From Life Cycle Assessment to Absolute Environmental Sustainability of Plastics from Alternative Carbon Feedstocks

Von der Lebenszyklusanalyse zu absoluter ökologischer Nachhaltigkeit von Kunststoffen aus alternativen Kohlenstoffquellen

Von der Fakultät für Maschinenwesen der
Rheinisch-Westfälischen Technischen Hochschule Aachen
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Aachen, im Februar 2024 *Marvin Bachmann*

"In nature, nothing exists alone."

Rachel Carson, *Silent Spring*, 1962

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Notation

Abbreviations and Acronyms

ADP	Abiotic resource depletion
BADGE	Bisphenol A diglycidyl ether
BFG	Blast furnace gas
Bio-waste	Organic fraction of municipal solid waste
BOFG	Basic oxygen furnace gas
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CFB	Pressurized direct oxygen-steam blown circulating fluidized bed
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_2-eq	CO_2-equivalent
COG	Coke oven gas
DAC	Direct air capture
DFB	Atmospheric indirect air-blown dual fluidized bed
DRM	Dry reforming of methane
EO	Ethylene oxide
EoL	End-of-life
GDP	Gross domestic product
GHG	Greenhouse gas
GWI	Global warming impact
GWP	Global warming potential
H_2	Hydrogen
H_2/CO ratio	Hydrogen-to-carbon-monoxide
HDPE	High-density polyethylene
HPT	High-performance plastics
JRC	Joint Research Center
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LUC	Land-use change
MDI	Methylene diphenyl diisocyanate

Mill gas	Steel mill off-gas
N_2	Nitrogen
N-Cycle	Biogeochemical flow of nitrogen
NGCC	Natural gas combined cycle
OCT	Olefins Conversion Technology
ODP	Ozone depletion potential
pBPGE	p-ert-Butyl phenyl glycidyl ether
P-Cycle	Biogeochemical flow of phosphorus
PEI	Polyetherimide
PES	Polyethersulfone
PSU	Polysulfone
PO	Propylene oxide
POX	Polyoxazolidinone
PSA	Pressure swing adsorption
PUR	Polyurethane
SOS	Safe operating space
TCM	Technology Choice Model
TDI	Toluene diisocyanate
TEA	Techno-economic assessment
TRL	Technology readiness level
UNEP	United Nations Environment Programme
WGS	Water-gas shift

Vectors and Matrices

A	Technology matrix
B	Elementary flow matrix
c_{imp}	Upper bounds for environmental impacts
c_{tech}	Upper bounds for technologies
h	Environmental impacts
h_{GHG}	Climate change impact
Q	Characterization matrix
s	Scaling vector
x	Gross output vector
$x_{plastics}$	Total global plastics production
y	Final demand

Abstract

Plastics have become indispensable part of our modern society, but their environmental impact has raised concerns globally. Efforts to reduce greenhouse gas emissions encompass the production of plastics from alternative carbon feedstocks, namely plastic waste, biomass, CO_2, and steel mill off-gases (mill gas). Previous studies have shown the climate benefits of using these feedstocks, but this thesis identifies critical scientific gaps in the current assessment practice. These scientific gaps include unexplored environmental synergies, disregarded system-wide environmental impacts, and insufficient consideration of other environmental impacts than climate change.

To address these scientific gaps, this thesis explores environmental synergies from combined utilization of biomass and CO_2. The results show that combined utilization saves about 13 % more greenhouse gas emissions than the individual utilization of either biomass or CO_2. In addition, combined utilization saves about 25 % of limited resources and mitigates burden shifting from climate change to other environmental impacts.

Furthermore, this thesis conducts a comparative life cycle assessment of alternative syngas pathways, considering both direct environmental impacts and system-wide environmental consequences. The results identify bio- and mill gas-based syngas as the most climate-beneficial options, although system-wide impacts diminish these benefits. System-wide environmental impacts result from using limited feedstocks that have already been used in other applications. Accordingly, this thesis highlights the need to consider the conventional use of limited feedstocks in life cycle assessments.

Lastly, this thesis assesses the absolute environmental sustainability of plastics from alternative carbon feedstocks. Combining a model of the global plastics industry with the planetary boundary framework, this thesis determines the planetary footprints of plastics from fossil and alternative sources. The results demonstrate that the current fossil-based plastics industry is highly unsustainable, while a balanced solution involving improved recycling technologies, biomass utilization, and carbon capture and utilization can lead to a scenario in which plastics comply with their assigned safe operating space in 2030. However, technological improvements alone cannot address the predicted increase in plastic demand by 2050. Therefore, society must change its perception of plastics as cheap and disposable and embrace their value to support the transition towards an environmentally sustainable plastics industry.

Kurzfassung

Kunststoffe sind trotz ihrer Umweltauswirkungen zu einem unverzichtbaren Bestandteil unserer modernen Gesellschaft geworden. Um die Treibhausgasemissionen der Kunststoffindustrie zu verringern, wurden Strategien zur Herstellung auf Basis alternativer Kohlenstoffquellen wie Kunststoffabfälle, Biomasse, CO_2 und Hüttengase vorgeschlagen. Frühere Studien haben die Klimavorteile der Nutzung dieser Rohstoffe gezeigt. Allerdings identifiziert diese Arbeit kritische wissenschaftliche Lücken in der aktuellen Bewertungspraxis, einschließlich unerforschter ökologischer Synergien in der Nutzung alternativer Rohstoffe, nicht berücksichtigte systemweite Umweltauswirkungen und eine unzureichende Bewertung anderer Umweltauswirkungen als die des Klimawandels.

Um die derzeitige Bewertungspraxis zu verbessern, untersucht diese Arbeit Umweltsynergien durch die kombinierte Nutzung von Biomasse und CO_2. Die Ergebnisse zeigen, dass die kombinierte Nutzung 13 % mehr Treibhausgasemissionen einspart als deren individuelle Nutzung. Darüber hinaus spart die kombinierte Nutzung etwa 25 % an begrenzten Ressourcen und mindert die Verschiebung der Umweltauswirkungen vom Klimawandel zu anderen Umweltkategorien.

Weiterhin führt diese Arbeit eine vergleichende Ökobilanz alternativer Synthesegas-Verfahren durch, wobei sowohl direkte als auch systemweite Umweltauswirkungen berücksichtigt werden. Die Ergebnisse zeigen, dass bio- und hüttengasbasiertes Synthesegas die klimafreundlichsten Optionen sind, obwohl systemweite Umweltauswirkungen diese Vorteile verringern. Systemweite Umweltauswirkungen resultieren aus der Verwendung von limitierten Rohstoffen. Daher unterstreicht diese Arbeit die Relevanz der Betrachtung der konventionellen Nutzung limitierter Rohstoffe in Ökobilanzen.

Zuletzt bewertet diese Arbeit die absolute Umweltverträglichkeit von Kunststoffen aus alternativen Kohlenstoffquellen. Durch die Kombination eines globalen Modells der Kunststoffindustrie mit dem Planetary Boundary Framework bestimmt diese Arbeit die planetaren Fußabdrücke von Kunststoffen. Die Ergebnisse zeigen, dass die aktuelle fossilbasierte Kunststoffindustrie stark unnachhaltig ist, während durch eine ausgewogene Lösung aus verbesserten Recyclingtechnologien und der Nutzung von Biomasse und CO_2 bis 2030 eine absolute Umweltverträglichkeit erreicht werden kann. Allerdings können technologische Verbesserungen allein den vorhergesagten Anstieg der Kunststoffnachfrage bis 2050 nicht bewältigen. Daher muss die Gesellschaft ihre Wahrnehmung von Kunststoffen als Wegwerfprodukt ändern, um den Übergang zu einer ökologisch nachhaltigen Kunststoffindustrie zu unterstützen.

CHAPTER 1

Introduction

Plastics are versatile, durable, and cheap and have therefore found their way into every aspect of our modern lives. We encounter plastics as packaging in supermarkets, lightweight materials in cars and bikes, or insulation for our homes. Due to their unique property profiles, plastics are nowadays also used in advanced applications such as medical and electrical devices, aviation, and aerospace. Accordingly, the global demand for plastics has doubled from 234 Mt in 2000 to 460 Mt in 2019 and is expected to double again before 2050.[1] Meanwhile, global plastic waste more than doubled from 156 Mt in 2000 to 353 Mt in 2019.[1] These sharp increases in production volumes and waste streams raise concerns among society, industry, and policymakers about the environmental impacts of plastics.[2]

The environmental impacts of plastics are manifold and include harm to wildlife and human health, nature loss, and climate change.[2] Therefore, the United Nations Environment Programme pledged to tackle the triple planetary crisis of habitat loss, plastic pollution, and greenhouse gas (GHG) emissions from plastics production and end-of-life treatment.[2] While habitat loss and plastic pollution are mostly related to mismanaged disposal of plastics, 90 % of GHG emissions are caused by fossil resources that supply both energy and carbon feedstock.[1,3] The fossil-based plastics industry currently emits about 1.8 Gt of GHG emissions annually, which is expected to increase by two to four times by 2050 if plastics production and waste treatment remain unchanged.[4,5] Changing the process energy supply from fossil to renewable energy can reduce life-cycle GHG emissions by more than 60 %, albeit these savings would not even match the increase in plastics demand by 2050.[4] The remaining GHG emissions result from using fossil resources as carbon feedstock. Accordingly, alternative carbon sources are needed to decouple plastics from fossil feedstocks and further reduce plastics GHG emissions.

Various alternative carbon feedstocks are emerging with circular technologies such as plastic recycling, bio-based production, and carbon capture and utilization (CCU).[6–11] Plastic recycling closes the carbon cycle by reprocessing plastic waste via mechanical or chemical treatment and returning the carbon into the plastics value chain. Bio-based technologies such as gasification, fermentation, or anaerobic digestion convert biomass and bio-waste into chemical intermediates that can be further processed into plastics. Similarly, CCU technologies produce chemical intermediates by capturing and converting CO_2 from industrial point sources or ambient air. Furthermore, using the carbon monoxide in industrial off-gases from steel production as a carbon feedstock for plastics is currently being discussed as an option to exploit synergies between industry sectors.[12–16]

All alternative carbon feedstocks have been shown to reduce the GHG emissions of plastics compared to their fossil-based counterparts.[4,5,17–22] However, GHG reductions are not guaranteed as they depend on the GHG intensity of the energy and material requirements to supply and convert these alternative feedstocks. Therefore, previous studies applied life cycle assessment (LCA) to account for the environmental impacts of plastics along their life cycle.[18–21] However, despite the well-established ISO standards for LCA[23,24], LCA studies often differ in underlying assumptions and data and require subjective methodological choices hampering the comparison of studies and technologies. In addition, previous studies individually assess alternative feedstocks and do not evaluate potential environmental synergies from combined use, which may decrease feedstock consumption and environmental impacts. Furthermore, the literature focuses on plastics production and neglect that alternative feedstocks are limited and often already used elsewhere. However, the limitation and conventional use of alternative feedstocks have to be considered to derive a sound understanding of the system-wide environmental consequences of alternative plastics production.

Besides considering the entire life cycle, LCA also aims to capture all environmental impacts to identify potential burden shiftings, i.e., reducing one impact while increasing others. However, recent studies on plastics focus on climate change and often exclude other environmental impacts.[4,5] This climate change bias is particularly critical since alternative resources have been shown to shift environmental burdens.[25–27] Furthermore, even the studies that do assess environmental impacts other than climate change do not quantify whether burden shifting would compromise absolute environmental sustainability, i.e., endanger the resilient state of the Earth-system. Consequentially, a pathway that reduces plastics' GHG emissions while mitigating burden shifting to a sustainable level is still open.

To meet this challenge, this thesis analyzes the environmental impacts of GHG mitigation pathways for plastics from alternative carbon feedstocks. For this purpose, we[a]

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[a] This thesis is written in the *pluralis modestiae*, first to avoid the excessive use of passive voice and second to emphasize that the research behind this thesis is done in collaboration with colleagues and my supervisor. The contribution of the author is pointed out in the beginning of each chapter.

build and use bottom-up models based on the Technology Choice Model (TCM)[28], allowing for a consistent assessment of alternative pathways for plastics. Chapter 2 presents an introduction to the fundamentals of LCA, absolute environmental sustainability assessment, and the TCM. Furthermore, Chapter 2 provides an overview of the current state of the fossil-based plastics industry and covers details on all alternative feedstock prospects mentioned above.

A motivating case study on a novel high-performance thermoplastic polymer demonstrates the GHG mitigation potential of biomass utilization and highlights the need to assess burden shifting in Chapter 3. In Chapter 4, we analyze the combined use of alternative carbon feedstocks to quantify synergies for mitigating environmental impact using polyurethane as a case study. Furthermore, we conduct a comparative LCA of alternative carbon feedstocks for syngas as a key chemical intermediate for the plastics industry in Chapter 5. In particular, we assess the system-wide environmental consequences of using limited feedstock for GHG mitigations. In Chapter 6, we combine a global model of the plastics industry with the planetary boundary framework to evaluate the absolute environmental sustainability of GHG mitigation pathways for plastics. Finally, the results of this work are summarized, and conclusions are drawn in Chapter 7.

Chapter 2

Assessment of environmental impacts of plastics

The following chapter provides a general overview of the plastics industry and a literature review of the current practice for assessing plastics' environmental impacts. Section 2.1 reviews the current state of the fossil-based plastics industry and future prospects for alternative carbon feedstocks. Section 2.2 elaborates on the environmental assessment of the plastics industry using life cycle assessment, the planetary boundary framework, and the Technology Choice Model. In Section 2.3, we review the current practice of assessing alternative carbon feedstocks for plastics and identify critical knowledge gaps in this assessment practice. Finally, Section 2.4 highlights how this thesis contributes to closing these critical knowledge gaps in the subsequent Chapters 3 to 7.

2.1 Fossil-based plastics and alternative carbon feedstocks

The following sections[a] describe the current state of the fossil-based plastics industry (Section 2.1.1) and introduce four alternative carbon feedstocks proposed in the liter-

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[a] Minor parts of these chapters are reproduced from:

> Bachmann, M., Völker, S., Kleinekorte, J., Bardow, A. (2022). Syngas from what? Comparative Life Cycle Assessment for Syngas Production from biomass, CO_2, and steel mill off-gases. *Submitted to ACS Sustainable Chemistry and Engineering*

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Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

ature: Plastic waste recycling, biomass, carbon dioxide (CO_2) via carbon capture and utilization, and steel-mill off-gases (Section 2.1.2).

2.1.1 The current plastics industry

The plastics industry today produces more than 350 Mt of plastics per year with a global market size of about 600 billion U.S. dollar, making it one of the world's largest industries.[29,30] The economic success story of the plastics industry began between the 1920s and 1950s when new findings on the structure of plastics[31–33] and advances in plastics synthesis[34–36] led to pioneering large-scale synthesis of polyvinyl chloride, polystyrene, polyethylene, polypropylene, and others. These pioneering syntheses were followed by catalysis and efficiency improvements allowing for low-cost production and resulting in a compound annual growth rate of 8.4 % between 1950 and today. This growth rate corresponds to roughly 2.5 times the compound annual growth rate of the global gross domestic product.[37]

Today, the consumption level of plastics ranges from 55-80 kg per capita and year in high-income countries to as little as 4 kg per capita and year in low-income countries. However, while growth rates in high-income countries are beginning to stagnate, they sometimes exceed values higher than 10 % per year in low-income countries.[38] These high growth rates result from plastics' wide range of potential applications: About 60 % of plastics are used for packaging, construction, and transportation, while the rest is used for textiles and electronics, consumer products, agriculture, and others (see Figure 2.1).[1] In these applications, plastics often improve the system performance by replacing or enhancing other bulk materials. In particular, plastics serve as lightweight materials in the transportation sector to reduce weight or as insulation for buildings to reduce energy demands.[38]

Each application requires a different type of plastic. Polyolefins, including low- and high-density polyethylene and polypropylene, represent the largest share of plastics with more than 40 %, followed by polyester, polyamide and acrylic fibers, polyvinyl chloride, polyethylene terephthalate, polystyrene, and polyurethanes (see Figure 2.1). In addition, a variety of other plastics exists, including engineering plastics such as polycarbonate and poly(methyl methacrylate) or high-performance plastics such as polyetherimide.

Plastics offer exceptional features comprising an excellent performance-to-weight ratio, high durability, and low processing temperatures compared to other bulk materials. Furthermore, each type of plastic provides unique properties, including good thermal and electrical insulation behavior, chemical resistance, rigidity, or flexibility.

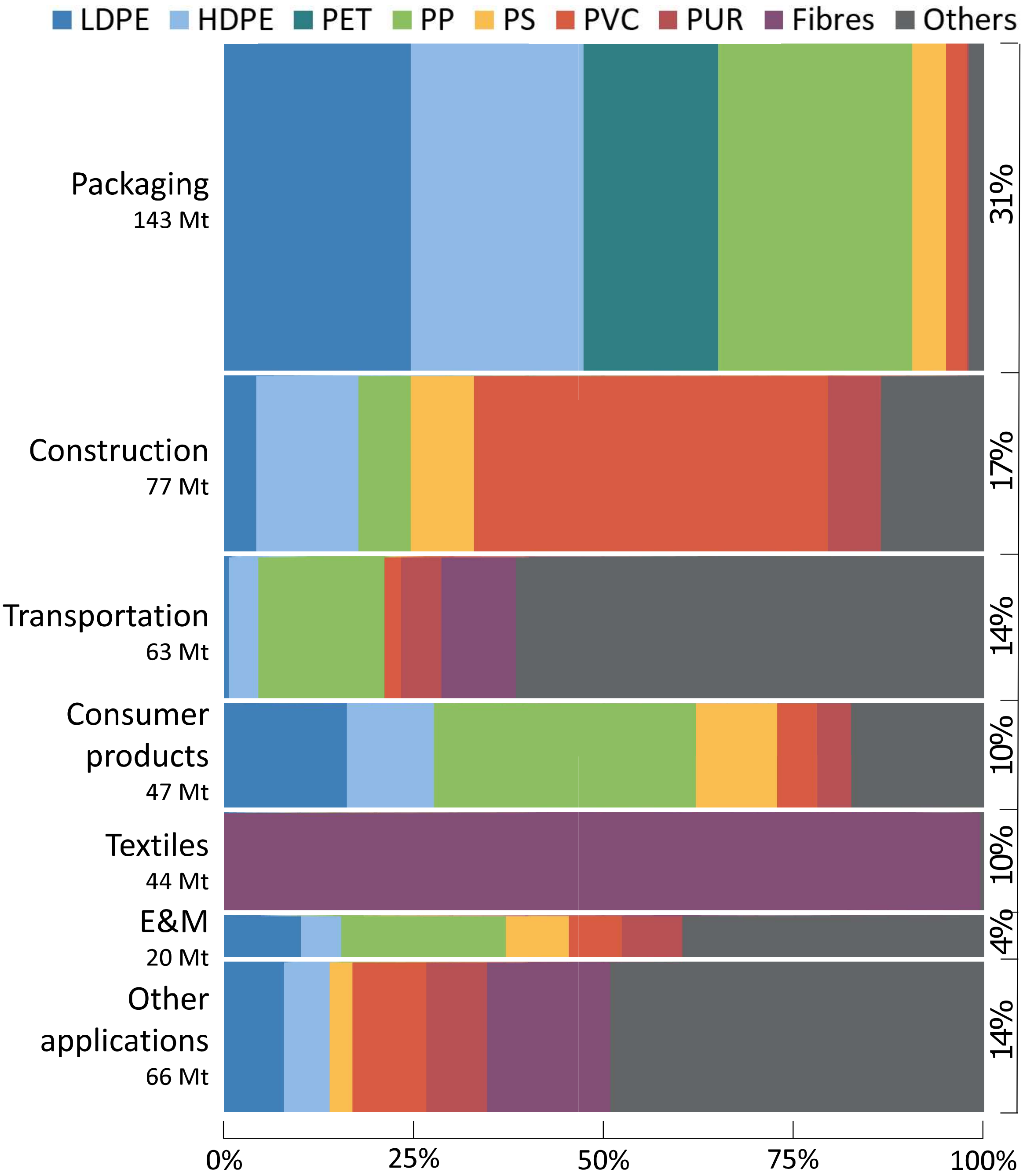

Figure 2.1: Market share by weight for the main plastic types and applications adapted from the Global Plastics Outlook.[1,39] Abbreviations: LDPE = low-density and linear low-density polyethylene, HDPE = high-density polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PVC = polyvinyl chloride, PUR = polyurethane, E&M = electronics & machinery.

