprint) OR (global AND warming AND potential) OR (cradle AND gate) OR (cradle-to-gate) OR (greenhouse gas) OR (GHG) OR (GWP)) AND TS=((biochemical) OR (bio-chemical) OR (bioplastic) OR (bio-plastic) OR (biocomposite) OR (bio-composite) OR (biolubricant) OR (bio-lubricant) OR (biosurfactant) OR (bio-surfactant) OR (biopolymer) OR (bio-polymer) OR (biomaterial) OR (bio-material) OR (biofiber) OR (bio-fiber) OR (biobased) OR (bio-based) OR (bio AND based)). Additionally, a search string was used including: AND TS=(algae), to include studies using algae as a feedstock. There was no publishing year limit and we included all languages and document types. The search resulted in a total of 1,349 studies, published between 1978 – 2023 (March 1st).

Screening and inclusion of prospective LCA studies. Based on abstract screening, we excluded studies on bio-based fuels to focus on emerging bio-based materials only, resulting in 428 studies. From these, 130 studies were selected for the analysis based on the following two criteria: (1) the study carried out an LCA with a prospective character, meaning the study assessed an emerging technology or material with a TRL below 9 modelled to a mature state in the future; and (2) the bio-based product is a 'drop-in' of a fossil-based product, meaning it has the same chemical structure, or it can be compared to a fossil-based product which has the same function (decision trees: Supplementary Figures in S2.1).

Framework: collection and harmonization of prospective LCA results. To carry out the analysis, the studies were aligned concerning the functional unit, biogenic carbon accounting and system boundaries. The following standardization approach was adopted:

1. Biogenic carbon emissions were considered CO_2-neutral, because CO_2 is taken up by growing biomass and released again at the end of the product life cycle. We consider this assumption defensible, as the considered biomass feedstock has a short rotation period - of typically one year (in line with the GWP_{bio} accounting approach by Cherubini et al. (2011)) and temporary carbon storage in the bio-products is not considered relevant, as the materials considered are typically short-lived (in line with Guest et al. (2013)), such as single use plastics.
2. The system boundary was set to cradle-to-grave by aligning end-of-life biogenic and fossil carbon emissions. From the papers, GHG emissions were extracted from cradle-to-gate (including biogenic carbon if it was subtracted from the GHG footprint at the gate) and an equal incineration end-of-life scenario based on the chemical structure of the product was added. Here, we accounted for CO_2 emissions of the end-of-life incineration, but left all other waste treatment

processes outside the system boundary, for both the bio-based products and their fossil-based counterparts.

3. For 10% of the studies the environmental impacts of the fossil-based counterparts were not given. These environmental impacts were calculated in SimaPro 9.1 software by applying impact assessment method matching the study's impact assessment method (e.g. ReCiPe 2016 (Huijbregts et al. 2017)) on LCI datasets from Ecoinvent 3.7 (Ecoinvent 2020) that fit within the same system boundaries.

For each study, we extracted the life cycle impact values of all the impact categories mentioned for the new bio-based products and its fossil-based alternatives (Zuiderveen et al. 2023a), either from the text, tables or graphs using WebPlotDigitizer (https://automeris.io/WebPlotDigitizer/). The categories of global warming, acidification, eutrophication, non-renewable energy use, ozone depletion and photochemical ozone formation contained a relatively large number of data values ($n \geq 50$) and are displayed in Figure 2.3. The predicted mean and 95% CI calculated for the other impact categories' RRs (which all had $n \leq 30$) can be found in Supplementary Figure S2.10. The functional unit was taken as reported by the study with 95% of the studies applying functional units in weight (kg), 3% in area (m^2) and 2% in volume (m^3). We also included in our database (i) the product category (bio-adhesive (incl. lubricants), bio-chemical, bio-composite, bio-fiber, bio-polymer, bio-refinery), (ii) the feedstock type (pure feedstock 1st generation, pure feedstock 2nd generation, agricultural & forestry residues, waste streams (including industrial side stream, municipal waste and food processing waste), 3rd generation), (iii) the original TRL (TRL 1 to 3, TRL 4 to 5, and TRL 6 to 9) and projected TRL. Definitions of the TRL groups were based on Moni et al. (2020) (Supplementary Figure S2.2). For example, a study based on lab- or experimental data was considered a TRL 1 to 3, and a study based on process data by simulation of the design was considered a TRL 4 to 5.

Statistical Analysis

Response Ratios. We calculated ln-response ratios to evaluate the change in environmental impacts between an emerging bio-based material and its fossil-based counterparts. The response ratio provides a measure of the relative change in environmental impacts. The response ratio (RR, dimensionless) was calculated as:

$$RR = \ln\left(\frac{X_B}{\bar{X}_F}\right) \qquad \textbf{equation 2.1}$$

where x is the environmental impact of the emerging bio-based product (B) and the fossil-based counterparts (F). Positive values for RR ($RR > 0$) indicate a larger footprint of the bio-based materials. Negative values for RR (RR < 0) indicate a smaller footprint of the bio-based materials. RR close to zero (RR ≈ 0), indicate no change in footprint. Throughout the text, the RR numbers are back-transformed using Euler's number (e) and are reported as the percentage change from the fossil-based counterparts.

Linear mixed models. Linear mixed models are an extension of regression models, and particularly useful for non-independency in data as they allow for random and fixed effects. If within one study the environmental impact of multiple products can be extracted, these footprints are non-independent. Hence, study identity is taken into account as random effect. Likewise, there are 98 different bio-based products. Footprints representing the same product are non-independent and therefore also taken into account as random effect. A random-effects model was ran to determine the mean RR across all studies and product types. Arithmetic average RRs were separately calculated per bio-based product with corresponding 95% confidence intervals (i.e., the ratio of the sum of RRs per bio-based product to the total number of corresponding bio-based product). Single linear mixed-effects models (LMM) were ran to assess the relationship between the RR of GHG, NREU, acidification, eutrophication, ozone depletion and photochemical ozone formation footprints and the key parameters, respectively product category, feedstock type and original TRL. Additional single linear mixed-effects model was ran to further explore the relationship between the RR of GHG footprints and GHG emission related to Land Use Changes (included/excluded in the study). Model fit of each of the mixed-effects models was assessed using the omnibus F test based on the Satterthwaite's approximation to the denominator degrees of freedom. The analysis was carried out in *R v.4.1.3* (R Core Team 2022), using the *lme4* package (Bates et al. 2015) to fit the LMM models, *lmerTest* (Kuznetsova et al. 2017) to perform F-tests and *ggplot2* (Wickham 2011) to generate figures.

Data availability

The supporting data generated in this study are provided in the Supplementary Information. The data collected in this study are available in the *figshare* repository (DOI: https://doi.org/10.6084/m9.figshare.22795184)(Zuiderveen et al. 2023a).

Code availability

The code to conduct the analysis is available in the *figshare* repository
(DOI: https://doi.org/10.6084/m9.figshare.22795184)(Zuiderveen et al. 2023a).

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3.

Ex-ante life cycle assessment of polyethylenefuranoate (PEF) from bio-based monomers synthesized via a novel electrochemical process

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3.1. Abstract

An ex-ante Life Cycle Assessment was conducted to assess the cradle-to-factory gate environmental impact of polyethylenefuranoate (PEF). The two monomers used to synthesize a 100% bio-based PEF, namely 2,5- furan dicarboxylic acid (2,5-FDCA) and mono ethylene glycol (MEG), are synthesized simultaneously from a novel electrochemical reactor using bio-based raw materials. The technology is currently at a low Technological Readiness Level (TRL 2-3), and was scaled up to a theoretical TRL4 using process design. The purposes of this study are two folds: 1) to identify the significant environmental issues at an early development stage and 2) to gain insights into and experience of ex-ante assessment for a low-TRL bio-based innovation. The electrochemical technology investigated offers the opportunity of electrification of the chemical sector in the future. Ex-ante LCA was applied based on recently suggested TRL-frameworks. Primary data from the foreground system, covering the electrochemical reactor and the downstream purification processes, were obtained from lab-scale experiments and conceptual design. Five environmental indicators were assessed: namely, climate change, non-renewable energy use (NREU), acidification, eutrophication and land use. The results show that the electricity demand from the electrochemical reactor is the most important contributor of the environmental impacts, yet downstream processes contribute significantly as well. Future scenarios show that a carbon neutral electricity in 2050 could help to significantly reduce the climate change impact (by up to 60%). As a proof-of-concept, the assessed electrochemical reactor shows its important potential of the electrification of the chemical sector for monomer and polymer production, provided that a zero emission electricity in the future can be achieved.

3.2. Introduction

The 21st-century is marked by growing concerns about climate change and the need to mitigate it becomes more urgent every passing day. Current climate change problems require radical new ways of living, producing and consuming. In order to achieve this, the Paris Agreement and the Sustainable Development Goals (SDGs) were set up; and at EU level, the Bio-economy Strategy was developed aiming at advancing the deployment of a sustainable European bio-economy (European Commission 2018). A bio-economy shifts from a fossil-based economy to a bio-based economy and offers potential solutions for climate change and related problems such as limited resources, biodiversity loss and ecosystem degradation. Key to this strategy is the development of bio-based materials using sustainable and clean technologies (European Commission 2017). The chemical industry is one of the primary industries producing the building blocks for many materials, such as plastics. This industry, including the petrochemical sector, accounts for 30% of the total industry energy-use and is responsible for 18% of direct industrial GHG emissions globally (IEA 2020). In order to lower the climate change impact of the chemical industry and to shift to a bio-economy, one of the grand challenges today within the chemical sector is to design green and sustainable materials and clean technologies (Aeschelmann and Carus 2015). Within this context, the Horizon 2020 TERRA project was set up exploring two strategies to lower climate change impact of plastic production. Firstly, it uses biomass as a feedstock for the synthesis of a 100% bio-based PEF polymer, and secondly, it explores an electrochemical conversion technology producing it.

One of the strategies is to produce materials from other resources than fossil fuels. Bio-based production of ‘drop-in’ chemicals or new materials offer a huge potential (Strengers & Elzenga 2020). The Horizon 2020 TERRA project aimed at producing bio-based chemicals (mono-ethylene glycol (MEG) and 2,5- furan dicarboxylic acid (2,5-FDCA)) which can be polymerized to PEF, an important and 100% bio-based future alternative to PET-plastic (Polyethylene Terephthalate). The global production of PET was over 50 million metric tonnes in 2016 (Zander et al. 2018) and its demand is increasing 8% per year for fibres (CIRFS 2016) and 4.8% for packaging (PlasticsEurope 2017), making it the most important polyester and the third most important polymers demanded by the market after polyethylene and polypropylene. PEF is reported to have better barrier (especially its oxygen barrier), mechanical and thermal properties compared to PET (Burgess et al. 2014). It also has the similar processability and therefore can be converted into end products using the same infrastructure. If fully recycled, the biogenic carbon embedded in the material could be potentially “locked” in the technosphere, offering a long-term carbon sink in a circular economy.

Apart from developing new bio-based materials, another strategy to reduce climate change impact is to decarbonize the processes in the chemical industry by electrification (Schiffer and Manthiram 2017). A large part of the energy consumed by the chemical industry is associated with heat requirements of thermochemical processes. Presently, though there are few solutions to acquire affordable low-carbon and high entropy heat, a more promising solution is the use of green electricity as it is becoming more and more accessible and affordable. Developing electrochemical reactions could be one of the alternative ways to replace the heat demand with electricity. The Horizon 2020 TERRA project developed a new electrochemical conversion technology. However, although the core technology may be very promising, the downstream processes could still be complexed and energy intensive, as well as the acquisition and pre-treatments of bio-based feedstock which may also contribute to significant environmental impacts (Morales et al. 2015). It is therefore important to understand whether this alternative electrochemical PEF synthesis route could really offer opportunity of decarbonisation and reduced climate change impact, from a system point of view and in its early-development stage.

One comprehensive method to assess the environmental impact of a product is Life Cycle Assessment (LCA). The methodology is based on systems thinking, which evaluates the whole supply chain of a product and analyses possible trade-offs. LCA offers the possibility of identifying environmental hotspots - especially important in early-stage processes - securing sustainability and avoiding lock-ins (Keijer et al. 2019). The life cycle environmental impacts of PEF are, to a large extend, still unknown due to early development phase of the material. One publicly available LCA of PEF, obtained from 2,5-FDCA sourced from first generation biomass (corn) and fossil and bio-based based MEG (70% and 100% bio-based content, respectively) conducted by Eerhart, Faaij & Patel (2012), analysed PEF could potentially reduce non-renewable energy use (NREU) by 40-50% and greenhouse gas (GHG) emissions by 45-55% compared to fossil fuel based PET. The study analysed a chemical conversion of corn-based fructose into furanics to produce hydroxymethylfurfural (HMF) and the air oxidation of HMF to FDCA, based on proof-of-concept experimental data from Avantium Chemicals B.V. (Eerhart et al. 2012). Just recently a comparative LCA for different types of bio-plastics was published by the Joint Research Center, including an early-assessment of PEF; It found an impact of 554 kg CO2 eq. per 1000 litres of beverage by means of 0.5 litre single-use bottles from cradle-to-grave, based on thermodynamic routes for FDCA, from a mix of maize, wheat and potatoes, and MEG from sugarcane via bio-ethanol (Nessi et al. 2020). Unlike the separate conversions of MEG and 2,5-FDCA, as reported in current literature, the electrochemical process developed by the TERRA-project aimed to innovate a ground-breaking synthesis route using a one-step reactor to produce MEG and 2,5-FCDA simultaneously (Figure 3.1).

The purpose of this study is to carry out an early-stage environmental assessment in order to understand the environmental impact of the proposed TERRA technology and to identify the environmental hotspots, using the method of ex-ante Life Cycle Assessment (LCA). When this study was prepared, the Technology Readiness Levels (TRL) of the TERRA technology was estimated at 2-3, which could be scaled up to a TRL-4 including process design. TRL is a method to define different levels of maturity of the technology. TRL 2-3 is an experimental phase, demonstrating the proof-of-concept. There are practical and methodological challenges to perform a technology assessment at very early development stage, e.g. limited data availability, scaling issues and assumptions with often large uncertainties (Moni et al. 2020). This study is an attempt to fill the knowledge gap of understanding the environmental impact at an early developmental stage by using data obtained from process design. A conceptual pilot design, based on the functional principles of the TERRA process, including all recovery and upgrading steps is modelled. Using process simulation data could provide valuable insights into the environmental impacts in the early development stages (Fernandez-Dacosta et al. 2019) and promotes responsible research and innovation (van den Hoven and Jacob 2013). The aim of this study is twofold: (1) it assesses a technology which offers the opportunity of electrification of the future bio-based chemical sector and (2) the ex-ante LCA is applied based on recently suggested TRL-frameworks. The experience gained from this study will provide further recommendations for a TRL-based ex-ante LCA.

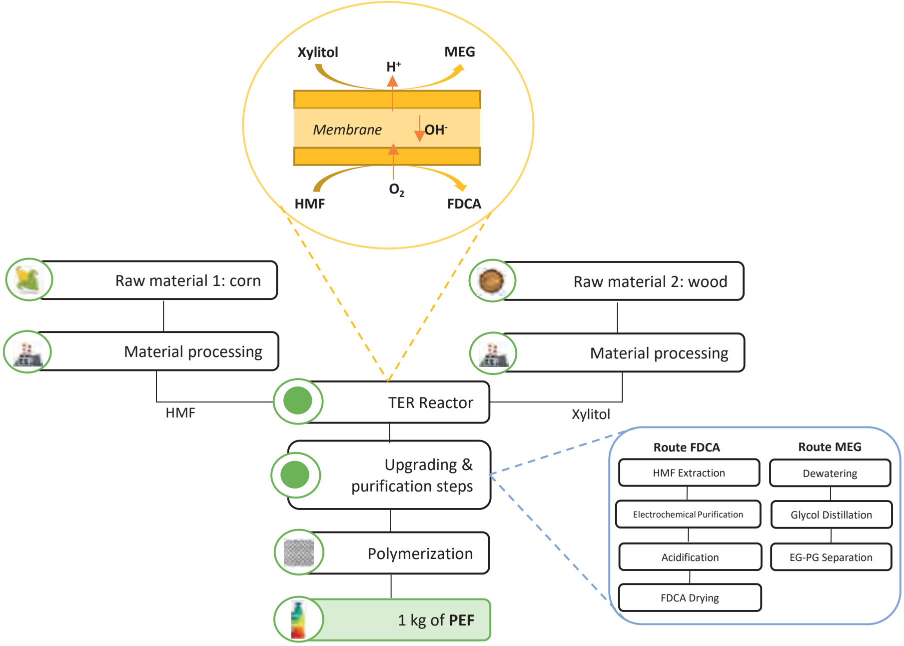

Figure 3.1: Simplified scheme of PEF production based on TERRA process.

3.3. Material and Methods

Ex-ante LCA

Ex-ante LCA is used to evaluate the environmental impact of an early-stage technology. Technologies assessed in an early developmental stage can have many (positive) future implications in regard to their environmental impact. It allows for comparison of different pathways, optimisation of supply chains and highlights possibilities for environmental improvement (Moni et al. 2020; Buyle et al. 2019) . Yet ex-ante LCA involves many challenges. Summarized these are the comparability of technologies, data availability, scaling issues and uncertainties. Apart from process changes and technological validation, process synergies and numerous external developments should be accounted for but are often highly uncertain (Moni et al. 2020).

Currently there is no consensus on a uniform framework for ex-ante LCA, but many have been recently proposed (Buyle et al. 2019; Moni et al. 2020; Thonemann et al. 2020), nonetheless, only a few bring it into practice (Piccinno et al. 2016; Simon et al. 2016; Tecchio et al. 2016). Previous research proposed frameworks defining ex-ante LCA by the different stages of technological development (Thonemann et al. 2020; Thomassen et al. 2019). Gavankar et al. (2014) applied TRLs to a case study on carbon nanotubes and recently van der Hulst et al. (2020) suggested a systematic approach defined by TRL ratings, applying it on a case study of CIGS solar photovoltaic laminate (Gavankar et al. 2015; van der Hulst et al. 2020). Technology Readiness Levels are based on 9 levels : TRL 1 to 3 define the lab phases, 4 to 6-7 includes process design and early pilot phase and TRL 9 means the technology is ready for commercial application (Thonemann et al. 2020). Our study is an attempt to assess a TRL2-4 technology.

By going from TRL 2-3 to TRL 4 in an ex-ante LCA, the design has to deal with upscaling and process changes based on a proven concept. Process design and simulation can support the LCA framework at an early developmental level (Righi et al. 2018). A conceptual pilot design, based on the functional principles of the TERRA process, including all recovery and upgrading steps is modelled (see section TERRA process). In order to go from TRL 4 to TRL 5 a miniplant should be evaluated and TRL 6 would cover the start of a pilot phase (Buchner et al. 2019). To go to a TRL 9 rating, apart from process changes to full-scale and technological validation, process synergies and external developments should be taken into account. Learning curves from previous similar technologies could be used at an industrial stage (Buyle et al. 2019). Our research contributes to the ex-ante LCA community and specifically to the TRL-based frameworks by defining the process by Technology Readiness Levels (TRLs). Our contribution is performing a case-study and exploring how to deal with a TRL 2-3 technology "upscaled" to TRL4. To scale up from a 50kt pilot plant to a 200kt plant was beyond the scope of this research due to very high uncertainties and data unavailability.

Goal and scope definitions

The goal of this study is to assess the environmental impact of a PEF polymer based on a novel electrochemical process at an early developmental stage and to identify potential environmental hotspots. The LCA is conducted using the ISO standards (ISO 14040: 2006 and ISO 14044: 2006). The focus of this study is an electrochemical process for the simultaneous production of bio-based monoethylene glycol (MEG) and bio-based 2,5-furan dicarboxylic acid (2,5-FDCA), the building blocks for PEF. Based on the decision context, the ex-ante LCA conducted is an attributional LCA.

The functional unit is 1 kg of PEF produced from first and second generation biomass and via the electrochemical TERRA process. A cradle-to-factory gate life cycle is assessed including (1) feedstock extraction, (2) monomers production and (3) polymerization. Biomass feedstock is assumed to be obtained from Europe, or if data is not available, (background) data is based on global average (commodity) supply. The TERRA reactor is assumed to be located in the Netherlands. For all other background data, average technology of 2010-2019 in Western Europe is assumed. Since the goal of this study is to prepare for potential process optimization, capital goods are excluded from the system boundary.

Foreground data for the Life Cycle Inventory (LCI) were collected from internal data from Avantium B.V. and personal communications with experts. Process design and simulation were modelled in ASPEN©Plus and Excel. Background data were collected from Ecoinvent databases (version 3.3) (Wernet et al. 2016), Agri-Footprint (version 1.0) (Durlinger et al., 2017) and literature data. Details on the data sources are reported in the next section.

The characterization methods used were ReCiPe Midpoint H (2016), IPCC 2013 GWP 100a and Cumulative Energy Demand (CED). Five environmental impact categories were selected: climate change (GWP, kg CO2 eq./FU), non-renewable energy use (NREU, MJ/FU), acidification (kg SO_2 eq./FU), eutrophication (kg PO_4^{3-} eq./FU) and land use (kg C deficiet). Greenhouse gas emissions and energy depletion (NREU) are the two most common environmental indicators in an ex-ante LCA and can provide an accurate prediction for the impacts of unscaled production of bio-based innovation (Fernandez-Dacosta et al. 2019). However, bio-based products have been shown to present environmental trade-offs. Acidification, eutrophication and land use are often neglected in an early stage assessment but are important impact categories for especially bio-based material (Broeren et al. 2017). We have not included direct or indirect land use changes (LUC or iLUC), although they can contribute notably to climate change (De Rosa et al. 2016). However, land use change emissions are spatially-explicit and because neither the final specific feedstock is known nor its geography, including LUC or iLUC introduces very high uncertainty when proving meaningful assessment for a technology at a very low TRL level. With the selection of environmental indicators, we aim to capture both expected benefits and potential downsides of TERRA PEF. Table 3.1 presents all five impact categories, their corresponding impact assessment methods and their definitions.

Table 3.1: the impact categories analysed and their units, the methods used for each impact category and their definitions.

Impact Categories	Unit	Impact assessment method	Definition
Non-renewable energy use (NREU)	MJ	Cumulative Energy Demand (Frischknecht et al. 2007)	Primary energy demand including fossil energy, nuclear energy and non-renewable biomass energy (Frischknecht et al. 2007).
Climate change (GHG emission)	kg CO_2 eq.	GWP 100a (IPCC, 2013)	Greenhouse gas emissions
Freshwater eutrophication	g PO_4 3- eq.	ReCiPe 2016 Midpoint (H) (Huijbregts et al. 2017)	Overflow of nutrient in freshwater ecosystems caused by e.g. phosphates and nitrates, measured in PO_4 3- equivalents (Helmes et al. 2012).
Terrestrial acidification	g SO_2 eq.	ReCiPe 2016 Midpoint (H) (Huijbregts et al. 2017)	Acidified soil due to pollution measured in SO_2 Equivalents (Roy et al. 2014)
Land use	kg C deficit	ILCD 2011 Midpoint + (Milà I Canals et al. 2007)	Land to produce biomass either in terms of occupied land in m2 of crop or land that is to be transformed, expressed in kg carbon deficiency (Milà I Canals et al. 2007).

Life Cycle Inventory

Figure 3.2a and 3.2b provide a schematic representation of the cradle-to-factory gate production process of PEF. The LCA is scoped to account for:

1) Feedstock production, including the production of 5-HMF and xylitol.
2) The TERRA process, which contains the electrochemical reactor and the downstream separation and purification steps to produce the two monomers MEG and 2,5-FDCA.
3) PEF polymerization.

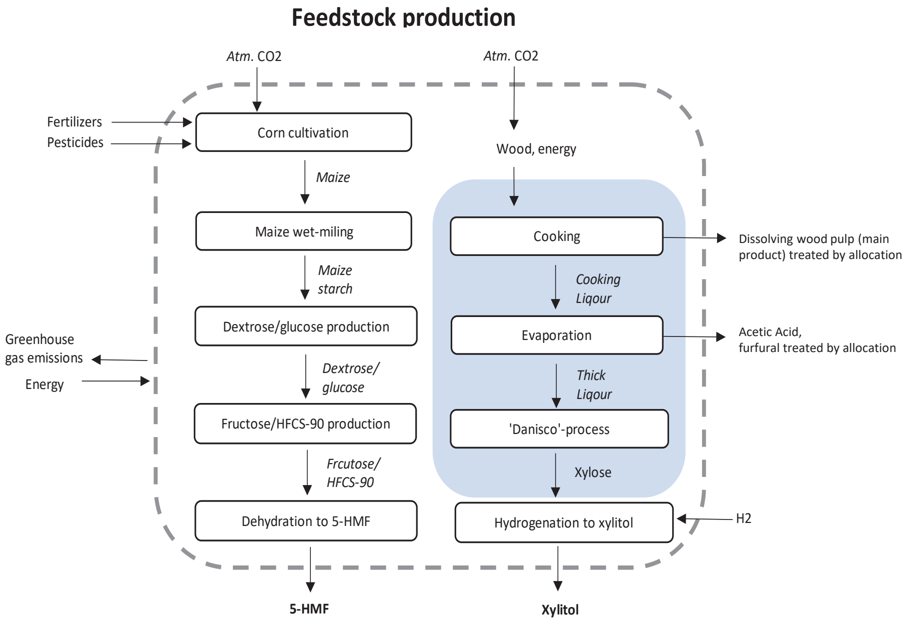

Figure 3.2a: schematic representation of raw material acquisition for 5-HMF and xylitol. Boxes in blue indicate multiple processes which were treated as one-unit process in the LCA model.

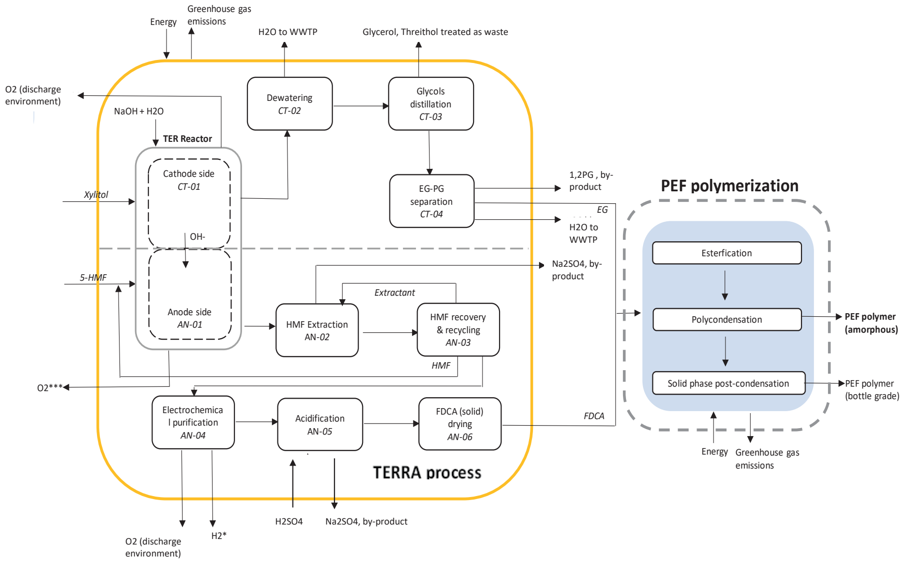

Figure 3.2b: schematic representation of TERRA process and polymerization steps. Boxes in blue indicate multiple processes which were treated as one-unit process in the LCA model.

Table 3.2: summary of data used in the baseline analysis in this study. See detailed description in subsections.

	Data source	**Notes**
Feedstock		
Glucose production	Literature, complemented with ecoinvent 3.3	From European Corn based on Tsiropoulos et al. (Tsiropoulos et al. 2013) For corn cultivation, energy and GHG emissions are taken from Tsiropoulos et al. (Tsiropoulos et al. 2013) For the other impact categories, the Ecoinvent French average corn production is assumed. See Table 3.3.
Fructose/HFCS-90	Own Model	Modified based on calculations Eerhart, Faaij & Patel. (Eerhart et al. 2012)
5-HMF (dehydration)	Own Model	Based on industry: Dumesic and Roquette processes. (Chheda et al. 2007)
Xylose production	Modified Ecoinvent 3.3 / Literature	From European wood pulp from via viscose production in Europe. Modified literature data from Shen et al. (2010) based on a European production.
Xylitol (hydrogenation)	Own Model	Based on standard industrial process described in literature.
TERRA process		
TERRA Reactor	Own Model	Primary data collected from Avantium.
Recovery and upgrading of MEG and FDCA	Own Model	Based on process simulation.
Wastewater treatment	Ecoinvent 3.3	Average Europe without Switzerland.
Electricity	Ecoinvent 3.3	Dutch electricity production, from grid.
Steam	Ecoinvent 3.3	Steam production, as energy carrier, in chemical industry [RER]
Polymerization		
PEF polymerization	Ecoinvent 3.3	Europe. Modified Based on PET polymerization.

The TERRA technology is based on an experimental and conceptual design. Process modelling and simulation were carried out in ASPEN©Plus and Excel. Table 3.2 provides a summary of the main data sources including the synthesis routes and the background infrastructure (electricity, heat and steam). This section explains feedstock production (for both 5-HMF and xylitol), the conceptual design of the TERRA process and the polymerisation step.

Feedstock supply

Raw material acquisition includes biomass production, transportation and the processing steps to obtain 5-HMF and xylitol - the two raw ingredients fed into the TERRA reactor. Production of 5-HMF is based on corn, xylitol is based on lignocellulosic biomass. First and second generation biomass feedstock rise to different challenges (see Discussion section). Assessment of xylitol involved high uncertainties regarding xylose production and xylitol conversion. Details on feedstock(s) can be found in next sections, and Supplementary S3.1.

5-HMF (hydroxymethylfurfural)

5-HMF production steps included corn cultivation, glucose processing and fructose dehydration. Corn cultivation is assumed to take place in Europe. The LCA included corn harvesting, transportation to the Netherlands (assuming a transportation distance of 850 km by truck) and wet-milling. Corn starch is further converted into sugars (dextrose or glucose) via enzymatic hydrolysis (Tsiropoulos et al. 2013). In order to obtain fructose (90% High Fructose Corn Syrup, HFCS-90), the glucose stream goes through isomerization, refining and evaporation stages (Vink and Davies 2015). Because of limited data availability, the corn sweetener refining is solely based on its most energy intensive step: evaporation of water after isomerization and separation (Eerhart et al. 2012). 5-HMF can be obtained by selective dehydration of fructose/HFCS-90 (HFCS 90% fructose). 5-HMF is not a bulk chemical and therefore LCA data in literature is scarce. Hence, dehydration of 5-HMF is based on a process described by Roquette and Dumesic (Chheda et al. 2007), excluding phase separation and production purification because of limited data availability. Table 3.3 gives a summary of 5-HMF process data.

Xylitol

Xylitol can be processed via hydrogenation of xylose, isolated from xylan-rich biomass. There is little known about the industrial xylose production in the public domain. Xylose can be synthesized by sulphuric acid hydrolysis (TSAH) from lignocellulosic material. However, because this process demands high acid and water input and is regarded as energy intensive, it is not conceived viable for our model (Zhang et al. 2014).

Alternatively, xylose can be produced as a by-product of viscose production (Shen et al. 2010). In viscose production, xylose is recovered from the C5 fraction of the wood pulping process using a patented technology (see the "Danisco process" in Figure 3.2). To our knowledge, this is so far the largest commercial scale xylose production.

Table 3.3: Summary of data and intermediate results on sub-processes for the baseline analysis, from corn cultivation (cradle) to 5-HMF, per kg PEF (as the FU)

Baseline	**NREU (MJ)***	**GHG emissions***	**Eutrophication****	**Acidification****	**Land use****
		(kg CO2 eq.)	**(g PO_4^{3-} eq.)**	**(g SO_2 eq.)**	**(kg C deficit)**
Total glucose production (including corn cultivation, wet milling and starch to glucose conversion)	8.5	0.88	0.157 [2]	7.08 [2]	1.09 [2]
From glucose to fructose [1]	5.65	0.23	<0.001	<0.1	<0.001
Dehydration of fructose to 5-HMF [2]	1.52	0.04	<0.001	<0.1	<0.001
Cradle to factory gate 5-HMF production	13.69	1.14	0.16	7.1	1.1

[1] results from own model using Vink and Davies (Vink and Davies 2015), and Ecoinvent 3.3 as the background data, see the text; [2] Own model based on Chheda et al., (Chheda et al. 2007), see the text

* NREU en GHG emissions is based on values proposed by Tsiropoulos et al., (Tsiropoulos et al. 2013) based on sub-division: 6.9 MJ/kg glucose.

** Baseline impacts on eutrophication, acidification and land use are based on corn cultivation from Ecoinvent 'Maize, at farm, France'.

Four viscose LCI/LCAs reported in literature were compared: viscose from Ecoinvent (version 3.3, based on generic technology), Viscose Asia, Viscose Austria and Modal Austria. The latter three are based on the specific production from Lenzing AG, one of the largest viscose producers in the world (Shen et al. 2010). Supplementary S3.1 covers the details of the environmental impact of these four viscose LCA datasets. The environmental impact of xylose as a by-product of viscose is determined by economic allocation. Allocation based on the physical relationship of energy/exergy does not apply because both products (viscose and xylose) are not energy products. System expansion is also not applicable because xylose is always made from processing wood (Shen et al. 2010). Based on the prices over the last ten years (2008-2018), on average the economic allocation factor for xylose is found to be 4%. The sensitivity of the allocation factors for xylose is examined in the Discussion section. Table 3.4 presents the environmental impact of 1 kg of xylose from viscose production.

Currently there is no LCA data available on the conversion process of xylose into xylitol within the public domain. Therefore, the LCA includes a simplified process based on a preliminary hydrogenation step of xylose to xylitol described by a patent of Melaja & Hamalainen (Melaja & Hamalainen 1975). Excluded were the fractionation and crystallization steps because the purity requirement is presumed not to be as high as for food-grade products.

Table 3.4: Environmental impacts allocated to 1 kg xylose based on wood pulp and viscose production using an allocation factor of 4%.

	NREU (MJ/kg xylose)	**GHG emissions (kg CO_2 eq./ kg xylose)**	**Eutrophication (g PO_4^{3-} eq.)**	**Acidification (g SO_2 eq.)**	**Land use (kg C deficit)**
Impact of Xylose from viscose production	8.5* (up to 40)**	-0.11 * (up to 1.7)**	0.191***	27***	1.22***

* Data source Shen et al. (Shen et al. 2010), lower value: Lenzing Austria Viscose is used as the baseline, ** the upper value represents the allocated impact using Lenzing Viscose Asia(Shen et al. 2010). *** Based on Ecoinvent (v3.3) process "Viscose fibre {GLO} viscose production".
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The TERRA Process

The TERRA process is subdivided into three sections (see Figure 3.2b): (1) electrochemical reactor, (2) MEG separation and purification and (3) 2,5-FDCA separation and purification. A detailed description of separation and purification steps is given in Textbox 1. The TERRA reactor is further discussed in the next section and a short process overview is given. The process design is based on experimental and theoretical data for a continuous production.

TERRA Reactor

The electrochemical TERRA reactor supports the simultaneous conversion of xylitol into MEG and HMF into FDCA, separated by a porous membrane. The electrochemical reactor follows Eq. (1a) and Eq (1b) in the cathodic and anodic compartment respectively, with electrons flowing to the cathode, and a global cell reaction of Eq. (1c):

The cathodic half reaction being: (1a)

$$C_5H_{10}O_5\text{ (XYL)} + 3H_2O + 4e^- \rightarrow C_2H_6O_2\text{ (EG)} + C_3H_8O_2\text{ (PG)} + 4OH^-$$

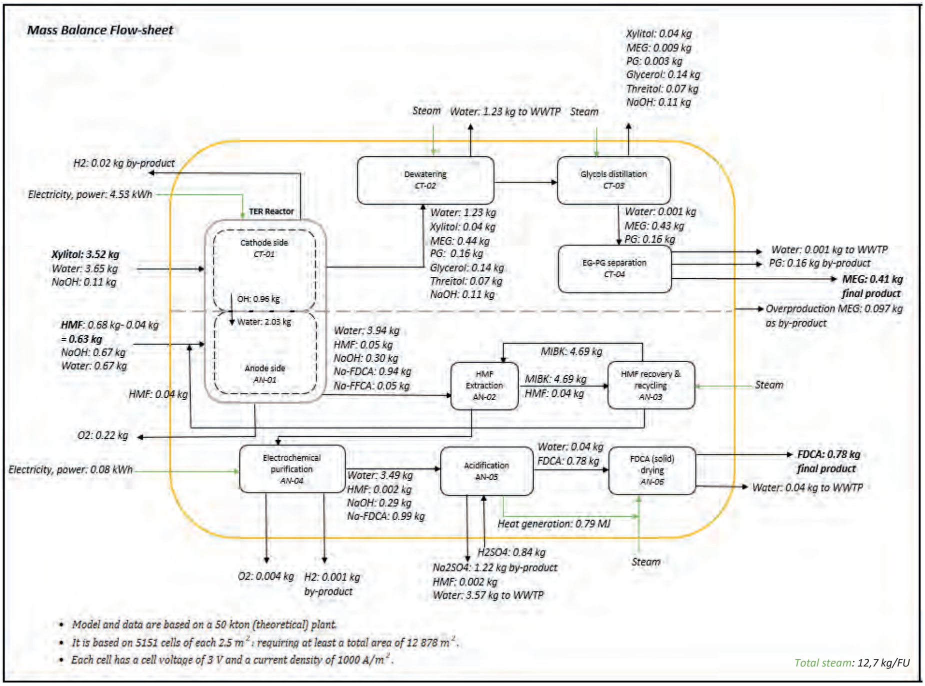
And the anodic half reaction: (1b)

$$C_6H_6O_3\text{ (HMF)} + 6OH^- \rightarrow C_6H_4O_5\text{ (FDCA)} + 4H_2O + 6e^-$$

Giving a global cell reaction of: (1c)

$$2HMF + 3XYL + H_2O \rightarrow 2FDCA + 3MEG + 3PG$$

The TERRA reactor simulation model is based on a 50 kilo metric tonne (kt) (theoretical) plant. A detailed mass balance flow-sheet is given in Figure 3.3. The pilot design is based on cells of 2.5m^2 with a total of 5151 cells requiring an area of at least 12,878m^2. The 50 kton/year pilot plant based on 8000 operating hours. Each cell has a cell voltage of 3V and a current density of 1000 A/m^2. FDCA and MEG production are each based on a faradaic yield of 50%.



- *Model and data are based on a 50 kton (theoretical) plant.*
- *It is based on 5151 cells of each 2.5 m^2: requiring at least a total area of 12 878 m^2.*
- *Each cell has a cell voltage of 3 V and a current density of 1000 A/m^2.*

Figure 3.3: mass balance flow sheet of the TERRA process, all inputs and outputs are normalized to 1 kg of PEF. Green arrows represent energy-related streams (with a total of 12.7 kg/FU). See abbreviations explained in Figure 3.2

Textbox 1: Separation and purification steps TERRA process

Cathode-side: recovery of MEG

There are three major steps to purify MEG from the cathode effluent stream (see Figure 3):

Dewatering. The outflow at the cathode effluent contains much water (56 wt%). The dewatering step is based on heat (in the form of steam) needed to evaporate water, including heat transfer and boiler efficiency of both 70%. All MEG recovery unit-processes assume a multi-effect evaporation unit, which means a high steam efficiency (1 kg of steam to evaporate 2.5 kg water). In the baseline scenario the water is removed to a European wastewater treatment plant before being discharged into the environment.

Glycol distillation. During this step MEG and PG are recovered from a polyol mixture containing xylitol, glycerol, threithol and the electrolyte sodium hydroxide. The remaining polyol bottom fraction is a waste stream as it has a very low concentration of organic matter and cannot be further recovered in the current design. The heat requirement for the distillation is obtained from industrial steam.

EG-PG separation. The last recovery step is the separation of MEG and PG. PG is a valuable by-product and is treated by system expansion and avoids the production of PG produced from fossil fuel resources. Polymerization of PEF requires a fixed ratio between MEG and FDCA, which is 1:2.5 (by weight). Excess of MEG is therefore also modelled by system expansion by substitution and avoids the production of EG produced from fossil fuels.

Anode side: recovery ofFDCAThere are four major steps to purify 2,5-FDCA from the anode side (see Figure 3.3):

HMF extraction & recovery. This step is based on liquid- liquid extraction to extract the excess HMF. It is assumed that the MIBK solvent is constantly recycled and re-used. Solvent losses are negligible. About 90% (by weight) of the excess HMF can be extracted and used again in the TERRA reactor (anodic side). Steam is required to generate heat for solvent recovery.

Electrochemical purification. The remaining HMF and Na- FFCA impurities are selectively converted into Na-FDCA by electrochemical purification. H_2 evolution during this step is treated by system expansion by substitution by avoiding industrial H_2 produced from steam reforming of natural gas. The outflow of this process contains mainly Na-FDCA (in water) and traces of HMF and NaOH.

Acidification. This step recovers FDCA from Na_2-FDCA by adding H_2SO_4 (0.84 kg H_2SO_4/kg PEF) which also leads to 1.22 kg H_2SO_4/kg PEF as a by-product which is modelled in LCA by system expansion by substitution. During this step, FDCA precipitates and is removed by filtration. The water goes through a wastewater treatment plant. The acidification step leads to large quantities of waste water: 3.57 kg waste water/kg PEF. A large amount of heat is generated upon acidification which is directly re-used during the next step of drying, assuming a heat transfer efficiency of 70%.

FDCA (solid) drying. The remaining water (5 wt%) in FDCA is removed in this step. The input is steam to evaporate water, partly covered by heat (0.8 MJ) generated in the acidification step.

Overview of process design

5-HMF and xylitol are continuously fed into the electrochemical rector. MEG is obtained in the cathodic compartment. The mono sodium salt of FDCA (Na-FDCA) in the anodic compartment. The two compartments are separated by a membrane. Porous metallic electro-catalysts drive the reactions. At the cathode, the major by-products are hydrogen,1,2-propylene glycol, threitol and glycerol. In order to obtain purified MEG, from the effluents (glycols/polyols stream) of the cathode water is first removed through a sequence of evaporation columns. Next, the glycol fraction is separated from the heavy polyols via distillation. During the last step, MEG is separated from 1,2- PG (1,2-propylene glycol) with a purity of 99.8%.

In the effluents from the anode, the excess 5-HMF is removed from the stream containing Na-FDCA through liquid-liquid extraction via MIBK (methyl isobutyl ketone) solvent. The by-products at the anode are oxygen and the sodium salt of formyl furancarboxylic acid (Na-FFCA). In the next step, the HMF-free stream is sent to an electrochemical purification reactor, where the aldehyde impurity is selectively oxidized into the sodium salt of FDCA. After the electrochemical treatment, Na-FDCA is acidified with H2SO4, converting the salt into 2,5-FDCA and generating Na2SO4 as by-product. Upon acidification, 2,5-FDCA precipitates out and can be removed from the aqueous stream through filtration. The purified 2,5- FDCA solid is washed with water in washing drums to remove remaining impurities and finally it is sent to a dryer for complete removal of water.

PEF polymerization

Polymerization of PEF occurs via nFDCA + nEG → PEF + (2n-1)H_2O. The current stage of development makes it difficult to estimate the required energy for polymerization. Research suggests a lower temperature and a faster operation time compared to conventional PET polymerization (Ma et al. 2012). However, because of insufficient data a more conservative method was chosen: PEF polymerization is estimated by assuming similar energy requirements as for the petrochemical polymerization of PET. Ecoinvent data (v3.3) on PET polymerization was modified to use in the baseline (see Table 3.2). Amorphous PET polymerization can be divided into two unit-processes: (1) esterification and (2) poly-condensation (PlasticsEurope 2017). For polymerization, a molar ratio of 1:1 FDCA:MEG is applied.

Multifunctionality

According to the ISO procedure (ISO 14040: 2006 and ISO 14044:2006), allocation should be avoided by subdivision or system expansion. If system expansion or subdivision is not applicable, allocation by partitioning is applied. In this study, we follow the ISO allocation procedure for multi-output processes. Whenever possible, system expansion by substitution is prioritised.

From the TERRA reactor, we applied system expansion by substitution for the output flows of H_2, Na_2SO_4, PG and the surplus of MEG; these by-products were modelled as avoided burdens. Specifically, the avoided processes are, based on Ecoinvent 3.3 data and PlasticsEurope data:

- H_2 based on hydrogen by steam reforming (Hydrogen (reformer) E, industrial data 2.0),
- Na_2SO_4 based on global production by three production routes: from natural occurring Na_2SO_4, as by-product of other processes and from industrial production (Mannheim process, sodium sulphate | market for | APOS, U),
- PG based on oxidation of propylene oxide (global market, Propylene glycol, liquid | market for propylene glycol | APOS, U).
- The surplus of EG is based on oxidation of ethylene oxide (global market, ethylene glycol | market for | APOS, U).

Additionally, three allocation methods were tested. Economic, mass and calorific value based allocation were adopted to understand the sensitivity of the results towards allocation strategy.

Biogenic carbon removal

In this study, biogenic carbon removed from the atmosphere during biomass cultivation is accounted for. The embedded biogenic carbon is calculated based on the molecular formulation of the polymer, which leads to 1.96 kg CO2 eq./kg PEF. This approach maintains carbon balances by keeping track of the physical carbon flow in each substance flow within the cradle-to-gate boundaries. The approach is in line with e.g. the European Commission's Product Environmental Footprint, which states that bio-based carbon contained in products shall be deducted when calculating GHG emissions

(European Commission 2009; Saouter E et al. 2013), and with PAS 2050 on carbon footprints, which states that carbon storage in products should be calculated based on the amount of carbon contained in the product (PAS2050 2011). It has also been applied in other LCAs of bio-based materials (Cok et al. 2014; Kim and Dale 2008; Tsiropoulos et al. 2015; Broeren et al. 2017; Vink and Davies 2015). Note that carbon removed from the atmosphere can be emitted again if it is fully oxidised (as CO2) during the product's end-of-life which is outside the scope of this paper. In addition, emissions caused by (indirect) land use change are not included. The results of GHG emissions (i.e. Climate change impact) are reported for both with biogenic carbon removals (the default) and also without (expressed as 'Gross GHG emissions').

3.4. Results

The cradle-to-gate environmental impacts of TERRA PEF for the five selected environmental impact categories are presented in Table 3.5. Figure 3.4 shows the breakdown in life cycle stages and key processes. The TERRA process itself (both 2,5-FDCA and MEG production) is the most important contributor for all categories (63-88% of the impacts) except for land use, which is dominated by the agriculture phase attributed to the feedstock production (xylitol and 5-HMF). Land uses of corn production and wood production account for 65% and 30% of the total land use impact, respectively. In the other four impact categories, the feedstock production accounts for 10-35% of the total impacts. The production of 5-HMF contributes 17% and xylitol 13% to the total NREU impact. For acidification, the impact contributed by feedstock production is 34%: 5-HMF production accounts for 18% and xylitol production for 16%. The environmental impacts of the polymerisation step are insignificant (<5% of the total impacts). Since the TERRA process alone takes the lion's share of the impacts in the four categories, in next sections the detailed interpretations of the NREU, the GHG emissions, the acidification and the eutrophication are presented.

Table 3.5: Cradle-to-factory gate environmental impact of 1 kg of TERRA PEF

Impact category	Unit	Impact
Climate change of which:	kg CO_2 eq	4.2
- Biogenic carbon removals		-1.9
- Gross GHG emissions w/o biogenic carbon removals		6.1
Non-renewable energy use	MJ	98
Freshwater eutrophication	g PO_4^{3-} eq.	7.5
Terrestrial acidification	g SO_2 eq.	39.8
Land use	kg C deficit	15.5

NREU and GHG emission of the TERRA process

The results on 2,5-FDCA and MEG processing can be separately evaluated. The total electricity requirement of the TERRA reactor is partitioned between the cathodic and anodic side, based on the total output mass of the main products. Overall, a large part of the impacts is caused by the electrochemical reactor's electricity demand. However, 2,5-FDCA production contributes to more than half of the impacts (see Figure 3.4). Downstream purification of 2,5-FDCA involves sophisticated design and requires multiple steps, nonetheless, electricity use at the anode side dominates the impact: it accounts for nearly 70% of the NREU or 60% of the GHG emissions of 2,5-FDCA production. This is largely caused by a larger allocation factor, 66% is assigned to 2,5-FDCA, based on mass allocation. Allocation based on the physical relationship of energy/exergy does not apply here because both products are not energy products. The second biggest impact for 2,5-FDCA processing originates from the acidification step, it contributes 7% to NREU and 13% to GHG emissions impact. This impact is mainly caused by wastewater treatment (66% for NREU and 58% for GHG emissions).

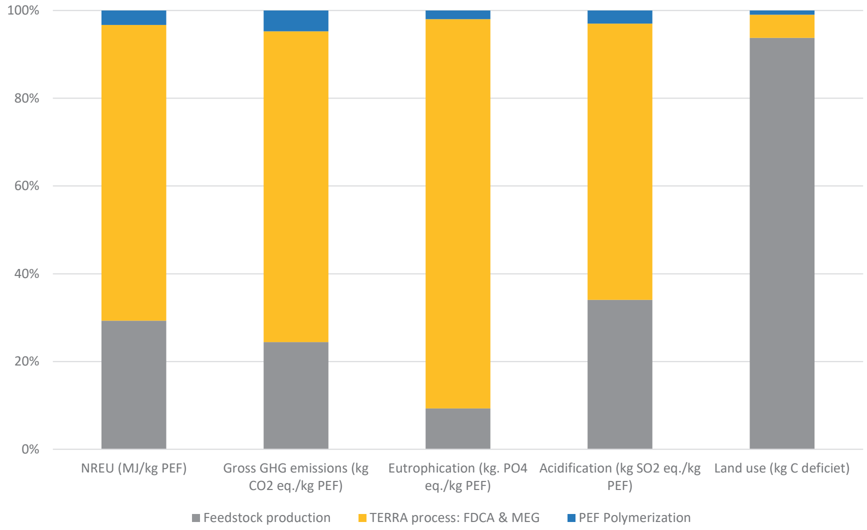


Figure 3.4: Breakdown of Cradle-to-factory gate environmental impacts of 1 kg TERRA PEF polymer by production phases. "Gross GHG emissions" do not take into account biogenic carbon removal. "Net GHG emissions", in which the biogenic carbon removals are accounted for, can be found in Table 3.5.

The impact of MEG production shows a similar pattern (see Figure 3.5): 57% of the NREU is attributed to the reactor itself, dominated by its electricity use. A substantial part (65%) of the impact is attributed to the heat requirements during recovery (dewatering 33% & glycol distillation 32%). Likewise, of the total gross GHG emissions related to MEG production, 74% results from the recovery steps (glycol distillation 50% and dewatering 24%, see Figure 3.5c). Nearly half of the GHG emissions from the distillation process originate from steam production, which is based on combustion of natural gas. About 43% of the GHG emissions of the distillation step are caused by waste treatments (both waste water and hazardous waste incineration, see Figure 3.5c). In terms of technological improvements, a higher selectivity towards EG/PG and therefore fewer by-products, could potentially mean a lower impact from the glycol distillation step. For example, by applying another electrode or improved reaction conditions within the process. Furthermore, increasing reactant concentration and reducing the amount of water in the system could positively impact the results.

Eutrophication and acidification of the TERRA process

The TERRA process plays a key role in the eutrophication (88%) and acidification (63%) impact of PEF (see Figure 3.4). For both 2,5-FCDA and MEG production, wastewater treatments (WWT) during the purification and recovery phases contribute most substantially. WWTs account for 60% of the total cradle-to-factory gate eutrophication impact and for 24% to total acidification impact. In the case of acidification, the impact mainly originates from corn cultivation (ammonia as fertiliser), heat production from coal and sulfur dioxide production (for xylose production).

Modelling wastewater treatment was based on background data from Ecoinvent, assuming an average Europe WWT plant. However, in order to treat such a large quantity of wastewater (approx. 5 kg wastewater/kg PEF), an on-site WWT facility built at the production site can be expected. This could lead to reduced impacts since wastewater from the TERRA process contains less complexed organic compounds compared to municipal wastewater. For a TRL 2-3 technology, a detailed design of an on-site WWT plant is beyond the scope. Nevertheless, some possibilities of process optimisation are explored in the Discussion Section.

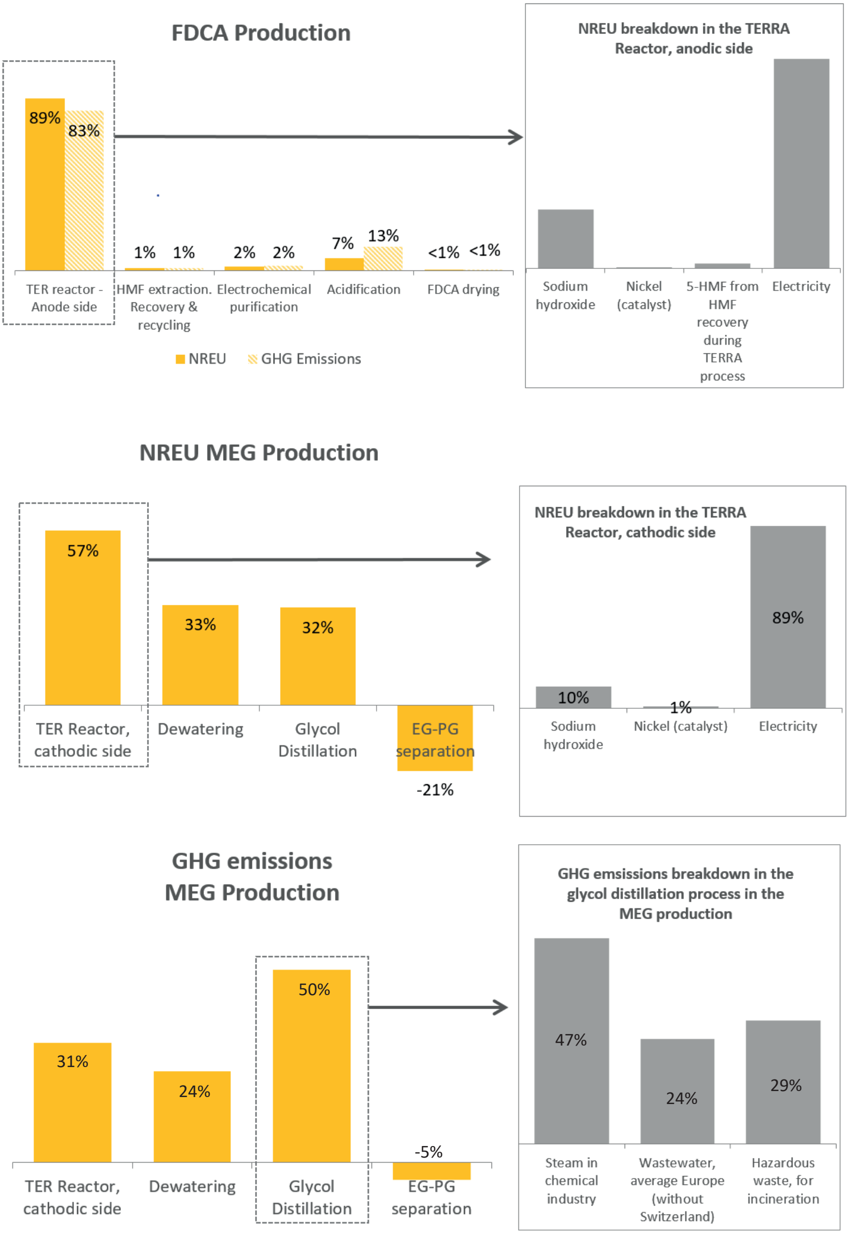


Figure 3.5 Breakdown of NREU and GHG emissions of FDCA and MEG in the TERRA reactor (allocation based on the mass outputs). 5a (top): Breakdown for FDCA production in the TERRA process, on the left: contribution in percentage by the major processes; on the right: breakdown NREU of anodic side of TERRA reactor (the breakdown of GHG emissions shows the similar pattern). 5b (middle): NREU of MEG production in the TERRA process. Due to system expansion of PG, the process of EG-PG separation receives a credit. 5c (bottom): GHG emissions of MEG production in the TERRA process.

3.5. Discussion

Future scenarios: renewable electricity

One of the core motivations of developing electrochemical process' is its accessibility to renewable electricity in the future. Within this study, future scenarios were developed to evaluate the environmental impact of the future TERRA PEF, increasing the share of renewable electricity in our electricity mix. Four different future electricity scenarios were based on the ambition of the 2019 Dutch Climate Agreement (Rijksoverheid 2019) (see Supplementary Table S3.1 for detailed scenarios). Two scenarios were developed for both near-term future 2030 and medium-term future 2050 (European Commission 2018; Capros et al. 2013; European Commission 2016; Government of the Netherlands 2016; van den Hoven and Jacob 2013). The selection of these years were based on (1) the full development of a low level technology to commercial scale, which will take at least 10 years, and (2) the milestones set by many climate policies and laws for 2030 and 2050 (Rijksoverheid 2019).

The future electricity scenarios were directly applied to the electricity consumption of the TERRA reactor and indirectly to the electricity consumption for the production of NaOH. NaOH is the second largest NREU contributor to the TERRA reactor (Figure 3.5). The assumptions of fuel mix and the updated LCA results are shown in Table 3.6. By 2050, the entire electricity grid of the Netherlands would become carbon neutral. As a result, the impact of NREU of TERRA PEF would decrease to 46 MJ/kg PEF, representing a reduction of 53%. The impact of GHG emissions (including biogenic carbon removal) would decrease to 1.68 kg CO2 eq., representing a total reduction of 60%.

Alternative allocation

Allocation strategies highly influence the results, especially in early-phase assessments. There are many uncertainties within the process and regarding products which are not embedded in the market yet. The baseline scenario adopted system expansion by substitution for H_2, Na_2SO_4, PG (propylene glycol) and the excess of EG (ethylene glycol) from the TERRA reactor. Approximately 28% of the total impact of the TERRA PEF (at the point of substitution) can be avoided by avoided burdens. Alternatively, if mass allocation is applied, it results in a substantial decrease of NREU impact by 39%. This decrease is mainly the result of the relatively high co-production contribution of sodium sulphate. Per kg of PEF 1.22 kg of Na_2SO_4 is produced. Similarly, applying economic allocation results in an increase of NREU by 20%, mainly because FDCA is very valuable. Another allocation strategy can be applied to deal with side streams originally treated as waste in the baseline. Allocation by calorific values leads to a slight decrease of NREU by 6%. This strategy assumes waste within the TERRA process to be burned, including extra by-products (the polyol side stream with organic contamination, discussed in Textbox 1).

Figure 3.6 provides a summarised overview of the variation of the cradle-to-factory gate NREU of 1 kg TERRA PEF, resulting from future electricity scenarios, a different source of xylose with higher impact, and various allocation approaches adopted for the by-products from the TERRA process. It can be concluded that regardless of the data uncertainty and different choices of allocation approaches, the access to renewable electricity in the future is key to a successful sustainable innovation.

Model uncertainties and limitations conceptual chain design

Biomass feedstock

The feedstock supply is a combination of first and second generation biomass. The use of first generation biomass is an important strategy in bio-plastics but has the drawback of being in competition with our food and feed system (Lambert and Wagner 2017). Xylitol and xylose were used as a model compound to represent the mixed hemicellulose sugars. Lignocellulosic biomass has the potential of lowering GHG emissions and does not directly compete with food production (Patel et al. 2016).

Table 3.6; Cradle to factory gate NREU and GHG emissions of TERRA PEF based on four future electricity scenarios in the Netherlands versus the 2018 baseline.

	2018 Baseline	**2030 low ren: 23.5%**	**2030 high ren: 43.5%**	**2050 ren: 86%**	**2050 ren: 100%**
Total renewable share	13.6%	23.5%	43.5%	86%	100%
Emission factor (kg CO_2 eq./kWh)	*0.59*	*0.54*	*0.334*	*0.0275*	*0.0014*
NREU of TERRA PEF (MJ/kg PEF) (reduction compared to the baseline)	98	83 (↓ 15%)	70 (↓ 28%)	**59 MJ/kg (↓ 39%)**	**46 MJ/kg (↓ 53%)**
Gross GHG emissions of TERRA PEF (kg CO_2 eq./kg PEF)	6.1	6.0 (↓ 2.3%)	5.7 (↓ 6.2%)	**4.5 (↓ 26%)**	**4.0 (↓ 34%)**
Net GHG emissions of TERRA PEF (kg CO_2eq./kg PEF), with biogenic carbon removal	4.2	4.0 (↓ 3.5%)	3.8 (↓ 8.8%)	**2.7 (↓ 37%)**	**1.7 (↓ 60%)**

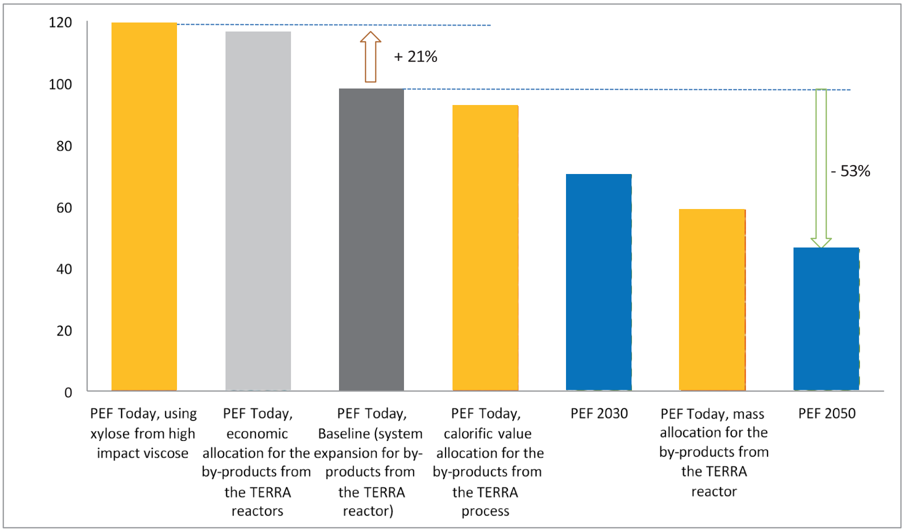


Figure 3.6; Results on cradle-to-factory gate NREU (MJ/kg) of TERRA PEF based on different allocation approaches, future electricity mixes and a higher impact sourced xylose.