In addition, plastics can be combined to fulfill several functions, thus offering much more design freedom than other conventional materials.[40]

Today, the chemical industry consumes about 31 EJ[b] of fossil resources annually. These fossil resources comprise crude oil, coal, and natural gas. The highest share of these resources is consumed by plastics production for energy purposes and as its primary chemical feedstock. In fact, virtually all plastics are produced from these three fossil resources.

The primary feedstock crude oil is separated by distillation in petroleum refineries, yielding naphtha and other saturated hydrocarbons (see Figure 2.2). The subsequent cracking of naphtha leads to a mixture of olefins, aromatics, and other short-chain hydrocarbons, which are used as monomers for plastics production.[41] Monomers are subsequently converted to plastics via polymerization. Alternatively, olefins and aromatics can also be produced from methanol via the methanol-to-olefins and methanol-to-aromatics processes, allowing coal and natural gas to be incorporated into the plastics supply chain. Converting coal and natural gas to methanol requires syngas as an intermediate product, which can be produced via steam reforming, partial oxidation, or gasification. Coal gasification combined with the methanol-to-olefins process is currently done exclusively in China, where abundant coal availability lowers the methanol production costs.[38,42]

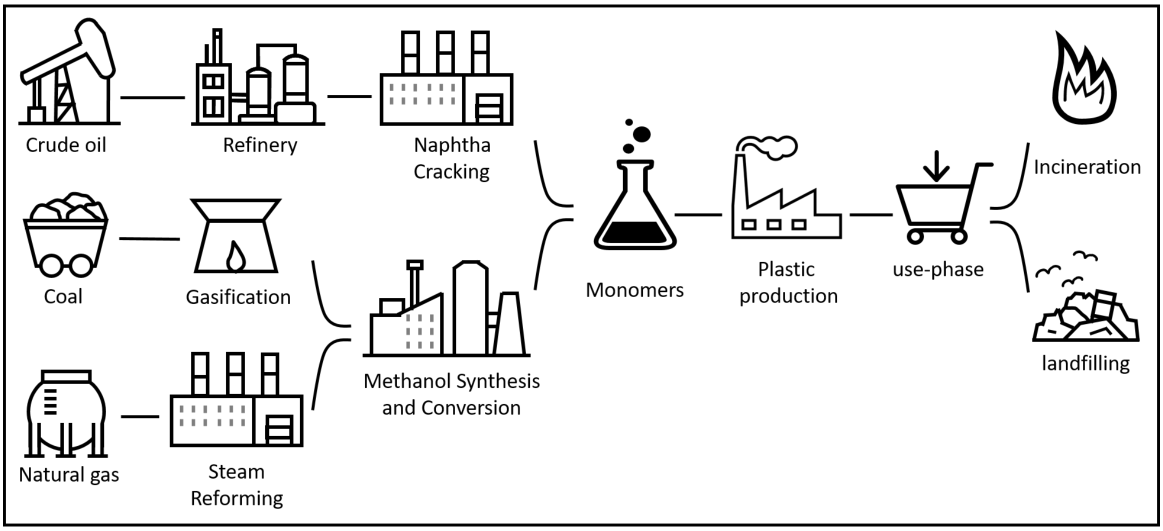

Figure 2.2: Schematic flow diagram of today's plastics industry.

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[b] Calculated based on the primary demand of crude oil, coal, and natural gas from the International Energy Agency

Today's plastics industry can be considered an almost entirely linear system, meaning that fossil resources are extracted from the environment, converted to plastics, and landfilled or incinerated at the end of their life cycle (see Figure 2.2). The linear system contradicts usual waste hierarchies, which prefer waste prevention and reuse, followed by recycling, recovery, and disposal by landfilling.[43,44] Still, landfilling is the number one treatment technology globally, with about 50 % of plastics being landfilled, whereas 19 % are incinerated, and 22 % are disposed of in uncontrolled dumpsites.[1]

In the European Union, landfill bans and other restrictions have raised the share of incineration with energy recovery to 48 %, making it the number one plastic treatment technology in Europe.[45] Although the shift from landfilling to incineration with energy recovery is in line with the waste hierarchy, it increases system-wide GHG emissions from plastics.[45] Incineration increases GHG emissions since bounded carbon is released as CO_2 into the environment. Contrarily, plastic incineration commonly generates heat and electricity and, therefore, receives a GHG credit for reducing the demand of fossil-based energy carriers for conventional generation. However, higher shares of renewable energy generation result in a lower GHG credit, reducing the environmental benefit of waste-derived heat and electricity. Overall, plastics generated 1.8 Gt of GHG emissions in 2019, of which 90 % came from producing and converting fossil resources.[1] If plastics production and waste treatment remain linear, these GHG emissions are expected to rise to 4.7-6.5 Gt by 2050 due to the increasing plastic demand.[4,5]

To reduce GHG emissions, the plastics industry must overcome its dependence on fossil resources for energy and feedstock supply. Zheng et al. found that changing the energy supply from fossil to renewable energy in 2050 can reduce life-cycle GHG emissions by 51-62 %.[4] Still, absolute GHG emissions in 2050 would double the current values due to the feedstock-related emissions to meet the increasing plastic demand. Reducing feedstock-related emissions requires alternative and circular technologies that allow for switching from fossil to alternative carbon feedstocks (see Figure 2.3). However, circular technologies, including mechanical and chemical recycling, make up only 14 % of the plastic treatment in the European Union and 5-23 % globally.[37,45] The reasons for the low shares of alternative carbon sources are manifold and are detailed in the following section.

2.1.2 Alternative carbon feedstocks for plastics

The following section provides an overview of alternative carbon sources and the technologies to convert or separate them into feedstock for plastics production.

Alternative 1: Plastic waste

The linear plastics industry introduced in Section 2.1.1 produces so-called virgin-grade plastics. Virgin-grade plastics come straight from the manufacturer and have not been reprocessed yet. This practice was state of the art until the end of the 1980s and is still common practice today.[46] In contrast, plastic recycling yields so-called recyclates, or secondary or recycled plastics, that are returned to the plastics value chain and reduce the consumption of virgin feedstock. Plastic recycling began in the early 1990s with the introduction of the resin identification codes in the USA and the German “Grüner Punkt”, the license symbol of the first plastic collection and recycling system, which has been adopted by many other countries worldwide.[47]

Unfortunately, today’s global recycling rates for plastics remain low, ranging from 5-23 %, depending on the recycling rate definition.[1,5,37,45,48] For instance, according to the Organisation for Economic Co-operation and Development, about 55 Mt of the total 353 Mt of plastic waste was recycled in 2019, corresponding to a 15 % recycling rate.[1] However, including recycling losses and residues reduces the effective recycling rate to 9 %. Furthermore, effective recycling rates vary widely across regions, ranging from 14.2 % in the European Union to 4.5 % in the United States.[39] Whether regions have adopted plastic recycling systems depends on several factors, including historical infrastructure, regulations, local population density, and costs.[1] For instance, densely urbanized countries promote plastic recycling and incineration systems, while countries with lower population densities rely on landfilling as their primary disposal method with about two-thirds lower cost.[1]

The recyclability of plastic waste depends on the plastic type and several other factors, e.g., the presence of contaminants or additives such as plasticizers, antioxidants, or stabilizers.[49] The shares of plastic types in plastic waste (see Figure 2.2) differ from the virgin market shown in Figure 2.1. The differences in shares result from the increasing plastic demand combined with deviating lifetimes of plastic types and applications. While plastic packaging with high shares of polyethylene, polypropylene, and polyethylene terephthalate have an average lifetime of about six months, polyurethane and polycarbonate applications in the construction sectors last about 35 years on average.[1] Therefore, plastic types for packaging are more dominant in plastic waste, which must be considered when designing recycling systems and selecting recycling technologies.

Generally, two types of recycling technologies exist: mechanical and chemical (see Figure 2.3). In addition, incineration with energy recovery is often referred to as thermal recycling. However, incineration cannot provide a carbon feedstock and is therefore not considered in detail here.

In mechanical recycling, plastic waste is pre-sorted by plastic type, cleaned, shredded, and melted by extrusion.[38] Mechanical recycling requires pure plastic monostreams with only minor impurities and is therefore often used for plastic packaging such as PET bottles. The recycling process leaves the chemical structure of the plastic intact, which requires less energy than breaking the strong polymer backbone by chemical recycling. Thus, mechanical recycling is often the simpler and cheaper source of secondary plastics. However, secondary plastics from mechanical recycling often suffer from degradation mechanisms and impurities that remain in the chemical structure, resulting in lower performances than virgin material.[8]

In contrast, chemical recycling generally converts the plastics back to monomers or even smaller chemical building blocks, which can then be reprocessed to the original virgin material.[38] Thus, secondary plastics from chemical recycling exhibit the same performance as virgin material. However, as mentioned above, the main challenge for chemical recycling is breaking the polymer backbone, which includes a strong carbon-carbon bond for most plastics. To break this backbone, several approaches exist, ranging from thermochemical routes such as pyrolysis or gasification to solvolysis or enzymatic hydrolysis.[50] These technologies offer the advantage of deconstructing

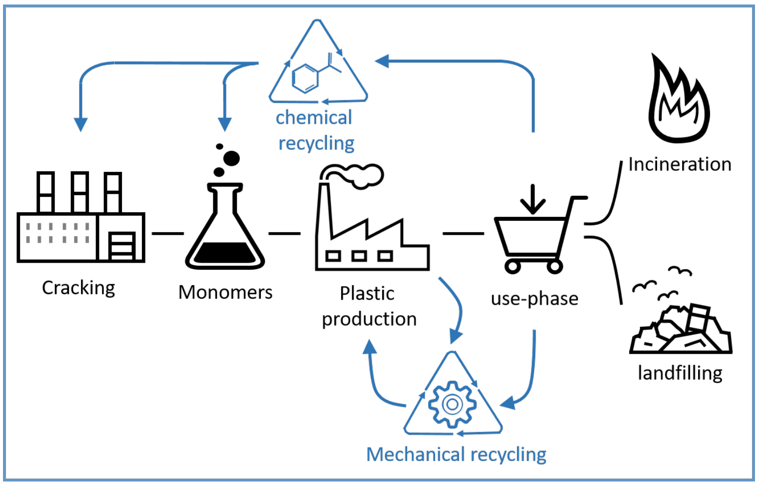

Figure 2.3: Schematic flow diagram of the plastics industry based on recycling.

(mixed) plastic waste unsuitable for mechanical recycling, e.g., multilayer films or thermosets.[11] Thus, chemical recycling can extend the lifetime of plastics that otherwise would have ended in landfills or incinerators. However, most chemical recycling technologies are still emerging and are therefore rarely used on an industrial scale.[11,51,52]

Recycling returns plastics to their value chain, closes the carbon cycle, and reduces virgin feedstock consumption. Moreover, the alternative carbon feedstocks presented in the rest of this section substitute fossil resources in virgin plastic production. These alternative carbon feedstocks are biomass, CO_2 via carbon capture and utilization, and steel mill off-gases.

Alternative 2: Biomass and bio-waste

Biomass is seen as an essential building block toward a more sustainable chemical industry.[53] In particular, biomass has become increasingly important as low-carbon energy and raw material source.[54] Biomass is considered low-carbon as it absorbs CO_2 from the atmosphere during the growth phase. The amount of CO_2 absorbed depends on the carbon content of the biomass. In addition, the carbon footprint of biomass depends on cultivation and logistical efforts, e.g., harvesting methods, gathering efforts, or fertilizer and pesticide application (details in Section 2.2.1).[55]

Bioplastics can substitute fossil plastics while retaining their desirable material properties. However, the term bioplastics is often misleadingly used in the literature:[56] On the one hand, bioplastic refers to plastics produced from biomass.[57] These plastics have the same durable and non-degradable properties as fossil-based plastics. On the other hand, the term bioplastics is also used for biodegradable plastics produced from both fossil resources and biomass.[6] To counteract this misunderstanding, we refer to plastics produced from biomass as bio-based plastics, whereas this thesis does not consider biodegradable plastics. Production capacities of biodegradable plastics represent only 0.3 % of total plastics, and their environmental impacts have become controversial owing to issues related to biodegradation in natural environments.[1]

Different types of biomass can be used to produce plastics: edible biomass such as sugarcane, corn, and wheat, lignocellulosic biomass like energy crops and forest residues, or the organic fraction of municipal solid waste (bio-waste).[58] Furthermore, algae biomass is another feedstock solely produced as an energy source or raw material.[59] Using edible biomass as feedstock for plastics may lead to direct competition with the food industry[60], and studies on algae biomass show a wide range of energy yields suggesting high uncertainties in its environmental impact.[59] Therefore, we focus on lignocellulosic biomass and bio-waste as feedstock for plastics in this thesis. Both feedstocks offer the potential for large-scale application.[61,62]

Biomass demand increased owing to the growing role of biofuels for transportation and bioenergy to provide low-carbon electricity and heat.[63] For instance, global biomethane production in 2020 showed a double-digit rise, which is also expected for the following years. Overall, the total global bioenergy consumption is anticipated to double from 42 EJ in 2021 to 80 EJ in 2030.[63]

In contrast, bio-based plastics represented only a minor share of 0.6 % of total plastics in 2019.[1] While growth rates of bio-based plastics are also high, they don't differ much from fossil-based plastics.[1,39] The reasons why bio-based plastics represent only a minor share of the plastics market are manifold, ranging from the innate variability of biomass resources to higher investment costs and lower efficiencies of the bio-based processes.[58,63,64] In particular, the lower efficiency is related to the composition of biomass: While plastics were designed to be efficiently produced from hydrocarbons from fossil resources, biomass consists mainly of partially oxidized hydrocarbons. Since bio-based plastics today are predominantly bio-based versions of conventional plastics, their production requires reducing the biomass's oxygen content.[58] Reducing the biomass oxygen content is typically done by decarboxylation, which results in direct CO_2 emissions and lowers the overall carbon efficiency. Alternatively, novel plastics can be designed with higher oxygen contents, such as polylactic acid and polyhydroxyalkanoates. However, this thesis focuses on conventional plastics, whereas novel plastics are out of the scope due to their low production volume.

To produce bio-based plastics, biomass needs to be converted into chemical intermediates first. Three suitable intermediates stand out that can be integrated into the value chain of plastics: ethanol, syngas, and methane. Ethanol is produced via fermentation by bacteria or yeast and can be dehydrated to ethylene monomers (see Figure 2.4).[65] Syngas is produced from biomass via gasification. Gasification can thermo-chemically convert biomass directly into syngas at high temperatures and in the presence of a gasifying agent such as oxygen or steam.[61] Syngas can be converted to methanol in subsequent process steps, which can then be further processed to monomers as described in Section 2.1.1. A common process for methane production is anaerobic digestion (not shown in Figure 2.4 for simplicity). Anaerobic digestion decomposes biomass in the absence of oxygen by anaerobic microorganisms[66] and has attracted much attention recently as a method for energy recovery from bio-waste.[67] Methane can either be converted to syngas in conventional steam reformers or directly to ethylene via oxidative coupling. All technologies presented above have already been applied on an industrial scale.[68–70]

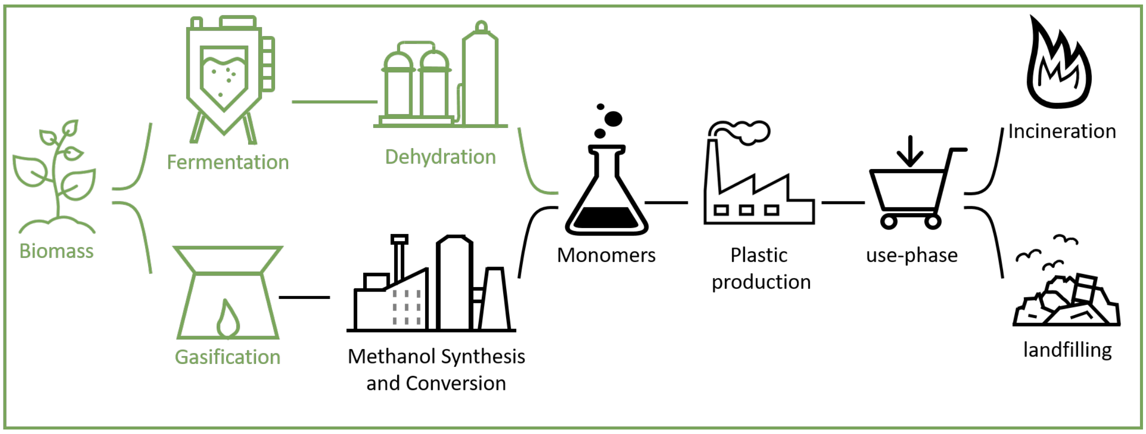

Figure 2.4: Schematic flow diagram of a bio-based plastics industry.