In this study, the uncertainty of the impact of xylose is strongly influenced by the type of viscose production. Ecoinvent viscose production is modelled based on global average viscose process, whereas Viscose Austria (used in the baseline) is based on a state-of-the-art viscose plant including an integrated pulp mill. It is highly optimized in terms of energy and material optimisation (Shen et al. 2010). Applying 4% economic allocation on viscose production using the Ecoinvent viscose dataset would result in a NREU of 27 MJ/kg xylose, a threefold higher impact compared to 8.5 MJ/kg xylose applied in the baseline. This will in turn lead to a significant increase of NREU by 21% for the TERRA PEF. Therefore, the source and production process of viscose is a sensitive assumption for the environmental impact of TERRA PEF.

Moreover, the sensitivity of the economic allocation factors was analysed. Based on the most recent available prices in 2018, a slightly higher allocation factor is obtained (6%), which leads to a slightly higher impact of xylose, namely, 12.95 MJ/kg xylose (vs. 8.5 MJ/kg xylose based on 4% allocation factor; see figure S3.1). However, the price fluctuations in xylose and viscose have insignificant effect on the total impact of TERRA PEF (e.g. less than 5% increase in NREU). It is concluded that the recent price fluctuation of xylose is not a sensitive parameter for the TERRA PEF.

Xylitol itself is not an ideal feedstock for large scale bulk chemical production. It is a valuable chemical from an economical point of view (Wright 2017). The baseline – xylose as a by-product of viscose production – is a well-considered choice but at the moment there is only a dominant market of xylose for high purity xylitol (used for e.g. sweetener in toothpaste). Xylose-xylitol was used as a model to represent mixed hemicellulose sugars but is unlikely to be used as an economically attractive feedstock. However, if a large scale lignocellulose-to-glucose technology could be developed and commercialized, a mixed C5/C6 sugar (side) stream from the hemicellulose fraction could be used for to produce MEG. The TERRA project has provided the proof-of-concept for the technical feasibility of the use of the C5/6 sugars in an electrochemical reactor.

TERRA technology

Potential environmental hotspots at this point of stage are (1) its electricity-use, which is one of the main contributors, (2) the complexity of purification and recovery steps, even though the TERRA cell simultaneously produces the two main products, and (3) the fossil-based heat used in the recovery and purification steps. In contrast, a powerful potential environmental advantage is the significant reduction in environmental impact when renewable electricity is used. Another potential advantage is the use of electrochemical cells within the chemical industry, and in this case, to produce the monomers of the new polymer PEF. From the work that has been done, recommendations to decrease environmental impact would be to (1) increase selectivity of the electrochemical reactor in order to reduce the amount of by-products, (2) search for clean and affordable feedstock based on lignocellulosic biomass, and (3) reduce the amount of wastewater by reducing the total water required in the process or by recycling water in the system.

Carrying out an ex-ante LCA has given methodological insights. First of all, the use of TRLs to define an ex-ante LCA is very helpful and practical, and makes it easier to compare ex-ante LCAs in the future. The use of process design and simulation software to go from lab-scale to a theoretical pilot-scale is highly recommended in an early-stage assessment. In addition, it is recommended to apply different allocation strategies and sensitivity analyses. Modelling second generation biomass can involve many uncertainties and asks for creative solutions. At last, besides GHG emissions and NREU impact, this study once again stresses the need to include more impact categories. Apart from the five categories included in the study, at least assessing its water footprint would be recommended in future research.

Quantifying process synergies and changes realising a full-scale TRL9 technology were beyond the scope of this study. However, these are important, especially from TRL 5/6 onwards (Piccinno et al. 2016). Process synergies influencing the environmental impact of the TERRA process would be 1) re-use of heat, 2) treatment of waste, 3) dealing with the generation of by-products, 4) treatment of water and 5) recovery of solvents (van der Giesen et al. 2020a). The re-use of heat is only marginally included in the conceptual process design, same applies to the treatment of waste. Within the baseline, four by-products (discussed in 4.2) were substituted resulting in a total NREU avoidance of 28% and all other by-products were treated as waste. However, in a sensitivity analysis the organic by-products after glycol distillation were burned with heat recovery. This led to a slight decrease of NREU by 6%. In addition, regarding the baseline scenario, all wastewater is treated and discharged to the environment, whereas in an industrial application water could be treated onsite for internal re-use. A sensitivity analysis was carried out on the environmental impact of wastewater treatment. An alternative scenario was modelled based on literature claiming to successfully reduce wastewater by 90%. Assuming 90% recycling of wastewater - excluding all needed extra steps, energy and capital costs for treatment - a theoretical maximum reduction of 89% for eutrophication impact and a reduced impact of 33% for acidification results.

Solvent recovery is an important factor in industrial chemical processes (Montazeri et al. 2016). Within the TERRA process, MIBK solvents were used for HMF extraction and recovery. In our model, the solvent separation and recycling is not included because of limited data availability. Nonetheless, the recyclability of the solvent is as a key issue (Turgis et al. 2018; McNeff et al. 2010). Furthermore, although scientific literature suggests successful liquid-liquid extraction of HMF using a water/DMSO and MIBK/2-butanol biphasic system, separating MIBK, 2-butanol, DMSO and HMF is not yet economically feasible (Teong et al. 2014). Further research should be carried out to apply this method successfully. In addition, there is also the issue of energy-intensiveness when using a high-boiling point solvent such as MIBK (Román-Leshkov et al. 2006). Nonetheless, separation of HMF from the product mixture is difficult, meaning, even though HMF would not be recovered from the organic solvent phase, it would be a better solution than to separate it via another more complicated route. Above mentioned is also an illustration of the uncertainties an early-stage LCA has to deal with.

Comparing TERRA PEF with other reported LCA for PEF

Very little research is done on the environmental impact of PEF, even though PEF has gained much interest and is regarded as a very promising polymer. There are different routes to produce the FDCA and EG building-blocks (Hwang et al. 2020), the present study is the first to report on the environmental impact of an electrochemical route. Eerhart et al. (2012) reported a cradle-to-factory gate LCA of a partly bio-based PEF obtained from 2,5-FDCA sourced from first generation biomass (corn) and fossil and bio-based based MEG. The study analysed a chemical conversion of corn-based fructose into Furanics to produce hydroxymethylfurfural (HMF) and the air oxidation of HMF to FDCA (Eerhart et al. 2012). Just recently a LCA report of the Joint Research Center (EU science hub)(Nessi et al. 2020) was published for a cradle-to-grave impact of 100% bio-based PEF. It was also an early-stage assessment. It assumed sugarcane for bio-MEG production and a mix of maize, wheat and potatoes for FDCA production. Conversion of HMF into FDCA was based on an oxidation process of p-xylene conversion in PTA production (Nessi et al. 2020). Figure 3.7 shows the comparison of the LCA results from the three studies, including the present one.

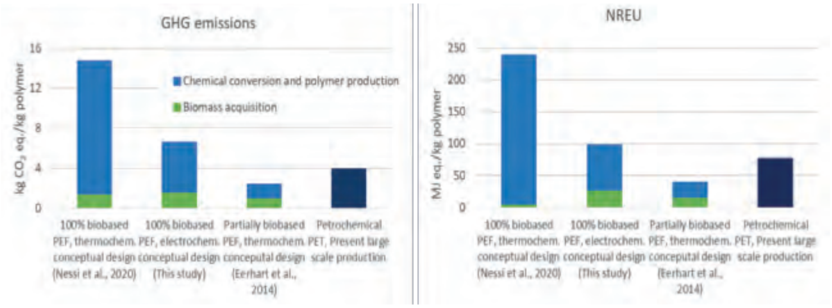


Figure 3.7: Cradle-to-factory gate results on NREU and GHG emissions of 1 kg PEF reported in different LCA studies (Nessi et al. 2020; Eerhart et al. 2012), this study and compared with those of PET (PlasticsEurope 2017; Shen et al. 2012). Impact from Nessi et al. (2020) was taken up to cradle-to-gate to harmonize results. To further harmonize the different results on PEF, the net GHG emissions are displayed, including the carbon credits from biogenic carbon storage.

The three studies differ substantially in terms of their LCA results. Both Eerhart et al. (2012) and this study reported the significant contribution from biomass production, whereas the JRC report identified the thermochemical conversion to play a dominate role (see Figure 3.7). This leads to a mixed conclusion when PEF based on the thermochemical route is compared with PET. PEF could offer nearly 50% impact reduction based on Eerhart et al. (2012), or could lead to a three-fold increase in environmental impacts according to the JRC report (Nessi et al. 2020). Eerhart et al. 2012) included a CHP for onsite power and heat. The CHP for burning humins, a process residue, made the process self-sufficient in terms of energy, and thus significantly reducing PEF's primary energy requirements.

The impacts of the electrochemical PEF identified by this study land somewhere in between (see Figure 3.7), with a somewhat higher impact compared to the current petrochemical PET, but substantially lower than the impacts reported by the JRC report (which is also an ex-ante LCA). Climate impact of PET and bio-PET (30% bio-based) ranges from 3,9 kg CO2 eq./kg polymer (PET) to 1.9-2.6 kg CO2 eq./kg polymer bio-PET (bio-based MEG made from sugarcane)(Shen et al. 2012; Tsiropoulos et al. 2015). However, on a kilogram basis PET and PEF are not comparable; it has not the same full functionalities such as barrier properties and thermal properties. Although the electrochemical conversion has the advantage of relying on electricity and the cell is highly efficient as it produces simultaneously two products, the downstream purification steps still consume a large amount of heat, similar to many thermochemical processes. Nevertheless, PEF is not a fully commercialised product; it is not yet able to compete with PET, whose production and supply chain have been optimised over many decades. The large differences observed from literature should not be interpreted black and white. These studies should be used to provide directions on future development to reduce the impacts and support responsible innovation.

3.6. Conclusions and recommendations

In this ex-ante LCA, the cradle-to-factory gate environmental impacts of PEF produced via a novel electrochemical process are assessed capturing a TRL2-4 technology from lab-scale proof-of-concept, conceptual design to up-scaled process design. This study has identified the TERRA process including the electrochemical reactor as the most crucial contributor to the environmental impacts. It contributes 63- 88% to four out of five impact categories studied, namely, NREU, GHG emissions, acidification and eutrophication. Biomass acquisition (corn production and forestry) is the most important player for land use impact. Xylitol and HMF productions (including biomass acquisition) account for 10-35% of the total impacts for the other impact categories. The polymerization step has insignificant impact (<5%).

As electrification is an important strategy to decarbonize the chemical industry, the assessment of the TERRA process demonstrated a great potential when a carbon neutral future can be realised. The study projected a substantially reduced overall impact (by 53% for NREU and up to 60% for GHG emissions) in the Netherlands by 2050 if the climate neutral targets of the power sector are realised. As a proof-of-concept, the electrochemical reactor could benefit greatly from a transition towards renewable electricity in the future.

Different allocation strategies, especially for the impact of xylose/xylitol, affect the LCA results significantly. However, they do not change the overall conclusions on the identified environmental hotspots (i.e. electricity use). In this study, xylitol was used as a model compound to approximate the mixed hemicellulose sugars. Shifting toward lignocellulosic biomass to produce glucose could replace corn feedstock for

2,5-FDCA production and a mixed C5/C6 sugar (side) stream from the hemicellulose fraction could be used for hydrogenation-hydrogenolysis to produce MEG. Future research should focus on clean and affordable hemicellulose sugars to replace xylitol.

Based on this early-stage assessment, recommendations can be made for future development of the TERRA process. Future development, beyond TRL 4, should pay attention to 1) increasing selectivity of the electrochemical reactor in order to reduce the amount of by-products and therefore reduce the energy requirements of downstream separation, 2) searching for clean and affordable feedstock based on lignocellulosic biomass and 3) reducing the amount of wastewater by reducing the total water required in the process, or by recycling water in the system. The latter would not only reduce NREU and GHG emissions, but also significantly decrease the acidification and eutrophication impacts of the future PEF.

Based on the experience gained from this case study, we propose the following principles for assessing bio-based innovation in an early development stage.

1. When an ex-ante LCA for bio-based innovation is conducted, always clearly report the TRLs. It helps to scope the research and makes it possible to compare across different early-stage assessments and to draw lessons in a systematic manner.
2. Simulated process design is proven to be very useful to fill in the data gaps for technologies with TRLs below 5 but higher than 3.
3. Like any scientific study, be transparent about the decisions in the research process. This is particularly important for ex-ante assessment where data uncertainties are often deemed to be high. For new bio-based feedstock (e.g. xylose), there are many challenges due to incomplete data availability.
4. Finally, do include more impact categories next to GHG emissions and energy-use, especially in regard to bio-based products, land use, acidification and eutrophication are important categories to spot on any potential environmental trade-offs.

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4.

Evaluating the environmental sustainability of alternative ways to produce benzene, toluene and xylene

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4.1. Abstract

The petrochemical industry can reduce its environmental impacts by moving from fossil resources to alternative carbon feedstocks. Biomass and plastic waste-based production pathways have recently been developed for benzene, toluene and xylene (BTX). This study evaluates the environmental impacts of these novel BTX pathways at commercial and future (2050) scale, combining traditional life cycle assessment with absolute environmental sustainability assessment using the planetary boundary concept. We show that plastic waste-based BTX has lower environmental impacts than fossil BTX, including a 12% decrease in greenhouse gas (GHG) emissions. Biomass-based BTX shows greater GHG emission reductions (42%), but causes increased freshwater consumption and eutrophication. Towards 2050, GHG emission reductions become 75% and 107% for plastic waste and bio-based production, respectively, compared to current fossil-BTX production. When comparing alternative uses of plastic waste, BTX production has larger climate benefits than waste incineration with energy recovery with a GHG benefit of 1.1 kg CO_2 eq./kg plastic-waste. For biomass (glycerol)-based BTX production, other uses of glycerol are favourable over BTX production. While alternative BTX production pathways can decrease environmental impacts, they still transgress multiple planetary boundaries. Further impact reduction efforts are thus required, such as using other types of (waste) biomass, increasing carbon recycling and abatement of end-of-life emissions.

4.2 Introduction

The petrochemical industry produces primary chemicals that form the building blocks for a wide range of products critical to our daily lives. At the same time, this industry is responsible for 7% of global industrial greenhouse gas (GHG) emissions and accounts for 14% of the world's oil demand (IEA 2018). These impacts relate largely to the use of fossil fuels as carbon feedstock (IEA 2022), consuming more than half of the sector's fossil input (Kätelhön et al. 2019). Therefore, shifting from fossil fuels to other carbon feedstocks, which includes biomass or recycled carbon sources, may reduce the GHG emissions and wider environmental impacts of this industry (Galán-Martín et al. 2021). At the European Union level, this shift has been advocated by several initiatives within the European Green Deal (European Commission 2019), including the chemical strategy (EC 2020) and its link with climate ambition, circularity ambition and overall sustainability of chemicals and materials.

Recently, novel production routes have emerged that use other carbon feedstocks for the aromatic petrochemicals benzene, toluene and xylene (Boulamanti and Moya 2017). These chemicals are known as BTX and account for 30 wt% of current petrochemical production (IEA 2018a). One of these routes is catalytic pyrolysis, a process that utilizes heat to convert feedstock into oil and aromatics in the absence of oxygen (Hulea 2018). Feedstocks that can be used to produce BTX via catalytic pyrolysis are biomass based (Yan and Li 2021; Sudolsky 2019; Ghorbannezhad et al. 2018a), such as woody biomass or sugarcane bagasse (Ghorbannezhad et al. 2018a), or plastic waste-based, such as high-density polyethylene waste (Gracida-Alvarez et al. 2019).

The few life cycle assessments (LCAs) on the environmental impacts of BTX production from alternative carbon feedstocks that have been performed mainly focused on climate change and have resulted in diverging outcomes. For biomass-based BTX, various authors found lower GHG emissions for BTX from pulpwood compared to their fossil products (Sudolsky 2019; Jiang et al. 2020), while BTX from wood chips in combination with CO_2 capture may even result in negative emissions (Yang et al. 2022). In contrast, Lin et al. (2015) found higher GHG emissions for starch-based p-xylene compared to petroleum-based p-xylene. LCA studies that compare alternative treatments of mixed plastic waste showed that chemical recycling, i.e., using plastic waste to produce chemicals, results in lower GHG emissions than incineration with energy recovery (Meys et al. 2020; van der Hulst et al. 2022). This finding points in the direction that BTX production might be a relatively climate beneficial use of mixed plastic waste (Vollmer et al. 2020). How plastic waste-based BTX compares to fossil BTX is, however, still unknown.

A thorough understanding of the wider environmental impacts of BTX production from alternative carbon feedstock and how these routes compare is currently lacking. In the European Union, the chemical strategy for sustainability has promoted a framework for safe and sustainable by design chemicals and materials (Caldeira et al. 2022; EC 2020) recommending to address sustainability by means of LCA, and evaluating environmental impacts applying absolute sustainability concepts (EC 2022). An absolute sustainability assessment can determine if the alternative production routes are sustainable without transgressing the planetary boundaries. The planetary boundaries framework has approximated safe operating spaces for humanity with respect to the functioning of the Earth (Steffen et al. 2015).

The goal of our study is to comprehensively assess the environmental impacts of BTX production from biomass and mixed plastic waste at a projected commercial scale for the current situation (year 2024) and at a future industrial scale (year 2050). We contrast these pathways to BTX production from fossil fuels. A prospective LCA was carried out employing two impact assessment methods: the ReCiPe and the European Commission Environmental Footprint (EF). Additionally, results were calculated adopting an absolute sustainability impact assessment method using the planetary boundary concept (PB-LCIA). We also explore the relative merits of using biomass and plastic waste as feedstocks for BTX production as compared to other common uses of these feedstocks.

4.3. Materials and methods

Goal and scope

The goal of the LCA is to perform a comparative assessment to evaluate the environmental impacts of BTX production scaled at a commercial scale (TRL 9, 2024) and at a future industrial level scale (2050), using mixed plastic waste (DKR350), biomass (crude glycerol) and fossil-fuels (oil) as a feedstock. The base commercial scale scenario and future industrial scenario are further explained in section ‘Estimates of future life-cycle impacts’ and Supplementary Information S4.1.5. The BTX production pathways (Figure 4.1) from mixed plastic waste (MPW) and biomass are both based on the Integrated Cascading Catalytic Pyrolysis (ICCP) process developed by BioBTX B.V. (hereafter: BioBTX), a company located in Groningen, the Netherlands. In this process, the feedstock is first heated in a pyrolysis step: the biomass and plastic molecules are cracked by heat, in the absence of oxygen. In a second step, the pyrolysis vapors released during this process are catalytically converted into aromatics, which are then separated from the non-condensable gasses, and collected (BioBTX 2022). For fossil BTX, the current conventional petroleum refinery route is included (PlasticsEurope 2013). The geographical scope is Europe for both the alternative BTX pathways and fossil-BTX, with the exception of specific processes that are known to occur in another part of the world (see Table 4.1).

The functional unit is “the production of 1 kg of mono-aromatics BTX” and the system boundary was set to cradle-to-grave, including CO_2 end-of-life emissions. BTX as platform chemical has many applications (Ghatta and P. Hallett 2023). Therefore, we accounted for CO_2 emissions by means of incineration, based on the chemical structure of BTX, but left all other waste treatment processes and emissions outside the system boundary. We included the CO_2 end-of-life emissions to align end-of-life biogenic and fossil carbon emissions, i.e. to include carbon uptake as well as its release. In case of biobased BTX, the carbon content is considered neutral as it originates from short-rotating crops (soy) (Guest et al. 2013a), and for MPW- and fossil BTX the embedded carbon is fossil-based. The use phase was excluded from the assessment based on equivalence. Furthermore, to deal with the multi-functionality, economic allocation was applied as it reflects socio-economic demands (Moretti et al. 2020). Allocation was performed for the by-products soybean meal, methyl esters, and bio-oil, treated as light fuel oil, using 2011-2021 prices. Details on the methods are described in Supplementary Information S4.1.

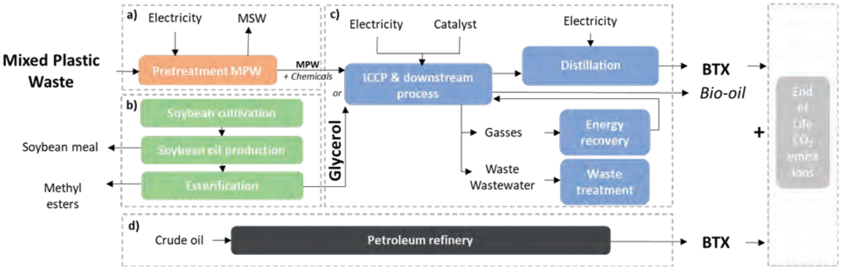


Figure 4.1. Simplified representation of Benzene-Toluene-Xylene (BTX) production pathways including a) Mixed Plastic Waste (MPW) handling, i.e. pretreatment, b) crude glycerol (biomass) production c) core processing for BTX production based on catalytic fast pyrolysis and d) petroleum refinery. ICCP = Integrated Cascading Catalytic Pyrolysis.

Inventory

The alternative BTX production (currently at pilot-scale) is scaled to a commercial level (TRL 9, 2024) and to a future industrial level (2050). Table 4.1 shows the compiling of the inventories described and an overview of the modelling assumptions. The prospective and future scenario is further described in section ‘Estimates of future life-cycle impacts'. To model background processes, the Ecoinvent database (v3.8) (Ecoinvent 2020), system model "cut-off", was used.

The mixed plastic waste used for BTX production was defined as "DKR-350", based on the set of quality standards called "Deutsche Kunststoff Recycling", which in the Netherlands represents the post-consumer mix of plastics that remains after the easily reusable plastics have been taken out (Brouwer et al. 2018). Following the "cut-off" approach, when MPW enters the system it was assumed to have no environmental burden because it is a waste stream. This approach is often applied in studies on chemical recycling of plastic waste (Jeswani et al. 2021; van der Hulst et al. 2022; Somoza-Tornos et al. 2020). Pretreatment impacts, i.e., sorting, were based on electricity needed to separate the plastics (Krüger 2020) and an additional step to remove the impurities (Jeswani et al. 2021). Transport of MPW from the sorting facility to the plant were based on a EURO6 truck assuming an average 50 km transport distance (Krüger 2020).

For the input of biobased BTX, crude glycerol production, the Ecoinvent process "Glycerine, esterification of soybean oil" from soybeans based on economic allocation from the USA was used. Following the PAS2050 guidelines (EC 2021), land use change emissions were assumed here to be zero for soybean production because it is on land that has not changed land use over the past 20 years. Glycerol transport by containership from USA to Europe was included. Crude glycerol can then directly be fed into the reactor without further pretreatment.

The ICCP process was obtained from BioBTX. The processes of biomass and MPW into BTX differ in energy and chemicals demand, but the catalyst use is similar. For the catalyst, a standard zeolite process in combination with bentonite (He et al. 2018), i.e., clay, was taken from Ecoinvent in a 20:80% ratio. Additionally, an on-site gas system was assumed to be installed for electricity generation to use the industrial plant's byproducts. An additional distillation step was applied to the BTX output to produce the mono-aromatics for further downstream uses. Here, the energy for a distillation step was calculated using the work of Piccinno et al. (2016) (Supplementary Information S4.1.4). Impacts from process waste was treated as municipal solid waste and incinerated. Wastewater was assumed to be treated according to the Ecoinvent process "average wastewater treatment" in Europe.

The fossil BTX pathway was modelled based on the Eco-profiles of PlasticsEurope on petroleum refining, producing benzene, toluene and xylene in a 48:33:19 weight ratio. This ratio was assumed to be the same for biobased BTX and MPW-BTX.

Table 4.1. Life Cycle Inventory (LCI) modelling assumptions and data sources of MPW-BTX, biobased BTX and fossil-BTX pathways.

Inventory	**Modelling assumptions**	**Source**
Mixed plastic waste	Cut-off approach: no environmental impact allocated to its production only pretreatment	-
Biomass	Glycerol as by-product of biodiesel production, economic allocation applied	Ecoinvent 3.8: Glycerine {US}| esterification of soybean oil
Transport (tkm)	MPW: Default scenario of transport from sorting place to the plant of 50 km (0.05 tkm) Bio (glycerol): Assumed transport from USA to the Netherlands (7.53 tkm)	Ecoinvent 3.8: Transport, freight, lorry >32 metric ton, euro6 {RER}| market for transport, freight, lorry >32 metric ton, EURO6 Ecoinvent 3.8: Transport, freight, sea, container ship {GLO}| market for transport, freight, sea, container ship
Pretreatment MPW	Electricity for sorting of MPW: 0.250 MJ/kg MPW Electricity additional sorting of MPW: 0.058 MJ/kg MPW	Jeswani et al. (2021), based on Krüger (2020) Jeswani et al. (2021)
Catalyst	As zeolite-bentonite powder (20:80 weight ratio)	Ecoinvent 3.8: Zeolite, Powder (RER) production; Activated bentonite (GLO), market group for.
Electricity (kWh)	Used in different processes, in total 1 kWh/kg MPW and 1.05 kWh/kg glycerol.	Ecoinvent 3.8: Electricity, medium voltage {Western Europe}| market group for.
Distillation	Based on energy needed for distillation (0.12-0.18 kWh/kg BTX) (Piccinno et al.,(Piccinno et al. 2016); See Supplementary Information S4.1.4)	Ecoinvent 3.8: Electricity, medium voltage {Western Europe}| market group for.
On-site gas system	Energy recovery of waste gasses, treated as natural gas. It covered 65% and 87% of electricity input for MPW- and biobased BTX, respectively. The on-site generated electricity required no additional fossil fuels. The carbon content of biobased BTX was considered biogenic.	Based on a Combined Heat and Power (CHP), electricity from natural gas (Ecoinvent 3.8) and a electricity efficiency of 28% (U.S. Department of Energy 2016)
Wastewater treatment	Treating separated wastewater (0.26-1 kg/kg BTX)	Ecoinvent 3.8: Wastewater, average {Europe without Switzerland}| treatment of wastewater, average
Waste	MSW incineration (0.23 – 0.34 kg/kg BTX)	Ecoinvent 3.8: Municipal solid waste {NL}| treatment of, incineration
Fossil BTX	Petroleum refinery (based a catalytic reformer and steam cracker)	Eco-profiles PlasticsEurope (PlasticsEurope 2013)

Table 4.1. Continued

Inventory	Modelling assumptions	Source
Resource use perspective	Incineration with energy recovery: MPW	Ecoinvent 3.8: Waste plastic, mixture {CH}| treatment of, municipal incineration; lower heating value DKR-350 mix (Brouwer et al. 2018) for energy recovery; Dutch incineration efficiencies (Corsten et al. 2013) (SI 4.1.8 for detailed data).
	Biogas from glycerol	Stucki et al. (2011); Ecoinvent 3.8: heat and power co-generation, biogas {RER}. See SI 4.1.8 for detailed data.
	Purification glycerol	Cespi et al. (2014) (SI 4.1.8 for detailed data)
	Avoided products: Bio-oil (0.08-0.14 kg CO_2 eq./kg BTX) Heat and electricity (0.5-1.1 kg CO_2 eq./kg MPW and 0.3-0.9 kg CO_2 eq./kg glycerol) Synthetic glycerol (3.1 kg CO_2 eq./kg glycerol)	Ecoinvent 3.8: • Light fuel oil {RER}| market for • Heat, district or industrial, natural gas {RER}| market group for • Glycerine {RER}| production, from epichlorohydrin

Prospective analysis

To project the maturing of the alternative BTX pathways from pilot to commercial and industrial level, we followed the framework by van der Hulst et al. (2020), which is a systematic procedure to assess future impacts of emerging technologies (Supplementary Information S4.1.5). To go from pilot to commercial level, the product output was scaled to 48 kton/year and process changes were introduced, including downstream steps, increased yield and energy input, and heat recovery (details can be found in Table S4.3 in S4.1.5). The industrial level (2050) included possible future external developments:

- Improvements due to technological advances were captured as improvements in energy intensity, assuming a reduction in energy input of 1% per year (Blok 2004; Bazzanella and Ausfelder 2017; IEA et al. 2013).
- Assessment of external developments for 2050 in the electricity sector were based on projections from the integrated assessment model IMAGE. IMAGE is an integrated assessment model to assess complex, large-scale environmental and sustainable development scenarios. Within this model, a future electricity mix is modelled based on drivers, such as costs and climate targets (Stehfest et al. 2014). Future developments were based on the Shared Socioeconomic Pathway (SSP) 2 representing a middle-of-the-road narrative committed to a long-term climate target of 2.6 W/m^2 in 2100 (SSP2 RCP2.6), consistent with the 2-degree target(van

Vuuren et al. 2017). The background datasets for the projected electricity market were systematically adapted using the approach of Mendoza Beltran et al. (2020).

- While in the commercial (2024) scenario, we accounted for CO_2 emissions by means of incineration of plastic waste at the end of life, this practice is likely to be reduced in the future (European Commission 2020a). We followed the 2°C-Circulair Economy scenario on plastic flows based on Stegmann et al. (2022) for the future (2050) scenario, assuming only 13% of plastic waste is burned or used for energy and 87% of the embodied carbon remains in the loop (Stegmann et al. 2022). We assumed that all the end products BTX is used for are plastics.

Life Cycle Impact assessment (LCIA)

we applied two LCIA methods: ReCiPe2016 Endpoint (H) and Midpoint (H) (V1.1) and the Environmental Footprint (EF) method. For the absolute environmental sustainability assessment, we implemented the PB-LCIA method. These methods are further explained below.