Alternative 3: CO_2 via carbon capture and utilization

The majority of all anthropogenic GHG emissions (74 %) is CO_2.[71] Capturing and utilizing this CO_2 as a carbon feedstock for polymers and other value-added products has received increased interest recently.[7] However, using CO_2 as a chemical feedstock is nothing new: For instance, for about a century, CO_2 has already been used in industrial scale for urea production.[72] The increasing interest in CCU stems from academia and industry, aiming to reduce the use of fossil resources and GHG emissions from the energy sector and so-called hard-to-abate sectors. In particular, these hard-to-abate sectors, namely the cement, steel, and chemical industries, suffer from inherent CO_2 emissions generated in non-combustion processes, which can only be reduced through substantial effort.[73] Capturing CO_2 and using it as a carbon feedstock can reduce overall GHG emissions, both by avoiding direct emissions and by replacing the conventional feedstock. As an alternative to CCU, CO_2 emissions can be captured and stored underground. This so-called carbon capture and storage (CCS) approach is recognized for playing a key role in decarbonizing the industrial sector.[74] However, CCS does not provide a carbon feedstock for plastics and is therefore not considered in this thesis.

The energy and industrial sectors mentioned above are large-scale CO_2 point sources, emitting over 50 % of the global anthropogenic CO_2 emissions.[71] However, the CO_2 concentration differs by point sources and thus also the best-suited capture technologies and the capturing efforts.[75] For example, the chemical industry includes several point sources that emit almost pure CO_2, such as ammonia or ethylene oxide plants. In contrast, off-gases from the cement and steel industries have CO_2 concentrations of 14-35 %, pulp and paper mills of 7-20 %, and coal and natural gas combined cycle power plants of 3-15 %. The most diluted CO_2 source is ambient air, with a concentration of about 400 ppm.[75]

In general, the energy efficiency of the separation process decreases with decreasing CO_2 concentration since more unwanted material needs to be processed.[76] Furthermore, the specific energy demand per kg CO_2 depends strongly on the capture technology. Several technologies for CO_2 capture have been developed, ranging from absorption and adsorption to membrane separation and cryogenic distillation.[77] The most common capture technology in industrial practice is amine scrubbing, which uses amine-based solvents for CO_2 absorption.[78] In the absorption phase of the amine scrubbing process, the CO_2 in the off-gas reacts with an amine solution containing, for example, monoethanolamine as the scrubbing agent. The absorption phase is carried out at low temperatures and high pressures. Afterward, the solution is desorbed at high temperatures and low pressures to reverse the reaction equilibrium. The amine scrubbing process achieves CO_2 concentrations higher than 99 % purity.

Besides applying CCU in urea production, a few other industrial applications exist, e.g., in the beverage industry or for enhanced oil recovery. Another CCU example in industrial application is the direct use of CO_2 in polyether polyol production.[79,80] Here, the CO_2 partially substitutes polyol momomers, e.g., fossil-based ethylene oxide or propylene oxide (see Chapter 4 for details). The resulting CO_2-based polyether polyols can produce polyurethanes. However, apart from the abovementioned examples, the industrial application of CCU has not become widely established yet.

A barrier to the industrial application is the relatively unreactive CO_2 itself, which in most CCU applications has to be activated by an additional energy carrier such as hydrogen (H_2).[7] Typical examples of CCU technologies using H_2 as an energy carrier are the Sabatier process for methane production, the direct catalytic hydrogenation of CO_2 to methanol, and the reverse water-gas shift (WGS) process and dry reforming of methane (DRM) for syngas production. These products can be integrated in the plastics supply chain to substitute fossil resources (see Figure 2.5). However, using H_2 requires large amounts of energy since H_2 is often provided via electricity-driven water electrolysis.

Alternatively, electrochemical CO_2 reduction uses electricity to convert CO_2 directly. For instance, CO_2-electrolysis reduces CO_2 to carbon monoxide (CO), and co-electrolysis converts CO_2 with water to syngas.[81,82] Studies have identified electrochemical pathways that convert CO_2 directly into monomers such as ethylene.[83] The direct reduction of CO_2 to CO and the co-electrolysis to CO and H_2 have shown significant progress in efficiency toward practical implementation.[84] The increasing efficiency of the CO pathway is shown by high Faradaic efficiencies of about 90 %

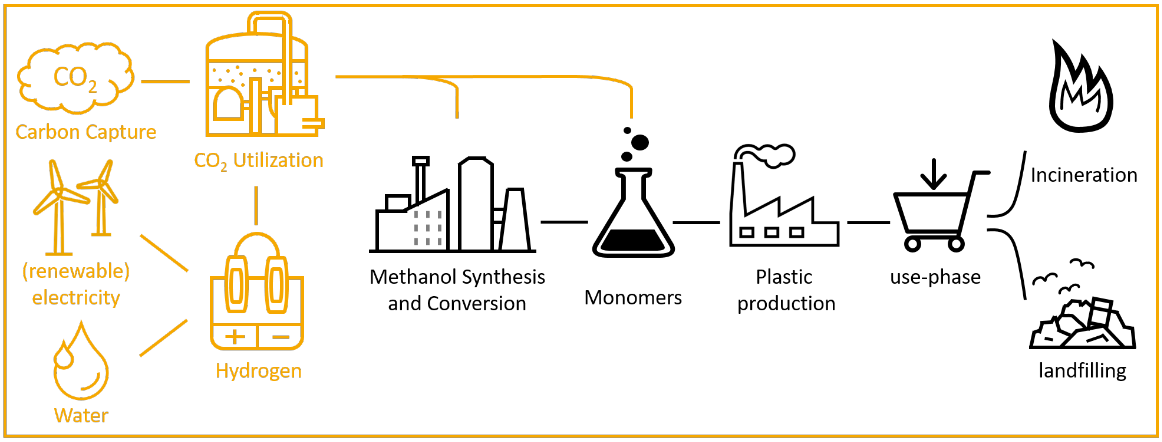

Figure 2.5: Schematic flow diagram of a plastics industry based on carbon dioxide and water.

and simultaneously low overpotentials of about 0.7 V.[81] Still, further development is required for industrial application as the current technology readiness level (TRL) is between 3-5.[85] In contrast, some H_2-based routes such as the Sabatier process have already reached TRL 9, meaning that large-scale operational facilities exist.

Alternative 4: Steel mill off-gases

Industrial symbiosis refers to the cooperation of traditionally separated industrial sectors through exchanging material and energy flows such as by-products or wastes.[86] The exchange is intended to save resources and meet environmental requirements while providing economic benefits. An example of industrial symbiosis with growing interest is the integration of the steelmaking and chemical industries (see Figure 2.6).[14,15,87,88] The steelmaking industry contributes around 7 % of the global anthropogenic GHG emissions, of which a large share results from the treatment of steel mill off-gas (mill gas).[71,89] To date, these gases are usually treated onsite for the steel mill's internal heat and power supply.[90] In contrast, novel approaches such as the Carbon2Chem®, the STEPWISE, or the Steel2Chemical projects are dedicated to using the valuable compounds (see Table 2.1) in such mill gases as feedstock for chemicals and polymers.[91–94]

Integrated steel mills currently produce over 90 % of the world's steel.[90] Integrated steel mills consist of pig-iron production and steel production, both of which emit large amounts of mill gases. In pig-iron production, coal is converted into coke at temperatures of around 1000 °C and in the absence of air. The process yields coke oven gas (COG), consisting mainly of H_2 and methane, with smaller amounts of CO, CO_2, nitrogen (N_2), and other compounds (see Table 2.1).[14] Afterward, the coke is

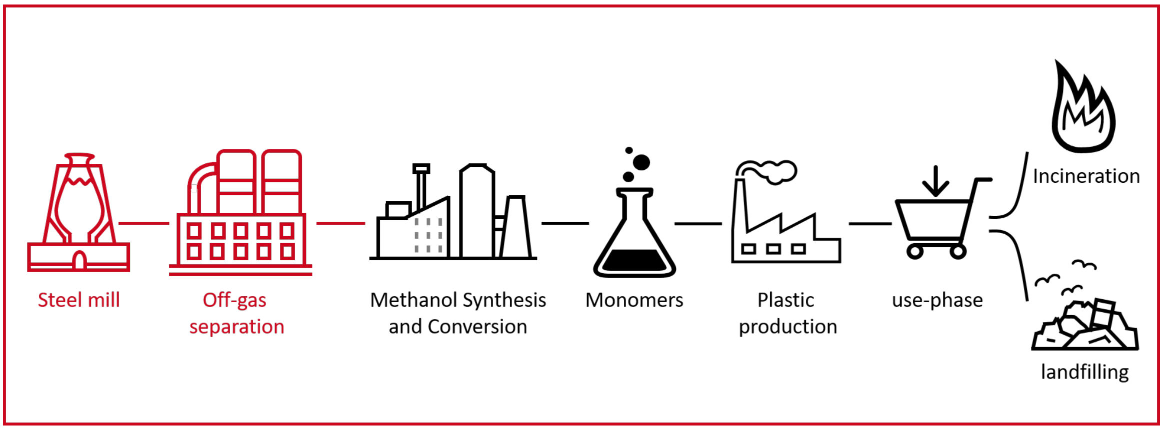

Figure 2.6: Schematic flow diagram of a plastics industry based on steel mill off-gases.

mixed with sintered iron ore and limestone, and the resulting mixture is reacted with air in the blast furnace. Combusting the coke yields carbon monoxide, which reduces the iron ore to pig-iron at temperatures up to 2000 °C. The remaining gas, called blast furnace gas (BFG), contains mainly N_2, CO_2, CO, and lower amounts of H_2 and other compounds.[14] The pig-iron still contains about 4 % carbon, which has to be reduced to gain steel. For this purpose, the pig-iron is mixed with steel scrap and oxidized with oxygen at around 1600 °C in the so-called Linz-Donawitz or basic oxygen process. The process yields steel, slag, and basic oxygen furnace gas (BOFG) with a high share of CO and lower amounts of CO_2, H_2, and other compounds. Approximately 50 Nm^3 of COG, 900 Nm^3 of BFG, and 50 Nm^3 of BOFG are produced per ton of steel, which are subsequently burned in the internal power plant to generate electricity and heat.

Table 2.1: Composition of steel mill off-gases as molar fraction (%).[14] Abbreviations: COG = coke oven gas, BFG = blast furnace gas, BOFG = basic oxygen furnace gas.

Compound	**COG**	**BFG**	**BOFG**
Carbon dioxide	1.2	21.6	20.0
Carbon monoxide	4.1	23.5	54.0
Hydrogen	60.7	3.7	3.2
Methane	22.0	-	-
Nitrogen	5.8	46.6	18.1
Other hydrocarbons	2.0	-	-
Oxygen & Argon	0.2	0.6	0.7
Water	4.0	4.0	4.0

To utilize mill gases in the chemical industry, the desired compounds, including CO_2, CO, or H_2, must be separated. The primary options for recovering these gases are the recovery of CO_2 from BFG, CO from BFG and BOFG, and H_2 from COG.[15] In principle, the CO_2 capture technologies described in the previous section are also suitable for mill gas separation. The separation of CO_2 via amine scrubbing as the most common absorption technology has already been described in the previous section. Absorption can also recover CO from BFG and BOFG. Today, absorption is commercially performed exclusively via the COPURESM (formerly COSORB) process, but hardly anything is known about it in the open literature. Alternatively, pressure or temperature swing adsorption can be used to recover CO, with pressure swing adsorption (PSA) as the more promising technology for industrial application.[15] PSA is also commercially used in H_2 separation from COG. Therefore, PSA is used in this thesis to separate mill gases. Alternatively, membrane separation can be employed, requiring multistage processes to reach the same H_2 purity and recovery as PSA. Cryogenic distillation, however, is rather seen as an additional purification step owing to its higher energy demand.[15]

The separated mill gases can be integrated into the plastics' supply chain via methanol (see Figure 2.6). However, even separated mill gases contain trace substances from steel production. These trace substances provide a challenge for proven catalyst systems in chemical production as they might be harmful or toxic to the catalyst.[95] Further challenges result from the high system dynamics when coupling several large production systems and the high H_2 demand, which can only be provided from the mill gases to a limited extent.[95]

Overall, producing plastics from alternative carbon feedstocks is challenging, yet offers potential to reduce the environmental impact of plastics. Alternative carbon feedstocks are suitable to substitute fossil resources in tomorrow's plastics industry (see Figure 2.7).

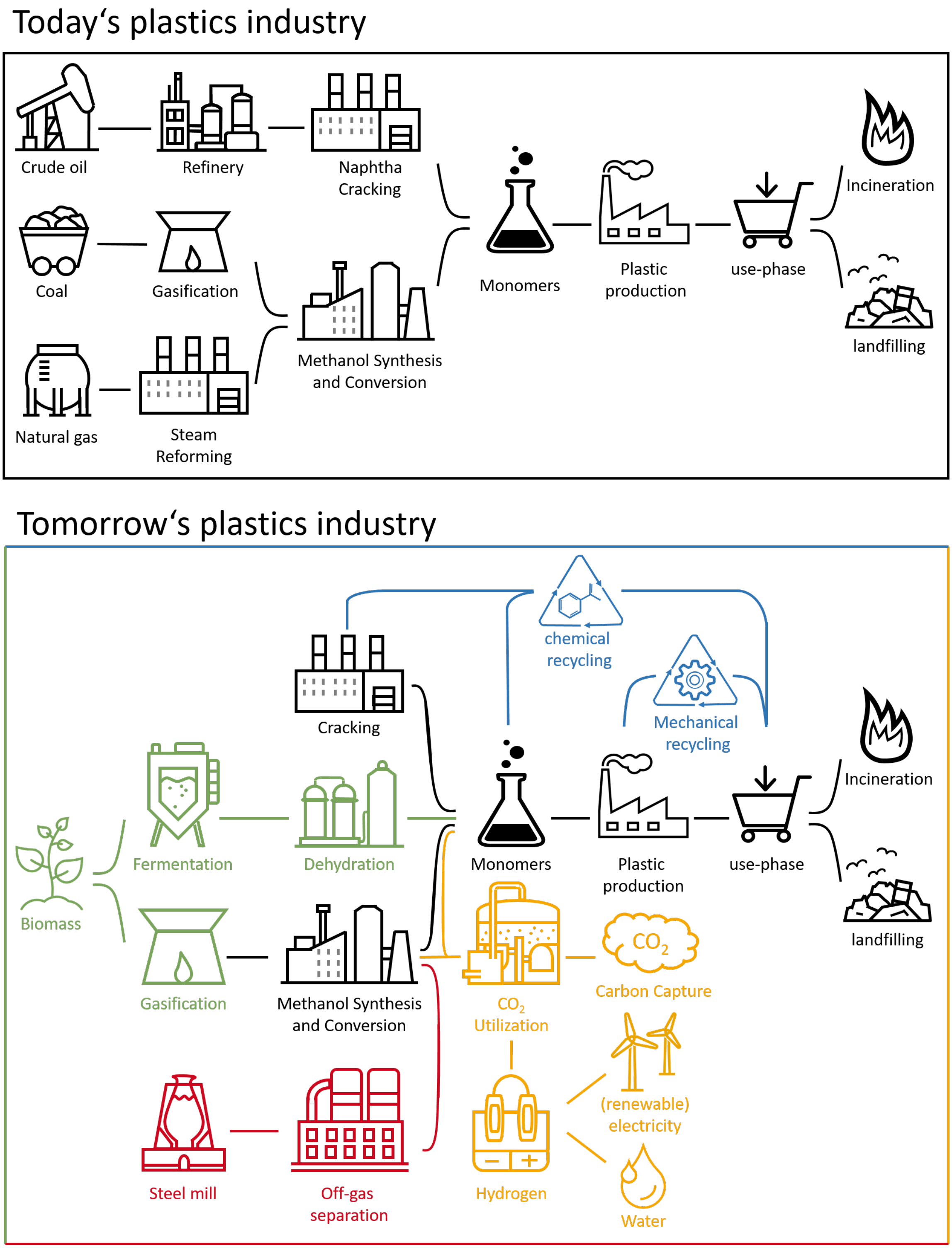

Figure 2.7: Schematic flow diagram of today’s plastics industry based on crude oil, coal, and natural gas (top) and tomorrow’s plastics industry based on renewable carbon feedstocks (bottom).

2.2 Assessing the environmental impacts of plastics: a review

The following section provides the basics for assessing the environmental impacts of plastics from alternative carbon feedstocks. Section 2.2.1 describes the fundamentals of LCA as a method for the comparative evaluation of environmental impacts between products and production systems. Furthermore, Section 2.2.1 elaborates on the drawbacks of LCA as a relative method for comparing environmental impacts. Afterward, Section 2.2.2 presents the planetary boundaries as an exemplary framework for absolute environmental sustainability assessment. Finally, Section 2.2.3 introduces the Technology Choice Model as a tool for the environmental optimization of production systems.

2.2.1 Fundamentals of life cycle assessment

LCA is a method that holistically accounts for the environmental impacts of products and services.[23] LCA considers the entire life cycle of a product, from the provision of energy and raw materials, through the manufacture and use of the product, to the recycling and the final disposal at the end of the life cycle. Thereby, LCA records all mass and energy flows exchanged with the environment throughout the product's life cycle. These flows include resource consumption of, for example, crude oil and ore, and emissions, such as CO_2 and methane. In an LCA, these mass and energy flows are translated into environmental impacts of the considered products. Examples of environmental impacts are climate change, toxicities, or resource depletion. The holistic approach of LCA aims to identify and avoid potential burden shifts between life phases and environmental impacts.

The International Organization for Standardization published the two complementary ISO standards 14040 and 14044, which define the principles and the framework of LCA and the requirements and guidelines for its implementation.[23,24] The ISO standards provide a standardized and scientifically sound basis that allows LCA to be used in industrial development processes, marketing strategies, and political decision-making.

An ISO-compliant LCA typically includes the following four phases (see Figure 2.8):

1. Goal and scope definition
2. Life cycle inventory analysis
3. Life cycle impact assessment
4. Interpretation

The following sections elaborate on these four phases of LCA.