Mid- and endpoint assessment

To determine environmental impacts at both mid- and endpoint level, the ReCiPe2016 Endpoint (H) and ReCiPe Midpoint (H) (V1.1) (Huijbregts et al. 2017) impact assessment methods were selected. A contribution analysis was done to research the contributions of the different processes and similarly, to identify the contributions of the midpoint indicators to each endpoint indicator. The assessments were carried out in the Activity Browser (Steubing et al. 2020), an open source LCA software built on Brightway (Mutel 2017). At midpoint level, we conducted an additional analysis using the EF method (Manfredi et al. 2012). This is the current method recommended by the European Commission for performing an LCA (EC 2021), and included in the context of the environmental sustainability step of the safe and sustainable by design recommendations (EC 2022).

Absolute environmental sustainability assessment

To evaluate the environmental impacts in relation to the planetary boundaries (Ryberg et al. 2018) we applied the planetary boundaries life cycle impact assessment (PB-LCIA) method. This method introduces PB-informed characterization factors (Ryberg et al. 2021) to connect to the elementary flows of the LCI and to map them onto the planetary boundaries' safe operating spaces (Ryberg et al. 2018, 2020). Nine PBs are defined in total, but we excluded novel entities and atmospheric aerosol loading because they have not yet been adequately defined. For biosphere integrity we followed the approach proposed in Galán-Martín et al. (2021), and updated it with more recent mean species abundance values from GLOBIO 3.5 (Schipper et al. 2016; Wilting et al. 2017).

The PB-LCIA results were compared with a safe operating space apportioned to the level of the product, i.e. 1 kg of BTX. For this downscaling we applied a two-step method that first allocates the safe operating space to individuals and then to the product (Hjalsted et al. 2021; Ryberg et al. 2020). We followed the approach described by (Tulus et al. (2021) defining a planetary boundary transgression level based on global population size and the price of BTX. Details on the PB-LCIA method are summarized in Supplementary Information S4.1.7.

To compare the results of the PB-LCIA method, another PB-based approach was used as well: a normalization-based method that adapts the PB-framework to the impacts of the LCIA method. Here, we applied the carrying capacity-based normalization factors for the Environmental Footprint midpoint categories (Bjørn and Hauschild 2015; Sala et al. 2020) (Supplementary Information Table S4.11).

Sensitivity analysis

To test the robustness of the results, a sensitivity analysis on key parameters and modelling choices were carried out. In general terms, the allocation strategy is key. In terms of material requirements, the glycerol source in biobased BTX is especially relevant, while the plastic waste input in MPW-BTX has no impact. In terms of production, electricity is key as well as yield, which represents both efficiency and energy requirements. In terms of EoL, the recycling strategy is relevant.

- Allocation methods: We tested different allocation methods beyond the default of economic allocation. The MPW-BTX allocation factor for BTX (0.79) was changed to 0.69 (mass allocation), 0.46 (energy allocation) and 0.33 (economic allocation based on bio-oil prices). The biobased BTX allocation factor for BTX (0.59) was changed to 0.48 (mass), 0.46 (energy) and 0.16 (economic, bio-oil prices). 'Bio-oil prices' refer to the market value of pyrolysis bio-oil, which is composed of light organics (Vural Gursel et al. 2019). The details are summarized in Supplementary Information S4.1.3.
- Glycerol source: We considered glycerol production from other feedstock besides soybeans from the USA, including glycerol from rapeseed oil (Sanz Requena et al. 2011), palm oil (Mekhilef et al. 2011), and cultivated at another geographical location, i.e. Brazil. This was modelled by replacing the default glycerine dataset with the following Ecoinvent 3.8 datasets: Glycerine {BR}| esterification of soybean oil; Glycerine {MY} | esterification of palm oil; Glycerine {Europe without Switzerland} | esterification of rape oil.
- Yields: the yields of the MPW- and biobased BTX production routes are uncertain. Based on expert judgement, we ranged the BTX yields from -10% to +20% compared

to default. This affected i) the amount of BTX product and waste gasses – and thus also the supply of electricity that could be generated on site (CHP) – and ii) the allocation factors. The latter now ranged from 0.77 – 0.84 for MPW-BTX and from 0.55 – 0.7 biobased BTX.

- Multiple electricity scenarios in 2050: Alongside the SSP2 'Middle of the road' baseline scenario of the electricity market of 2050, we tested a more optimistic pathway of 1.9 W/m^2 (RCP1.9) as well as a more conservative pathway of 4.5 W/m^2 (RCP4.5) in 2100 (Stehfest et al. 2014). The baseline scenario represents efforts to commit to a long-term climate target of 2°C, while RCP1.9 and RCP 4.5 include efforts resulting in an estimated global warming of up to 1.5°C and between 2.1 and 3.5°C, in 2100, respectively (Stehfest et al. 2014).
- Multiple recycling scenarios in 2050: Alongside the base 2°C-Circulair Economy scenario, we tested less optimistic scenarios based on SSP2 RCP4.5 and a 'worst case' narrative. The SSP2 RCP4.5 scenario included 14% chemical or mechanical recycling of plastics, 17% landfill stock and 69% littered or incineration with energy recovery. The 'worst case' scenario represented 100% littered or incinerated with energy recovery. The default Circular Economy scenario included 29% recycling, 58% landfill stock and 13% littered or incineration with energy recovery (Stegmann et al. 2022).

Resource use perspective

Biomass and mixed plastic waste can be used in a myriad of applications besides BTX production. To understand the relative merits of their use in BTX production, we assessed whether the production of BTX results in lower GHG emissions than other common applications of these feedstocks (Figure 4.2) following the approach by Hanssen and Huijbregts(Hanssen and Huijbregts 2019). For MPW (figure 4.2a) the alternative application was incineration of plastic waste (Ecoinvent 2020), with energy recovery based on average incineration efficiencies (Corsten et al. 2013). Landfilling was excluded because the EU guidelines state: 'landfilling is the least preferable option and should be limited to the necessary minimum' (EC 2023). For biomass (figure 2b), the two alternative uses of glycerol considered were (i) combustion of biogas (fermented from glycerol) (Stucki et al. 2011) to generate electricity and heat (Ecoinvent 2020), which we called "incineration with energy recovery", and (ii) purification towards 99.5-grade glycerol (Cespi et al. 2014). High-grade glycerol (99.5%) is alternatively still manufactured as synthetic glycerol, as medical and cosmetic applications need high quality glycerol (Attarbachi et al. 2023). This was modelled via the process of synthetization of propylene via epichlorohydrin (Ecoinvent 2020). See Supplementary Information S4.1.8 for further details. In this analysis, we accounted for fact that biomass or MPW-based products would substitute conventional fossil products (counterfactuals indicated in grey boxes) and therefore resulted in avoided emissions that were quantified using Ecoinvent data.

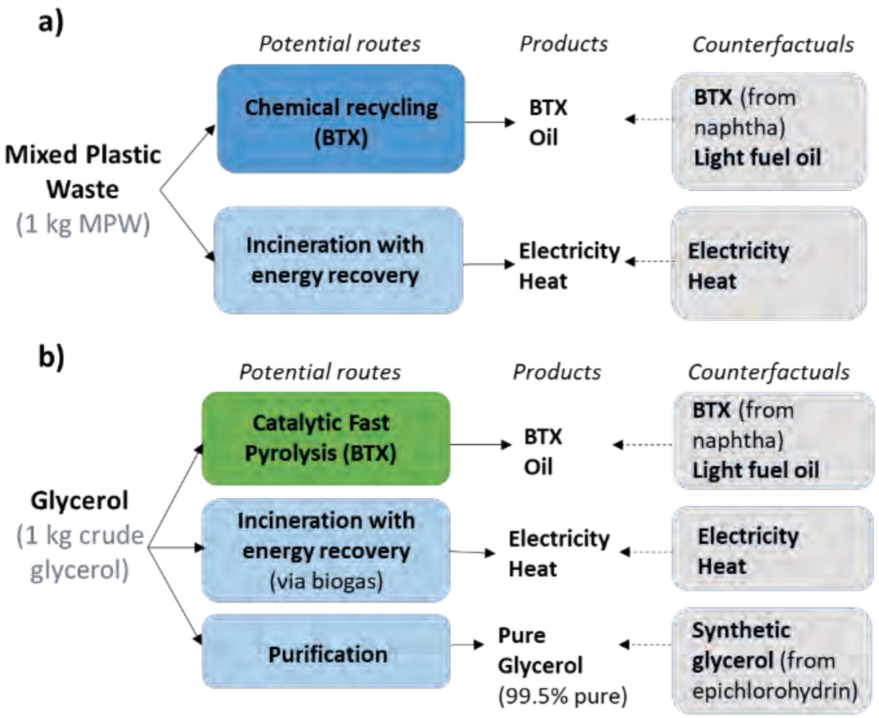


Figure 4.2. Representation of resource use perspective of (a) MPW and (b) glycerol as feedstock to produce BTX. In blue are the alternative uses producing other products (indicated by the arrow), the counterfactuals, i.e. the avoided products, are shown in the grey boxes. MPW = Mixed Plastic Waste; BTX = benzene-toluene-xylene.

4.4. Results

Mid- and endpoints impacts

Figure 4.3 shows the life-cycle impacts at endpoint (3a) and level midpoint (3b) of BTX produced from the different feedstocks. BTX from MPW resulted in the lowest potential impacts across the endpoint categories *human health*, *ecosystems quality* and *resource scarcity*, compared to the other BTX pathways (Figure 4.3a). Nonetheless, both alternative pathways came with trade-offs on the midpoint level (Figure 4.3b). MPW-BTX had the lowest predicted impact in all categories, except for *climate change* (and *freshwater eutrophication*, only at commercial level and compared to fossil-BTX). Here, biobased BTX resulted in the lowest GHG emissions, i.e., 3.0 kg CO_2-eq. per kg BTX

(Figure 4.4), mainly due to its biogenic carbon content, which leads to carbon neutral end-of-life CO_2 emissions. However, biobased BTX lead to higher impacts in multiple other midpoint categories: *land occupation*, *fine particular matter formation, freshwater eutrophication* and *water consumption*. These higher impacts result from agricultural practices, i.e. the cultivation and harvest of soybeans for the glycerol.

When applying the Environmental Footprint method at midpoint level (Supplementary information S4.2.2), the same trends were observed. Meaning, the biobased BTX pathway resulted in the lowest potential GHG emissions and fossil-BTX in the highest, while the MPW-BTX pathway had lower potential impacts across the other midpoints.

Estimates of future life-cycle impacts

Figures 4.3 and 4.4 show that environmental impacts are likely to reduce in the future, with negative GHG emissions for biobased BTX (-0.4 kg CO_2-eq/kg BTX). This is mainly related to the end of life carbon flows integrated in the future scenarios, which avoids 87% of embodied carbon to be re-emitted.

Overall, largest future reductions were seen for MPW-BTX, with midpoint impacts decreasing with 15-85%. In contrast, biobased BTX impact reductions ranged up to 30% (with the exception of 113% for GHG emissions) and fossil-BTX impacts reduced up to 56%. In all cases, though, water consumption increased, varying between 9-83% (Figure 4.3b). This is caused by foreseen carbon capture and storage (CCS) in the future electricity market.

Apart from the effect of carbon recycling, the future reduction potential of fossil-BTX is relatively low because the electricity use in fossil-BTX production makes up only 1% of the total energy input, as it mainly depends on gas and oil. Moreover, the future GHG emission reduction potential of MPW-BTX was expected to be larger. Yet, the waste gases that are used for energy purposes on-site lead nevertheless to emissions due to the fossil carbon content of mixed plastic waste.

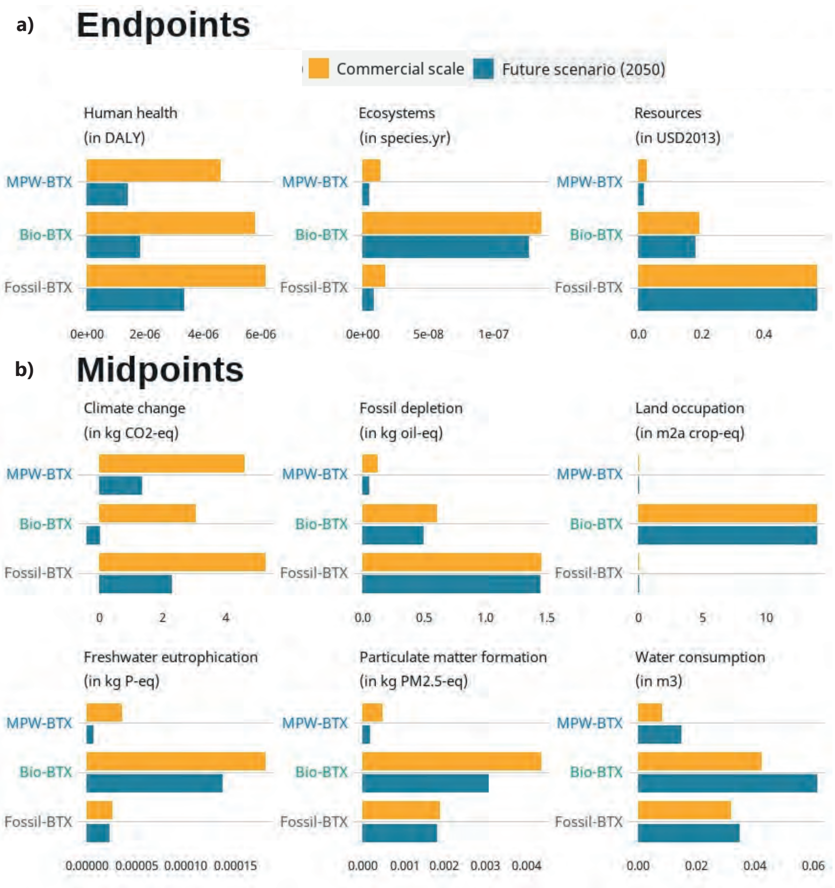


Figure 4.3. (a) Endpoint damage (exact numbers in S2.1), and (b) impacts of the six main contributing midpoint indicators of commercial (2024) level and future, industrial (2050) level BTX production from MPW, glycerol and fossil fuels. *Water consumption is contributing for ~1% to the endpoints ecosystems and human health, but it is the only impact category increasing in impact in the future and therefore shown here; the results of all midpoint impact categories are in Supplementary Information S4.2.2.

Process contributions to climate change impact

GHG emission reductions ranged between 42 and 113% for biobased BTX and 12 and 71% for MPW-BTX (Figure 4.4), compared to current fossil BTX production. For the current commercial scenario, the largest contribution to *climate change* for both MPW- and fossil-BTX is related to the embodied carbon released in the form of CO_2 at the end of life. The GHG emissions of MPW-BTX are mainly affected by the end of life treatment, rather than by the production process itself, which showed to be relatively low in GHG emissions. For biobased BTX, glycerol production contributed the most to *climate change*, and other midpoint categories, with 52% of it relating directly to soybean cultivation (Figure 4.4).

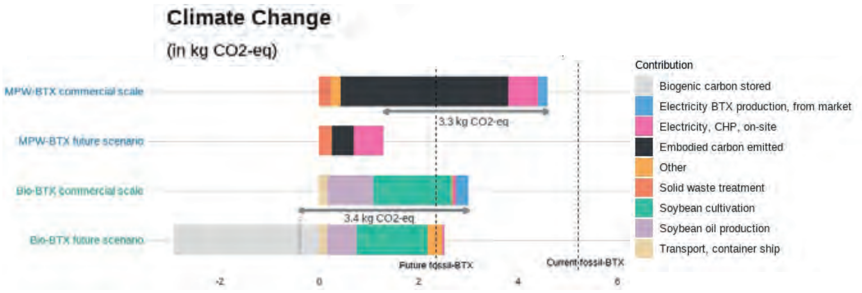


Figure 4.4. Process contributions to climate change impact of MPW, biomass and fossil-based BTX production pathways. The difference between current and future production is indicated with the grey arrow. CHP = Combined heat and power; MPW = mixed plastic waste.

Sensitivity analysis

The type of allocation method influenced the environmental impact estimations of the BTX production pathways. Depending on either mass, energy or economic allocation, climate change impact of biobased BTX production ranged from 1.1 to 3.0 kg CO_2-eq./kg BTX for the current scenario, and MPW-BTX production from 3.9 to 4.6 kg CO_2-eq./kg BTX (Supplementary S4.2.7). The default scenario, economic allocation based on light fuel oil prices, lead to results on the higher end of the ranges, while economic allocation based on bio-oil prices lead to the lowest results (Figure 4.5). Nevertheless the general conclusions did not change depending on allocation method.

Glycerol production has a large influence on the endpoint results of biobased BTX (Figure 4.5). Producing glycerol with other feedstocks than soybeans from the USA lead to potentially higher endpoint results, including GHG emissions. Largest GHG emissions result for glycerol from Brazilian soybeans or Malaysian palm oil, resulting in even 69-126% higher GHG emissions for biobased BTX compared to fossil-BTX. These higher predicted emissions were mainly due to clear-cutting of primary forest to arable land (Supplementary S4.2.6). The environmental impact of biobased BTX thus highly depends on the location and production of glycerol, and much less on the BTX production process itself.

The large impact of biomass input for biobased BTX is also identified by varying the parameter ‘yield’ (Figure 4.5). This has a larger effect on biobased BTX than MPW-BTX, because glycerol production has a relatively high impact, while plastic waste has no impact.

Depending on the future electricity scenarios, GHG emissions were lower ranging from 103-120% for biobased BTX and 34-46% for MPW-BTX, compared to future fossil-BTX production (Supplementary Information S4.2.4; Figure 4.5 for endpoint results). Future BTX production including electrification of the processes and a renewable energy mix can thus reduce impact on endpoint level, and mainly climate change impact.

The influence of carbon recycling on the results was further shown by testing alternative plastic recycling scenarios for 2050, which resulted in GHG emissions of -0.4 to 1.6 kg CO_2-eq/kg BTX for biobased BTX, 1.3 to 3.2 kg CO_2-eq/kg BTX for MPW-BTX and 2.3 to 4.1 kg CO_2-eq/kg BTX for fossil-BTX (Supplementary S4.2.5). The other recycling strategies increases the impact in the endpoint categories *Ecosystems* and *Human Health* (Figure 4.5). For biobased BTX, combining biomass use with plastic recycling could lead to a net carbon sink.

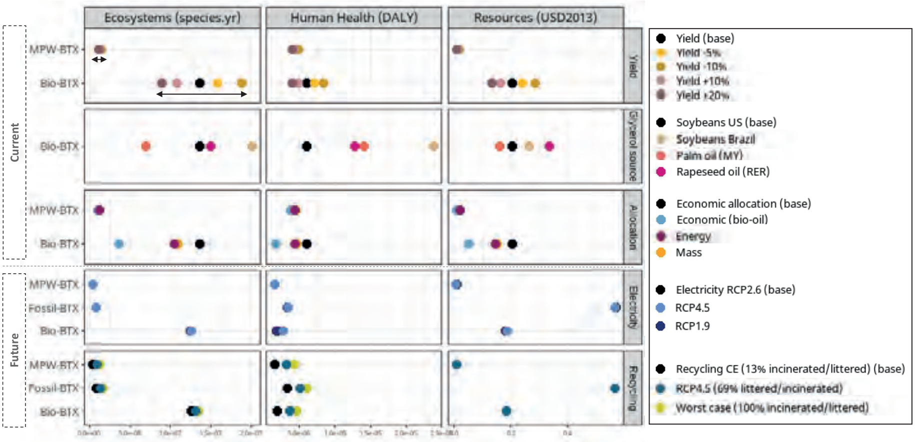


Figure 4.5: Sensitivity analysis results on endpoint level, varying key modelling parameters and scenarios. MY = Malaysia, RER = Europe.

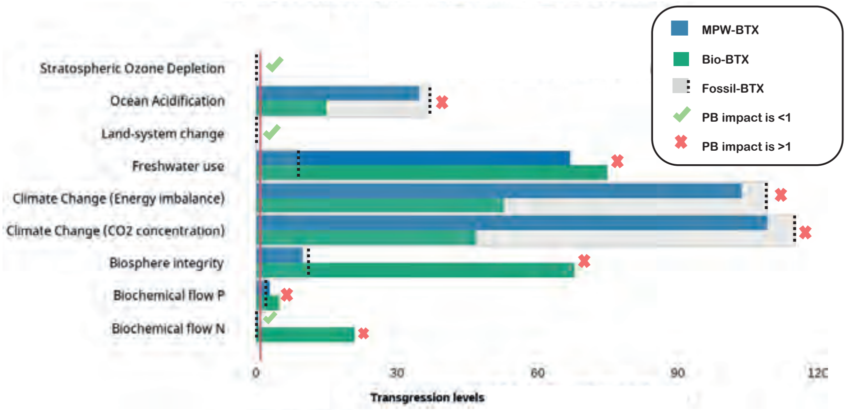
Planetary boundary impacts

The results from the PB-LCIA are presented in Figure 4.6a for the commercial (2024) scenario and in 6b for the future (2050) scenario. If the transgression level is >1, the BTX pathway overshoots the safe operating space that was allocated to BTX production. Only when all the transgression levels are <1, BTX production is predicted to be "absolutely" sustainable. At current commercial scale (Figure 4.6a), all BTX pathways transgressed at least six levels of the planetary boundaries, meaning none of the pathways are considered sustainable in absolute terms. The BTX pathways in the future scenario (Figure 4.6b) lead to the same conclusion, albeit that only three levels of the planetary boundaries were transgressed.

The *climate change* levels were transgressed up to 115 times, but the least by biobased BTX production due to its biogenic carbon content. Consequently, all pathways transgressed the levels of *ocean acidification* and *biosphere integrity*, as they are strongly affected by CO_2 emissions. In the future scenario, especially climate change (energy imbalance) and ocean acidification were affected due to carbon recycling, leading to transgression levels of <1. Furthermore, the *biosphere integrity*, *biochemical N* and *P flows* levels were specifically high for the biobased BTX pathway. Especially agricultural practices and land use related to soybean cultivation increased the impact for biobased BTX.

Transgression of planetary boundaries by BTX production pathways

a) PB-LCIA results of commercial (2024) scenario



b) PB-LCIA results of future, industrial (2050) scenario

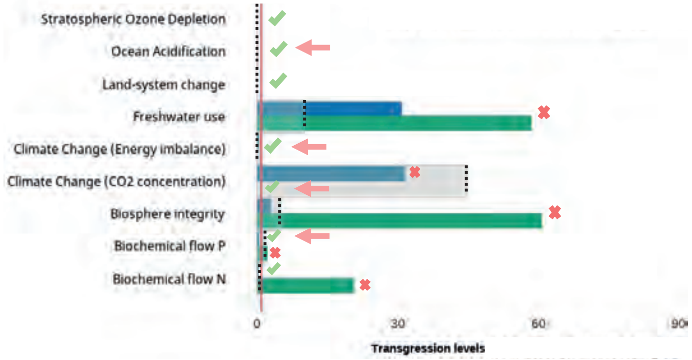


Figure 4.6. Transgression of planetary boundaries by BTX production pathways. (a) commercial (2024) scenario and (b) future, industrial scenario (2050, as described in section 'Estimates of future life-cycle impacts'). The green check marks indicate that the PB-LCIA result is <1. The red crosses indicate that the results are >1, and thus the BTX pathway is transgressing its share of safe operating space of that planetary boundary. The pink arrow indicates reductions in transgression levels to <1. BTX = benzene, toluene and xylene, MPW = mixed plastic waste. Exact numbers are given in Supplementary Information S4.2.3.

The application of the carrying capacity normalization factors to the EF results also identified *climate change* as the highest impacts category for all BTX pathways, as well as *ecotoxicity* and *land use* for biobased BTX. Interestingly, the normalization-method ranked particulate matter high in all BTX pathways. This category is related to atmospheric aerosol loading, which is not yet adequately defined and therefore excluded in this PB-LCIA assessment.

Optimal use of resources

Using MPW to produce BTX instead of incinerating it and recover energy, resulted in a GHG benefit of 1.1 kg CO$_2$-eq./kg mix plastic waste used (Figure 4.7a), mainly because incinerating plastic waste emits large amounts of CO$_2$. Figure 4.7b shows that the relative climate benefits of using MPW for BTX increases to 1.8 kg CO$_2$-eq./kg feedstock applying a 2050-projected renewable electricity mix. The main reason for this increase is that the GHG savings of energy recovery from incineration diminish in the future, as an increasingly cleaner electricity mix is substituted.

Figures 4.7c and 4.7d show that incineration with energy recovery or higher-grade glycerol has higher GHG benefits compared to BTX production. Here as well, the relative climate benefit for incineration with energy recovery is expected to decrease in the future due to a cleaner energy mix. For purification, the GHG benefit relates to the avoided conventional production of synthetic glycerol which is a GHG intensive process.

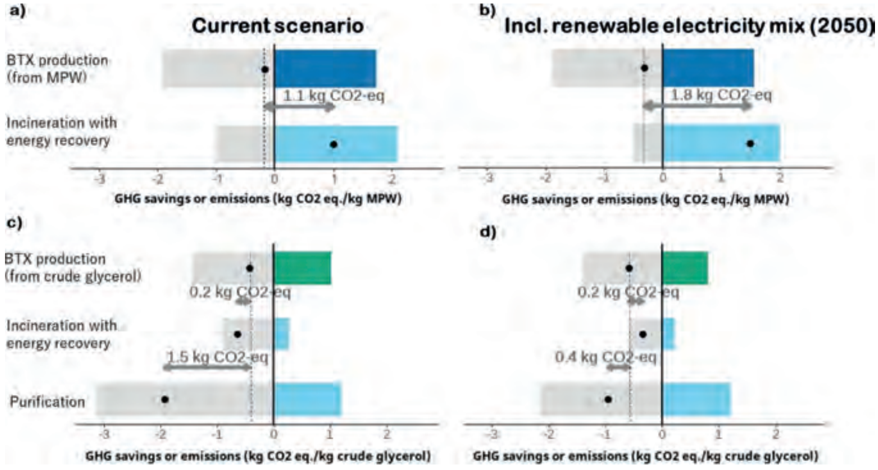


Figure 4.7. Climate change impact and savings for the use of (a, b) 1 kg of MPW and (c,d) 1 kg of crude glycerol, at current commercial scale and including a future renewable electricity mix (SSP2-RCP2.6, 2050). The black dot represents the GHG emissions minus the GHG saving potential. The arrow indicates the GHG benefit/disadvantage of BTX production compared to the other uses. BTX = benzene, toluene and xylene; MPW = mixed plastic waste.

4.5. Discussion & Conclusion

Environmental impacts

This is the first study to compare the environmental impacts of BTX production using three different carbon feedstocks. The environmental impacts (midpoint and endpoint) were lowest for future MPW-BTX, except for GHG emissions. Nevertheless, from a resource use perspective, MPW-BTX was favorable over waste incineration with energy recovery with a GHG benefit of 1.1 kg CO2 eq./kg plastic-waste, whereas using glycerol for BTX production resulted in a GHG disadvantage compared to other uses. These findings show the added value of multiple perspectives within performing an LCA.

Our results highlight the importance of including impacts beyond GHG emissions in environmental impact analyses, and shows the environmental trade-offs between the various feedstocks. In general, these trade-offs result from agricultural practices like fertilization and pesticide use that can increase eutrophication, acidification and ecotoxicity (Cucurachi et al. 2022).

We excluded Land Use Change (LUC) related emissions for glycerol production. Even though this is fair practice (PAS2050 2011), GHG emissions from LUC can play a big role with first generation biomass or when deforestation is involved (Khoo et al. 2016a; Vera et al. 2022; Wicke et al. 2011). This was also shown in the sensitivity analysis on different feedstocks for glycerol production, where impacts were predicted to be higher compared to soybean cultivation in the USA mainly as a result of clearing of the original vegetation, and in some cases even resulted in higher overall emissions compared to fossil-BTX. Moreover, LUC emissions can also encompass soil carbon losses and lost capacity of natural vegetation to sequester CO_2 (Daioglou et al. 2019; Kim and Kirschbaum 2015). These were not included due to modelling limitations implying that the GHG emissions of biobased BTX may be underestimated.

Climate change impacts

We found that especially the process-related emissions from production were low compared to fossil-BTX. According to literature on other BTX production pathways in development, process related CO_2 emissions are predicted at 2.21 kg CO_2-eq./kg BTX for a Diels-Alder route and 2.6 kg CO_2-eq./kg BTX for a methanol-to-aromatics route (Bazzanella and Ausfelder 2017). The current GHG emissions related to MPW- and biobased BTX processing were estimated between 0.7-1.3 kg CO_2-eq./kg BTX. This shows that the catalytic fast pyrolysis process has potential over these alternative routes.

There is a GHG benefit to treat MPW via chemical recycling to produce BTX. The result from this study's resource use perspective are in line with previous research on chemical recycling versus incineration with energy recovery (van der Hulst et al. 2022; Jeswani et al. 2021; Meys et al. 2020). In accordance with this study's GHG benefit of 1.1 kg CO_2-eq./kg waste feedstock treated to produce BTX, van der Hulst et al. (2022) estimated a GHG benefit of 0.82 kg CO_2-eq./kg waste feedstock treated for chemical recycling producing high value chemicals, and a 50% lower climate change impact for chemical recycling via pyrolysis was found by Jeswani et al. (2021). Even though direct comparison is not possible because different fossil-based chemicals are avoided, i.e. BTX, other high value chemicals or naphtha, these studies uniformly show emission saving potentials for chemical recycling when compared to incineration with energy recovery.

We did not find a GHG benefit to treat glycerol to produce BTX: purification of glycerol was the better option due the avoided conventional production of synthetic glycerol which is a GHG intensive process, which has become economically feasible (Attarbachi et al. 2023). Moreover, producing electricity from biogas is currently promoted in European renewable energy policies, because it displaces the use of fossil fuels in energy supply and contributes to GHG emission reductions (Scarlat et al. 2018), which makes glycerol as feedstock choice for BTX less logical. Due to limited data, the resource use perspective included GHG emissions only. Expanding the analysis to other environmental impacts, however, could generate further insights into the beneficial purposes of the feedstocks.

Whereas we found positive emissions for current biobased BTX production of 3 kg CO_2-eq./kg BTX, Yang et al. (2022) found negative emissions of –0.82 kg CO_2-eq./kg biobased BTX. The lower impact was mainly a result of the carbon credits from exported electricity that offset upstream emissions, i.e. substitution. In this study, if the by-products, i.e., bio-oil and the surplus of electricity, were substituted, this would result in a credit of 2.25 kg CO_2 eq./kg biobased BTX (Supplementary S4.3.3). Taking this credit into account, the GHG emissions of this study's biobased BTX are nevertheless still higher due to the high impact of soybean cultivation. In both cases, however, the credits would diminish towards 2050 if we assume electricity will be renewably produced. This highlights the added value of a future assessment.