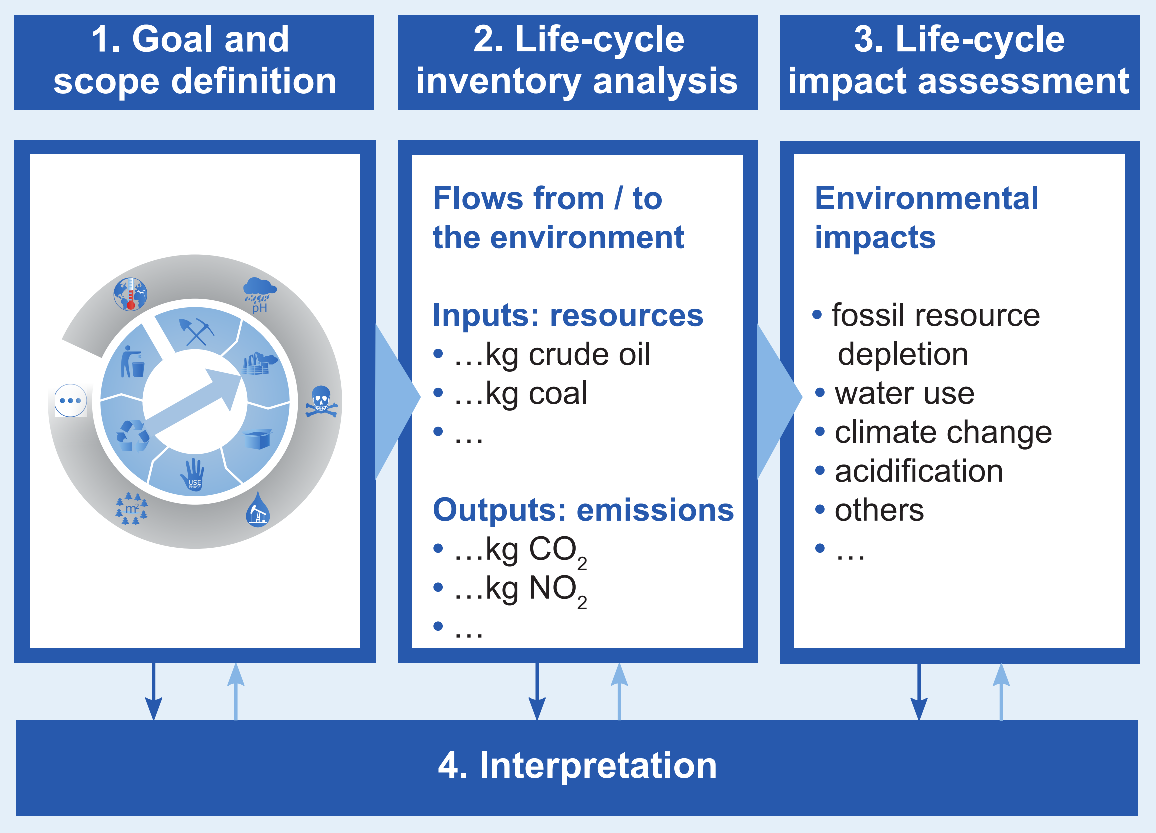

Figure 2.8: The four phases of life cycle assessment according to ISO standards[23,24] (adapted from Deutz.[96])

Goal and scope definition

The goal definition is the first step in every LCA.[97] The goal defines the scope of the study and is thus decisive for all following phases. Furthermore, the final results of the LCA are evaluated and interpreted in close relation to the goal. Therefore, a clear goal definition is essential for conducting an LCA. For detailed instructions on how to define the goal of an LCA study, the reader is referred to the ILCD Handbook.[97]

The goal definition is followed by the scope definition, including key elements of an LCA, such as the functional unit and the system boundaries. The functional unit provides the quantitative basis for an LCA, which is usually applied to compare the environmental impacts of product systems. For a meaningful comparison, the functions must be identical for the evaluated product systems and the reference processes (benchmarks). In this thesis, the functional unit often corresponds to a certain amount of plastic that all product systems must produce.

In addition, some product systems provide further functions which must be taken into account, e.g. the production of co-products, the provision of energy, or the treatment of wastes. In the plastics industry, the definition of the functional unit can get complex, as production systems typically serve multiple functions. For instance, plastics recycling treats plastic waste while simultaneously producing new plastics. Such processes are referred to as multifunctional processes. The ISO standards define several approaches to dealing with multifunctionality. In this thesis, the system expansion approach is preferred. The system expansion approach either expands the functional unit by including all other functions of the product system or gives a credit for producing co-products. The credit is given for avoiding the environmental impact of the conventional production of the co-product. In cases where system expansion is not possible, proportional allocation is applied in this thesis. Allocation partitions the environmental impacts of a product system between co-products based on factors such as the co-products' mass, energy content, or economic value.

The system boundary determines which phases and processes of the product's life cycle are included in the assessment. Generally, LCAs should always consider the product's entire life cycle. However, in certain cases, a reduced system boundary is sufficient to reach the goal of the study. For instance, a so-called cradle-to-gate system boundary neglects all emissions after the "factory gate", i.e., emissions that occur in downstream processes, in the use phase, and during the recycling and the final disposal. Such a cradle-to-gate system boundaries are suitable for comparative LCAs in which the post-gate life cycle is identical for all systems under consideration. For example, suppose fossil-based plastics are compared with chemically identical bio-based plastics. In that case, assessing the life cycle from raw material extraction to the factory gate is sufficient since all subsequent environmental impacts are identical. However, this approach explicitly applies to comparative LCAs only, whereas absolute environmental assessments should consider all life cycle phases for which data is available (*cf.* Section 2.2.2).

The system is often divided into the foreground and the background system. The foreground system is the system of primary concern to the LCA practitioner. In contrast, the background system consists of processes over which the LCA practitioner has no or only indirect influence. In this thesis, the foreground system corresponds to the part of the system that was modeled based on process data. For the background system, we use datasets from LCA databases such as GaBi or ecoinvent.[98,99]

Life cycle inventory analysis

The second phase of LCA is the life cycle inventory analysis. The life cycle inventory analysis determines the life cycle inventory (LCI) of all processes within the system boundaries. The LCI consists of all flows that are exchanged between the product system and the environment, further referred to as elementary flows. Elementary flows are either natural resources consumed by or emissions from the product system. In contrast, flows that are exchanged between processes within the product system are called intermediate flows.

Measuring elementary flows directly is usually preferable to ensure high data accuracy. Alternatively, elementary flows can be approximated using industrial, simulation, or laboratory data. Furthermore, computer-aided estimation methods are an emerging tool for generating LCI data.[100] In addition, LCA databases can be used to retrieve unit process data and so-called aggregated datasets. Aggregated datasets summarize the elementary flows of the complete upstream or downstream life cycle of a product or service. Therefore, aggregated datasets are usually applied to model the background system.

In practice, incomplete datasets are common. For instance, industrial datasets often contain information on intermediate flows, while elementary flows are not or only partially covered. Here, mass and energy balances are useful to check consistency and identify missing elementary flows.

Life cycle impact assessment

In the third phase of an LCA, the life cycle impact assessment (LCIA), the elementary flows of the LCI are translated to environmental impacts. Environmental impact categories are, for example, climate change, eutrophication, acidification, and resource depletion (see Tables C.2 and C.3). The contribution of an elementary flow to an impact category is described by so-called characterization factors. For instance, GHG emissions are characterized by their global warming potential to assess their impact on climate change. The overall environmental impact corresponds to the sum of all characterized elementary flows.

As mentioned earlier, the holistic approach of LCA aims to identify potential burden shifts between environmental impact categories. Thus, LCA practitioners should strive to consider all environmental impacts. For this purpose, LCIA methods are proposed in the literature, consisting of characterization factors for multiple environmental impact categories. Examples of LCIA methods are CML, ReCiPe, or USEtox.[97] In this thesis, we apply all methods recommended in the framework of the Environmental Footprint 3.0.[101,102] The Environmental Footprint methodology has been developed by the Joint Research Centre (JRC) of the European Commission and represents a state-of-the-art compilation of LCIA methods. The LCIA methods were chosen based on several factors, i.e., completeness, relevance, robustness, transparency, applicability, acceptance, and suitability for communication. Based on these factors, the JRC defined three recommendation levels for LCIA methods: Level I is assigned for LCIA methods that are recommended and satisfactory, level II is recommended but in need of some improvements, and level III is recommended but to be applied with caution. The impact categories of the Environmental Footprint 3.0 methodology and their recommendation levels are summarized in Tables C.2 and C.3.

The Environmental Footprint 3.0 method only recommends LCIA methods at midpoint level. Midpoint-level methods are designed to have their indicator somewhere along an elementary flow's impact pathway.[103] In contrast, endpoint indicators aim to quantify how elementary flows affect the so-called areas of protection, i.e., human health, natural environment, and natural resources. While midpoint-level methods generally have a lower modeling uncertainty due to their stronger relations to the elementary flows, endpoint-level methods are often more understandable as they give a sense of the environmental relevance of an elementary flow.

Interpretation

The interpretation is the final phase of an LCA. Here, the results of the LCI and the LCIA are interpreted with regard to the goal of the study. In the interpretation, LCA practitioners evaluate the robustness of the results to draw conclusions and provide recommendations. The robustness is evaluated regarding the assumptions made in the previous LCA phases, the completeness and consistency of the underlying data, the uncertainty, and the sensitivity of critical parameters. In particular, critical parameters are identified in so-called hot spot analyses where the practitioners investigate processes and elementary flows that contribute significantly to the overall LCA result.

The recommendations of LCAs are increasingly used to inform decision-making on multiple levels, e.g., between products or on a company or national level.[104,105] However, it is often difficult to draw clear recommendations from LCA results as many LCAs identify environmental trade-offs between alternative product or production systems. For instance, a novel product may emit less GHG than the benchmark but simultaneously increases other environmental impacts such as land use.

Table 2.2: LCIA methods with recommendation level I & II from the framework of the Environmental Footprint 3.0 adapted from Fazio et al.[102] Further information on the LCIA methods can be found in the original source.

Impact category	**Indicator**	**Unit**	**Recommended LCIA method**	**Recommendation level**
Climate change	Radiative forcing as Global Warming Potential (GWP100)	kg CO_2-eq	Baseline model of 100 years of the IPCC (2013)	I
Ozone depletion	Ozone Depletion Potential (ODP)	kg CFC-11eq	Steady-state ODPs as in WMO (1999)	I
Particulate matter/Respiratory effects	Human health effects associated with exposure to $PM_{2.5}$	Disease incidences	PM method recommended by UNEP (2016)	I
Ionising radiation, human health	Human exposure efficiency relative to U235	kBq U^{235}	Human health effect model by Dreicer et al. (1995)	II
Photochemical ozone formation	Tropospheric ozone concentration increase	kg NMVOC eq	LOTOS-EUROS as applied in ReCiPe 2008	II
Acidification	Accumulated Exceedance	mol H+ eq	Accumulated Exceedance by Seppälä et al. (2006) and Posch et al. (2008)	II
Eutrophication, terrestrial	Accumulated Exceedance	mol N eq	Accumulated Exceedance by Seppälä et al. (2006) and Posch et al. (2008)	II
Eutrophication, aquatic freshwater	Fraction of nutrients reaching freshwater end compartment (P)	kg P eq	EUTREND model by Struijs et al (2009) as implemented in ReCiPe (2008)	II
Eutrophication, aquatic marine	Fraction of nutrients reaching marine end compartment (N)	kg N eq	EUTREND model by Struijs et al (2009) as implemented in ReCiPe (2008)	II

Table 2.3: LCIA methods with recommendation level III from the framework of the Environmental Footprint 3.0 adapted from Fazio et al.[102] Further information on the LCIA methods can be found in the original source.

Impact category	**Indicator**	**Unit**	**Recommended LCIA method**	**Recommendation level**
Human toxicity, cancer effects	Comparative Toxic Unit for humans (CTUh)	CTUh	USEtox 2.1. model by Rosenbaum et al. (2008)	III
Human toxicity, non- cancer effects	Comparative Toxic Unit for humans	CTUh	USEtox 2.1. model by Rosenbaum et al. (2008)	III
Ecotoxicity freshwater	Comparative Toxic Unit for ecosystems (CTUe)	CTUe	USEtox 2.1. model by Rosenbaum et al. (2008)	III
Land use	Soil quality index	Dimensionless, aggregated index	Soil quality index based on LANCA	III
Water use	User deprivation potential	kg world eq. deprived	Available WAter REmaining (AWARE) in UNEP (2016)	III
Resource use, minerals and metals	Abiotic resource depletion	kg Sb eq	CML Guinée et al. (2002) and van Oers et al. (2002).	III
Resource use, energy carriers	Abiotic resource depletion – fossil fuels	MJ	CML Guinée et al. (2002) and van Oers et al. (2002).	III

LCA offers two options to analyze the relevance of this burden shifting by setting the burden shift into perspective: weighting and normalization. Weighting aggregates environmental impacts across impact categories to determine an environmentally beneficial ranking of alternatives. An example of a frequently used weighting approach is the Eco-indicator 99, where endpoint categories are aggregated into a single-score value.[106] The Eco-indicator 99 provides weighting factors to simplify the interpretation of LCA results. Using the Eco-indicator 99 or other single-score approaches may be better than letting decision-makers choose relevant impacts themselves.[107] However, determining weighting factors for the design of these single-score approaches still requires value choices and is, therefore, highly subjective.

Normalization compares LCA results to a reference system to understand the relative magnitude of environmental impacts. However, most reference systems rely on environmental assessments of larger anthropogenic systems and regions.[108] For instance, the normalization factors of the Environmental Footprint methodology were calculated based on the apparent consumption of the European Union in 2010.[108] Thus, normalization helps to grasp the magnitude of an environmental impact but so far lacks to interpret this magnitude in terms of absolute environmental sustainability. In particular, LCA lacks thresholds whose exceedance would make a system unsustainable.

Overall, LCA is a well-established method to compare the environmental impacts of alternative products or systems. However, LCA's relative evaluation of environmental impacts is insufficient to assess the relevance of burden shifting. Assessing the relevance of burden shifting requires planetary thresholds for normalization to determine an environmental impact's relevance in terms of absolute environmental sustainability. The following section therefore introduces the planetary boundaries as an example of an absolute environmental sustainability framework that provides planetary thresholds.

2.2.2 The planetary boundary framework

Considering environmental indicators in decision-making has certainly contributed to improving the eco-efficiency of products.[109] However, the increasing eco-efficiency cannot keep up with the growth of the global economy. In fact, incremental efficiency improvements in the past have not led to long-term declines in energy and resource use and associated environmental impacts, as increases in consumption typically outpace these improvements. Thus, the total anthropogenic environmental impacts are steadily increasing. These growing environmental impacts have reached a scale that can destabilize critical biophysical systems and trigger irreversible environmental changes that will be catastrophic for humanity.[110]

Rockström et al. defined the planetary boundary framework[c] to identify key Earth-system processes that must be maintained to avoid these catastrophic environmental changes.[110] The authors identified nine critical Earth-system processes, including the core boundaries of climate change and biosphere integrity (see Figure 2.9, details in Appendix D.2.1). Steffen et al. defined the latter as core boundaries, providing the overarching planetary-level system within which the other Earth-system processes operate.[111] Thus, these two boundaries are strongly connected to all other boundaries. In addition to the nine global boundaries, regional boundaries have been defined for some Earth-system processes. For further information about these regional boundaries, the reader is referred to Steffen et al.[111]

Rockström et al. aimed to quantify global limits to human activities to avoid destabilizing the Earth-system processes at a planetary scale.[110] These global limits jointly define the so-called safe operating space (SOS) for humanity and have been determined for seven of the nine Earth-system processes. Steffen et al. updated this quantification and found that at least four boundaries, including the two core boundaries, are already transgressed.[111] These transgressions are particularly critical as each boundary has initially been defined under the strong assumption that none of the other boundaries have been transgressed. In contrast, the authors caution that if one boundary is transgressed, the others are more likely to also exceed their thresholds, owing to the interconnectivity of the planetary boudaries. Thus, the interconnectivities between the boundaries may even reduce the remaining SOS. Furthermore, recent literature also indicates that the planetary boundary of novel entities is also already transgressed.[113] For a detailed discussion on the Earth-system process of novel entities, please see Section 6.5.

Ryberg et al. developed LCIA methods that link the planetary boundary framework to LCA.[114] The methods enable the quantification of planetary footprints, which is a significant step in assessing the absolute environmental sustainability of products. Other LCIA methods have been added or updated, e.g., to quantify changes in biosphere integrity or reduce the uncertainty in quantifying the biogeochemical flow of nitrogen.[115–117] Please note that absolute environmental sustainability assessments

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[c] Parts of this chapter are reproduced from:

> Bachmann, M., Zibunas, C., Hartmann, J., Tulus, V., Suh, S., Guillén-Gosálbez, G., Bardow, A. Towards circular plastics within planetary boundaries. *Nature Sustainability*, 1-12, 2023.

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

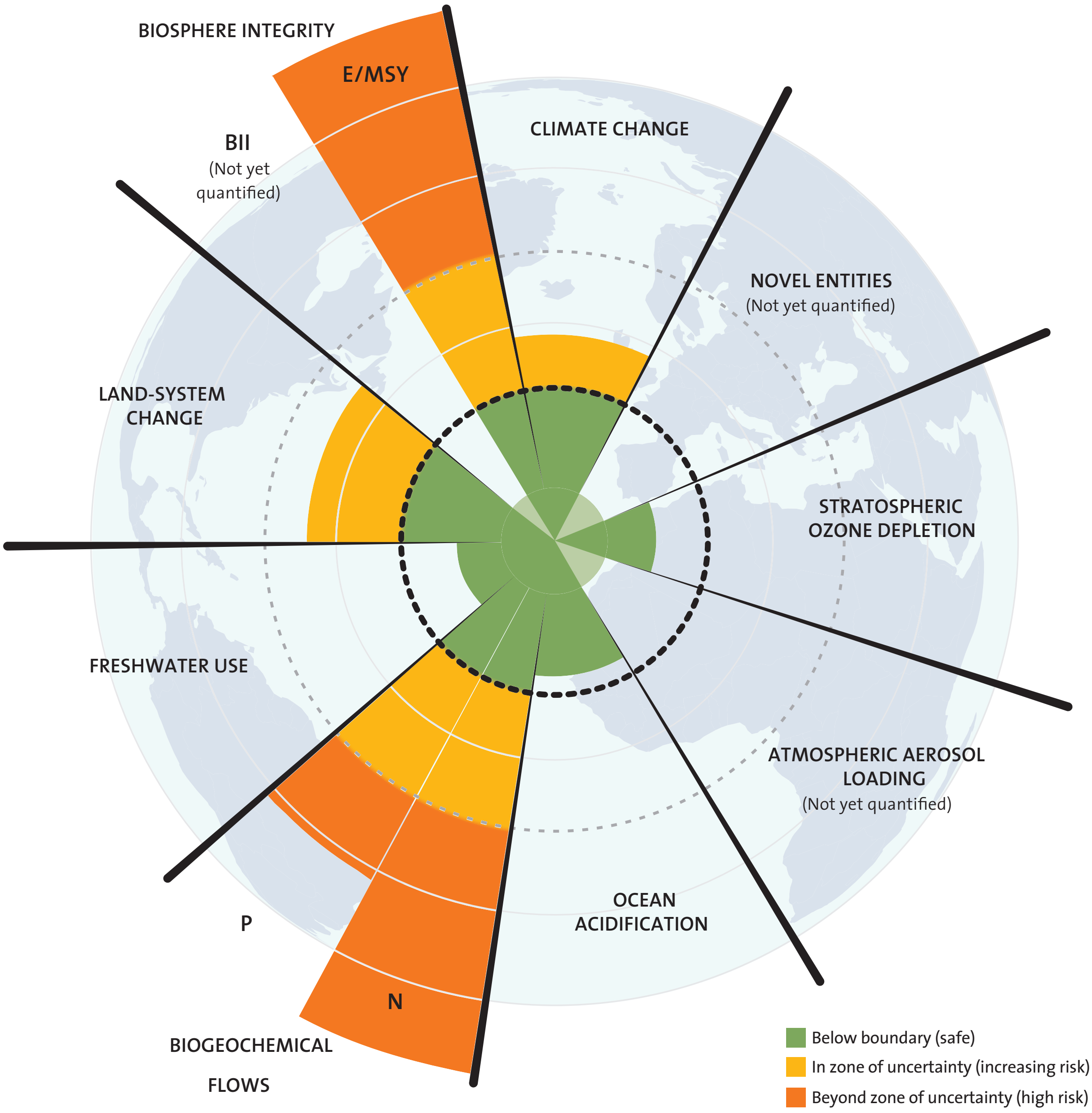

Figure 2.9: The nine Earth-system processes of the planetary boundary framework adapted from Lokrantz and Azote based on Steffen et al.[111,112] Abbreviations: E/MSY = Extinctions per million species per year, BII = Biodiversity Intactness Index, P = Phosphorus, N = Nitrogen

should, if possible, always consider the entire life cycle of the product under study, as every life cycle phase contributes to the absolute environmental impact. In contrast, comparative LCAs can neglect identical life cycle phases (see Section 2.2.1 for details).