The largest share of emissions of biobased BTX originated from glycerol production. Lower GHG emissions in Yang et al.'s work were also a result of the feedstock selection of wood chips (Yang et al. 2022). In line with this, lower climate impacts were also found for pulpwood as a feedstock in an intermediate biobased BTX production

(Akanuma et al. 2014; Sudolsky 2019). Due to limited process and technology data, we did not further research woody biomass as a feedstock.

In the future scenario, we applied the default economic allocation ratio, which is based on the average of 2011-2021 prices. Ideally, as economic allocation reflects socio-economic demands, future pricing was considered in the 2050 scenario. However, there is a large uncertainty regarding price forecasting, as it depends on many factors, such as fluctuations, policy, and technology development (Broeren et al. 2014).

For both fossil and MPW-BTX, a large share of their climate change impact related to the embodied carbon released at the end of life. End-of-life emissions are, however, often not included in petrochemical GHG emissions reporting (IEA 2020; Carus et al. 2020). In our current commercial (2024) scenario, it was assumed that all carbon embodied in the products would eventually end up in the atmosphere. Large reductions in the future scenario were, therefore, mainly a result of continuous carbon recycling, avoiding 87% of the embodied carbon to be emitted. Preventing the end products, for which BTX is used, from being burned or incinerated for energy is thus pivotal in reducing the environmental impact of both fossil as well as renewable BTX production.

Absolute Sustainability

Even though the alternative BTX pathways showed lower environmental impacts compared to fossil-BTX pathway, at least three planetary boundaries were transgressed. Tulus et al. found that most of 492 globally produced chemicals transgress multiple planetary boundaries (Tulus et al. 2021). A study on the petrochemical industry replacing fossil feedstock with carbon via carbon capture and utilization (CCU) technologies demonstrated emission reductions from 25% up to 100%, though in the best case it still exceeded biosphere integrity (Galán-Martín et al. 2021). These and our findings highlight the relevance of complementing LCA with an absolute environmental sustainability assessment to further support decision making towards the development of environmental sustainable production chains. Whereas LCIA helped to understand what the hotspots in the BTX production chain were, the PB-LCIA showed that further reduction is still necessary to stay within the planetary boundaries.

The share of safe operating space depends on downscaling of the safe operating space; it can thus vary per study and has a large influence on the results. Here, we used the transgression levels defined by Tulus et al. (2021) based on equality and economic value of 2018. Whether a more expensive product is allowed to take up more safe operating space is in the end a political question, and ideally different downscaling perspectives are therefore considered. In general, downscaling of planetary boundaries is still in its infancy, and future research should be dedicated exploring alternative definitions of transgressions levels.

Recommendations for a sustainable future of BTX production

For both alternative BTX pathways, the feedstock choice has a large influence on the environmental impacts, i.e. the fossil carbon content in plastic waste for MPW-BTX and biomass cultivation for biobased BTX. Therefore, to further reduce environmental impacts of the MPW-BTX production, the GHG emissions related to the embodied carbon at end-of-life should be further avoided, i.e., by re-using and recyling plastics and other products BTX is used in. If 100% of the embodied carbon remains in the system, GHG emissions could be 0.86 kg CO_2-eq/kg MPW-BTX, i.e., 83% lower than current fossil BTX production. Furthermore, the emissions related to the on-site electricity production from the waste gasses could be abated by, for example, CCS or CCU technologies. Theoretically, this could save a further 0.6 kg CO_2-eq/kg BTX leading to 0.26 kg CO_2-eq/kg MPW-BTX, though this excludes the environmental impacts of CCS and CCU (de Kleijne et al. 2022; Yang et al. 2022). Alternatively, it might be possible to use the waste gasses as feedstock for other production, such as methanol, to keep the carbon in the loop (Im-orb and Arpornwichanop 2020).

Increasing the share of biogenic carbon content in plastics could further reduce the GHG impact of MPW-BTX. If 45% of the mixed plastic waste would be sourced from biomass, future MPW-BTX could decrease to -0.4 kg CO_2-eq. (Supplementary Information S4.3.2), comparable to future biobased BTX's impact. Chemical recycling of bio-based plastics could thus combine the benefit of biogenic carbon with carbon recycling, which could result in long-term CO_2 sequestration from the atmosphere (Stegmann et al. 2022). This would, however, require the use of sustainably sourced biomass and further exploration of the potential associated trade-offs with other environmental impacts.

To further reduce environmental impacts of the biobased BTX production, other bio-based feedstocks could be considered. In general, research showed that the use of woody biomass or agricultural residues, such as sugarcane bagasse or corn stover, can lead to lower GHG emissions, eutrophication and land use impacts than the use of first generation biomass (Morales et al. 2015; Wellenreuther and Wolf 2020; Ögmundarson et al. 2020). The use of these feedstocks could lower the GHG emissions of the BTX's feedstock phase by 74-95%, compared to soybean glycerol (Supplementary Information S4.3.2) (Balasundram et al. 2020; Ghorbannezhad et al. 2018b; Mendes et al. 2016). When residue biomass is considered to have no environmental impact, i.e. “zero-burden” approach (Corona et al. 2018), it would lower the GHG impact of biobased BTX production with at least 1.4 kg CO_2-eq./kg BTX. Further development of low impact lignocellulose-based BTX production to a commercial scale would therefore be recommended.

In view of the feedstock supply, there are factors of influence that should be further researched to support policy recommendations. In regard to glycerol, there is pressure from competing technologies for renewable diesel, which do not produce glycerol as a by-product (Attarbachi et al. 2023), plus, glycerol has a relatively high price. Moreover, there are many other glycerol applications being developed or promoted that might have larger environmental benefits (Chilakamarry et al. 2021; Scarlat et al. 2018). Plastic waste has a GHG benefit compared to incineration with energy recovery and is abundant. Either based on current plastic waste management trends (Geyer et al. 2017) or a middle-of-the-road development scenario (Stegmann et al. 2022), by 2050, 40% to 58% of the generated plastic waste would be required to meet BTX demands (Supplementary Information S4.3.3). However, there could be ‘competition’ with mechanical recycling to retrieve plastics or chemical recycling producing other high value chemicals and fuels (Vollmer et al. 2020; Zhao et al. 2022). Moreover, policy actions targeting plastic use, such as reducing single-use plastics (European Commission 2020c), may result in lower amounts of feedstock availability. Hence, future studies to assess holistically the cost-benefit and trade-offs at macro scale of the different choices will be necessary.

A combination of strategies proves to be key to reach a low-emission industry. Our findings imply that the use of alternative carbon feedstock, electrification of the processes and a renewable electricity mix could reduce emissions of BTX production up to 21-58% in 2050, compared to fossil BTX production. Including carbon recycling of 87% can reduce GHG emissions even up to 75-107% by 2050. In contrast, solely decarbonizing energy supply reduces GHG emissions by 8-20%. To further minimize emissions, recycling and/or CCS technologies could be used to abate end-of-life and process emissions (Meng et al. 2023).

Overall, the combination of methods applied in our research offered complementary insights on the sustainability of the alternative BTX pathways. In the context of the safe and sustainable by design recommendations (Caldeira et al. 2022), combining a LCA and absolute sustainability assessment gives insights into whether one product design is more sustainable than the other and whether it stays within the planetary boundaries. Overall, more systemic changes would be necessary for BTX production to stay within the planetary boundaries, such as the use of other types of waste biomass, increasing carbon recycling and the abatement of end-of-life impacts, alongside reducing product demand (Bachmann et al. 2023; Meng et al. 2023). To conclude, a future BTX production combining strategies including alternative carbon feedstock helps the petrochemical industry to become more sustainable. Holistic assessments similar to the one presented herein can guide research and policy in their support to develop more sustainable aromatics and other petrochemicals.

Data Statement

All relevant data supporting the findings of this study are available within the article and its supplementary information files.

Acknowledgment

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5.

Land-use change emissions limit climate benefits of bio-based chemicals

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5.1. Abstract

Petrochemicals are used in manufacturing thousands of daily products with fossil fuels as carbon feedstock. Transitioning to renewable carbon feedstocks is crucial to reduce greenhouse gas (GHG) emissions. Biomass is a potential option, but the GHG benefits of bio-based products are debated, particularly due to the risk of large emissions from land use change (LUC). Here, we analyzed the GHG life cycle emissions of bio-based primary chemicals via 30 different routes using sugarcane, grasses, woody crops and agricultural residues as biomass feedstock, and their potential contribution to climate change mitigation when applied at global scale. Spatially explicit LUC emissions were included by using the LPJml model coupled with IMAGE, under scenarios limiting global warming to well below 2°C, and over a 30-year evaluation period. We avoided indirect LUC emissions in feedstock production by only considering abandoned agricultural land, marginal land, managed and degraded forests. Results show on average that 63% of GHG emissions from bio-based chemical routes relate to LUC emissions. While 27 out of the 30 bio-based routes have lower GHG emissions compared to their fossil-based equivalents without LUC emissions, this reduces to 5 out of 21 routes, when including LUC emissions. When residue-based routes are also considered, the number increases to 13 out of 30 routes. Bio-based chemical production is most effective when using residues, and if crops are used, they should be cultivated in locations leading to minimal land-use change impacts. Our results appear to be particularly sensitive towards the assumed evaluation period of 30 years and the default chemical production conversion efficiencies. We also found that the global petrochemical industry's GHG emissions can be reduced from 6% to 0.4% with residue feedstocks, and for global petrochemical ethylene production from 2.2% to 1.2% by using sugarcane and from 2.2% to 1.8% using grasses. Our findings imply careful selection of land area, biomass feedstock and chemical production route to achieve significant climate change mitigation potentials.

5.2. Introduction

Globally, thousands of different synthetic materials are produced from six main chemicals: methanol, ethylene, propylene, benzene, toluene and xylene (IEA 2018). The petrochemical sector that produces these six chemicals covers 12% of the world's crude oil demand (IEA 2018), and emits around 4% of global greenhouse gas (GHG) emissions, even not accounting for upstream and downstream processes in the supply chain (Bauer et al. 2022). While these emissions associated with petrochemical production processes can be reduced via electrification (Schiffer and Manthiram 2017) and carbon capture and storage (Kätelhön et al. 2019), they do not fully eliminate the sector's reliance on fossil feedstock (Schiffer and Manthiram, 2017), which accounts for 58% of the sector's fossil input (IEA 2021). Therefore, to achieve net-zero GHG emission chemicals by 2050, in line with the Paris Agreement (UNFCCC 2015), the petrochemical sector needs to transition away from fossil feedstocks.

Alternative renewable carbon sources for the chemical industry include: (i) plastic waste streams, via chemical recycling (ii) atmospheric CO_2, obtained via direct air capture (DAC) or (indirectly) from biomass combustion or gasification, which can be utilized via various carbon capture and utilization (CCU) technologies (Lange 2021; Huo et al. 2023), and (iii) sustainably sourced biomass (Lopez et al. 2023; Gabrielli et al. 2023). Plastic waste re-used as feedstock via chemical recycling is still an upcoming technology, involving high energy requirements and uncertainty (Stegmann et al. 2022), but can contribute to net-zero emissions in the chemical industry (Saygin and Gielen 2021). In regard to CCU options, previous research has shown that few options for chemical production are likely to reach net-zero emissions by 2050 (de Kleijne et al. 2022), and that DAC/CCU technologies applied in the chemical industry are currently energy- and resource-intensive and costly (Meng et al. 2023). It may nevertheless still be part of a multifactorial solution in petrochemical industry (Huo et al. 2023).

Biomass is often considered a sustainable feedstock for producing products such as primary chemicals (European Commission 2018; Strengers and Elzenga 2020). The sustainability of using biomass and the availability of sustainable biomass is, however, highly debated, due to concerns on GHG emissions from land use change (LUC) (Akkari et al. 2018; Searchinger et al. 2008) and trade-offs with biodiversity and environmental impacts like eutrophication (Zhang et al. 2021; Zuiderveen et al. 2023b). LUC emissions relate to changes in carbon-stocks due to changes on land, i.e., by burning of original vegetation, soil carbon losses, or the diminished capacity of natural vegetation to sequester CO_2 (Vera et al. 2020; Gerssen-Gondelach et al.

2017; Hanssen et al. 2020), and can significantly contribute to global GHG emissions (Qin et al. 2024).

Existing sustainability assessments of biomass-based feedstocks in the petrochemical industry have indicated that bio-based chemicals could reduce climate change, ocean acidification and biodiversity loss compared to fossil-based production (Galán-Martín et al. 2021) and likely have a higher GHG emission reduction potential compared to CCU options (Gabrielli et al. 2020). Yet, these studies do not account for LUC emissions. For specific petrochemical industry end-products, such as plastics, global analyses have been conducted that include LUC emissions (Zheng and Suh 2019), though not all studies do (Meys et al. 2021). Zheng and Suh (2019) showed that biomass can play an important role in reducing GHG emissions of the plastics sector, but only considered generic LUC emissions without accounting for spatially explicit differences. They noted that the land-use implications of a large-scale shift to biomass-based plastics call for a more extensive analysis of LUC emissions. Studies on energy production from biomass have shown that LUC emissions substantially contribute to overall climate impacts, but that they highly depend on biomass cultivation location, previous land cover type, handling of original vegetation and the evaluation period considered (Elshout et al., 2015; Daioglou et al., 2017; Hanssen et al., 2020). For bio-based chemicals, however, the implications of consistently including LUC emissions on GHG footprints and mitigation potentials remain to be fully assessed.

Here, we comprehensively included spatially explicit LUC emissions in the life cycle GHG emissions of bio-based production of the six base chemicals from the petrochemical industry. Thirty different chemical production routes are considered and four sources of biomass feedstock, i.e., sugarcane, grasses, woody crops and agricultural residues. For sugarcane, grasses and woody crops, we only considered marginal and abandoned agricultural land and managed and degraded forest areas to avoid indirect land-use change effects, i.e., avoiding biomass cultivation for chemicals replacing food production thereby causing emissions elsewhere by conversion of natural habitat to cropland (Searchinger et al. 2008). Life cycle GHG emissions of the bio-based chemicals include emissions from (i) land use change, (ii) biomass cultivation and processing, (iii) chemicals production and (iv) CO_2 emissions related to the embedded carbon in the chemicals released at the end of life. Based on current production volumes, location-specific emission factors per feedstock type and chemical route, we also determined the global climate change mitigation potentials of biobased compared to fossil based production in the petrochemical industry.

5.3. Methods

Bio-based petrochemical production routes

We analysed the six largest petrochemicals by global production volume (IEA 2022) that contain carbon, i.e., ethylene and propylene (the olefins), benzene, toluene and xylene (also known as 'BTX'; the aromatics) and methanol. Together these chemicals account for two-thirds of total global chemical production (IEA 2018). We refer to them in this study as the 'primary chemicals'. Ammonia is also on this list of chemicals by largest production volume, but was excluded here as it does not contain carbon. We assessed several routes to produce the six primary chemicals from biomass instead of fossil fuels (Supplementary Figure S5.5.1). We selected these routes based on technological maturity, i.e. a reported technological readiness level (TRL) of 6 or higher, and on data availability for the inventory modelling.

Each route starts from one of four biomass types (Figure 5.1): (i) first-generation biomass in the form of sugarcane, (ii) second-generation lignocellulosic biomass in the form of fast-growing grasses (switchgrass, Miscanthus) or (iii) woody crops (willow, poplar), and (iv) agricultural residues. These biomass types were selected to avoid direct competition with food production. With these different biomass types, four intermediate 'chemical feedstocks' are produced: bio-ethanol, bio-methanol, bio-naphtha and bio-oil (Figure 5.1). Bio-methanol is produced via biomass gasification of woody crops (Kajaste 2014) or lignocellulosic material (Sikarwar et al. 2016). Bio-methanol is unlikely to be produced from sugarcane, because the yield of wood-based methanol is about two times higher compared to sugar crops (Bertau et al. 2014). Bio-ethanol is produced by fermentation of sugarcane (Dale 1987), or via simultaneous saccharification and fermentation of woody crops or grasses (Lynd et al. 1991), bio-oil via fast pyrolysis of woody biomass (Vispute et al. 2010), and bio-naphtha via syngas production and subsequent Fischer-Tropsch synthesis (Oliveira et al. 2021). Except for the bio-methanol, further steps are needed to get to the primary chemicals: ethylene and propylene can be produced via methanol-to-olefins conversion routes (MTO) (Mohsenzadeh et al. 2017) and BTX via methanol-to-aromatics routes (MTA) (Bazzanella and Ausfelder 2017). Ethylene and propylene can also be produced from ethanol via catalytic dehydration and catalytic conversion respectively (Oliveira and van Dril 2021). BTX is produced by catalytic upgrading of bio-oil (Yang et al. 2022). Bio-naphtha can be used to produce both ethylene, propylene and BTX via catalytic cracking, similar to conventional petrochemical production (de Jong et al. 2020). Taken together, all feasible combinations amount to 30 different biomass-to-primary-chemical routes. Detailed descriptions of each chemical processing step are given in Supplementary Information S5.1.3.

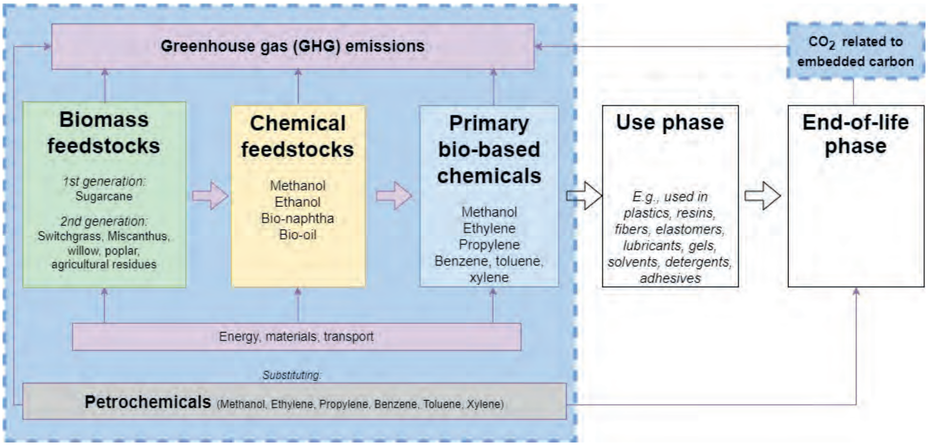

Figure 5.1: Overview of biomass-to-primary-chemicals production routes and associated GHG emissions. The blue dashed lines show the system boundaries of our analysis. The use phase is indicated for clarity but excluded from the analysis. Note that we also include release of embedded CO_2. CO_2 emissions related to the embedded carbon in the chemical product released at the end of life are accounted for, but the waste treatment processes are left outside the system boundary. An overview of each route can be found as Supplementary Figure S5.1, technical descriptions are given in Supplementary Information S5.1.3.

Life cycle greenhouse gas emissions of bio-based chemical production

The life cycle GHG emissions per primary bio-based chemical are expressed as an emission factor (EFs). They encompass land-use change, supply chain and end-of-life emissions related to the embedded carbon in the product (Eq. 5.1). Each contribution to the EFs is discussed in the next sections.

$$EF_{f,pc} = Em_{LUC,f,pc,x,t} + Em_{cult,f,pc} + Em_{chem,pc} + Em_{embedded,pc} \qquad \textbf{equation 5.1}$$

Where $EF_{f,pc}$ is the emission factor for each primary chemical per feedstock type and per bio-based primary chemical route (kg CO_2-eq./kg chemicals); $Em_{LUC,f,pc,x,t}$ are the LUC emissions per bio-based primary chemical route (pc) depending on feedstock (f), location (x) and considered evaluation period (t) (kg CO_2-eq/kg chemical); $Em_{cult,f,pc}$ are the emissions of biomass cultivation per feedstock type, per bio-based chemical route (kg CO_2-eq./kg chemical); $Em_{chem,pc}$ are the supply chain emissions per bio-based chemical route (kg CO_2-eq/kg chemical); $Em_{embedded,pc}$ are the emissions related to embedded carbon released at the end of the product's life (kg CO_2-eq/kg chemical) per primary chemical (pc).

Land use-change emissions

We determined LUC emissions based on the difference in carbon stock between the biomass plantation and that of a benchmark of continued natural vegetation growth at each potential production site, following Hanssen et al. (2020):

$$Em_{LUC,f,t,x,pc} = \frac{\Delta C_{f,t,x} \cdot r}{Y_{f,x} \cdot t \cdot \eta_{f,pc}} \quad \textbf{equation 5.2}$$

Where $Em_{LUC,f,t,x,pc}$ are the LUC emissions per feedstock type, per location (grid cell) and per bio-based primary chemical route over a considered evaluation period (kg CO_2-eq/kg chemical); ΔC is the difference in carbon stocks between the feedstock plantation and the natural vegetation regrowth benchmark after 30 years (tonne C/ha); r molar ratio between CO_2 and C (dimensionless); Y is the yield (in tonne wet biomass/(ha x yr)); η the conversion efficiency of biomass feedstock to the primary chemical (in tonne primary chemical/tonne wet biomass); and t is the evaluation period (30 years as a default). The subscripts represent: (f) feedstock type, i.e. sugarcane, grasses or woody crops; (t) considered period related to the natural vegetation regrowth benchmark; (x) the specific grid cell; (pc) primary chemical via a specific production route. Note that per feedstock crop all the relevant grid cells were always considered, i.e., the crop specific LUC emissions are mutually exclusive.

Carbon stock data and crop yields were based on datasets used by Hanssen et al. (2020), which was derived from the IMAGE integrated assessment model (Stehfest et al. 2014) coupled to the global vegetation and hydrological model LPJml (Müller et al. 2016; Beringer et al. 2011). Note that by comparing biomass plantation carbon stocks to a hypothetical benchmark of natural vegetation growth, we account for carbon stock changes during initial conversion to a plantation, but also for the so-called 'foregone sequestration', i.e., the lost sequestration capacity of natural vegetation due to the use of the land for plantations. We assumed that the original vegetation is burned when a cultivation site is established, releasing the initial carbon-stock as CO_2. We did not consider the re-use of initial biomass for other purposes, such as bio-energy, because the stem fractions of the included land areas amounted to only 3% of all initial carbon stock loss. The potential available agricultural residues were based on 0.75 EJ/year, assuming 4% of current available biomass supply for energy purposes (19.2 EJ/year (Hanssen et al., 2019); Supplementary S5.1). We assumed no land-use change emissions were allocated to residual biomass, in line with Hanssen et al. (2019, 2020). Biomass to chemical conversion efficiency was collected from published data (Supplementary Table S5.2).

Emissions of biomass production

Emissions of biomass cultivation are regularly included in GHG footprint calculations and were obtained from various literature sources. For sugarcane, fertilizer emissions were taken from Hanssen et al. (2020). For woody crops and grasses, fertilizer emission data were averaged from data on willow or (organic) grass production from Ecoinvent 3.8 (Ecoinvent 2020) and from Hanssen et al. (2020). For each biomass feedstock, emissions from harvesting, mowing, tillage and tractor use (Ecoinvent 2020) were included (Supplementary Table S5.1). Cultivation emissions of residues were calculated based on corn stover, applying an allocation factor of 0.1 (market value-based) to the emissions of corn production (Wang et al. 2014).

$$Em_{cult,f,pc} = \frac{Em_{fert,f} + Em_{agri,f}}{\eta_{f,pc}}$$ **equation 5.3**

Where $Em_{cult,f,pc}$ are the emissions of biomass cultivation per feedstock type and per bio-based primary chemical route (kg CO_2-eq./kg chemical); $Em_{fert,f}$ the feedstock-specific fertilizer emissions (kg CO_2-eq./kg wet biomass); $Em_{agri,f}$ the emissions from agricultural practices such as mowing (kg CO_2-eq./kg wet biomass); and $\eta_{f,pc}$ the conversion efficiencies (η) from wet biomass to chemical feedstock and to primary chemical (kg chemical/kg wet biomass).

Emissions of primary chemical production

The emissions of primary chemical production were obtained by modelling inventories per chemical processing step. The chemical process inventories included energy input in terms of heat, steam, and electricity and, when available, material input in terms of chemicals and catalysts. Inputs were collected from published data (all inputs, by-products and other related data are shown in Table S5.1 with references). The emissions of the inputs and background processes were taken from the Ecoinvent database v3.8 (Ecoinvent, 2020) as system model 'at point of substition (APOS)'. In the default scenario, system expansion with substitution of the by-products was used to deal with multi-functionality, as recommended by the ISO-standards (ISO 2006a, 2006b). The use phase was excluded from the assessment based on equivalence.

$$Em_{chem,pc} = \frac{(Em_{energy,cp} + Em_{material,cp} + Em_{transport,cp})}{\eta_{f,cp}}$$ **equation 5.4**

Where $Em_{chem,pc}$ are the supply chain emissions of each chemical production step per bio-based chemical route (kg CO_2-eq/kg chemical); Em_{energy} the emissions related to the energy requirements in terms of heat, steam or electricity (kg CO_2-eq/kg chemical), $Em_{material}$ the emissions of material inputs, such as catalysts (kg CO_2-eq/kg chemical); and $Em_{transport}$ the emissions of transport including truck, barge and freight (kg CO_2-eq/kg chemical). Emissions were divided by the conversion efficiencies (η) from wet biomass to chemical feedstock and to primary chemical (kg chemical/kg wet biomass).

A first drying step was included in all processes, except for sugarcane. The energy needed to reduce the original moisture content to 10% was calculated based on work of Piccinno et al. (2016) (Supplementary Information S5.1). We assumed that the biomass is dried on-site by air to half of its moisture content (Shinners et al. 2011), and that the heating energy to dry to other half was provided by burning biomass, based on the energy content of the feedstock (Inventory Table in Supplementary S5.1). The extra biomass needed for heating was therefore included. Transportation of the biomass to the refinery was assumed as 550 km truck and 459 km barge (in tkm/kg dry biomass) based on the current number of refineries globally, area per continent and the averaged distance (in tkm/kg chemical) (Supplementary Table S5.1). Shipping the final chemicals was based on the average distance (11,241 km) between China, USA, Brazil and the EU (The Netherlands).

Emissions of embedded carbon in the primary chemicals

The majority of the fossil carbon involved in conventional primary chemical production ends up in the final product. In bio-based chemicals, this embedded carbon has a biogenic origin, which means that different carbon accounting applies, as explained below. To account for this difference, we specifically include the release of embedded carbon at the end-of-life stage (see Figure 5.1), assuming all carbon is directly emitted to the atmosphere at the end of life (thus implicitly assuming 100% incineration). The emissions were based on the chemical structure of the primary chemicals following equation 5.5.

$$Em_{embedded,pc} = \left(\frac{M_C}{M_{total}}\right) \cdot r \qquad \textbf{equation 5.5}$$

Where $Em_{embedded,pc}$ are the emissions related to embedded carbon released at the end of the product's life (kg CO_2-eq/kg chemical) per primary chemical (pc), i.e. methanol, ethylene, propylene, BTX); M_c is the carbon mass (g/mol) of the primary chemical; M_{total} the total weight of the primary chemical (g/mol); and r the molar ratio between CO_2 and C, which is 3.66 (dimensionless).

In terms of biogenic carbon accounting we follow the approach by Cherubini et al. (2011) and we assumed emissions of embedded biogenic carbon are CO_2-neutral, based on the conditions that (i) the biomass feedstock has rotation period of 5 years or less (Cherubini et al. (2011), and (ii) the chemical end-product has a lifetime of 10 years or less (Guest et al. 2013), as is typical for thermosets, thermoplastics or fibers.

Climate change mitigation potential of bio-based chemical production at scale

Switching from fossil to bio-based feedstocks for in the petrochemical industry could help mitigate climate change. To estimate the potential global contribution that bio-based chemicals could have towards climate change mitigation, we calculated the total amount of GHG emissions that could be saved when switching from fossil feedstocks to bio-based ones. We determined the global climate mitigation potentials per primary chemical route as described in equation 5.6. We only included the primary chemical routes that showcased complete global production volumes with emission factors lower than their fossil-based benchmark. Note that the primary chemical routes' global mitigation potentials are mutually exclusive, except for the residue-based routes.

$$CMP_{pc} = \sum_{x} \left(EF_{f,pc,x} \cdot P_{pc,x} \right) - Em_{fossil} \qquad \textbf{equation 5.6}$$

Where CMP_{pc} is the climate change mitigation potential of the primary bio-based chemical per chemical route (Gt CO_2-eq/Global production volume); $EF_{f,pc}$ the emission factor per bio-based primary chemical, feedstock and route (eq. 5.1) (kg CO_2-eq./kg chemical); $P_{pc,x}$ the potential production volume per grid cell (x) per primary chemical route (kg chemical), which is further described by equation 5.7; and Em_{fossil} are the total GHG emissions based on global production volume of the specific petrochemical that is replaced (Gt CO_2-eq/Global production volume).

The fossil pathway represents the current petrochemical production of cracking naphtha, from crude oil, and the supply chain GHG emissions were taken from Cullen et al. (2024). The GHG emissions of fossil-based chemical production included the supply chain emissions and CO_2 emissions from embedded carbon in the chemicals released at the end of life. For the fossil-based counterparts of the bio-based chemicals, all embedded carbon is emitted to the atmosphere (see eq. 5.5).

First, emissions per primary chemical route were determined by adding up the emissions from biomass cultivation, chemical production and the CO_2 emissions related to the embedded carbon in the chemicals released at the end of life. Second, the emission factors, including spatially explicit LUC emissions, were calculated and shown against their corresponding production potentials, resulting in 'emission-supply curves'. These were determined by sorting the grid cells by ascending emission factor and summing the corresponding production potentials across these cells. The chemical production potential per grid cell was derived as equation 5.7. The routes that could not cover complete global production volumes with emission factors lower than their fossil-based benchmark were omitted for further analysis. For the global climate change mitigation potentials, summation was done up to the production volumes required for global production demand, which were based on volumes of methanol, ethylene, propylene and BTX of 2022 (Statista 2023).

$$P_{f,pc} = A_x \cdot Y_{f,x} \cdot t \cdot \eta_{f,pc} \qquad \textbf{equation 5.7}$$

Where $P_{f,pc}$ is the total production volume per chemical per route per feedstock (Gt per chemical/yr); A is the area (in ha); Y the yield of the feedstock (tonne dry biomass/(ha x yr)); t the evaluation period (30 years); and η the conversion efficiency of the biomass feedstock to the primary chemical (tonne primary chemical/tonne wet biomass).