The planetary boundary LCIA methods can quantify the planetary footprints of anthropogenic systems such as the plastics industry. However, these systems usually represent only a fraction of all human activities. Consequentially, these systems should operate within an assigned share of the SOS to be considered absolutely environmentally sustainable.[118] Previous studies determine such shares by so-called downscaling principles, e.g., via historical emission data, economic indicators, or population data. Downscaling is widely discussed since the original boundaries were not designed to be downscaled, and the assigned share of SOS is highly selective to the selected downscaling principle. However, as mentioned above, decision-making usually takes place at a sub-global level. Thus, decision-making requires downscaling the planetary boundaries from the global level to the level of consideration.

Several approaches and frameworks have been proposed to operationalize the planetary boundaries at a sub-global level.[119–124] For instance, Häyhä et al. proposed a framework to scale the planetary boundaries from the global to a national level addressing bio-physical, socio-economic, and ethical dimensions.[119] Hjalsted et al. proposed a two-step approach that first scales down the planetary boundaries to the level of individuals and then scales up to the level of consideration.[124] However, despite these ongoing efforts, there is no scientific consensus on how to assign ecological budgets to industrial sectors. As we aim to assign an ecological budget to the global plastics industry (details in Section 6.3), we discuss ethical downscaling concepts regarding their applicability for assigning an ecological budget to industrial sectors in the following.

Previous research applies downscaling principles based on four ethical concepts: Egalitarian, inegalitarian, prioritarian, and utilitarian.[118,124] Egalitarian principles aim for an equal distribution of resources between all humans.[125] A common egalitarian approach is equal per capita allocation to reflect the population distribution in regionalized assessments.[126,127] However, to use egalitarian principles for allocating environmental budgets across industry sectors, they must be combined with other downscaling principles.[118]

Grandfathering, as an example of inegalitarian principles, is another commonly applied approach to assigning ecological budgets.[123,128,129] Grandfathering allocates the SOS by the proportion of an industry's contribution to the total anthropogenic environmental impact.[118] Thus, grandfathering requires data for the environmental impacts of the industry and the total anthropogenic environmental impacts. For climate change, the data availability of GHG emissions is sufficient in most cases, whereas other environmental impacts are less studied. Therefore, less data is available for these other environmental impacts, making grandfathering difficult to implement for other Earth-system processes than climate change.

Grandfathering is based on the concept of acquired rights and favors industrial sectors with high environmental impacts.[130] In turn, grandfathering disfavors historically disadvantaged regions and industries that have already reduced their environmental impacts. Disregarding this historical responsibility is seen as unjust.[131]

In contrast, downscaling by prioritarian principles such as historical debt favors historically disadvantaged entities, e.g., regions or industries, by allowing them to overcome their historical disadvantages.[118] However, in addition to the status quo data, prioritarian downscaling requires historical data, which is often not available for industrial sectors.

Another example of the prioritarian principles is the capability approach that assigns a lower share of the SOS to entities with greater capacity to reduce environmental impacts. The capability approach has been used in regionalized assessments using per capita gross domestic product (GDP) indicators.[123] Kulionis et al. applied this approach within a regionalized assessment to allocate a country's ecological budget between industrial sectors.[132] They translated the per capita GDP to the share of value-added per employee as an indicator of an industry's ability to pay for mitigation efforts. The authors argue that high-income industrial sectors such as the pharmaceuticals industry usually have a high value-added per employee and a great capacity to reduce environmental impacts. While abundant data is available to calculate this indicator, we cannot endorse the authors assumption of a direct correlation between an industry's value-added per employee and its (partially inherent) environmental impacts. The capability approach rather needs to be adjusted by considering the industry's technical potential to reduce environmental impacts. However, an adjusted approach requires data for the technical mitigation potential of all industrial sectors, which is uncertain or often unknown.

The last ethical concept is utilitarianism. Utilitarian principles are designed to maximize aggregated total utility, i.e., the sum of the welfare of all affected stakeholders.[133,134] Parameters have been discussed to quantify welfare, e.g., happiness or the satisfaction of (fundamental) human needs and preferences.[135,136] In practice, economic indicators are often used to quantify human preferences, while indicators for happiness and fundamental human needs are less studied in the context of the planetary boundaries.[118,137] An example of a well-suited economic indicator for allocating ecological budgets to industrial sectors is consumption expenditure. Consumption expenditure is a reliable indicator of human preferences for which sufficient data is available. Therefore, we use consumption expenditure to assign a share of the SOS to the plastics industry and discuss its sensitivity. For further details on this approach, the reader is referred to Section 6.3 of this thesis.

2.2.3 The Technology Choice Model

In this thesis, we aim to identify suitable GHG mitigation pathways for plastics. However, as discussed in Section 2.1, a multitude of options exist for integrating alternative carbon feedstocks into the plastics value chain. Furthermore, the plastics industry is a complex and highly interconnected system, making it challenging to calculate GHG savings manually. Therefore, we apply mathematical optimization using the Technology Choice Model[d] (TCM) to identify the most promising technologies for a given objective, e.g., climate change mitigation.[28] The model enables a detailed accounting of mass and energy flows throughout the plastics supply chain and identifies the optimal choice of technologies for a given objective, e.g., climate change mitigation. The TCM provides numerous possibilities for expansion, allowing for the assessment of costs and marginal abatement costs, conducting multi-regional studies, and performing prospective LCAs, among other features. In this thesis, the TCM is applied as is, and for a comprehensive exploration of potential extensions, readers are directed to Kätelhön's work.[138]

The TCM is based on the computational structure of LCA and combines bottom-up LCA models with linear optimization.[139] The TCM represents production systems by four basic entities: technologies, the final demand, intermediate flows, and elementary flows. These entities are adapted from the ISO standard for LCA and discussed in the following.[23,24]

Technologies transform inputs of energy, materials, or other goods and services into products. In this thesis, technologies represent, e.g., the conversion technologies for CO_2 and biomass. Multiple technologies interact to generate the output of the production system, hereafter named the final demand. Inputs and outputs of technologies can be further divided into intermediate flows and elementary flows (for details see Section 2.2.1.

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[d] Major parts of this section are reproduced from:

> Bachmann, M., Kätelhön, A., Winter, B., Meys, R., Müller, L.J., Bardow, A. Renewable carbon feedstock for polymers: environmental benefits from synergistic use of biomass and CO_2. *Faraday Discussions*, 230, 227-246, 2021.

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

The technology matrix A includes all technologies of the production system as well as all intermediate flows. All flows are represented by the rows of the A matrix, while its columns represent the technologies. In the A matrix, a coefficient a_{ij} corresponds to an intermediate flow i that is either produced ($a_{ij} > 0$) or consumed ($a_{ij} < 0$) by technology j. The final demand for intermediate flow i is described by coefficient y_i in vector y.

Elementary flows are included in the elementary flow matrix B. Similar to the A matrix, b_{ej} describes an elementary flow e that is either taken from ($b_{ej} < 0$) or emitted ($b_{ej} > 0$) to the environment by technology j. To assess the environmental impacts of a production system, elementary flows are characterized by the characterization matrix Q. Here, a coefficient q_{ze} represents the characterization factor of elementary flow e to the environmental impact category z.

As mentioned above, the TCM employs linear optimization to identify the technology mix with the lowest environmental impact. In this thesis, the objective function for the optimization is chosen as the environmental impact of the production systems, which can be calculated as

$$h = Q \cdot B \cdot s \tag{2.1}$$

The scaling vector s scales the amount of inputs and outputs per technology in the A matrix. In this thesis, we mostly minimize the climate change impact of considered production systems. All other environmental impacts are then calculated after the optimization.

In this case, the optimization problem is generally defined as follows:

$$\begin{aligned} \min h_{GHG} &= q_{GHG} \cdot B \cdot s && (2.2) \\ \text{s.t. } A \cdot s &= y && (2.3) \\ s &\leq c_{tech} && (2.4) \\ q_z \cdot B \cdot s &\leq c_{imp} && (2.5) \\ s &\geq 0 && (2.6) \end{aligned}$$

h_{GHG} represents the climate change impact for the production of the final demand y (Equations 2.2 - 2.3). A specifies the technology matrix and c_{tech} the upper bounds for the scaling vector s (Equation 2.4). In this thesis, upper bounds limit the availability of resources or utilities, e.g., biomass or renewable electricity. Furthermore, Equation 2.5 defines additional constraints such as upper bounds for environmental impacts c_{imp}. In addition, the entries of the scaling vector must be positive to avoid unphysical results (Equation 2.6).

2.3 Scientific gaps in the current assessment practice

In Section 2.3.1, we review LCA studies of alternative carbon feedstocks for plastics or intermediates in the plastics supply chain to identify scientific gaps in the current state of the environmental assessment. These scientific gaps are summarized in Section 2.3.2.

2.3.1 The current assessment practice

The following section briefly summarizes the current status of the environmental assessment of plastic waste recycling, biomass utilization, carbon capture and utilization, and steel mill off-gas separation for plastics production.

Environmental assessment of plastic waste recycling.

Section 2.1.2 has shown that in addition to landfilling and incineration, two process types exist for treating plastic waste: mechanical and chemical recycling. Early LCA literature reviews have shown that mechanical recycling reduces GHG emissions compared to other treatment technologies for plastic waste as mechanical recycling substitutes virgin plastics production.[25,140,141] However, GHG reductions depend on the virgin material substitution factor, i.e., the amount of virgin plastic that is replaced by recycled plastic.[141] Michaud et al. assessed eight LCA studies comparing mechanical recycling with landfilling, incineration with energy recovery, and pyrolysis for several types of plastics.[25] They found that mechanical recycling provides climate benefits compared to all other treatment technologies for most plastic types except polyvinyl chloride, as polyvinyl chloride is harder to mechanically recycle than other plastics.

However, mechanical recycling is only applicable to plastic mono-streams. Therefore, a more recent study by Faraca et al. assessed mechanical recycling, including the sorting and pretreatment of mixed plastic waste.[142] They found that climate benefits from mechanical recycling decrease with lower sorting efficiencies since more residuals have to be treated after recycling, and less virgin plastic is substituted.

Furthermore, Lazarevic et al. found that the climate benefits of mechanical recycling depend on assumptions about the energy efficiency of plastic waste incineration and the organic contamination of plastic waste.[141] Higher energy efficiencies reduce the net GHG emissions of plastic waste incineration as higher credits are given for electricity and heat generation. Thus, higher energy efficiencies reduce the climate benefits of mechanical recycling compared to incineration. In addition, higher organic contamination and lower substitution factors generally increase environmental impacts of mechanical recycling. Yet, for climate change, the authors did not notice a change in preferences between mechanical recycling and the other treatment technologies when assessing these parameters.[141] In contrast, for other environmental impacts, changes in preferences have been identified .

In general, LCA studies on plastic waste treatment tend to focus on GHG emissions, whereas other environmental impacts are less studied.[25,141] Michaud et al. found that only four of the eight evaluated studies have assessed other environmental impacts, e.g., abiotic resource depletion (ADP), water consumption, acidification, and eutrophication.[25] While the assessment of ADP also indicates mechanical recycling as the most environmentally beneficial, no clear preference could be identified for any treatment technology regarding the other environmental impacts.

Contradictory results for other environmental impacts are also found in more recent LCA studies: Jeswani et al. found that mechanical recycling and pyrolysis lead to higher environmental impacts than incineration with energy recovery in acidification, eutrophication, photochemical ozone formation, and human toxicity.[20] In contrast, Khoo et al. show that mechanical recycling decreases acidification compared to incineration with energy recovery.[143] Furthermore, Bora et al. show that mechanical recycling does not cause burden shifting compared to incineration and pyrolysis in all impact categories except ionizing radiation.[144]

These contradictory findings may result from methodological variation in LCA studies on plastic waste treatment, e.g., varying assumptions for energy substitutes. Laurent et al. found that many studies lack compliance with the LCA ISO standards.[145] Pires Costa et al. added that available studies lack holistic consistency and representativeness due to limited data availability and reliability.[146] Despite the ongoing efforts for improvement[11,146,147], these methodological inconsistencies compromise the validity and reliability of the LCA studies for plastic waste treatment.

Furthermore, Darvidson et al. argue that a direct comparison between mechanical and chemical recycling technologies has no value.[148] In contrast, chemical recycling should be considered an additional technology to treat the residues of mechanical recycling or mixed plastic waste unsuitable for mechanical recycling. By combining mechanical and chemical recycling, Meys et al. found that recycling is the key enabler for net-zero GHG emission plastics when also combined with other alternative carbon feedstocks, i.e., biomass and CO_2.[5] However, Meys et al. did not assess a potential burden shift from GHG emissions to other environmental impacts.

Overall, the literature highlights the environmental potential of plastic waste recycling. While mechanical recycling shows climate benefits compared to other treatment technologies, such as landfilling and incineration, its effectiveness depends on sorting efficiency and the substitution of virgin plastic. Furthermore, combining mechanical and chemical recycling, along with alternative carbon feedstocks, has been shown to significantly reduce GHG emissions within the plastics industry. However, the assessment of other environmental impacts in LCA studies on plastic waste treatment remains limited, and contradictory findings exist regarding acidification, eutrophication, or human toxicity. Unfortunately, the lack of methodological consistency compromises the validity of these studies.

Environmental assessments of biomass and bio-waste utilization.

The previous section has identified methodological variation and a lack of consistency in the environmental assessment of plastic waste recycling. These methodological inconsistencies can also be observed in the environmental assessment of bio-based plastics.[6,55,56] Pawelzik et al. argue that the inconsistencies result from the fact that the ISO standards do not elaborate on critical aspects of biomass utilization.[55] In particular, LCA studies on bio-based plastics differ in methodological choices for determining the environmental impacts of biomass cultivation. The environmental impacts of biomass cultivation depend on cultivation efforts, e.g., harvesting methods, emissions from transport and storage, or application of fertilizers and pesticides.[149] Furthermore, environmental impacts depend on the carbon content of the biomass and potential land-use change (LUC) emissions.[55] We further elaborate on these two critical aspects in the following:

During the growth phase, biomass sequesters CO_2 from the atmosphere. The amount of CO_2 sequestered depends on the carbon content of the biomass. Some LCA practitioners do not consider this carbon uptake as it is assumed that the biogenic carbon sequestered during the growth phase is released back to the environment at the end of the product's life cycle.[150] Thus, biomass utilization is considered carbon neutral. In contrast, this carbon uptake can be considered as a negative CO_2 flow in the LCI of biomass cultivation. Pawelzik et al. provide an extensive discussion on the two approaches for considering carbon storage in bio-based materials.[55] They observed a clear trend towards accounting for the biomass carbon uptake and recommend to follow this approach. Accordingly, we credit the sequestered CO_2 as a negative emission in this thesis.

In addition, biomass cultivation for plastics production leads to LUC, i.e., the transition from the current use of land to the cultivation of biomass as feedstock.[55] LUC may lead to unintended environmental impacts, including nutrient depletion, water consumption, and biodiversity loss. In addition, LUC alters the carbon content of the soil, leading to carbon emissions.

LCA literature typically differentiates between direct and indirect LUC emissions (see Figure 2.10). Direct LUC emissions occur when biomass cultivation alters the carbon content of the soil where the cultivation takes place. Indirect LUC emissions occur when biomass cultivation displaces other crops since these crops must be cultivated elsewhere to meet their demand. This displaced cultivation may also change the carbon content of the soil, resulting in additional carbon emissions. In particular, indirect land-use change effects are critical if the displaced crop cultivation proceeds in regions with high soil-bound carbon content, such as tropical rain forests.

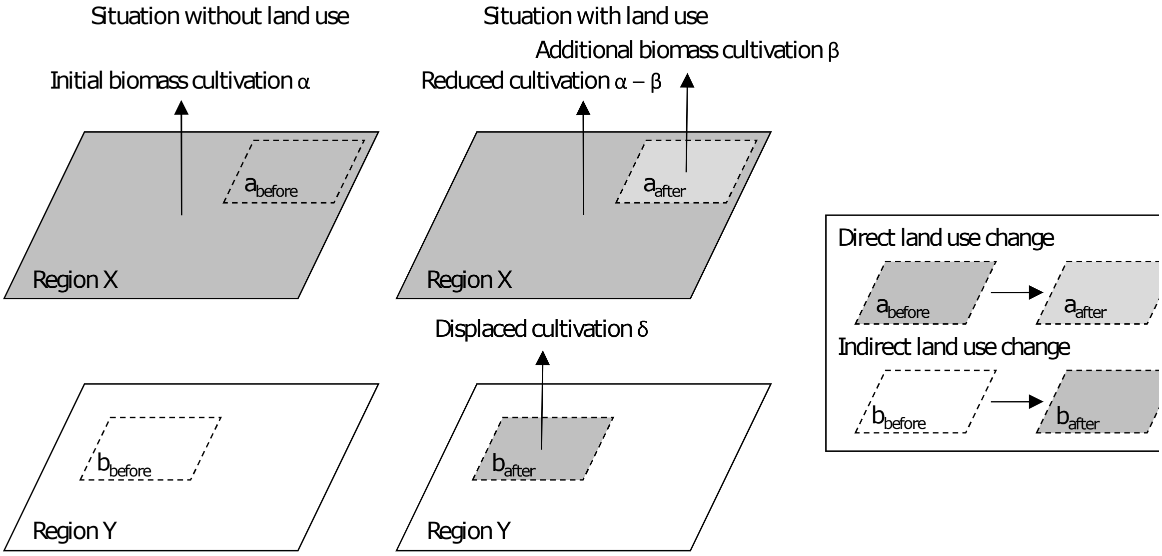

Figure 2.10: Direct and indirect land use changes adapted from Schmidt et al.[151]. The land under study is the area "a". The shaded squares represent land in use.

Thus, bio-based plastics may come at the cost of additional land use and related environmental impacts.[55] In this thesis, we either consider LUC or clearly state why we neglect it depending on the purpose of the chapter.

Using biomass for material purposes does not necessarily lead to indirect LUC emissions. In fact, the historical emissions data of the Intergovernmental Panel on Climate Change shows a declining trend of GHG emissions from LUC over the last century due to yield improvement and reduced deforestation rates.[152,153] Still, Hedegaard et al. found that by 2030, the amount of biomass available for energy or material purposes will be physically and economically constrained.[154] Agora Industry added that biomass demand could massively outstrip its supply, even when considering non-virgin biomass sources such as organic wastes.[155] Accordingly, biomass utilization for plastics production will most likely happen at the expense of alternative biomass applications, potentially leading to undesirable environmental consequences. Still, many LCA studies evaluate bio-based plastics without considering the limited availability of biomass. Accordingly, undesirable environmental consequences may go undetected.

Due to these methodological inconsistencies, LCA studies of bio-based plastics generally show a wide range of environmental impacts, making it difficult to draw general conclusions about their environmental performance.[26] For instance, Spierling et al. conducted a literature review on 29 LCA studies of bio-based plastics and found a range in GHG emissions of -0.3 to +11.9 kg CO_2-eq per kg plastic.[6] In contrast, the GHG emissions of the fossil-based counterparts range between 1.6 to 6.4 kg CO_2-eq per kg plastics. Thus, bio-based plastics show a lower minimum and higher maximum value for GHG emissions than fossil-based plastics. A literature review by Weiss et al. confirms this wide range of GHG emissions for bio-based plastics.[26] Still, the review concludes that one kilogram of bio-based material, on average, saves about 3 kg CO_2-eq.

Similar to LCA studies of plastic waste recycling, LCA studies of bio-based plastics focus primarily on climate change.[6,56] For instance, Bishop et al. analyzed 44 LCA studies on bio-based plastics, which all assess indicators for climate change.[56] In contrast, the most prevalent impact categories besides climate change were considered in less than 30 studies. These categories include acidification and eutrophication, resource depletion, and photochemical oxidant formation. While the study by Bishop et al. confirms the need to assess environmental impact categories more comprehensively, they do not assess whether bio-based plastics induce burden shifting from climate change to other environmental impacts.

Weiss et al. found that most LCA studies on bio-based materials indicate burden shifting when switching from fossil- to bio-based feedstocks.[26] On average, environmental impacts increase in eutrophication and stratospheric ozone depletion, whereas impacts in acidification increase or decrease depending on the case.

Walker et al. observed a prevailing scientific consensus that bio-based plastics perform better than fossil-based plastics in climate change and fossil resource depletion.[156] In contrast, LCAs tend to reveal that fossil-based plastics outperform bio-based plastics in impact categories such as eutrophication and acidification. However, their literature review on LCA studies of bio-based plastics does not reliably support this hypothesis, as results show a significant range in every impact category.

In summary, the assessment of bio-based plastics faces methodological inconsistencies, particularly in determining environmental impacts of biomass cultivation and the consideration of carbon uptakes. Furthermore, LUC emissions can significantly contribute to the carbon footprint of biomass. These inconsistencies contribute to a wide range of environmental impacts observed in LCA studies, making it difficult to draw general conclusions about the environmental impacts of bio-based plastics. Furthermore, the focus of LCA studies has primarily been on climate change, with limited consideration of other impact categories. While there is a prevailing scientific consensus that bio-based plastics perform better in terms of climate change and fossil resource depletion, the results vary across different impact categories, indicating the need for further standardization in assessment practices.

Environmental assessment of carbon capture and utilization.

CCU has already shown great potential to reduce GHG emission of chemicals[27,157] and plastics[158]. CCU reduces GHG emissions by removing CO_2 from point sources or the air and avoiding GHG emissions from conventional production. However, adopting CCU technologies does not guarantee net GHG savings.[159] Rather, net GHG savings can only be achieved if GHG reductions are higher than the additional GHG emissions from CO_2 capture and conversion, which depend strongly on the efficiency and the energy supply.[17]

Accordingly, the environmental assessment of CCU should involve multiple key aspects, including the CCU and the conventional technology, the CO_2 source, and the energy supply. Assessing each of these process steps involves pitfalls, which have led to methodological inconsistencies in the environmental assessment of CCU technologies.[160] To address these inconsistencies, a guideline was developed for conducting LCAs for CCU.[159] Please note that this thesis only elaborates on exemplary inconsistencies relevant for this thesis, while reference is made to the guideline for a complete analysis.

A particular methodological inconsistency pertains to determining the environmental impact of CO_2 as a feedstock. For CO_2-based processes, CO_2 is mainly captured from industrial point sources.[161] Since CO_2 from industrial point sources is a waste stream that is otherwise released into the atmosphere, most studies credit captured CO_2 as a negative emission.[159,161] However, several studies follow the assumption that the CO_2 feedstock is readily available and that utilizing the CO_2 results in negative GHG emissions of -1 kgCO_2-eq per kg CO_2 used.[161] In contrast, capturing CO_2 requires heat and electricity, leading to indirect emissions. Therefore, this thesis also account for the elementary flows from the additional electricity and heat demand for CO_2 capture. This approach represents a simplified calculation of the system expansion approach via substitution, where the emissions of the original point source without capture are subtracted from the emissions of the point source with CO_2 capture. However, the simplified calculation is mathematically equivalent and therefore leads to the same elementary flows (see Figure 2.11).

Substitution allocates the emission reductions of the CO_2 capture to the feedstock, whereas the emissions of the main product remain unchanged.[161] Therefore, the approach may lead to a negative elementary flow for CO_2. However, a negative CO_2 flow should not be misinterpreted as CCU being a carbon-negative technology. To be carbon-negative, a technology needs to physically and permanently remove CO_2 or other GHG from the atmosphere.[162] Accordingly, a negative CO_2 flow simply means that emissions are reduced by capturing CO_2.

An additional inconsistency in the environmental assessment of CCU technologies results from the assumptions on energy supply. The conversion of the chemically rather inert CO_2 normally requires highly energetic co-reactants such as hydrogen.[7] Since using hydrogen from today's largely fossil-based production would usually increase GHG emissions,[163] several studies consider water electrolysis as an alternative hydrogen source. However, water electrolysis requires large amounts of electricity, and the environmental impacts of hydrogen from water electrolysis therefore strongly depend on the electricity source.

CCU applications mostly require low-carbon electricity to reduce GHG emissions, whereas grid electricity often results in the contrary. For instance, Thonemann et al. found that most CCU technologies reduce GHG emissions when considering the marginal German market mix as electricity source.[164] In their study, the marginal market mix contains 75 % wind electricity and 19 % natural gas. In contrast, if electricity from lignite is assumed as a sole source of electricity, the authors found that most CCU technologies increase GHG emissions compared to fossil-based production. Similarly, Kätelhön et al. assessed the climate change mitigation potential of CCU in

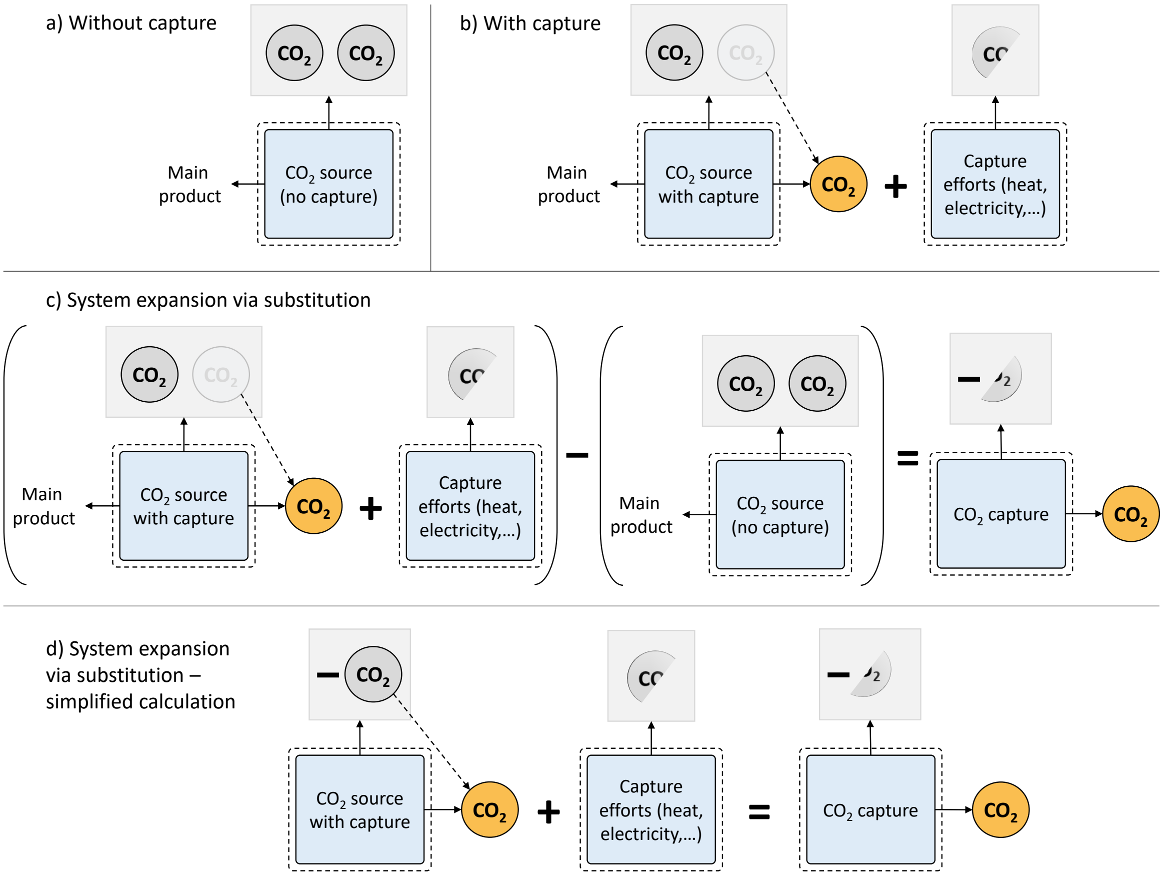

Figure 2.11: Determining the environmental impacts of the CO_2 as a feedstock for carbon capture and utilization adapted from Müeller et al.[161] (a) CO_2 source without capture, (b) CO_2 source with capture, (c) system expansion via substitution, where the environmental impacts of the CO_2 source without capture are substracted from the CO_2 source with capture, (d) simplified calculation of the system expansion approach via substitution.

the chemical industry and found that CCU can reduce up to 3.5 Gt of annual GHG emissions in 2030.[17] However, in order to accomplish these reductions, approximately 18 PWh of low-carbon electricity are required, equivalent to 55 % of the projected global electricity generation by 2030. Using more than half of the global electricity generation for chemical production alone seems unlikely. Accordingly, large-scale production of CO_2-based chemicals will remain limited due to the limited availability of low-carbon electricity.

Other environmental impacts of CCU technologies are less studied and not clear.[165] For instance, some studies on CCU-based methanol identified hydrogen supply as the main contributor to an increased impact in water and mineral depletion, whereas all other environmental impacts are lower compared to the fossil-based production.[166] In contrast, Thonemann et al. found that all environmental impacts are worsened via CCU-based methanol.[27] For CO_2-based methane, other environmental impacts generally seem to be larger for CCU than conventional production, particularly for human toxicity, freshwater ecotoxicity and resource depletion.[165] Studies on other environmental impacts on other CCU products such as dimethyl carbonate also do not reveal a clear trend.[165]

Overall, the environmental assessment of CCU technologies identifies their potential to reduce GHG emissions in the plastics industry. However, methodological inconsistencies in previous LCA studies led to a wide range of potential environmental impacts. By following the methodological guidelines for LCA of CCU,[159] this work prevents these methodological inconsistencies. Additionally, the existing literature predominantly focuses GHG emissions, while the evaluation of other environmental impacts remains insufficiently addressed.

Environmental assessment of steel mill off-gas separation and utilization.

The steel industry directly emits about 2.1 Gt of GHG emissions per year.[167] These GHG emissions primarily originate from off-gas treatment from the coke oven, the blast furnace, and the basic oxygen furnace (see Chapter 2.1.2 for details).[71,89] One approach to reduce these off-gases and mitigate GHG emissions involves substituting the coke with alternative reducing agents such as biomass or hydrogen from water electrolysis.[168–171]

Alternative reducing agents have shown great potential for reducing GHG emissions compared to conventional steel production.[168–172] Using biomass as a feedstock for coke production can save up to 20 % of GHG emissions,[168] but bio-based steelmaking is currently limited due to the high price of biomass compared to fossil-based reducing agents.[169] Hydrogen-based steel production involves utilizing hydrogen to remove oxygen from the iron ore, and subsequently converting the resulting iron to steel in an electric arc furnace.[170] Steel scrap is often added to the electric arc furnace along with the iron to achieve desired compositions.

GHG reductions of hydrogen-based steel highly depend on the grid emission intensity and the amount of steel scrap used.[170] Vogl et al. have shown that for 25 % steel scrap charge, the break-even between conventional steel production and hydrogen-based steel is about 660 g CO_2-eq per kWh, which corresponds approximately to the power grid intensity of Poland. Higher steel scrap charges and lower grid intensities reduce GHG emissions of hydrogen-based steel, respectively. However, transitioning to alternative steel production requires significant structural changes and investments since the blast furnace has to be modified or replaced and biomass transportation networks or power grids have to be expanded.

Alternatively, the valuable compounds in the steel mill off-gas (mill gas) can be separated and used as feedstocks for chemical production as described in Chapter 2.1.2. These so-called polygeneration systems reduce GHG emissions by avoiding the combustion of valuable compounds and by substituting the conventional production of chemicals. However, since mill gas is conventionally combusted for on-site heat and electricity generation,[90] the missing energy has to be provided using alternative sources. In addition, the valuable compounds have to be separated, which results in additional electricity and heat demand. Accordingly, net GHG reductions can only be achieved if GHG emissions from additional energy provision are lower that the avoided emissions.

Several authors have shown that polygeneration systems can be environmentally beneficial.[19,173,174] For instance, Thonemann et al. compared the GHG emissions of integrated steel and methanol production to the stand-alone production of steel and methanol.[19] The authors found that the integrated production emits about 40 % less GHG emissions than conventional production if wind power is used as electricity source. Contrastingly, integrated production emits 41-47 % more GHG emissions according to the 2030 electricity grid forecasts, and the estimated break-even for the grid emission intensity is 230 g CO_2-eq per kWh.

Shin et al. conducted a study on methanol production from blended coke oven and Linz-Donawitz gas and found that the integrated production saves between 2 to 7 % of GHG emissions.[175] In their study, Shin et al. assumed natural gas as an energy substitute. Kleinekorte et al. determined climate-optimal production pathways for a combined model of the global steel and chemical industry.[174] The authors concluded that, under optimal conditions, GHG savings of up to 3.6 Gt CO_2-eq per year can be achieved compared to the business-as-usual. However, GHG reductions result mainly from using steel mill off-gases as a CO_2 point source for CCU-based processes. The actual integration only achieves 79 Mt CO_2-eq savings per year, corresponding to 4.5 % additional GHG savings compared to stand-alone industries.

Other environmental impacts of mill gas separation and utilization are generally less studied, and all of the previously mentioned studies focused solely on GHG emissions. Deng et al. conducted a regionalized LCA on an integrated steel and methanol production plant and compared the results to a conventional steel mill and a steel mill with an integrated combined cycle power plant.[176] Their analysis revealed that environmental impacts vary greatly by region due to the large difference in electricity impacts and credits for heat and methanol production. Although integrated production of steel and methanol generally results in lower GHG emissions, the trend for other environmental impacts varies significantly depending on the region. In certain regions, integrated steel and methanol production proved to be more environmentally preferable, while in others, the steel mill with an integrated combined cycle power plant was found to be the better option. However, it is important to note that the conventional steel mill was never the best choice in terms of environmental impacts.

In summary, the decarbonization of the steel industry can be achieved through two main approaches: replacing fossil-based reducing agents with renewable resources or utilizing the valuable components of steel mill off-gas in other industries. Literature suggests that the first approach offers greater potential for reducing GHG emissions, although it may involve higher costs. Alternatively, the utilization of steel mill off-gas in polygeneration systems for chemical and plastics production presents a promising interim solution for GHG reduction, but with variations in GHG emissions and other environmental impacts across studies and regions.

Assessment of environmental synergies between renewable carbon feedstocks.

The preceding sections have concentrated on assessing the environmental impact of chemicals and plastics production using a single renewable carbon feedstock. While all the discussed feedstocks have demonstrated potential for reducing GHG emissions in the plastics industry, their potential is limited due to either constraints in feedstock availability, such as renewable electricity, or the risk of shifting burdens from GHG emissions to other environmental impacts. However, combining multiple renewable carbon feedstocks and capitalizing on potential environmental synergies between them may decrease feedstocks dependence and mitigate burden shifting.

A prominent example for a concept that combines multiple renewable carbon feedstock is the bio-hybrid fuel approach.[177] The bio-hybrid fuel approach jointly utilizes biomass, CO_2, and renewable electricity to overcome feedstock limitations and produce renewable fuels at scales relevant for the mobility sector.[178] Ackermann et al. have shown that bio-hybrid fuels reduce GHG emissions compared to conventional gasoline by 95 % under best-case assumptions.[179] Even under worst-case assumptions, bio-hybrid fuels can still lower GHG emissions compared to conventional gasoline, but are surpassed by bio-ethanol, whose carbon footprint is about 50 % smaller.