We included land areas that do not potentially lead to indirect LUC or may interfere with food production, i.e. abandoned agricultural land, marginal land, managed and degraded forests. Therefore, grid cells classified as urban land, cropland, pastures, water bodies, forests, grass- and shrub lands were excluded. The classification of current and future land areas were derived from the SSP2 baseline scenario in the IMAGE integrated assessment model (Stehfest et al. 2014). Based on LPJml, areas with low yields, i.e. less than 2.5 tonne of wet biomass/ha x year, were excluded. (Part of) the grid cells that are protected natural land areas (UN WCMC 2020), such as parts of the Amazon, were also excluded.

Sensitivity analyses

To test the robustness of the results, sensitivity analyses on key parameters and modeling choices were performed, these included:

- Evaluation period: LUC emissions are sensitive to the time period over which they are amortized. To quantify the impact the evaluation period has on the LUC emissions, LUC emissions were calculated based on a 80-year evaluation time (Hanssen et al. 2020), instead of the default of 30-years.

- Conversion efficiencies: conversion efficiencies of biomass into primary chemicals depend on yield and selectivity of the processes, which varies across literature. For each process, data on conversion efficiencies of each chemical processing step was collected and minima and maxima were determined to calculate its impact on the total emissions per route and on the process-specific emissions. Details can be found in Supplementary Table S5.2.
- Cultivation emissions: cultivation practices vary across the globe, leading to varying emission. A sensitivity analysis based on minimum and maximum values collected from literature was carried out to analyze the influence of different emissions on the total emissions of each route. Details are summarized in Supplementary Information S5.1.5.
- Electricity in chemical processing: the current electricity mix was replaced by a cleaner electricity mix. Emissions of the cleaner electricity mix were based on the 'low emissions & carbon-neutral' dataset from Galán-Martín et al. (2021). This resulted in 0.04 kg CO_2-eq/MJ of electricity, instead of the default of 0.14 kg CO_2-eq/MJ. The emissions of the electricity inputs from the chemical processing inventories were replaced with emissions from the cleaner electricity mix.
- Allocation method: Allocation based on calorific value (in MJ/kg product) was tested beyond the default of system expansion by substitution of by-products. The by-products covered both chemicals and fuels. Energy products that were re-used in the process were not changed. Details are summarized in Supplementary Information S5.1.4.

5.4. Results

Land-use change emissions

Land-use change emissions associated with the production of biomass depend on biomass feedstock (Figure 5.2) and location (Figure S5.2), and range between 0.1 and 4.1 kg CO_2-eq./kg wet biomass. Median LUC emissions of woody crops were predicted to be the largest, followed by grasses and sugarcane, with median values of 1.7, 1.3 and 0.4 t CO_2/t wbm, respectively (Figure 5.2A). This is primarily a result of the lower yields of woody crops compared to especially sugarcane, and grasses (Supplementary Figure S5.2, and specifically map A, E and I).

The LUC emissions encompass contributions from initial carbon stock loss and foregone sequestration (Figure 5.2B), of which the latter is not regularly included.

By including both, we account for the fact that removing natural vegetation does not only release stored carbon but also eliminates the potential sequestration of carbon in the future, i.e., what could have grown in 30 years. On average, we find that the emissions related to foregone sequestration contribute for 32-48% to the overall LUC emissions per feedstock type (see also Supplementary Figure S5.3). Though the LUC impact remains substantial when considering only the carbon-stock losses resulting from land clearing, ignoring foregone sequestration could lead to underestimation of land-use change impacts.

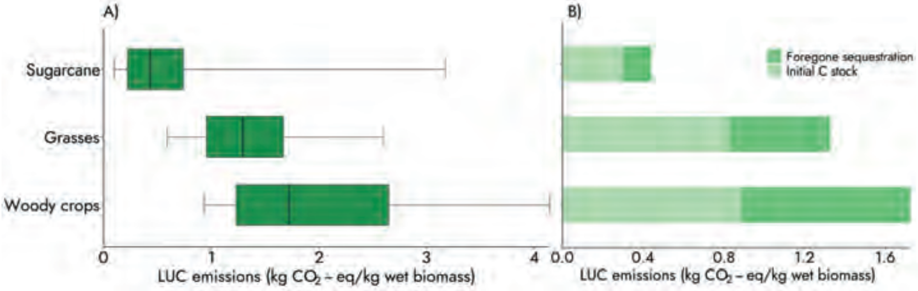

Figure 5.2: LUC emissions per feedstock type represented as (A) Boxplots (5,25,50,75,95 percentiles) of LUC emissions; and (B) contributions of initial C-stock loss and foregone sequestration to median LUC emissions. The initial C-stock loss relates to the initial biomass on-site that is removed to cultivate crops, and foregone sequestration relates to lost sequestration capacity of the natural vegetation by using the land as cultivation site. Note that the LUC emissions per feedstock type are mutually exclusive.

GHG footprints of bio-based primary chemicals

If we do not consider LUC emissions, 27 out of 30 bio-based routes are predicted to have lower GHG emissions compared to their fossil-based equivalents. For all bio-based routes, except for BTX production via the methanol-based route, we find lower supply chain emissions when compared to fossil-based production. In the production of ethylene, propylene and BTX, the lowest emissions are predicted for the naphtha-based routes. This is caused by two main factors: first, the process is well-developed, and allows for the simultaneous production of all three chemicals, thus distributing the environmental burdens among them. Second, the quantities of by-products generated in the naphtha-based routes offset the process emissions (2 kg CO_2-eq/kg chemical, while the process emissions are 1.6 kg CO_2-eq/kg chemical). Conversely, methanol-based routes producing olefins and aromatics demonstrate the highest emissions, primarily due to their relatively low conversion efficiencies.

Adding LUC emissions, we find that in most cases this is the largest contributor to overall bio-based chemical production emissions for all investigated routes, except for residues-based options (Figure 5.3). LUC emissions are therefore critical in determining whether these bio-based chemicals have lower or higher emissions compared to their fossil-based counterfactuals. Adding LUC emissions based on the 5% grid cells with the lowest LUC emissions, we find that 5 of the 21 chemical production routes (excluding the residue-based routes) result in lower life cycle GHG emissions compared to the fossil benchmark, which thus have the potential to reduce GHG emissions. Apart from the residues, promising routes include the sugarcane-based routes and the grasses-based (via naphtha) routes.

These findings imply that in terms of climate change, the use of residues in bio-based primary chemical production is favored over sugarcane feedstock, which is favored over second generation lignocellulosic crops. This finding is explained by LUC emissions dominating the life cycle GHG emissions for sugarcane, grasses and woody crops feedstocks. In case of sugarcane-based routes, the lower LUC emissions were predominantly a result of sugarcane's higher yields compared to the second generation crops, and to a lesser extent due to its application in further processing as wet biomass, therefore requiring overall lower amounts of biomass.

Sensitivity analyses

Considering a longer evaluation period leads to lower LUC emissions (Figure 5.4), because the emissions are amortized of a longer period. By applying an 80-year evaluation time on LUC emissions based on the 50% grid cells with the lowest LUC emissions, we find that EFs now become lower than the fossil benchmark for these three routes. Overall, we find that life cycle GHG emissions are on average 54% lower compared to the GHG emissions based on a 30-year evaluation period, considering LUC emissions based on the 50% grid cells with the lowest LUC emissions (Supplementary Table S5.7).

By applying a range of conversion efficiencies in each chemical process step, we observe that total emissions vary, potentially reaching up to almost three times the default emissions in case of ethylene from woody crops (Figure 5.4), or approaching zero or even negative emissions in case of the residues-based naphtha-route (due to the offset of emissions by by-products).

Sensitivity analyses on cultivation emissions (-5 to +6%) and renewable electricity use (reductions of 6% on average) demonstrate less influence on the life cycle GHG emissions compared to evaluation period and conversion efficiencies (Figure 5.4). Applying a calorific-based allocation method predicts on average 13% (-10 to +17%) higher GHG emissions compared to the GHG emissions based on system expansion by substitution of by-products. The outlier is the naphtha-route using residues, which is thirteen times larger as a result of the relatively large substitution impact of its by-products.

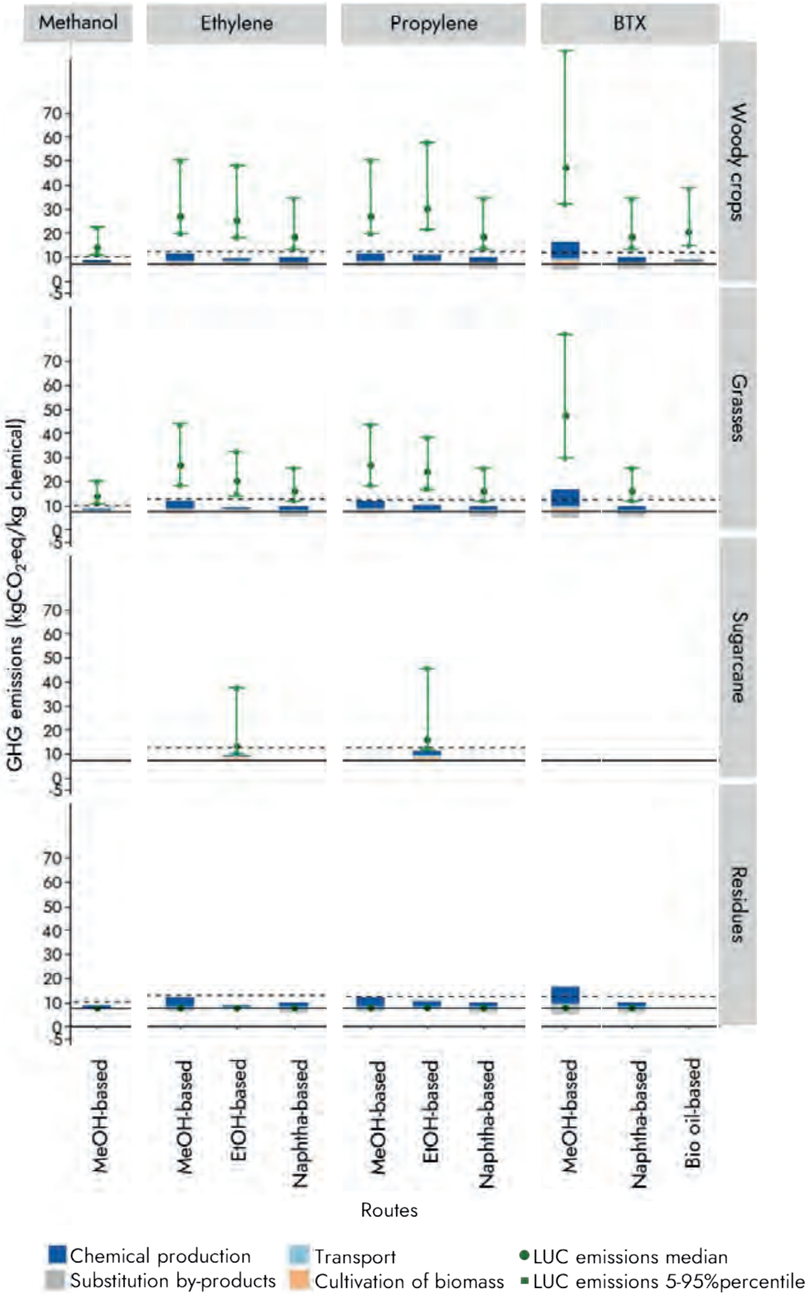

Figure 5.3: Total GHG emissions per stage (chemical production, cultivation of biomass, substitution of by-products & transport), presented per production route and feedstock type. LUC emissions are represented as a green line (range of total LUC emissions), dot (total LUC emissions based on median values) and square (total LUC emissions based on 5-95%-percentile values). The dotted black line represents the GHG emissions of the fossil-based chemical.

Global climate change mitigation potentials of bio-based primary chemicals

To assess the global climate change mitigation potential of each bio-based primary chemical route, we derived emission-supply curves that show the increase in emission factor of bio-based chemicals with cumulative production of the chemical (three curves are shown Figure 5.5). This increase is due to LUC emissions varying with location and crop yield. From the 30 emissions-supply curves (Supplementary Figure S5.6), the residue-based routes, the naphtha-based routes using grasses, and the sugarcane-based ethylene route show the largest potential to mitigate global climate change. Figure 5.5A shows that enough abandoned agriculture and marginal land is available to supply for sugarcane-based ethylene production with EFs lower than fossil-based ethylene, up to current ethylene production volumes. When also considering degraded and managed forests, up to 0.8 Gt ethylene can be produced annually with lower EFs than fossil-based ethylene, a more than tripling of current production. Ethylene produced from grasses as feedstock shows climate change mitigation potential, but further growth in production volume would lead to higher EFs compared to fossil-based ethylene (Figure 5.5B). Woody crops-based ethylene, when grown in specific locations, can lead to lower EFs compared to fossil-ethylene, but the largest share of the EFs are higher (Figure 5.5C).

Our findings indicate that life cycle GHG emissions from global petrochemical production can be mitigated from 6% to 0.4% using residue-feedstocks, and global petrochemical ethylene production from 2.2% to 1.2% by using sugarcane as feedstock, and from 2.2% to 1.8% using grasses (Figure 5.6). There are sufficient residues available to replace global production volumes (Supplementary Figure S5.6, last three panels). When sugarcane or grasses are used, the global mitigation reduction potential ranges from 19-45%. Note that per route the global climate change mitigation potential is calculated, but the land cannot be utilized multiple times. As the considered land covers can only be used once, global production based on crops with low EFs is limited. This implies careful selection of land area, biomass feedstock and chemical production route to achieve significant climate change mitigation potentials.

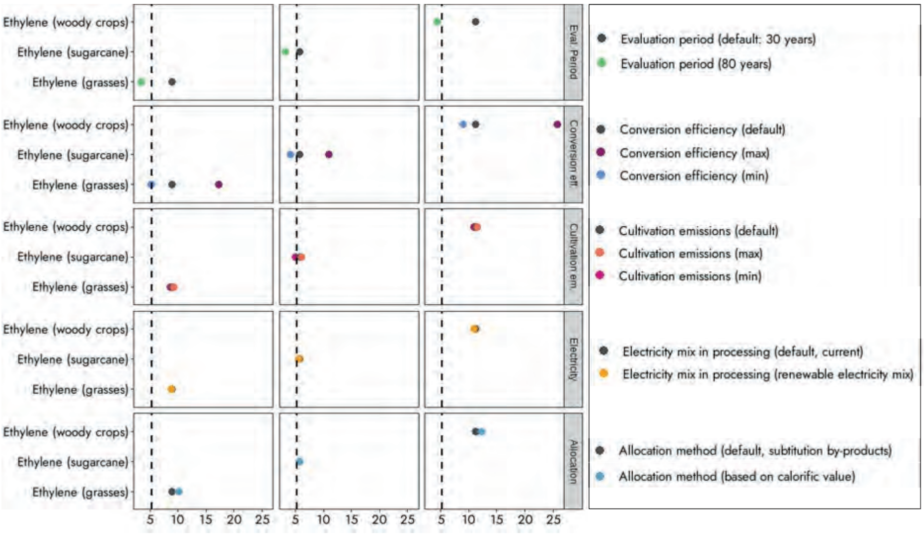

Figure 5.4: Sensitivity analyses and their impact on the total GHG footprints shown for three routes: ethylene based on (i) woody crops (via naphtha-route), (ii) sugarcane (via EtOH-route) and (iii) grasses (via naphtha-route). Dashed line represents life cycle GHG emissions of fossil-based ethylene. Sensitivity analyses include: 80-year evaluation period for LUC emissions, ranges in regard to conversion efficiencies in chemical processing and cultivation emissions, electricity in chemical processing replaced by a cleaner electricity mix, allocation based on calorific value. Note: All LUC emissions considered in the GHG footprints are based on median values, i.e., based on the 50% grid cells with the lowest LUC emissions. LUC emissions based on an 80-year evaluation period per feedstock type (based on the 5%, 50% and 95% of grid cells with the lowest LUC emissions, in kg CO_2-eq./kg wbm) are shown in Supplementary Figure S5.4. Further details can be found in Supplementary Tables S5.2,4-6. Sensitivity analysis results on total GHG footprint of all routes are shown in Supplementary Figure S5.7-10.

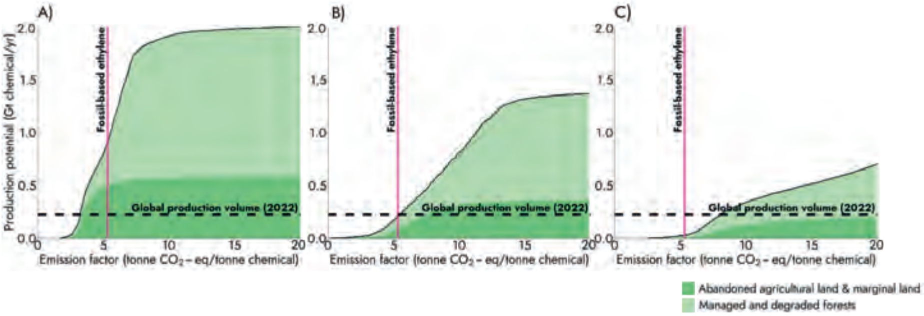

Figure 5.5: Three emission supply curves of A) Sugarcane-based ethylene via the EtOH-route; B) Grasses-bases ethylene via naphtha-route; and C) Wood crops-based ethylene via naphtha-route. The dashed line shows the global production volume of ethylene (2022); the pink line represents the fossil-based emission factor (in t CO_2-eq/t ethylene). The emission factors are the emissions from land use change, biomass cultivation, chemical production and the CO2 emissions related to the embedded carbon in the chemicals released at the end of life (Eq. 5.5). The production potentials are based on the yields of the included land covers, multiplied by the biomass to chemical conversion efficiency (Eq. 5.7). The emissions supply curves of all routes and per feedstock are shown in Supplementary Figure S5.6.

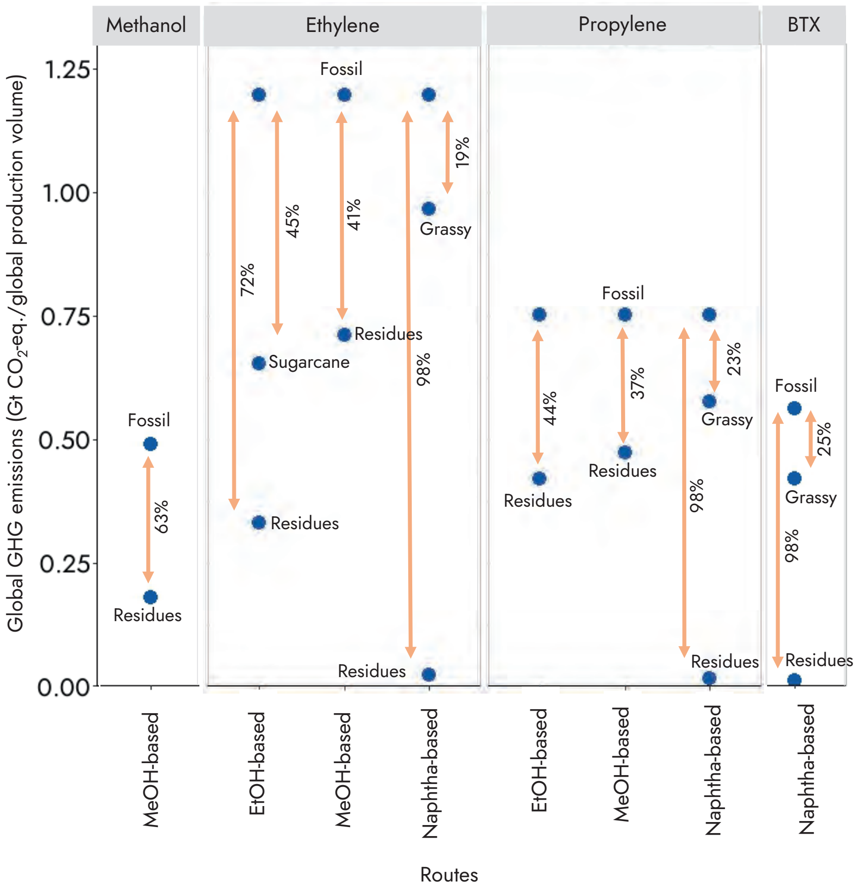

Figure 5.6: Global climate change mitigation potentials for residue-based methanol, ethylene, propylene and BTX via naphtha and MeOH-based routes; sugarcane-based ethylene via the EtOH-route; and grasses-based ethylene, propylene and BTX via naphtha-based route. The global climate change mitigation potentials were determined ascending emission factor, including spatial-explicit LUC emissions, and summing production potentials, up to the production volumes required for global production demand. Global production volumes of methanol, ethylene, propylene and BTX are from 2022 (Statista, 2023).

5.5. Discussion

Interpretation

Our results demonstrate that the life cycle GHG emissions of primary chemicals are predominantly determined by LUC emissions and to a lesser extent by chemical production. This implies that omitting LUC emissions in the assessment of bio-based production emissions can lead to misleading conclusions.

Other carbon footprint studies on alternative carbon feedstocks in the petrochemical industry found that biomass can contribute to a net-zero (Gabrielli et al. 2020) or planet-compatible chemical industry (Meng et al. 2023), yet these assessments did not include LUC emissions. We find on average that 63% of the GHG emissions of the bio-based primary chemical routes relate to LUC emissions (based on median LUC values). In contrast, work on bio-plastics' GHG footprints have showed for sugarcane-based PLA that 10% of life cycle emissions related to LUC, and in case of sugarcane-based PET, it varied between 1-17% (Zheng and Suh 2019).

The GHG footprints of bio-based chemical production varies across literature. On average, bio-based products that excluded LUC emissions reduce GHG emissions by 47% compared to their fossil-based counterparts (Zuiderveen et al. 2023b). We find that bio-based primary chemicals reduce GHG emissions on average by 56% compared to their equivalent petrochemicals while excluding LUC. Bio-based methanol, for example, showed 15% lower cradle-to-grave GHG emissions compared to fossil-based methanol (Montazeri et al. 2016), though it is unclear whether these studies included LUC emissions. In contrast, we find that bio-methanol from woody crops results in 44% higher GHG emissions compared to fossil-based methanol when accounting for LUC (based on the 5% grid cells with the lowest LUC emissions), but in 64% lower GHG emissions when excluding LUC.

We show that the GHG benefits of replacing petrochemicals with bio-based primary chemicals depend on (i) careful selection of cultivation sites to minimize LUC emissions and (ii) the use of carbon-efficient processes. Comparable in method to this study, Hanssen et al. (2020) have found that the range of negative emissions from BECCS by including spatially explicit LUC emissions also depends on cultivation location and evaluation period. A recent policy brief has indicated that the production of modern bio-fuels might even cause higher CO_2 emissions than those from burning fossil diesel primarily due to LUC emissions, and if averaged over a 30-year evaluation period (Merfort et al. 2023).

LUC emissions crucially depend on the assumption of evaluation period. Longer evaluation periods lead to lower LUC emissions. This finding is in line with other work, such as on bio-energy, indicating that a longer evaluation period can lead to substantially higher energy potentials at lower EFs (Hanssen et al. 2020). Different land-use projects vary in lifespan, and because this is often unknown, common practice is to apply a 20-year period was established by following IPCC guidelines (IPCC 1996). Studies have criticized the ambiguity of a 20-year harmonization (Maciel et al. 2022), suggesting that the evaluation period could be based on other factors, such as biophysical parameters (De Rosa et al. 2018) or policy goals (Valin et al. 2015). There are studies applying an 80-year evaluation period because it corresponds with the mitigation pathways' duration towards the year 2100 (Hanssen et al. 2020, 2021). Whereas agricultural cultivation sites can be in use for decades, land use after 30 years is in principal uncertain and there is no guarantee (U.S. EPA 2010). One could also argue that on the basis of discount rates (Newell and Pizer 2003), carbon emissions today have a different, more significant value than carbon emissions occurring in the future. This advocates for a shorter evaluation period rather than a longer one. We recommend it should be at least a point of sensitivity in LCA assessments of bio-based products, showing the variation in results by applying different evaluation periods.

There is not a consistent format to include LUC emissions in life cycle GHG emissions. We show how the outcomes of a global vegetation model coupled to an integrated assessment model can produce such results. This approach has already been applied, but on other applications of biomass, such as bio-energy (Elshout et al. 2015; Daioglou et al. 2017; Hanssen et al. 2020). Specifically, these LUC emissions, either based on the 5%, 50% or 95% of grid cells with the lowest LUC emissions, could be applied to other bio-based products' case-studies.

Limitations

In our study, no LUC emissions were assigned to residues. Although this is a commonly applied practice (Hanssen et al. 2019), technically when residues become a commodity, allocating LUC emissions would be required. Karras et al. (2022) have examined pricing for residue biomass, ranging from zero to one euro per kilogram dry matter, which could be used to economically allocate LUC impact to residues. Increase in GHG emissions of residues will decrease its climate change mitigation potential for bio-based production in the petrochemical industry, and should be further understood. The availability for residue-based primary chemical production should also be further understood. In our study, a share of 4% of global biomass residue supply otherwise used for energy purposes was assumed, which can sufficiently supply the bio-based primary chemical industry with feedstock. The availability of residues as feedstock for energy production has been researched (Daioglou et al. 2019; Kongchouy et al. 2021), and even though residues can potentially meet a significant part of global energy demand by 2050, potential biomass supply varies considerably between integrated assessment models (Hanssen et al. 2019; Rose et al. 2022). Uncertainty has also for example been indicated regarding the availability of waste biomass, such as food waste (Cristóbal et al. 2018).

Another limitation is the consideration of current chemical demand, which may increase towards the future. Following current trajectory, demand of the six main petrochemicals is set to increase by 30% by 2030 and 60% by 2050 (IEA 2018). Covering this growth in production volume considering EFs lower than their fossil-based equivalents is only possible for ethylene production from sugarcane (up to 0.8 Gt), implying limited future production potentials. Additionally, future demand with regard to other fossil-fuel products may also change. This would especially affect the GHG emissions of the bio-naphtha-based route, because in the future, the credits from avoided fossil-fuel products would diminish (if we are to follow future scenario's reducing fossil energy, e.g., (IEA, 2023)).

To systematically expand our study's LUC emission approach, a next step would be to broaden the analysis by including more crops, and specifically, to focus on the variation in crop yields and their geographical constraints. Multiple chemical production routes exist using, for example, corn, sugar beet or wheat as feedstock (Kuznecova et al. 2018), including efficient production routes that have been commercialized (Bazzanella and Ausfelder 2017). Moreover, sugarcane has a high yield but its cultivation is limited in temperate areas, whereas wheat and barley grows well in these areas (Beringer et al. 2011).

Finally, bio-based production can involve significant trade-offs with other environmental impacts such as freshwater eutrophication impact (Zuiderveen et al. 2023b). Especially impacts related to agricultural practices are relevant to further research, including ecotoxicity (related to pesticides) and eutrophication (related to fertilizers) (Ögmundarson et al. 2020), to understand the sustainability of bio-based chemical production and to reduce their environmental impacts.

Implications

Replacing fossil by bio-resources in the petrochemical industry can mitigate climate change, yet, land requirements limit the climate benefits of bio-based primary chemicals. We find that marginal and abandoned agricultural land and degraded and managed forest have relatively high LUC emissions under the assumption of a 30-year evaluation period. Bio-based chemical production is most effective when using residues, and if crops are used, it should be cultivated in locations leading to minimal land-use change impacts, requiring careful selection of cultivation site. Regardless, the focus should be on sourcing biomass sustainably. Overall, LUC emissions must be accurately accounted for to fully address the GHG footprint of bio-based chemicals. This is particularly important in environmental evaluations of bio-based chemical production, precisely because conversion efficiencies are often relatively low and land requirements for biomass feedstock therefore high.

The global supply of bio-based feedstock for the petrochemical industry, with lower EFs compared to fossil-based petrochemicals, is limited when evaluated over a 30-year evaluation period and constrained to using abandoned agricultural land, marginal land, and degraded and managed forests. Firstly, this implies consideration of variation of LUC emissions regarding evaluation periods in LCAs to better understand GHG benefits of bio-based chemicals. Secondly, it might imply that research entering a more political realm is required on division of bio-based feedstock over sectors - who should have priority? This topic is highly complex, and a sustainable bio-economy entails the design of policies that are able to capture these complexities and make a fair allocation of available resources to the different sectors. Thirdly, it implies the need for a combination of approaches to achieve further GHG emission reductions in the petrochemical industry.

A combination of approaches to achieve a net-zero petrochemical industry can include using bio- and waste-resources, improved end-of-life handling (such as recycling), the abatement of end-of-life emissions, and electrification of production processes with the use of renewable electricity mixes (Lange 2021). The latter can potentially lead to GHG emission reductions of up to 40% (Saygin and Gielen 2021). In this study, however, the climate change reduction potentials by applying renewable electricity mixes were limited. In general, most of the chemical production pathways are still traditional thermochemical routes (Palou-Rivera and Grieco 2022), which would require decarbonization. Recycling can lower GHG footprints of bio-based chemicals by 16% (Saygin and Gielen 2021). However, in the case of carbon-rich chemicals, such as primary chemicals, reduction potentials are much larger. Overall, a combination of measure is key in making the petrochemical industry more sustainable and circular and need to be further understood.

5.6. Conclusion

Overall, we show that replacing fossil-based petrochemical production with bio-based resources has the potential to mitigate global climate change, but careful selection of both cultivation sites and chemical production route is crucial. Our results imply that biomass as feedstock can play a role in transforming the chemical industry, but fully replacing global production with dedicated crops from abandoned and marginal lands is limited. Therefore, on the demand side, smaller volumes may be required considering the limitations in abandoned and marginal land availability, and on the product side, the development of more carbon-efficient processes are key.

Acknowledgement
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6.

Synthesis

6.1. Introduction

The petrochemical industry plays a critical role in modern economies by supplying the chemicals used across various manufacturing sectors, including plastics production. At the same time, the petrochemical industry contributes for about 4% of global anthropogenic annual greenhouse gas (GHG) emissions (Bauer et al. 2022) and is the largest industrial energy consumer, accounting for 14% of global oil consumption and 9% of global natural gas consumption (Meng et al. 2023). Mitigating GHG emissions in the petrochemical industry is particularly challenging due to its reliance on fossil fuels as both feedstock and source of energy.

Replacing fossil fuel use as feedstock in the petrochemical industry requires alternative carbon-rich feedstocks. Biomass could form a low-emission source of carbon as biomass captures CO_2 during growth. Aside from switching to a different carbon source, the environmental impact of chemicals production can be reduced by electrification using new processes and reactors that run on renewable electricity instead of fossil fuel (Schiffer and Manthiram 2017). These two strategies are typically combined in the development of emerging bio-based products.

The actual, full life-cycle environmental benefits of emerging bio-based products do, however, still need to be demonstrated. Doing this at an early stage of technology development is particularly important as it helps to prevent unforeseen environmental impacts and minimizes the risk of technological lock-ins (Cucurachi et al. 2022). While an increasing number of studies have been carried out to evaluate the environmental performance of emerging bio-based products (Aryapratama and Janssen 2017; Pachón et al. 2020; Müller-Carneiro et al. 2023; Moretti et al. 2021; Saavedra del Oso et al. 2023), their results vary strongly. This variability may arise from differences in biomass feedstock, land use changes and variations in biogenic carbon accounting practices (Guest et al. 2013a; Brandão et al. 2013), but also from uncertainty with emerging technologies and methodological challenges in prospective LCA (Tsoy et al. 2020). To understand if, and to what extent, emerging bio-based products have environmental benefits compared to their fossil-based equivalents, it is important to map and compare their environmental footprints.

The main aim of this thesis was to quantify the environmental footprints of emerging bio-based products for the chemical industry compared to their fossil counterparts. This synthesis chapter discusses the outcomes of the previous chapters in the context of the two research questions:

- How to assess the environmental consequences of early-stage chemical processes that produce bio-based products compared to their fossil counterparts (Section 6.2)?
- What are the environmental consequences of replacing fossil- by bio-based products in the chemical industry (Section 6.3)?

Policy implications based on my results are discussed in section 6.4, with a concluding section at the end (section 6.5).

6.2. Environmental assessment of early-stage technologies producing bio-based products

Prospective LCA evaluates the expected environmental impacts of novel products when developed and produced at scale in the future. Below, I elaborate on the insights I gained from applying a prospective LCA framework in practice. I will focus on (i) how to upscale from lab to industrial scale and account for future developments, (ii) how to systematically account for biogenic carbon and land-use change emissions in LCAs of biobased products, and (iii) how to assess possible burden shifting.

Key elements of a prospective LCA framework

To systematically upscale a new product from lab to industrial level, I used the framework of van der Hulst et al. (2020). This relatively new framework guides the LCA practitioners through two phases: (1) the upscaling, including process changes, size scaling and process synergies, and (2) industrial & future developments. Insights from applying this framework to advance the field of prospective LCA are discussed in the next two sections.

Step 1: How to upscale?

A prospective assessment ideally scales up the early-stage technology to the same technological maturity as a full-scale technology. However, upscaling can be challenging due to a lack of (industrial) data. In general, in chapter 2 I found no indication that the initial TRL of a technology introduces systematic bias in early-stage assessments, even though prospective LCAs based on lab-data may overestimate environmental impacts (Moni et al. 2020). However, development predictions could not be fully aligned across studies (Chapter 2), such as to what extent waste streams were recycled or heat integrated. Standardizing technology development predictions across studies remains challenging. A first step would be, to clearly report the TRLs in prospective LCAs. Chapter 3 indicated that this does not only help to scope prospective LCA research but also helps to compare across different early-stage assessments. Which upscaling steps are required, depends on the starting TRL. In Chapter 2, I recommended the development of technology-specific TRL guidelines, facilitating more comparable assessments. For example, the broad application of fermentation-based technologies (which compromised 55% of the data points in Chapter 2) involves different developmental stages, such as the requirement of bioreactors (Bazzanella and Ausfelder 2017), compared to electrochemical (Chapter 3) or thermochemical catalytic processes (Chapter 4). Similarly, the valorization of lignin involves multiple pretreatment steps like enzymatic hydrolysis, which is different from processing sugarcane (Ponnusamy et al. 2019). Overall, per emerging technology or bio-based product, specific upscaling steps are involved, depending on the data that is available.

Chapter 3 and 4 worked with primary lab or pilot data, collected from Avantium and BioBTX, and expert views to further upscale. These were crucial: detailed technical data is often unavailable and usually not within the LCA practitioners' expertise, while LCA can also assist product development at an early-stage to avoid lock-ins (Keijer et al. 2019). In Chapter 3, a combination of process design tools (ASPEN©Plus and Excel) and expert input (internal data from companies and expert consultations) was useful in modelling the inventory. In Chapter 4, remaining technical data gaps were covered using the framework from Piccinno et al. (2016), i.e. to approximate the heating energy for an additional up-scaled distillation step. Literature is available on upscaling, e.g. from more generic guidance (Buyle et al. 2019) to decision trees (Tsoy et al. 2020), or more thematically, specifically for novel bio-based products (Cucurachi et al. 2022). This technical part is ideally sufficiently dealt with, but depends on the data available for the LCA practitioner – differences in level of detail may, therefore, remain. Transparency on technology and proxy processes is therefore highly recommended (Adrianto et al. 2021).

Industrial processes are typically optimized for conversion and energy efficiency and upscaling of an emerging technology therefore needs to consider process synergies, e.g. the integration of heat and reduction of waste streams. In general, I found in Chapter 2 that in technical upscaling of emerging bio-based products, process synergies such as heat integration was included in 22% of the cases, recovery of solvents in 12%, treatment of waste including energy recovery in 22%, and recycling of waste streams in 40%. In other words, although 92% of the studies upscaled to a TRL 9 (based on production output and size), only 48% of them included one or more types of process synergies. This finding indicates differences in the level of detail of technical development of the products evaluated. To systematically upscale a technology, specifying the following three distinctive steps in technological development is recommended: size scaling, process changes and process synergies (van der Hulst et al. 2020). I found it fruitful to combine the use of expert views, process design, and covering the remaining technical gaps by approximation, e.g. based on the upscaling framework of Piccinno et al., (2016).

Step 2: How to include industrial & future developments?
Ideally, once the processes are upscaled, a prospective LCA includes modelling of improvements of technological industrial maturation (Buyle et al. 2019) and future developments (Arvidsson et al. 2017). Chapter 2 discussed that a prospective LCA requires temporal alignment, when compared at a future point in time, of both the emerging technology as well as the fossil baseline product, and should consider changes in both the foreground and background systems. A prospective LCA deals with a technology at a future point in time (van der Giesen et al. 2020), yet industrial learning (in the foreground data) and external developments (in the background data) are often not included (Parvatker and Eckelman 2019). Studies have recommended how to include future scenarios for foreground and background data (Bisinella et al. 2021a), e.g. based on policy reports (Chapter 3) or key parameters (Steubing and de Koning 2021). Whereas external developments constituted a relatively small part in Chapter 3 (a renewable electricity mix for 2030 and 2050 based on policy reports), in Chapter 4, a more comprehensive assessment was carried out. A future electricity mix (2050) was included based on projections from the integrated assessment model IMAGE (Stehfest et al. 2014), as well as a future recycling scenario, which was based on a 2 °C-Circular Economy scenario on future plastic flows (Stegmann et al. 2022). The background datasets were adapted using the approach of Mendoza Beltran et al. (2020), which integrates Ecoinvent databases with IMAGE data. This approach has demonstrated to be useful in recent other prospective LCAs as well (van der Hulst et al. 2022; Georgiades et al. 2023; Zhong et al. 2021). Industrial learning was accounted for by applying generic future energy reductions of 1% per year (Blok 2004; Bazzanella and Ausfelder 2017), i.e. lowering the energy requirements in the core chemical foreground processes. Industrial learning is still relatively unexplored, though studies exist on learning curves for technology development (Bergesen and Suh 2016; Thomassen et al. 2020). Future research is therefore recommended towards developing technology-specific learning curves, to be systematically applied in prospective LCA studies.

Overall, I found the framework of van der Hulst et al. (2020) useful as a systematic approach for prospective LCA, and I would recommended to further develop technology-specific TRL guidelines and open prospective LCA databases, covering both foreground data, such as data repositories including a diverse representation of emerging materials and technologies (Moni et al., 2020), as well as background data, such as the efforts of Mendoza Beltran et al. (2020) by integrating Ecoinvent databases with IAM data.

Biogenic carbon accounting and land-use change emissions

Products based on biomass instead of fossils as a feedstock bring specific challenges regarding their environmental assessment. With regard to assessing GHG footprints these are: (1) biogenic carbon accounting and (2) land-use change emissions. The following sections provide insights and recommendations to address these aspects.

Biogenic carbon accounting

Carbon embedded in bio-based products has a biogenic origin, i.e., it is obtained from biomass that sequesters CO_2 during growth, as opposed to fossil-based products, which contain fossil carbon. For biogenic carbon, carbon sequestration during biomass growth equals emissions of embedded carbon at the end of life. To reflect this balance, I consistently applied the following accounting approach throughout Chapters 2 to 5: (i) The system boundary was set to cradle-to-grave by assuming the embedded carbon in the chemicals to be released at their end of life in the form of CO_2 (explained in the next paragraph); (ii) Biogenic carbon emissions were considered CO_2-neutral because CO_2 is taken up by biomass and released again at the end of the product life cycle. These assumptions apply when (1) the considered biomass feedstock has a short growing time of typically one year (in line with the GWP_{bio} accounting approach by Cherubini et al. (2011)) and when (2) the bio-based products are typically short-lived (i.e., the temporary carbon storage is not relevant, <10 years (Guest et al. 2013a)), such as single-use plastics. This was the case for the assessed bio-based products across Chapter 2 to 5.

The embedded carbon in many products, such as solvents or plastics, end up in the environment in the form of CO_2 within a relatively short period, e.g. via incineration of waste (Scown 2022). In regard to petrochemicals, which are used in the manufacturing of a myriad of products, it is complicated to assess their actual end-of-life management (Caldeira et al. 2022). To account for these CO_2 emissions, the embedded carbon in the chemicals can be assumed to be released at their end of life based on the chemical structure of the chemical. The following formula (Equation 6.1) was applied in Chapter 2 to 5 to the fossil-based products:

$$Em_{embedded\ carbon} = \left(\frac{M_C}{M_{total}}\right) \cdot r \qquad \textbf{equation 6.1}$$

Where $Em_{embedded\ carbon}$ are the emissions related to embedded carbon released at the end of the product's life (kg CO_2-eq/kg chemical); M_c is the carbon mass (g/mol) of the primary chemical; M_{total} the total weight of the primary chemical (g/mol); and r the molar ratio between CO_2 and C, which is 3.66 (dimensionless).

This standardization approach is useful because (1) it is a simple calculation method, (2) it avoids complication of chemical application in a myriad of end-products and their numerous end-of-life handling. Ideally waste disposal is fully addressed, and to calculate the global warming potential, the GWP_{bio} indicator can be used for bio-based products with storage periods and biomass growing time of >10 years (Guest et al. 2013b). Moreover, it is recommended to avoid the often applied '-1/0'-approach, which assigns credits for carbon uptake in biomass while not considering its release (also based on findings from Chapter 3, where two accounting approaches were tested). This could lead to biogenic carbon mismatch and potential misleading results regarding negative GHG emissions. In the best case, bio-based production is carbon-neutral, which may result in negative emissions when applying additional measures, such as CCS combined with bio-chemical production (Jiang et al. 2020), circularity measures combining plastic recycling with high biomass content (Stegmann et al. 2022) or bio-char (e.g., co-product in pyrolysis) incorporation into soil (Jeswani et al. 2022), and only if the products have a long lifetime.

Additionally, a large share of fossil-based chemicals' GHG emissions is related to the end of life, because of their high carbon content (Chapter 3 to 5). Whereas for bio-based products these emissions were considered carbon-neutral, fossil-based chemicals' emissions related to the embedded carbon were 48-70% of their total emissions per functional unit (Chapter 4 and 5). Chapter 5 calculated that petrochemical production contributes 6% of global life cycle GHG emissions annually (2022), while others have estimated this contribution to be 3 to 4% (Bauer et al. 2022; IEA 2018). The latter were direct GHG emissions, i.e., Scope 1, the difference may therefore arise from the inclusion of the end-of-life CO_2 emissions related to the embedded carbon in Chapter 5, or from upstream emissions. Fossil petrochemicals are significantly impacted by the management of carbon at the end of life stage (IEA 2022). Meng et al. (2023) have shown that for life cycle emissions of ethylene and propylene, feedstock and end-of-life emissions are most important. Serpell et al. (2021) highlighted how the end-of-life emissions of petrochemicals are influenced by their disposal methods, with incineration leading to significant CO_2 emissions. Overall, these findings underscore the need to include end-of-life stage in especially LCAs on bio-based versus fossil chemicals. More broadly it implies abatement of end-of-life emissions, e.g., waste incineration with CCS technologies (Bisinella et al. 2021b), and improved waste management strategies, such as recycling (Chapter 4) or re-use, to mitigate climate change impacts.

Land-use change emissions

As many sources of biomass require additional land for cultivation, a second element relevant in the GHG emissions of bio-based products is land-use change (LUC) emissions. LUC emissions relate to carbon stock losses due to removing of original vegetation (Fargione et al. 2008; Searchinger et al. 2008) or the lost capacity of natural vegetation to sequester CO_2 (Righelato and Spracklen 2007). GHG emissions resulting from land use changes can significantly impact the GHG emissions of bio-based products, or even outweigh the GHG savings (Searchinger et al. 2008; Nong et al. 2020).

The methodological novelty of chapter 5 is its systematic inclusion of LUC emissions for bio-based chemicals, with spatially explicit modelling of LUC emissions for thirty different chemical production pathways. The LUC emissions were based on: (1) land availability and land cover types, (2) spatially explicit carbon stocks and (3) crop-specific yield estimates (Hanssen et al. 2020), which were obtained from the global vegetation and hydrological model LPJml (Beringer et al. 2011; Müller et al. 2016) coupled to the integrated assessment model IMAGE (Stehfest et al. 2014). The LUC emissions (Equation 6.2) included the emissions due to land clearing (carbon stock loss) and the differences in carbon stocks between the feedstock plantation and the natural vegetation regrowth benchmark over a period of 30 years (foregone sequestration), i.e., the lost sequestration capacity of natural vegetation due to the use of the land for plantations. A 30-year evaluation time reflects a typical plantation lifetime. Only abandoned agricultural land, marginal land, managed and degraded forests were included, to avoid indirect LUC emissions. Spatially explicit LUC emissions were calculated for three types of feedstock: sugarcane, grasses (switchgrass and miscanthus), and dedicated woody crops (willow and poplar). These emission values can be systematically applied by multiplication with the conversion efficiencies of chemical production (tonne product/tonne dry biomass).

$$Em_{LUC,f,x,p,t} = \frac{\Delta C_{f,t,x} \cdot r}{Y_{f,t,x} \cdot t \cdot \eta_{f,p}} \qquad \textbf{equation 6.2}$$

Where $Em_{LUC,f,t,x,p}$ are the LUC emissions per feedstock type, per location (grid cell) and per bio-based primary chemical over a considered evaluation period (kg CO_2-eq/kg chemical); ΔC is the difference in carbon stocks between the feedstock plantation and the natural vegetation regrowth benchmark after 30 years (tonne C/ha); r molar ratio between CO_2 and C (dimensionless); Y is the yield (in tonne wet biomass/(ha x yr)); η the conversion efficiency of biomass feedstock to the primary chemical (in tonne product/tonne wet biomass); and t is the evaluation period (30 years as a default).

The subscripts represent: (f) feedstock type, i.e. sugarcane, grasses or woody crops; (t) considered period related to the natural vegetation regrowth benchmark; (x) the specific grid cell; (p) the product.

A longer evaluation period leads to lower LUC emissions, because the emissions are amortized over a longer period. This finding corresponds with other research, such as on bio-energy (Hanssen et al. 2020). Different land-use projects vary in lifespan, and commonly, a standard evaluation period of 20-years is applied, based on IPCC guidelines (IPCC 1996). However, the ambiguity of this 20-year standard has been criticized (Maciel et al. 2022), proposing other consideration to set the evaluation period, e.g., policies (Valin et al. 2015) or biophysical parameters (De Rosa et al. 2018). Some studies have applied an 80-year evaluation period to align with mitigation pathways toward 2100 (Hanssen et al. 2020, 2021). While agricultural sites can be used for decades, land use after 30 years is uncertain (U.S. EPA 2010). Additionally, discount rates imply that current carbon emissions have a greater impact than future ones (Newell and Pizer 2003), supporting a shorter evaluation period. I recommend to consider evaluation period at least as a point of sensitivity in LCA assessments to show variation in GHG footprints.

There are different modeling approaches to estimate LUC emissions, such as using Integrated Assessment Models (IAMs) (De Rosa et al. 2016), and specific guidelines (European Commission 2010), yet there is not a consistent format to include LUC emissions in life cycle GHG emissions. Chapter 5 demonstrated how the outcomes of a global vegetation coupled to an IAM can produce such results. This approach has already been applied, but on other applications of biomass, such as bio-energy (Elshout et al. 2015; Daioglou et al. 2017; Hanssen et al. 2020). The LUC emissions values from Chapter 5 can be directly applied in other bio-based products' case-studies. To systematically expand this approach, a next step is to include additional crops and their respective conversion routes, and specifically, to focus on the variation in crop yields and their geographical constraints (e.g., sugarcane has a high yield but its cultivation is limited in temperate areas, whereas wheat grows well in those areas (Beringer et al. 2011)).

Beyond climate change impact

When evaluating the environmental benefits of bio-based products, it is important to not only address GHG emissions. Efforts should be made to avoid possible burden shifting to other impact categories. The significance of environmental impacts beyond climate change for the bio-based products I studied is discussed in the following section. In addition, the combination of prospective LCA with absolute sustainability assessment that I performed in this thesis provides further insights into the sustainability of emerging bio-based products.

Other environmental impacts

The necessity of including impact categories beyond global warming was emphasized in chapters 2 to 4. GHG emission reductions for bio-based products compared to their fossil-based counterfactuals were found, yet higher impacts were predicted in other impact categories, such as eutrophication or land use. Most research is published on chemical industry's CO_2-emissions or their carbon footprint (Galán-Martín et al. 2021; Stegmann et al. 2022; Meng et al. 2023; Zheng and Suh 2019) and fewer studies include more environmental impact categories (Ögmundarson et al. 2020). Chapter 2 identified that a limited number of studies considered the impacts on land use, water use, and ecotoxicity. Yet, 'net-zero' emissions pathways for the chemical industry depend on land and water, with scarcity of these resources imposing serious constraints (Gabrielli et al. 2023). Only a few studies in Chapter 2 did report on land- and water use and indicated an increased impact for bio-based products. Chapter 4 projected increased water consumption of alternative BTX-production by 2050, which was attributed to anticipated carbon capture and storage (CCS) in the future electricity market (in line with previously noted hydrological constraints of CCS (Rosa et al. 2020)). Ögmundarson et al. (2020) highlighted that for bio-chemicals the most relevant impact categories are global warming, land use, water use, and eutrophication (due to fertilizer use) and ecotoxicity (due to pesticide use) for feedstock production. To minimize burden shifting, it is therefore crucial to include a variety of impact indicators, especially those relevant for feedstock production.

Absolute environmental sustainability assessments

Combining an LCA with an absolute sustainability assessment, as was done in Chapter 4, gives insights into whether one product design is more sustainable than the other and whether it stays within the planetary boundaries. An absolute assessment can assess whether a product is sustainable in absolute terms (Bjørn et al., 2019), i.e. comparison of environmental impacts to certain limits, thresholds or targets, in this case the Planetary Boundaries (Rockström et al. 2009). By doing this, we can assess whether the implemented strategies for reducing environmental impacts are sufficiently effective, or if premature conclusions of success are being drawn.

Different AESA methods are being developed linking the PB-framework to LCA. There is, however, currently no common framework to do that (Bjørn et al. 2019). Among the different methods, one approach is to adapt the PB-framework to the indicators of the LCA method. Work has been done on carrying capacity-based normalization references for the Environmental Footprint (EF) midpoint categories (Bjørn and Hauschild 2015; Sala et al. 2020). Another approach is to adapt the LCA metrics to the PB-framework; a method developed by Ryberg et al. (2018) proposed PB-informed characterization models defining characterization factors to map the elementary flows onto the PBs (Ryberg et al. 2018, 2020). Chapter 4 applied both PB-approaches. In general, they arrived at the same conclusions, but they cover different impacts and are not directly comparable. Currently there is a gap in how the two AESA methods exactly compare and how insights from each of these methods can support decision making, which requires further research. Further note that the current biodiversity intactness indicator for PB-LCIA includes only pressures from land use and climate change (Ryberg et al. 2018). Future research should aim to expand the PB Framework within LCA by developing biodiversity intactness indicators for additional stressors, such as nitrogen deposition and chemical pollution. The GLOBIO model could be used for this purpose (Schipper et al. 2016, 2020).

The absolute assessments also require downscaling of the planetary boundaries to product level. We applied the transgression levels defined by Tulus et al. (2021) based on equality (each person is entitled to have the same share of planetary boundary) and economic value of the chemical. There are, however, other downscaling principles rooted in different distributive fairness theories, such as principles based on concepts of fulfilment of human needs (Heide et al. 2023), sovereignty, capability to pay or reduce (Lucas et al. 2020), historical debt, or cost-effectiveness (van den Berg et al. 2020). The decision which downscaling principle to use is in the end a subjective question, and thus, it is important to consider various downscaling perspectives. The process of downscaling planetary boundaries is still in its early stages, thus necessitating future research to investigate alternative downscaling principles and definitions of transgression levels. Overall, absolute assessments can guide research and policy in their support to develop more sustainable chemical production: to understand if certain strategies are effective or need additional efforts to further decrease environmental impacts.

6.3. Environmental consequences of replacing fossil- by bio-based products in the chemical industry

Below, I discuss novel insights on what the environmental consequences are of replacing fossil products with bio-based ones. I will focus on (i) the GHG footprint of bio-based products, conducting an additional analysis based based on data from chapter 2 and 5, (ii) the environmental impacts of bio-based products beyond climate change, and (iii) the environmental impacts of bio-based products in the context of planetary boundaries.

The GHG footprint of bio-based products

Life-cycle greenhouse gas emissions for emerging bio-based products are on average almost halved in comparison with fossil-based products, as I showed in Chapter 2, based on reviewing 130 studies. However, only 13% of these studies accounted for LUC emissions. Here, an additional analysis contrasts the GHG footprints' response ratios when including or excluding LUC emissions (Figure 6.1a,b). Figure 6.1a presents the arithmetic averages of GHG emissions for bio-based products from sugarcane, grasses, woody crops and residues from studies that excluded LUC emissions. Figures 6.3b displays the arithmetic averages of GHG emissions for the same bio-based products, now including LUC emissions assuming a 30-year evaluation period. The LUC emissions of the crops were taken from Chapter 5, i.e., LUC emissions based on the 50% grid cells with the lowest LUC emissions considering abandoned agricultural land, marginal land and degraded and managed forests. These were added to the GHG emissions of the bio-based products by multiplying the LUC emissions (in kg wet biomass/kg bio-based product) with their respective conversion efficiencies.

On average, bio-based products, excluding LUC emissions, reduce GHG emissions by 47% (CI-95: -54 to -38%) compared to their fossil-based equivalents. Overall, 79% of bio-based products exhibit lower GHG footprints than their fossil-based alternatives. However, when LUC emissions allocated over a 30-year evaluation period are considered, the average GHG emission reduction is only 2% (CI-95%: -39 to 58%), which is not significantly different from zero (with 61% of the bio-based products resulting in lower GHG footprints than their fossil-based equivalents). However, by assuming an 80-year evaluation period (Figure 6.1c) or including LUC emissions based on the 5% grid cells with the lowest LUC emissions (Figure 6.1d), the average GHG emission reduction is 22% (CI-95%: -41 to 2%) and 18% (CI-95%: -41 to 13%), respectively. The LUC emissions relate to (i) the initial carbon stock losses associated with land use change and (ii) the foregone sequestration, i.e., the lost sequestration capacity of the natural vegetation over 30 years by instead using the land as cultivation site. Attributing LUC emissions to biomass products are often only related to initial carbon stock losses (Bhan et al., 2021). In Chapter 5, initial carbon stock losses contributed on average 65% to the LUC emissions, which therefore indicates that LUC emissions related to foregone sequestration have a significant impact and should be addressed. Overall, the GHG benefit for bio-based production strongly depend on LUC emissions, and consequently, how these are modelled in environmental assessments. Additional insights, together with those in Chapter 5, show that when LUC emissions are taken into account, bio-based products can lead to lower GHG emissions compared to fossil-based products, but it depends on the evaluation period, and requires careful selection of cultivation site and biomass feedstock to achieve significant climate change mitigation potentials.

In Chapter 2, the type of biomass feedstock did not explain the variance in GHG footprints. However, in the analysis with LUC emissions included, as presented in Figure 6.1b, the biomass feedstock does have significant influence (F-value: 32.9; *p*-value: 3.4e-16). Based on this and Chapter 5, I find that residue-based products have lower GHG footprints compared to GHG footprints of products from dedicated crops, and can reduce GHG emissions compared to their fossil-based equivalents.

Throughout Chapter 2 to 5, bio-based products' GHG footprints were compared to fossil GHG footprints. However, a study recently addressed the uncertainties in GHG emissions of petrochemical production, estimating a 34% uncertainty in total global emissions for 2020, and 15–40% uncertainties across many petrochemicals analyzed (Cullen et al. 2024). It may be interesting to address these uncertainties in a future comparison with bio-based products, re-performing the analysis from Chapter 2, and assigning weights based on Cullen et al. (2024) to the response ratios, i.e. taking into account the variance of fossil GHG footprints to better compare the GHG benefits of bio-based products.

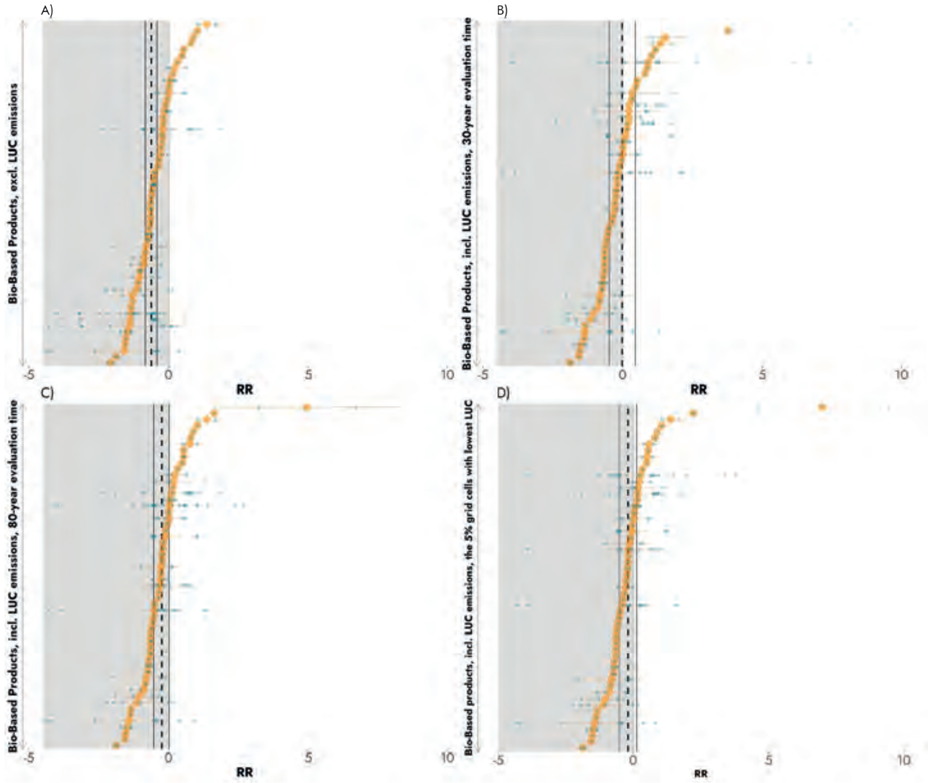

Figure 6.1: Response ratios (RRs) of GHG footprints of bio-based products compared to their fossil-counterfactuals, (a) ex- and (b) including LUC emissions based on (i) on foregone sequestration, (ii) initial carbon stock loss; (iii) the 50% grid cells with the lowest LUC emissions and (iv) allocated over a 30 years evaluation period; (c) including an 80-year evaluation period; (d) including LUC emissions of 5% grid cells with the lowest LUC emissions. RRs are defined as the natural-logarithm of the environmental impacts of the emerging bio-based product (X_B) divided by its fossil equivalent (X_F): RR = $\ln(X_B/X_F)$. The response ratios have a positive value (RR > 0) when the impact of the bio-based product is larger compared to its fossil equivalent, and a negative value (RR < 0) when the impact of the bio-based product is smaller. The encircled orange dots represent arithmetic average RRs per bio-based product with corresponding 95% CI as opaque orange error-bars. There is no 95% CI for bio-based products with n = 1. Black dashed line is the predicted mean RR based on a random-effects model including product type and study as random effects (for (a) RR=-0.62; (b) RR=-0.02; (c) RR=-0.25; (d) RR=-0.20), accompanied by two black lines as overall 95% CI (for (a) 95% CI: -0.84 to -0.41; (b) -0.49 to 0.46; (c) -0.53 to 0.02; (d) -0.53 to 0.12). In the grey area, the GHG footprints of the bio-based products are lower than their fossil counterparts, with a grey line at RR = 0 representing no difference in GHG footprint. For (a) 44 out of 56 products have GHG footprints lower than their counterfactual; (b) 34 out of 56; (c) 37 out of 56; (d) 37 out of 56. Studies from Chapter 2 were selected based on the following criteria: (i) derived from sugarcane, second generation dedicated crops, agricultural & forestry residues, and waste streams, and excluded LUC emissions in their original assessment; and (ii) studies were excluded if they did not specify conversion efficiencies. In case of agricultural & forestry residues and waste streams, LUC emissions did not play a role, in line with other research (Hanssen et al. 2020; Daioglou et al. 2015).

GHG emissions reduction through electrification and future electricity mixes

In the development of new technologies, electricity-driven processes are aimed at minimizing future environmental impacts by reducing reliance on fossil fuels. A key parameter in this switch to electrification is the GHG intensity of the future electricity mix. Here, I discuss the application and implications of different future electricity mixes (2030, 2050) for the environmental impacts of the emerging bio-based production, especially looking at the case studies presented in chapters 3 and 4.

In general, GHG emissions were predicted to be 40% higher (at a TRL-4 stage) for PEF (Chapter 3) and 42% lower for bio-BTX production (Chapter 4), compared to their fossil-based equivalents. In Chapter 3, the electricity demand of the electrochemical reactor was the largest contribution to its environmental impacts, especially for climate change. By applying a future (2030, 2050) electricity mix, bio-plastic PEF production resulted in climate change impact reductions up to 60%, i.e. at a low-TRL stage it was predicted to have 16% lower GHG emissions compared to fossil-based PET production. In Chapter 4, GHG emissions were predicted at -0.4 kg CO_2 eq./kg bio-based BTX toward 2050 (including a future renewable electricity and a future scenario on carbon recycling), in contrast to 5.2 and 2.3 kg CO_2 eq./kg current or future fossil-BTX production, respectively. A renewable electricity mix was especially effective because Chapter 3 and 4 assessed novel, electricity-driven processes. In contrast, solely decarbonizing energy supply reduces GHG emissions of fossil-based BTX production by 1% (Chapter 4) and chemical production (Chapter 5) on average by 6%, compared to applying current electricity mix. Mainly because the processes addressed required fossil-based heat and steam. Overall, it was shown that electrification of chemical processes (in combination with a renewable electricity mix) is a useful strategy in reducing GHG emissions of chemical production, which is in line with other research (Saygin and Gielen 2021; Schiffer and Manthiram 2017; Mallapragada et al. 2023). Novel bio-based production can lead to GHG emission reductions compared to current situation, but a greater potential is achieved in the future when future developments may become reality.