Navajas et al. conducted an LCA on hybrid power-to-methane systems utilizing CO_2 from biomass.[180] The power-to-methane system consumes surplus electricity from the grid by an electrolyzer unit to produce hydrogen, which is then converted to methane through a Sabatier process using CO_2 from biomass combustion. The biomass combustion also generates electricity, and excess CO_2 is assumed to be permanently stored. A comparative analysis with a reference system was performed, employing an electrolyzer unit that uses the same amount of surplus electricity to produce hydrogen stored and converted back to electricity. The functional unit of the assessment includes the amount of electricity generated by the reference system, the surplus grid electricity consumed, and the methane produced. The LCA indicates that the hybrid power-to-methane systems emit significantly fewer GHG emissions compared to the reference system, with cradle-to-grave GHG emissions even being negative due to the substantial amount of stored CO_2. However, Navajas et al. do not address whether a system that simply curtails surplus grid electricity and employs biomass combustion with CO_2 storage would yield even greater reductions in GHG emissions.

In the plastics industry, environmental synergies between renewable carbon feedstocks are generally less studied. As previously mentioned, Meys et al. conducted a study that evaluated the utilization of biomass and CCU for plastic production, along with plastic waste recycling, and their findings indicated that only by combining all feedstock, net-zero GHG emission plastics can be achieved.[5] Furthermore, the previous section discussed the use of biomass as a substitute for coke in the steel industry. Integrating biomass feedstock with mill gas separation and utilization for plastics production has the potential to significantly mitigate the environmental impacts associated with both steel and plastics. However, to the best of the authors knowledge, a combined assessment has not been conducted yet. Overall, environmental synergies between renewable carbon feedstocks are still poorly studied although they can play a decisive role in decarbonizing the plastics industry.

Approaches to handle burden shifting.

Several LCA studies on alternative carbon feedstocks for plastics indicate environmental trade-offs, i.e., burden shiftings from climate change to other midpoint indicators such as acidification or ionizing radiation. Accordingly, these studies could not provide clear recommendations for decision-making based on midpoint-level indicators. Therefore, they applied normalization and weighting approaches to handle burden shifting and identify the most promising alternatives.

For instance, Khoo et al., who assessed several plastic waste treatment scenarios, normalized their results to the current waste treatment system. Afterward, they defined weighting factors ranging from 1 for acidification to 3 for climate change and weighted the environmental impacts accordingly.[143] In addition, Schwarz et al. assessed the production and end-of-life treatment of multiple plastic types.[21] They weighted the environmental impacts by so-called shadow prices that should represent the economic damage per impact category. While the former is entirely subjective, we consider the latter semi-subjective since monetary factors differ by up to two orders of magnitude depending on the monetization method, resulting in considerable variability in weighting factors.[181]

An alternative approach to evaluating environmental impacts and trade-offs is by assessing them in relation to established environmental thresholds, such as the planetary boundaries. For example, Tulus et al. utilized the planetary boundary framework to analyze 492 fossil-based chemicals, including monomers and polymers, and discovered that over 99 % of these chemicals exceeded at least one planetary boundary.[182] Their findings highlights the significant environmental impact of fossil-based chemicals. Meng et al. argued that transitioning to circular plastics based on biomass, carbon capture and utilization (CCU), and recycling could have a positive effect on plastics' planetary footprints.[183]

In the study conducted by Galán-Martín et al., the planetary boundary framework was employed to assess the chemical industry and rank potential future supply chains based on their planetary footprints.[115] The findings revealed that the production of fossil-based chemicals alone accounts for approximately one-quarter of the entire safe operating space, raising concerns about its sustainability. Additionally, the authors observed that both bio-based production and CCU can substantially reduce the planetary footprints of chemicals. However, it is crucial to note that the reduction of planetary footprints relies on the availability of renewable resources, and bio-based production, in particular, carries risks to biosphere integrity.

Ranking by planetary footprints is a crucial first step in identifying promising pathways towards absolute environmental sustainability. However, ranking alone is insufficient to assess absolute environmental sustainability since the plastics industry represents only a fraction of all human activities. Consequentially, the plastic industry may operate within an assigned share of the safe operaing space to be considered absolutely environmentally sustainable (see Chapter 2.2.2 for details).

2.3.2 Scientific gaps

The literature review of exemplary LCA studies in Section 2.3.1 has confirmed that alternative carbon feedstocks can reduce plastics' life-cycle GHG emissions. However, the review identified the following major research gaps in the environmental assessment of alternative carbon feedstocks:

Lack of comparability: The efficiency of converting alternative carbon feedstocks to plastics varies among technologies. As the availability of alternative carbon feedstocks is limited, comparing conversion technologies in a consistent environmental assessment is crucial to identify the most suitable feedstock for plastic production. However, LCA studies on alternative carbon feedstocks are hardly comparable due to deviating assumptions and methodological variations. This lack of comparability applies to technologies that use the same feedstock but becomes even more apparent when comparing multiple feedstocks. Consequentially, the current lack of comparability hinders identifying the most efficient feedstock use. In fact, the current assessment practice lacks a systematic approach to comprehensively assess both GHG reductions and potential environmental trade-offs from alternative carbon feedstocks. Thus, it is currently poorly understood which feedstock is preferable for producing plastics from an environmental perspective.

Unexplored environmental synergies: Most LCA studies compare the environmental benefits of products from alternative carbon feedstocks to their fossil benchmark and quantify potential savings in GHG emissions. In addition, some studies compare the environmental benefits of multiple pathways for the same feedstock. Thus, the latter studies identify the most promising pathways for one alternative carbon feedstock. However, only a few LCA studies compare multiple alternative carbon feedstock in a consistent environmental assessment. As a result, environmental synergies between alternative pathways often remain unexplored. However, exploring potential environmental synergies is particularly important for the plastics industry, as other sectors are more efficient at avoiding GHG emissions by using alternative carbon feedstocks.[17,184]

Disregarded availability of limited feedstocks: As mentioned above, alternative carbon feedstocks are limited and usually already used elsewhere. Nevertheless, most studies focus solely on producing plastics or intermediates based on these feedstocks and neglect the limited availability. However, the limitation and the conventional use of these feedstocks should be considered to derive a sound understanding of the system-wide environmental consequences of producing plastics from alternative carbon feedstocks. Accordingly, the climate benefits of using alternative carbon feedstocks may be overestimated.

Climate change bias: LCA studies often focus on climate change since climate change is considered the primary environmental problem. Other environmental impacts are less studied and sometimes not discussed at all or only in the supporting information. While the spotlight on climate change may be justified by its immense importance for our planet, a climate change bias can miss potential burden shifts to other environmental impacts. A climate change bias is particularly critical when assessing alternative carbon feedstocks for plastics since the review has shown that using these feedstock leads to burden shifting.

Insufficient handling of burden shifting: Burden shifting has been identified for several alternative carbon feedstocks. Some LCA studies applied weighting and normalization to set the burden shift into perspective and to derive recommendations for promising pathways among technology alternatives. These studies either chose arbitrary weighting factors or applied weighting factors derived from methods such as monetization. However, both approaches are subjective and not based on scientifically sound environmental criteria.

Furthermore, LCA studies often assess the relative change in environmental impacts by normalizing their results to the benchmark process or environmental impacts of anthropogenic systems. However, neither approach can evaluate the relative magnitude of burden shifting regarding absolute environmental sustainability. Accordingly, the current practice of handling burden shifting is insufficient to understand the potential collateral damage from switching plastics' feedstock basis from fossil resources to alternative carbon feedstocks. Thus, the environmentally optimal pathway to a sustainable plastics industry is still open.

2.4 Contribution of this thesis

Section 2.3 has highlighted critical scientific gaps in the current environmental assessment of alternative carbon feedstocks for plastics. In particular, we found that most LCAs focus on commodity plastics and some engineering plastics, whereas high-performance thermoplastic polymer (HPT), also referred to as high-performance plastics, are currently underrepresented in LCA literature. Therefore, **Chapter 3** provides a motivating case study on polyoxazolidinone (POX) as a novel HPTs. POX serves as an excellent case study for this thesis, as POX can be produced largely from bio-based feedstocks. Accordingly, Chapter 3 demonstrates the GHG reduction potential of biomass utilization in HPT production. Furthermore, the case study exhibits burden shiftings induced by biomass utilization.

Subsequently, this thesis narrows the scientific gaps by providing the following contributions:

Chapter 4 – environmental synergies in polyurethane production: Chapter 4 investigates *unexplored environmental synergies* from the combined utilization of alternative carbon feedstocks. In particular, we assess if a synergetic use of biomass and CO_2 further reduces GHG emissions and saves renewable resources while potentially avoiding burden shifting. For this purpose, we quantify environmental impacts using a Technology Choice Model for the bio- and CO_2-based production of polyurethane. Polyurethane is particularly well suited as a case study since polyurethane production offers possibilities for both direct and indirect utilization of biomass and CO_2.

Chapter 5 - consistent life cycle assessment of syngas: In Chapter 5, we address the scientific gaps *lack of comparability* and *disregarded availability of limited feedstocks*. For this purpose, we evaluate the environmental impacts of syngas from multiple alternative carbon feedstocks in a consistent LCA. In particular, we consider that alternative carbon feedstocks can be limited and already used elsewhere by considering the conventional feedstock use in the assessment. We choose syngas as a case study since syngas is a key chemical intermediate for producing plastics from alternative carbon feedstocks. We build a bottom-up TCM of conventional and alternative syngas production, which allows for a systematic examination of GHG reductions and potential environmental trade-offs. Thereby, we ensure the comparability between the alternative production pathways.

Chapter 6 – towards absolute environmental sustainability for plastics: In Chapter 6, we address the *climate change bias* and improve the *insufficient handling of burden shifting* for the plastics industry. For this purpose, we assess the absolute environmental sustainability of the plastics industry using the planetary boundary framework. In particular, we focus on quantifying the extent to which renewable carbon feedstocks could help operating within the Earth's ecological budget. By quantifying the planetary footprints of plastics in multiple Earth-system processes, we assess the magnitude of potential burden shifts from climate change to other environmental impacts. The analysis builds on a global, LCA-compliant model of the plastics industry and applies utilitarian downscaling principles to assign an ecological budget to plastics.

Concluding, this thesis addresses the pressing environmental challenges of GHG emissions from plastic production by examining the potential of alternative carbon feedstocks. Through comprehensive LCAs and exploration of environmental synergies, this thesis emphasizes the importance of reducing environmental burdens holistically. In particular, the findings underscore the necessity of improved recycling technologies, a shift towards renewable carbon feedstocks, and a fundamental transformation in production and consumption practices to achieve a sustainable plastics industry.

Chapter 3

Bio-based high-performance plastics - a motivating example

The literature review in Section 2.3 has revealed that most LCA studies of the plastics industry focus on commodity plastics. For commodity plastics, the literature has proven that using renewable carbon feedstocks reduces GHG emissions. However, the properties of commodity plastics do not satisfy the requirements for advanced applications, e.g., in the aviation or electronics industry.[185] Such advanced applications require a more specialized property profile, combining low density and high thermal stability with high elasticity modulus and chemical resistance.[186] These characteristics are provided by high-performance thermoplastic polymers (HPTs, also referred to as high-performance plastics).[186,187]

In this chapter,[a] we demonstrate the GHG reduction potential of polyoxazolidinone (POX) as a novel HPT. POX can be produced to a large extent from bio-based feedstocks. Therefore, we use POX as a motivating example to illustrate the environmental benefits and drawbacks of bio-based production on a group of plastics that has hardly been studied.

In Section 3.1, we provide a brief introduction to the field of HPTs. Section 3.2 defines the goal and scope of the LCA, and Section 3.3 introduces the production systems of POX and its reference HPTs polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU). In Section 3.4, we assess the environmental impacts of POX compared to its reference HPTs, and Section 3.5 concludes the results of this study.

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[a] Major parts of this chapter are reproduced from:

> Bachmann, M., Marxen, A., Schomäcker, R., Bardow, A. High-performance, but low cost and environmental impact? Integrated techno-economic and life cycle assessment of Polyoxazolidinone as a novel high-performance polymer. *Green Chemistry*, 24(23):9143-9156, 2022.

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

3.1 Introduction

HPTs can be classified into semi-crystalline polymers, such as polyphenylene sulfide and polyether ether ketone (PEEK), and amorphous polymers, such as PEI, PES, and PSU (see Figure 3.1).[185] HPTs have superior chemical and mechanical properties at temperatures higher than 150 °C resulting from the high aromatic content in the polymer backbone.[185,187–190]

Commonly used HPTs are often produced from complex monomers and via multi-step synthesis. The more complex production of HPTs increases production costs compared to commodity plastics.[185] For example, the costs of PEI are about five to ten times, and the sales revenues are even up to twenty times higher than for polyethylene (1 - 2 € per kg).[191]

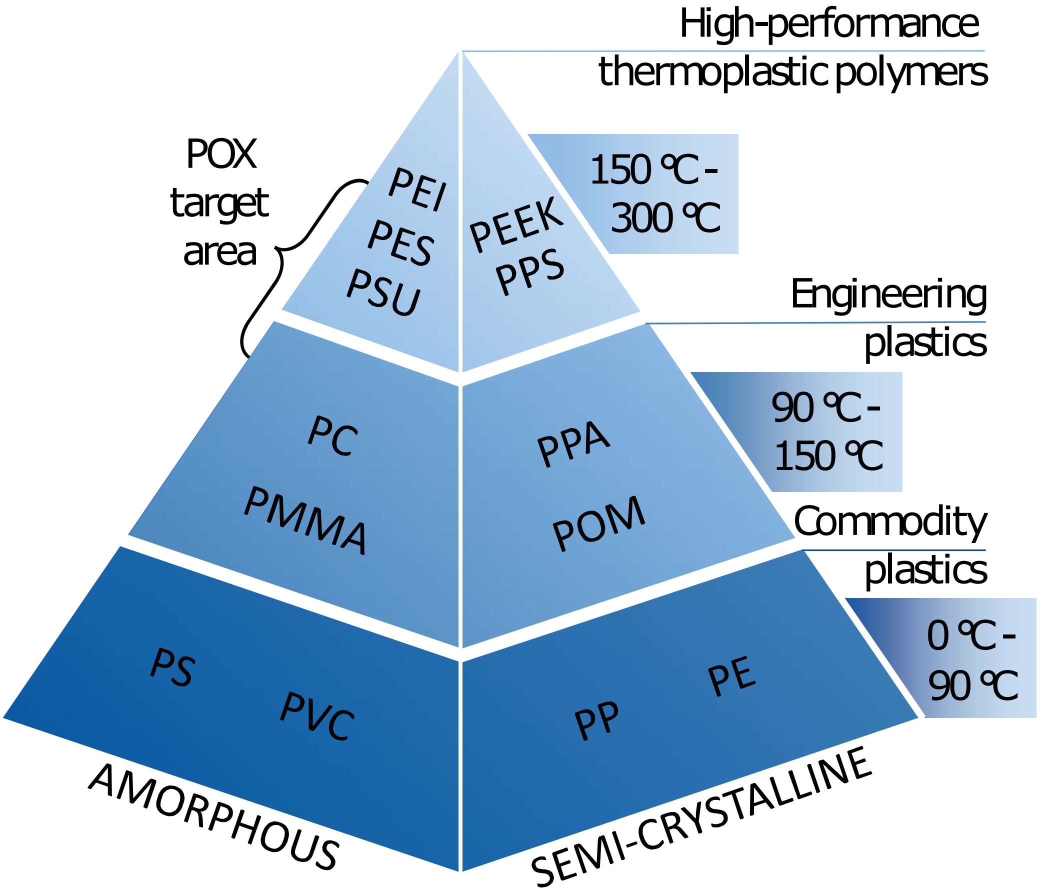

Figure 3.1: The polymer pyramid adapted from Yildizhan.[189] Temperature ranges given correspond to typical values of heat deflection temperatures and continuous use temperatures of the polymers.[190] For simplicity, only a few polymers are shown by their common abbreviation.

The multi-step production also leads to high environmental impacts.[98] HPTs have a significantly higher carbon footprint than commodity plastics.[98] Accordingly, HPTs offer great leverage for reducing GHG emissions. Still, the environmental impacts of HPTs have been neglected in recent studies of global polymer production due to their relatively small production volumes compared to commodity plastics.[4,5,17,192] However, HPT production volumes have risen sharply and will continue to rise due to increasing demands, e.g., in the electronics industry. For instance, the production volume of PEI is expected to increase by 4.5 % and that of PES by 5.9 % in the coming years.[193] In comparison, the global plastic market is expected to increase by an annual growth rate of 3.4 %.[194] Besides improving current HPTs, development should target novel HPTs with low costs and environmental impacts.

Recent advancements in catalyst technology and process engineering enable the production of POX as a new HPT.[195–198] POX has a similar chemical structure and mechanical and chemical properties within the same range as the commercial amorphous HPTs PEI, PES, and PSU (see Appendix A.2 for details). Thus, we define PEI, PES, and PSU as reference HPTs for POX in this study.

Compared to the reference HPTs, POX has key advantages during production by increased process efficiency due to a 1-step polyaddition without by-products and highly available inputs.[195–198] Thus, POX provides opportunities to reduce environmental impacts and costs compared to reference HPTs. Furthermore, in contrast to the reference HPTs, POX production is suitable for extrusion-based and solvent-free downstream processing (downstreaming).[199]

This chapter investigates the potential environmental impacts for a recently developed industrial-scale production process of POX.[200] We apply a comparative LCA based on ISO 14040/14044.[23,24] Thus, we assess whether POX reduces environmental impacts compared to reference HPTs. Furthermore, we evaluate the environmental impacts of integrating bio-based feedstocks in the supply chain of POX and its reference products.

3.2 Goal and scope definition

The presented study aims to compare the potential environmental impacts of fossil-based POX production to reference HPTs. Furthermore, this study assesses potential future environmental impacts based on renewable energy and biomass as feedstock. For this purpose, we conduct a comparative LCA of POX and its reference HPTs PEI, PES, and PSU. We follow the recommended procedure of Walker et al. and include all mandatory steps of the Product Environmental Footprint guidance in our assessment.[156]

Furthermore, POX can only achieve the potential environmental benefits if it is cost-competitive compared to the reference HPTs, as commercialization largely depends on economic performance. Therefore, the publication from which this chapter was reproduced also contains a techno-economic analysis (TEA). The TEA analyzes the cost of POX compared to the production costs of reference products by conducting a factorial-based cost estimation. For details, the interested reader is referred to the original publication.

Functional unit

We choose PEI, PES, and PSU as reference products for POX due to their similar properties (see Appendix A.2). However, each HPT can be further varied in essentially infinite chemical ways due to their flexibility in monomer and catalyst selection.[193] Thus, the considered polymers should rather be regarded as families of materials with a few common chemical characteristics than single products.