Trade-offs with other environmental impacts

The environmental impacts of emerging bio-based products beyond GHG emissions were assessed to gain a comprehensive understanding of their overall environmental benefits. Chapter 2 showed that emerging bio-based products have on average 37% lower (95% CI: -56 to -10%) non-renewable energy use (NREU) compared to their fossil counterparts. On the other hand, the NREU impact of the bio-plastic PEF (Chapter 3) showed an increase of 41%, compared to PET (Eerhart et al. 2012). However, it was assessed at a TRL-4 stage, meaning that future energy reductions are likely due to increased efficiencies at higher TRLs. Energy reductions can also happen with technological advances because of further technological maturity (Blok 2004). Overall, the NREU of emerging bio-based products was significantly different from zero, i.e. resulting in a lower impact compared to their fossil-based equivalents (Chapter 2).

Eutrophication impacts were on average 369% higher (95% CI: 163 to 737%) for bio-based products compared to their fossil counterfactuals (Chapter 2). Likewise, Chapter 3 and 4 found increased impact for freshwater eutrophication for bio-based PEF and BTX compared to their fossil-based counterfactuals. For the impact of acidification, ozone depletion and photochemical ozone formation, bio-based products from Chapter 3 indicated a 20-fold increase of terrestrial acidification of bio-PEF compared to PET, and Chapter 4 reported increased impact for bio-based BTX compared to fossil-based BTX in the categories of land occupation, fine particular matter formation, freshwater eutrophication, and water consumption. These higher impacts often result from agricultural practices, i.e., the cultivation and harvest of biomass. For instance, current fertilizer application in agriculture practices can lead to freshwater eutrophication (Zhang et al. 2021). To better understand potential burden shifting, it is crucial in prospective assessment of bio-based products to include impact indicators that are especially relevant for feedstock production.

The comparison of alternative carbon-rich feedstocks for BTX production in Chapter 4 showed that plastic waste-based BTX had the lowest predicted impact across all categories, except for climate change (bio-BTX had the lowest GHG emissions, but plastic-waste based BTX still had lower emissions compared to fossil-based BTX). The environmental benefits of using plastic waste for chemical production have been demonstrated by other studies (van der Hulst et al. 2022; Meys et al. 2020; Jeswani et al. 2021). All these findings, together with results from Chapter 2 and 3, indicate that even when the GHG footprints of bio-based products are lower than those of their fossil-based counterparts, environmental trade-offs in other impact categories should not be overlooked. We should be careful shifting environmental impacts to other domains while aiming to reduce GHG emissions. Nevertheless, burden shifting may be unavoidable, imposing the question to what extent it is acceptable. Endpoint assessment and absolute assessments are helpful to put burden shifting into context.

Absolute assessment within LCA

Generally, the environmental impacts of product A to those of product B are compared in an LCA. However, when a product is environmentally friendlier than another, this does not automatically mean it is sustainable. When combined with an absolute environmental impact assessment, it can provide a deeper understanding of whether the reduced impacts are sufficient, ensuring that they do not exceed any planetary boundaries. Tulus et al. (2021) argued that the vast majority of 492 conventional chemicals exceed at least one or multiple planetary boundaries. Sustainable alternatives are being explored for different chemicals (D'Angelo et al. 2021; Vázquez and Guillén-Gosálbez 2021), plastics (Bachmann et al. 2023) or the petrochemical sector as a whole. Galán-Martín et al. (2021) found that replacing fossil-based feedstock by CO_2 and biomass in the petrochemical industry reduce impacts significantly but still exceeds the biodiversity planetary boundary. Likewise, in Chapter 4 it was found that while alternative BTX production pathways can lead to lower environmental impacts for multiple impact categories, they still transgressed multiple planetary boundaries, namely climate change, freshwater use and biosphere integrity, i.e. biodiversity loss. In other words, integrating planetary boundaries into LCA may lead to different conclusions than conventional LCA approaches. To achieve absolute sustainability, the chemical industry should adopt impact reduction strategies that extend beyond merely transitioning to bio-based feedstocks. Effective solutions should prioritize minimizing impacts in critical categories, such as climate change and biodiversity loss.

6.4. Policy implications

Bio-based products

Replacing fossil by bio-resources in the chemical industry can mitigate climate change, yet, land requirements limit these climate benefits. LUC emissions alongside supply-chain emissions must be accurately accounted for to fully address the GHG balance. Bio-based chemical production is most effective when utilizing residues or waste streams, and if crops are used, selecting appropriate locations for cultivation to minimize LUC emissions is crucial. Careful selection of land area, biomass feedstock and carbon-efficient chemical production route is required to achieve significant climate change mitigation potentials.

Policy should target bio-based production based on residues and crops with low LUC emissions as feedstock. To support policy, the feasibility for residue-based primary chemical production should be further understood. Even though residues can potentially meet a significant part of global energy demand by 2050 (Hanssen et al. 2019), potential biomass supply varies substantially between Integrated Assessment Models (Rose et al. 2022). There is also uncertainty regarding the availability of other waste streams, such as industrial food waste. Furthermore, limited physical accessibility of marginal lands for dedicated crops might be an issue (Cristóbal et al. 2018), emphasizing the complexity of logistics when scaling up bio-based production. Other technical challenges may remain concerning process conversion technologies, which require the development of carbon-efficient processes.

The potential for biomass to replace fossil feedstock in the entire petrochemical industry is constraint by the availability of abandoned agricultural and marginal lands (Chapter 5). This finding might imply questions in the political domain, particularly regarding the division of bio-based feedstock over sectors. Determining sectoral priorities for bio-based feedstock use is a highly complex issue, but developing a sustainable bio-economy requires policies that address these complexities and ensure the fair allocation of available biomass resources.

The end-of-life phase, i.e., waste management, is critical in both fossil-based and bio-based products. This emphasizes the need for comprehensive LCAs, including cradle-to-grave system boundaries, to inform sustainable strategies in both bio-based and fossil-based product sectors. Recycling of petrochemical products, such as plastics, is crucial to reach a low-carbon sector, and should be further addressed in policy initiatives at both national and EU levels.

Trade-offs between environmental impacts related to bio-based production, such as climate change vs. eutrophication, should not be overlooked. Strategies to decrease these environmental impacts are, for example, recycling of bio-based plastics to reduce primary biomass feedstock production (Stegmann et al. 2020) or decreasing fertilizer application (Zhang et al. 2021). Overall, the focus should be on sourcing biomass sustainably, contributing positively to climate targets while protecting the environment. There are policies supporting this aim, such as The Farm to Fork Strategy (European Commission 2020b) that have set ambitious goals to substantially reduce fertilizer use (20%), and the EU Forest Strategy, to support sustainable forest management including biodiversity protection (European Commission 2021).

A net-zero chemical industry

A net-zero chemical industry based on biomass would require a combination of mitigation strategies. The adoption of bio-based feedstocks, process electrification, and a renewable electricity mix can reduce emissions for chemical production. Our findings also indicate that carbon recycling and mitigation of end-of-life emissions need to be addressed. Implementing recycling and/or carbon capture and storage (CCS) technologies (Bisinella et al. 2021b) are required to further limit end-of-life emissions. Integrating biomass feedstocks with plastic recycling could further lower the GHG footprint of chemical production, as it can function as a carbon sink (Stegmann et al. 2022). Additionally, prolonged product life (on the production side) and decrease in production volume (on the consumption side) are strategies to further explore. Production volume reduction pathways have shown to be effective in e.g., plastic production (Bachmann et al. 2023) and the petrochemical industry (Meng et al. 2023). On a global scale, petrochemical industry's emissions (6% of global GHG emissions in 2022) can be reduced to to 0.4% with residue feedstocks, and for global petrochemical ethylene production from 2.2% to 1.2% by using sugarcane and from 2.2% to 1.8% using grasses (Chapter 5). Combining biomass with other viable feedstocks, such as CO_2 (Huo et al. 2023), can be part of a multifactorial solution for the chemical industry. Overall, combining biomass with other sustainability strategies is crucial to significantly reduce the environmental impacts of the chemical industry, and their implementation should be further targeted in research and policies.

Better, but not good enough

The planetary boundaries framework can be used to set global goals for reducing environmental impacts. Whereas LCA helps to understand what the hotspots in a production chain are, an absolute assessment can show whether reductions are still necessary to stay within the planetary boundaries. In line with The Safe and Sustainable by Design (Caldeira et al. 2022), we recommend to integrate absolute assessment in LCA assessment. Further exploration is needed on how to do this, i.e. standardization of AESA methods. Absolute assessments can support policy in understanding if certain strategies are effective or need additional efforts to further decrease environmental impacts, e.g., in relation to biosphere integrity. Overall, a fossil-free society is ultimately a key requirement to stay within planetary boundaries. Bio-based chemical production can reduce environmental impacts in the petrochemical industry, yet further sustainability improvements are still required.

6.5. Conclusions

I arrive at the following main conclusions with my research:

- On average, greenhouse gas life cycle emissions for emerging bio-based products are halved compared to their fossil-based equivalents. By systematically including emissions from land use change for the same chemicals, based on sugarcane, grasses and woody crops, I find GHG emission benefits may reduce to virtually zero, including both carbon stock losses and foregone sequestration and assuming a 30-year evaluation period. My findings imply that emerging bio-based products offer GHG benefits relative to their fossil-based equivalents when emissions from land use change are not at stake. However, when LUC emissions are included, careful selection of land area, biomass feedstock, chemical production route is required to achieve significant (global) climate change mitigation potentials.

- There is a large variation in environmental impacts between individual bio-based products. This implies the necessity of a case-by-case evaluation of emerging bio-based products. To comprehensively assess the environmental impacts, their full life cycle should be considered, including CO_2 emissions associated with the embedded carbon of the product, consistent biogenic carbon and LUC accounting, and comprehensive prospective upscaling by applying prospective LCA frameworks.
- Bio-based products have trade-offs with other environmental impacts. For eutrophication, we found statistical evidence for an increase (on average, 369%) in emerging bio-based footprints, indicating that environmental trade-offs should not be overlooked.
- Combining an LCA with an absolute sustainability assessment gives insights into whether one product design is more sustainable than the other and whether it stays within the planetary boundaries. Our results imply that further impact reduction efforts, e.g., in regard to biodiversity loss, are necessary for bio-chemical production to stay within the planetary boundaries.
- Almost none of the emerging bio-based products reach net-zero emissions. Net-zero or even negative emissions were predicted for (i) bio-BTX production, requiring second-generation feedstock, electrification of the core process, a renewable electricity mix and increased carbon recycling; and (ii) for bio-based primary chemicals, involving residues as feedstock and the offset of by-products' emissions. Overall, a combination of mitigation measures is essential to achieve a low-emission petrochemical industry. These measures include chemical sector electrification, utilizing waste biomass (e.g., agricultural residues) as a feedstock, increasing carbon recycling and mitigating end-of-life emissions.

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Appendices

Appendix 1. Research Data Management Plan

The research in this thesis has been carried out under the RDM policy of the Radboud Institute for Biological and Environmental Sciences, version 5 April 2023. Data and supplementary information used or generated in this thesis can be accessed in the following way:

Chapter 1	No data were produced.
Chapter 2	Zuiderveen, E. A. R., Kuipers, K. J., Caldeira, C., Hanssen, S. V., van der Hulst, M. K., de Jonge, M. M., Vlysidis, A., van Zelm, R., Sala, S., & Huijbregts, M. A. (2023). The potential of emerging bio-based products to reduce environmental impacts. *Nature Communications*, 14(1), 8521. Data were published in the article and supplementary information: 10.1038/s41467-023-43797-9. The dataset in this study is available in the *figshare* repository: Zuiderveen, E. A. R. et al. The Potential of Emerging Bio-based Products to Reduce Environmental Impacts Dataset. figshare (2023). 10.6084/m9.figshare.22795184. The code to conduct the analysis is available in the figshare repository: 10.6084/m9.figshare.22795184.
Chapter 3	Zuiderveen, E. A., Ansovini, D., Gruter, G. J. M., & Shen, L. (2021). Ex-ante life cycle assessment of polyethylenefuranoate (PEF) from bio-based monomers synthesized via a novel electrochemical process. *Cleaner Environmental Systems*, 2, 100036. All data were published in the article and the supplementary information: 10.1016/j.cesys.2021.100036.
Chapter 4	Zuiderveen, E. A., Caldeira, C., Vries, T., Schenk, N. J., Huijbregts, M. A., Sala, S., Hanssen, S. V., & van Zelm, R. (2024). Evaluating the Environmental Sustainability of Alternative Ways to Produce Benzene, Toluene, and Xylene. *ACS Sustainable Chemistry & Engineering*, 12(13), 5092-5104. All data were published in the article and the supplementary information: 10.1021/acssuschemeng.3c06996.
Chapter 5	Zuiderveen, E. A. R., Caldeira, C., Sala, S., van Zelm, R., Huijbregts, M. A. J., Hanssen, S. V. (2024). Land-use change emissions limit climate benefits of bio-based. In preparation. Data related to this chapter will become publicly available upon acceptance of the article.
Chapter 6	Figure 3 in Chapter 6 is generated from data from Chapter 5 and the dataset: Zuiderveen, E. A. R. et al. The Potential of Emerging Bio-based Products to Reduce Environmental Impacts Dataset. Figshare (2023). 10.6084/m9.figshare.22795184.

Appendix 2. Supplementary Information to Chapters 2-5

The Supplementary Information to Chapters 2–5 can be obtained as a single PDF file from the Radboud Repository at:

https://books.radbouduniversitypress.nl/index.php/rup/catalog/view/Environmental-footprints/Supplementary_Information/226

Summary

The petrochemical industry is an important facilitator of our modern society by producing thousands of products. At the same time, the petrochemical industry is a major contributor to climate change, and thereby co-responsible for an unprecedented threat to our society. Decarbonizing the petrochemical industry is essential to achieve net-zero greenhouse gas (GHG) emission targets and to substantially reduce its environmental impacts. Key strategies to make this industry more sustainable might include the use of biomass feedstock and developing new and cleaner technologies. The sustainability of bio-based chemicals and their expected environmental benefits is, however, currently under discussion, as (1) the environmental consequences of emerging bio-based technologies at a future, more technological developed level are uncertain, and (2) the potential tradeoffs between climate change, biodiversity loss, water availability, and pollution of replacing fossil feedstocks by bio-based resources in the chemical industry are still to be fully investigated. The main aim of my thesis is to quantify the environmental footprints of emerging bio-based products for the petrochemical industry compared to their fossil equivalents, which represent a pivotal element for evidence-based support of current and future policies.

Chapter 2 presented a large-scale systematic analysis of the environmental benefits and trade-offs of emerging bio-based products compared to their fossil-based equivalents. In total, 98 different bio-based products were analyzed, gathered from 130 studies that were consistently aligned regarding biogenic carbon accounting, end-of-life treatment and system boundaries. Greenhouse gas (GHG) footprints of bio-based products are on average 45% (52% to 37%; 95% confidence interval (CI)) lower compared to their fossil-based equivalents. I found, however, a large variation across individual bio-based products, with none of them reaching net-zero emissions. I also showed an increase in eutrophication impact (369%; 163% to 737% as 95% CI), indicating that environmental trade-offs should not be overlooked. My findings imply that evaluation on an individual product basis is required, and more radical product developments are needed to reach climate neutral targets.

Chapter 3 assessed the environmental impacts of the novel bio-plastic polyethylenefuranoate (PEF), in terms of climate change, non-renewable energy use (NREU), acidification, eutrophication and land use. My main aim was to upscale the lab-scale electrochemical technology using process design to identify hotspots in this novel production route. The results show that the electricity demand from the electrochemical reactor contributes for 63–88% in each impact category, except

for land use. Production of xylitol and hydroxymethylfurfural (HMF), including biomass production of corn and woody biomass, account for 10–35% across the impact categories, and up to 65% for land use. My results suggest to (i) increase the selectivity of the electrochemical reactor to minimize waste products and thus lower the energy requirements for downstream separation, (ii) search for a clean and cost-effective feedstock derived from lignocellulosic biomass rather than xylitol, and (iii) reduce the amount of wastewater by either reducing the total water usage in the process or implementing water recycling within the system, in particular to reduce eutrophication impact. When applying a renewable electricity mix for the year 2030 and 2050, I obtained up to 16% lower GHG emissions for the bio-plastic (TRL 4) compared to the fossil-based plastic PET. My findings imply that while further improvements are necessary, electrochemical reactors based on biomass input present a potential viable route in future plastic production.

Chapter 4 analyzed the environmental impacts of benzene, toluene and xylene (BTX) from biomass and mixed plastic waste at a projected commercial scale (2024) and at a future industrial scale (2050). I combined prospective LCA with an absolute environmental sustainability assessment using the planetary boundary concept. For the projected commercial scale in 2024, I found that plastic waste-based BTX has lower environmental impacts than fossil-based BTX across all environmental impact categories, including a 12% reduction in GHG emissions. Biomass-based BTX has a GHG emission decrease of 42%, but an increase in freshwater consumption and eutrophication impact compared to plastic waste-based and fossil-based BTX. In 2050, GHG emissions are expected to further reduce to 75 and 107% for plastic waste and bio-based production, respectively, compared to current fossil-based BTX production, including a future renewable electricity-mix and increased recycling. While alternative BTX production pathways can decrease environmental impacts, they still transgressed at least freshwater use and biosphere integrity. Further impact reduction efforts are required, for instance, by using other types of (waste) biomass, e.g., wood chips, and abating the CO_2 emissions related to the release of the embodied carbon, e.g., by further increasing the recycling rate.

Chapter 5 assessed the impact of LUC emissions on the life cycle GHG emissions of six key chemicals in the petrochemical industry at a global scale. I analyzed 30 different routes using sugarcane, grasses, woody crops and agricultural residues as biomass feedstock, including spatially-explicit LUC emissions using the LPJml model coupled with the integrated assessment model IMAGE, under scenarios limiting global warming to well below 2°C, and over a 30-year evaluation period. Results show on average that 63% of GHG emissions from bio-based chemical routes relate to LUC emissions. While 90% of the routes have lower GHG emissions compared to their fossil-based equivalents when excluding LUC emissions, this drops to 27-43% when including them. The results demonstrate a large variation in GHG emissions when applying different evaluation periods and chemical production conversion efficiencies. Bio-based chemical production is most effective when using residues, and if crops are used, they should be cultivated in locations leading to minimal land-use change impacts. The global petrochemical industry's GHG emissions can be reduced from 6% to 0.5% with residue feedstocks and to 3% by replacing ethylene with bio-based resources. My findings imply that careful selection of land area, biomass feedstock, and chemical production routes is required to achieve significant climate change mitigation.

Chapter 6 reflected on the lessons learned. Emerging bio-based products offer GHG benefits compared to fossil-based equivalents, but land requirements can limit these climate benefits. There is a large variation in environmental impacts between individual bio-based products. This indicates that case-by-case evaluation of bio-based products is necessary, including full life cycles, CO_2 emissions from embedded carbon of the product, consistent biogenic carbon accounting, and comprehensive upscaling using prospective LCA frameworks. Other impact categories, such as freshwater eutrophication, can have a significant impact and must also be systematically addressed. Sustainable biomass sourcing is crucial to address these trade-offs between climate change and other environmental impacts, including land-based biodiversity impacts. Almost none of the emerging bio-based products achieve net-zero emissions, indicating that more radical product developments are needed to meet climate-neutral targets. To transform the petrochemical industry into a more sustainable sector, a combination of mitigation measures is key. These measures include the electrification of processes, utilizing waste biomass (such as agricultural residues) as a feedstock, further increasing carbon recycling and mitigating end-of-life emissions.

Samenvatting

De petrochemische industrie vormt de basis van onze moderne samenleving met de productie van talloze producten die we dagelijks gebruiken. Tegelijkertijd draagt deze industrie bij aan klimaatverandering en speelt zij een rol in een van de grootste crises van onze tijd. Het verduurzamen van de petrochemische sector is daarom essentieel om de uitstoot van broeikasgassen terug te dringen en de impact op het milieu te verminderen. Twee belangrijke strategieën voor verduurzaming van de petrochemische industrie zijn het gebruik van biomassa als grondstof en de ontwikkeling van schonere technologieën. De duurzaamheid van biomaterialen, en de verwachte milieuwinst die ze opleveren, blijven echter onderwerp van discussie. Dit komt doordat (1) de milieueffecten van nieuwe op biomassa gebaseerde technologieën onzeker zijn op grotere, technologisch verder ontwikkelde schaal, en (2) de afwegingen tussen klimaatverandering, biodiversiteitsverlies, waterschaarste en vervuiling bij de vervanging van fossiele grondstoffen door biomassa in de chemische industrie nog onderzocht moeten worden. Het hoofddoel van mijn proefschrift is het kwantificeren van de milieugevolgen van nieuwe biomaterialen voor de petrochemische industrie en het vergelijken van deze effecten met die van fossiele materialen. Deze inzichten zijn van cruciaal belang om beleid te ondersteunen dat gericht is op het verduurzamen van de chemische industrie en het realiseren van een duurzame toekomst.

Hoofdstuk 2 presenteert een uitgebreide systematische analyse van de milieugevolgen van nieuwe biomaterialen, in vergelijking met hun fossiele tegenhangers. In totaal werden 98 verschillende biomaterialen onderzocht, verzameld uit 130 studies, en geharmoniseerd op het gebied van biogene koolstofberekeningen, de eindelevensfase van het product, en de systeemgrenzen van de levenscyclusanalyse. De broeikasgasemissies van biomaterialen blijken gemiddeld 45% lager te zijn dan die van fossiele alternatieven (met een variatie van 52% tot 37% binnen een betrouwbaarheidsinterval van 95%). Er werd echter veel variatie tussen de individuele biomaterialen gevonden, waarbij geen enkel biomateriaal netto-nul emissies behaalt. Verder werd een aanzienlijke toename in eutrofiëringeffect (369%, variërend van 163% tot 737% met 95% BI) vastgesteld, wat erop wijst dat naast broeikasgasemissies andere milieueffecten niet over het hoofd gezien mogen worden. De bevindingen benadrukken het belang van een evaluatie van de milieueffecten op productniveau en geven aan dat ingrijpende productinnovaties noodzakelijk zijn om klimaatneutrale doelstellingen te realiseren.

Hoofdstuk 3 analyseert de milieueffecten van het nieuwe bio-plastic polyethyleenfuranoaat (PEF) op het gebied van klimaatverandering, niet-hernieuwbaar energiegebruik, verzuring, eutrofiëring en landgebruik. Het hoofddoel was het opschalen van de laboratoriumschaal elektrochemische technologie met behulp van procesengineering, om knelpunten in deze nieuwe productieroute te identificeren. De resultaten tonen aan dat het elektriciteitsgebruik van de elektrochemische reactor verantwoordelijk is voor 63–88% van de milieu-impact in elke categorie, behalve voor landgebruik. De productie van xylitol en hydroxymethylfurfural (HMF), inclusief de biomassa van maïs en houtige biomassa, draagt voor 10–35% bij aan de impact in de verschillende categorieën, en tot 65% in landgebruik. De bevindingen wijzen erop dat (i) de selectiviteit van de elektrochemische reactor verhoogd moet worden om afvalstromen te minimaliseren en zo het energiegebruik bij latere scheidingsprocessen te verlagen, (ii) er gezocht moet worden naar duurzamere en kosteneffectieve grondstoffen, zoals lignocellulose biomassa in plaats van xylitol, en (iii) de hoeveelheid afvalwater verminderd kan worden door het totale watergebruik in het proces te beperken of waterrecycling te implementeren, vooral om de eutrofiëringsimpact te reduceren. Bij de toepassing van een hernieuwbare elektriciteitsmix voor de jaren 2030 en 2050 resulteerde dit in een vermindering van de broeikasgasemissies met tot wel 16% voor het bio-plastic in vergelijking met het op fossiele brandstoffen gebaseerde plastic PET. Mijn bevindingen impliceren dat, hoewel verdere verbeteringen nodig zijn, elektrochemische reactoren met biomassa als input een veelbelovende route kan bieden voor de toekomstige productie van plastic.

Hoofdstuk 4 onderzoekt de milieueffecten van benzeen, tolueen en xyleen (BTX) uit biomassa en gemengd plastic afval op een technologisch geprojecteerde commerciële schaal (2024) en op een toekomstige industriële schaal (2050). Hierbij combineerde ik prospectieve LCA met een absolute milieuduurzaamheidsbeoordeling volgens het concept van 'de planetaire grenzen'. Voor de geprojecteerde commerciële productie in 2024 toonde mijn analyse aan dat BTX uit plastic afval lagere milieueffecten heeft dan BTX uit fossiele bronnen in alle impactcategorieën, waaronder een reductie van 12% in broeikasgasemissies. BTX uit biomassa vertoonde zelfs 42% lagere broeikasgasemissies, maar leidde tot een toename van zoetwaterverbruik en eutrofiëringsimpact in vergelijking met zowel BTX uit plastic afval als fossiele BTX. In 2050 wordt verwacht dat de broeikasgasemissies verder zullen dalen, met respectieve verlagingen van 75% en 107% voor BTX uit plastic afval en biomassa, vergeleken met de huidige fossiele BTX-productie, dankzij de toepassing van een hernieuwbare elektriciteitsmix en verhoogde recycling. Hoewel deze alternatieve BTX-productieroutes milieueffecten kunnen verminderen, overschrijden ze nog steeds de planetaire grenzen op het gebied van zoetwatergebruik en biosfeerintegriteit. Verdere inspanningen zijn dus nodig, bijvoorbeeld door alternatieve soorten (afval)biomassa, zoals houtsnippers, te gebruiken als grondstof en door de CO_2-emissies die gepaard gaan met de koolstof in het product te beperken, bijvoorbeeld door het recyclingpercentage verder te verhogen.

Hoofdstuk 5 beoordeelt de invloed van LUC-emissies (emissies door landgebruiksverandering) op de totale broeikasgasemissies van de levenscyclus van zes belangrijke chemicaliën in de petrochemische industrie op wereldwijde schaal. Ik analyseerde 30 verschillende routes met suikerriet, grassen, houtgewassen en agrarische reststromen als biomassagrondstof, inclusief ruimtelijk expliciete LUC-emissies met behulp van het LPJml-model gekoppeld aan het geïntegreerde beoordelingsmodel IMAGE, met scenario's die de opwarming van de aarde beperken tot ruim onder 2°C, en een evaluatieperiode van 30 jaar. De resultaten tonen aan dat gemiddeld 63% van de broeikasgasemissies van de biomassaroutes gerelateerd is aan LUC-emissies. Terwijl 90% van de routes lagere broeikasgasemissies heeft dan hun fossiele tegenhangers wanneer LUC-emissies worden uitgesloten, daalt dit percentage tot 27-43% wanneer LUC-emissies worden meegenomen. Er werd een grote variatie geconstateerd in broeikasgasemissies wanneer verschillende evaluatieperioden en conversie-efficiënties bij de chemische productie werden toegepast. De biomassaroutes om de zes chemicaliën te produceren zijn het meest effectief wanneer reststromen worden gebruikt, en wanneer gewassen worden ingezet, dienen deze te worden verbouwd op locaties met zo min mogelijk landgebruiksverandering. De wereldwijde broeikasgasemissies van de petrochemische industrie kunnen worden verminderd van 6% naar 0.5% door het gebruik van biomassareststromen als grondstof, en naar 3% door de productie van ethyleen te vervangen door een biomassaroute. Mijn bevindingen impliceren dat een zorgvuldige selectie van landgebruik, biomassa als grondstof en productieroute essentieel is om substantiële klimaatmitigatie te realiseren.

Hoofdstuk 6 reflecteert op de belangrijkste lessen geleerd uit de voorgaande hoofdstukken. Nieuwe biomaterialen bieden weliswaar lagere broeikasgasemissies dan hun fossiele tegenhangers, maar veranderingen in landgebruik kunnen deze klimaatvoordelen beperken. Er is veel variatie in de milieueffecten tussen verschillende biomaterialen, wat aantoont dat een grondige evaluatie van individuele biomaterialen noodzakelijk is. Idealiter omvat dit de volledige levenscyclus, de CO_2-emissies die vrijkomen uit de ingebedde koolstof van het product, consistente berekeningen van biogene koolstof en uitgebreide opschalingsmodellen binnen prospectieve LCA. Andere milieueffecten, zoals eutrofiëring van zoetwater, kunnen aanzienlijke gevolgen hebben en moeten systematisch worden aangepakt. Duurzame biomassawinning is van cruciaal belang om de afwegingen tussen klimaatverandering en andere milieueffecten, zoals de impact op biodiversiteit, effectief aan te pakken. Bijna geen enkel nieuw biomateriaal bereikt netto-nul emissies, wat aangeeft dat ingrijpendere innovaties nodig zijn om daadwerkelijk klimaatneutrale doelen te behalen. Voor de verduurzaming van de petrochemische industrie is een combinatie van maatregelen noodzakelijk. Deze omvatten de elektrificatie van productieprocessen, het gebruik van afvalbiomassa (zoals agrarische reststromen) als grondstof, verdere verbeteringen in koolstofrecycling en het verminderen van emissies aan het einde van de productlevenscyclus.

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About the author

Born in Amsterdam in 1992, I followed an interdisciplinary bachelor majoring in chemistry at the University of Amsterdam, after which I studied one year of the master's program Theoretical and Computational Chemistry at KU Leuven and obtained a joint Master’s degree at the University of Amsterdam and the Vrije Universiteit in Chemistry (*cum laude*), focusing on energy and sustainability. During my master research at the Copernicus Institute of Utrecht University, I got acquainted with Life Cycle Assessment, a method to calculate the environmental impact of a product, which I was very enthusiastic about. In 2020, I started my PhD project at the Radboud University Environmental Science department and in collaboration with the Joint Research Center, the EU-science hub of the European Commission, at the directorate Sustainable Resources in Italy. Researching the environmental impact of bio-based materials was both an intellectual and personal challenge that I enjoyed, which I finished in the summer of 2024. During my PhD, I also published poems to translate scientific and technical knowledge about the climate crisis into pieces aiming to resonate on a more emotional level. Currently, I am finishing writing my debut novel ‘De Rest is Naakt’, that will be published in the spring of 2025 at Prometheus.

List of publications

Peer-reviewed journal publications:

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