As the functional unit for comparison, we choose 1 kg of HPT. We model the production of the base resin without any additives since compounding depends on the application. We choose a mass-based functional unit since, in TEA, materials are usually compared per unit of mass. However, HPTs are also frequently replaced on a molded part-specific basis so that volume rather than mass can be the decisive unit. The density of POX (1.2 g/cm^3)[199] is lower than its reference products (1.24 - 1.37 g/cm^3)[190], while the mechanical and chemical stability is on par (details in Appendix A.2). Thus, less material could be required for the same molded part when substituting the reference products with POX. Therefore, a mass-based functional unit allows for a conservative assessment of the reduction potential of POX.

Scope of the life cycle assessment

For the comparative LCA, we apply cradle-to-grave system boundaries, including the supply chain, production, and final disposal (see Figure 3.2). The use phase is assumed to be identical and is thus neglected from the assessment. However, depending on the HPT application, the use phase may have a significant influence on the life-cycle environmental impacts. Therefore, please note that the absolute environmental impacts of HPTs are higher when considering the entire life cycle. At the same time, HPT might replace other materials that are environmentally more harmful, leading to environmental benefits from the use phase. This analysis needs to be carried out for each application. Accordingly, in this study, relative savings refer only to the system boundaries of HPT production and disposal.

We included the disposal in the assessment as bio-based production may lead to negative GHG emissions from cradle-to-gate due to the biomass carbon uptake. Negative GHG emissions might lead to the false conclusion that bio-based plastics represent carbon sinks. In contrast, net-negative GHG emissions can only be achieved by permanent carbon storage, e.g., by using negative emission technologies such as bioenergy with carbon capture and storage.[162]

As the foreground system, we modeled the fossil-based supply chain and included options to integrate bio-based chemicals: methanol, carbon monoxide, aniline, ethanol, and glycerol. For the background system, we used aggregated GaBi datasets because they are both high quality and industrially validated.[98] If available, we used datasets for the region of Germany. Otherwise, we used European data. Furthermore, we neglect plant construction in the foreground system because the environmental impacts of plant construction are typically small for chemical products and probably similar for all HPTs.[201]

For bio-based chemicals, we account for the CO_2 absorbed from the atmosphere during the biomass growth phase as described in Section 2.3.1. For absorbing 1 kg of CO_2, we give a credit of 1 kg CO_2-equivalent emissions (CO_2-eq) as negative GHG emissions. Furthermore, we consider LUC emission using aggregated datasets from the LCA database GaBi.[98] In addition, we conduct a sensitivity analysis on LUC emissions in Appendix A.5.

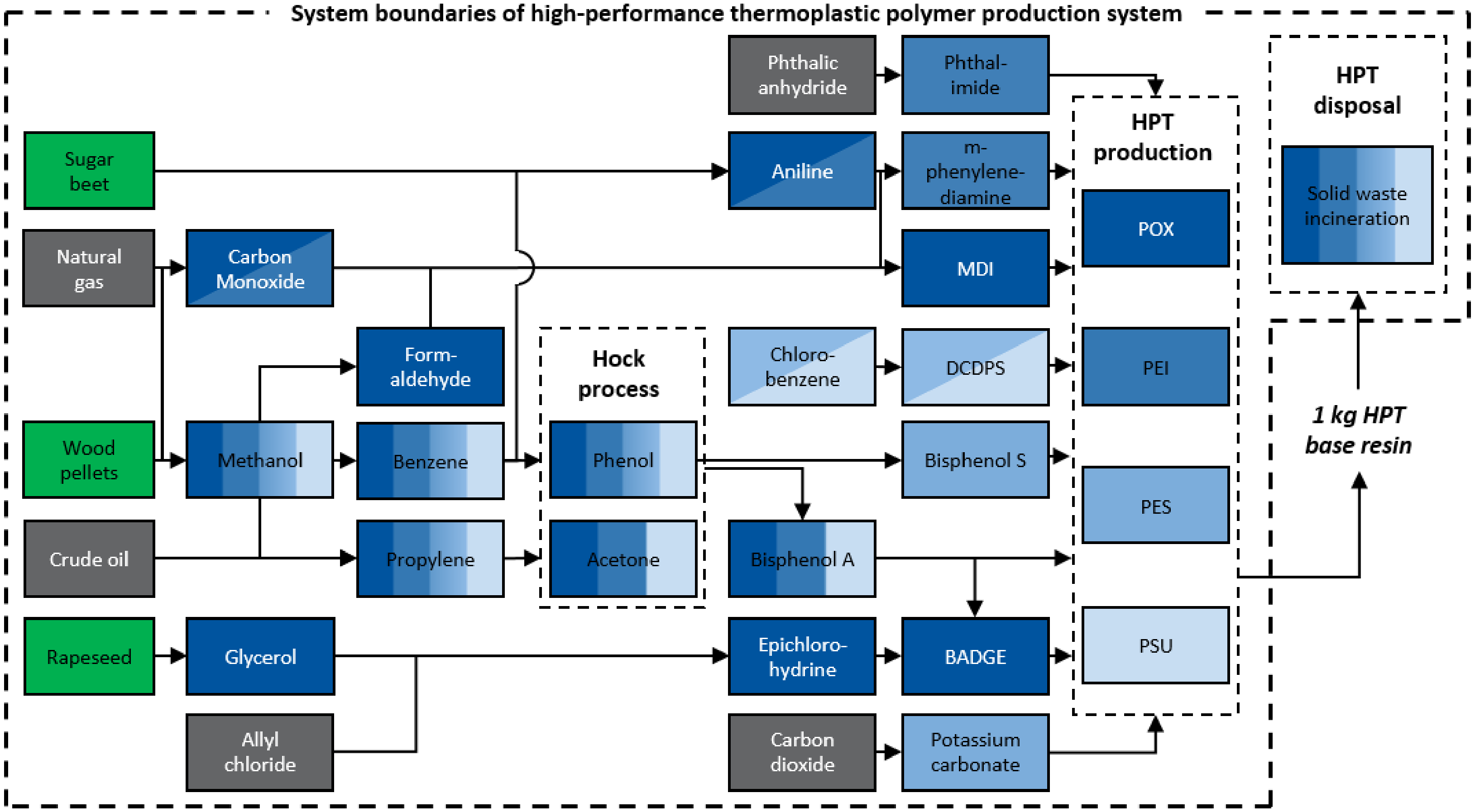

Figure 3.2: Cradle-to-grave system boundaries of the high-performance thermoplastic polymer production system. For better readability, only the most important carbon-containing chemicals and polymers are shown. Each HPT is shown in a shade of blue. If a chemical in the supply chain has the same shade of blue as the HPT, the chemical is part of the supply chain of the HPT. Fossil-based feedstocks are highlighted in grey and bio-based feedstocks in green. Further abbreviations: MDI = Methylene diphenyl diisocyanate, DCDPS = 4,4'-Dichlorodiphenyl sulfone, BADGE = Bisphenol A diglycidyl ether.

For the environmental impacts of PEI, an aggregated dataset is available in GaBi.[98] However, aggregated datasets do not provide insights into a product's production and supply chain. Thus, the aggregated dataset cannot be applied to fulfill the goal of this study and assess the bio-based production of PEI. Furthermore, for PES, no datasets are available in commercial databases. A dataset for PSU is available in ecoinvent.[202] However, the dataset is modeled based on stoichiometry and, therefore, only represents a rough estimate of the environmental impacts of PSU.[203] Thus, the PSU dataset does not meet the required technical appropriateness for a consistent assessment of all HPTs. Accordingly, we modeled the production of PEI, PES, and PSU to identify environmental hotspots, enable insights into their supply chains and ensure a high and consistent data quality.

The Life Cycle Inventories of HPT production are based on patents and experimentally validated process simulations conducted by Covestro Deutschland AG and NexantECA.[193,199] According to Parvatker et al., process simulations are the most accurate method to generate Life Cycle Inventories if actual plant data is missing.[204] Therefore, the data quality is regarded as sufficient to assess the environmental impacts of the considered HPTs.

The supply of process steam and electricity in the HPT production and supply chains assumes a natural gas boiler with an efficiency of 95 % and the 2019 electricity grid mix from GaBi.[98] Additionally, we assess the environmental impacts of future HPT production by assuming low-carbon power for electricity supply represented by current wind power and process steam production via electric boiler with 95 % efficiency as a best-case assumption for GHG emissions. Furthermore, we use biogas as a renewable alternative to natural gas if high-temperature heat is required. Accordingly, this study assesses four scenarios of HPT production, summarized in Table 3.1.

The production of POX does not result in any by-products. However, both the reference HPT production and the supply chains yield by-products, thus making these

Table 3.1: Production scenarios of high-performance thermoplastic polymers.

Scenario	**Feedstock type**	**Electricity source**	**High-temperature heat source**
Conventional	Fossil	Grid mix 2019	Natural gas
Biomass	Biomass		
Renewable energy	Fossil	Low carbon (represented by wind power)	Biogas
Renewable carbon and energy	Biomass		

processes multifunctional. We solve the multifunctionality problem by giving a credit for the avoided conventional production whenever possible. If no conventional process exists or sufficient data on the conventional process is not available, we apply mass allocation. For the given product system, the impact of this allocation is expected to be small due to the small amounts of by-products.

POX has a lower melting temperature (∼170 °C) compared to the reference products (∼180 - 220 °C), which promises lower environmental impacts in further processing steps, e.g., by injection molding. However, detailed modeling of further processing requires defining the application, as it influences crucial process parameters such as the number of pieces and storage conditions. Due to the variety of HPT applications, this study avoids determining a single application and focuses on the materials. Therefore, we do not consider further processing in this study.

Depending on the application, the use phase may determine the life cycle emissions of HPTs, e.g., if used in lightweight construction. Here, HPTs compete with other advanced materials that may emit more GHGs during production but further reduce the weight of the final product compared to HPTs. Thus, use phase emissions of HPTs might be higher compared to other materials, resulting in trade-offs between life cycle phases.[205] These trade-offs strongly depend on the application and other parameters like the lifetime of the materials. However, to the best of the authors' knowledge, no study exists that quantifies the life cycle emissions of HPTs compared to other advanced materials. We assume that the environmental impacts of the use phases of POX and reference HPTs are similar and can thus be neglected in a comparative LCA. The similar density and mechanical and chemical properties of HPTs support this assumption.

We do not consider recycling in our assessment due to the poor data availability on the recyclability of HPTs. However, by applying simplified assumptions for the recycling efficiency of PSU, Schwarz et al. found that the environmental impacts of HPTs are the lowest if primary recycling (dissolution or closed-loop mechanical recycling) is used due to the high environmental impacts of the PSU production phase.[21] Primary recycling requires either pure or well-sorted PSU mono streams. Decreasing sorting efficiency negatively affects the environmental impacts of PSU recycling to the extent that primary recycling may perform worse than other recycling technologies.[21] However, the collection and sorting efficiencies of HPTs are limited, as HPTs are primarily applied in smaller quantities compared to commodity plastics. Thus, depending on the application, the environmental impacts from the collection and separation of HPTs may outweigh the environmental benefits of HPT recycling.

As end-of-life treatment, we consider incineration. We adapted the incineration model from Meys et al.[5], which followed Doka.[206,207] The model accounts for all environmental impacts of flue gas emissions, flue gas cleaning, and the disposal of residuals. Potential energy production from incineration is not considered, and all emissions are allocated to the waste treatment representing a worst-case assumption.[206,207] Furthermore, we assume that non-usable by-products and wastes from HPT production and their supply chains are treated by incineration. We apply the incineration model to close the mass balances for all unit processes.

As impact assessment methods, we use all methods recommended by the Joint Research Center in the framework of the Environmental Footprint 3.0.[101,102] In Chaper 3.4, we show the impact category of climate change as a primary driver for the development of the novel HPT. Bio-based processes tend to shift environmental burdens from climate change to other impact categories, particularly acidification and eutrophication (see Section 2.3.1).[208] Consequentially, we also assess acidification and eutrophication in Section 3.4. All other environmental impacts can be found in Appendix A.7.

3.3 Production of high-performance thermoplastics

To assess POX's environmental and economic performance compared to the reference HPTs, Covestro Deutschland AG provided us with energy and material requirements for an industrial-scale POX process.[199] Each step of the POX process has already been proven on a lab or pilot scale. Thus, the present inventory data is regarded as suitable for evaluating the potential impacts of an up-scaled industrial process (see Table 3.2 and 3.3).

The production of the reference products PEI, PES, and PSU is modeled using process data from NexantECA.[193] The NexantECA data contains detailed information about reactants and utilities such as electricity, heat, and cooling demands. However, the data does not always include information about auxiliary materials such as chain stoppers. Therefore, the data were checked for consistency and adjusted or extended if necessary. In addition, the reference products are standard commercially available HPTs without additives, thus ensuring a consistent comparison with POX.

Table 3.2: Life cycle inventory of polyoxazolidinone (POX), polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU) - part 1. Positive values represent products, and negative values represent inputs.

Function	**Input**	**Value**				**Unit**	**Modelled as**
		POX	PEI	PES	PSU		
Products	Polyoxazolidinone	1,000	-	-	-	kg	Modeled using industry data
	Polyetherimide	-	1,000	-	-	kg	Modeled using NexantECA data
	Polyethersulfone	-	-	1,000	-	kg	Modeled using NexantECA data
	Polysulfone	-	-	-	1,000	kg	Modeled using NexantECA data
By-products	Dilute nitric acid (60 %)	-	2,200	-	-	kg	GaBi - DE: Nitric acid (60 %)
Reactants	Bisphenol A diglycidyl ether	-549	-	-	-	kg	Modeled using NexantECA data
	Methylene diphenyl diisocyanate	-420	-	-	-	kg	Modeled using NexantECA data
	Bisphenol A	-	-412	-	-526	kg	Modeled using NexantECA data
	Phthalic anhydride	-	-550	-	-	kg	GaBi - DE: Phthalic anhydride
	n-Methyl phthalimide	-	-70	-	-	kg	Modeled based on stoichiometry
	m-Phenylenediamine	-	-192	-	-	kg	p-Phenylenediamine used as proxy
	Nitric acid	-	-2,500	-	-	kg	GaBi - DE: Nitric acid (98 %)
	Caustic soda	-	-300	-	-105	kg	GaBi - DE: Sodium hydroxide (caustic soda) mix (100%)
	4,4’-Dichlorodiphenyl sulfone	-	-	-631	-662	kg	Modeled using NexantECA data
	4,4’-Dihydroxydiphenyl sulfone	-	-	-550	-	kg	Modeled using NexantECA data
	Potassium carbonate	-	-	-286	-	kg	Modeled using ecoinvent data

Table 3.3: Life cycle inventory of polyoxazolidinone (POX), polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU) - part 2. Positive values represent products, and negative values represent inputs.

Function	**Input**	**Value**				**Unit**	**Modelled as**
		POX	PEI	PES	PSU		
Chain stopper	p-tert-Butylphenyl glycidyl ether	-28	-	-	-	kg	BADGE used as proxy
	Triethylamine	-	-11	-	-	kg	Modeled using ecoinvent data
	Methyl chloride	-	-	-6	- 7	kg	Modeled based on stoichiometry
Catalyst	Others	-3	-	-	-	kg	POX catalyst is confidential, other catalysts are not considered
Solvents	Benzonitrile	-10	-	-	-	kg	Modeled based on stoichiometry
Utilities	Electricity	-2,036	-6,545	-6,160	-6,160	MJ	GaBi - DE: Electricity grid mix /DE: Electricity from wind power
	Steam, medium pressure	-6,648	-22,400	-20,000	-18,000	kg	GaBi - DE: Process steam from natural gas 95 % or modeled separately (details in Appendix A.1)
	Cooling water	-116	-732	-628	-610	Nm^3	GaBi - DE: Tap water from surface water
	Fuel gas	-	-651	-56	-51	kg	GaBi - DE: Natural gas mix
	Inert gas	-	-0.1	-0.1	-0.1	kg	GaBi - DE: Nitrogen (gaseous)

The modeling of POX is described in detail below. For the reference products, see Appendix A.4. POX can be produced via many routes, the most promising being the 1-step polyaddition of diisocyanates and di-epoxides.[195,209] The main limitation of this route is the required chemoselectivity since trimerization of isocyanates in POX polymerization leads to the formation of insoluble products. Recent developments have identified a catalyst system and reaction conditions for a highly selective formation of the oxazolidinone group via polyaddition.[195,209] This development enables the production of linear POX with a high molecular weight, which can be thermally processed in subsequent steps.

We modeled the POX production as a 1-step polyaddition of bisphenol A diglycidyl ether (BADGE) and methylene diphenyl diisocyanate (MDI) with p-tert-butyl phenyl glycidyl ether (pBPGE) as chain terminator (see Figure 3.3 and Figure 3.4). The mass balance is derived from the reaction stoichiometry for a POX composition with a molecular weight of 15,000 g/mol. Deriving the mass balance from reaction stoichiometry and assuming complete conversion is reasonable since no by-product and other residues are expected in industrial practice. Benzonitrile is used as the reaction solvent. After heated premixing of BADGE with catalyst, benzonitrile, and the first charge of chain terminator, the mixture is passed to a reactor where MDI is added, and polymerization is initiated. Polymerization is ended by adding a second charge of the chain terminator.

POX is purified by extrusion-based downstreaming, which enables a high processing temperature and, thus, a low viscosity of the reactor slurry. Therefore, the extrusion-based downstreaming allows for a high solid reaction content of 50 wt-% between reactants and benzonitrile. For benzonitrile recovery, we assumed a solvent recovery rate of 99 % as a standard value in industrial practice.[199] The provided energy requirements for the extrusion-based process are based on process simulations conducted in the commercial flowsheeting software Aspen Plus®.[199]

The reactants of POX production result from a complex supply chain that causes a high share of POX's overall environmental impact (see Figure 3.2). Accordingly, changes in the supply chain from fossil-based to renewable feedstock may reduce the overall impact. Thus, we modeled the supply chain of POX and assessed the environ-

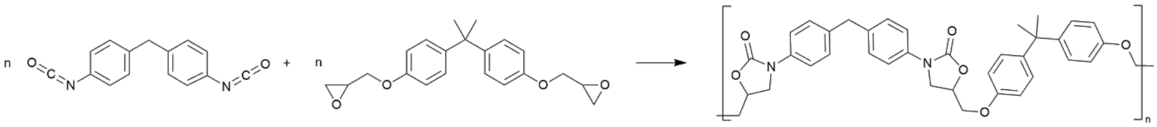

Figure 3.3: Chemical reaction of diisocyanate and diepoxide to polyoxazolidinone.

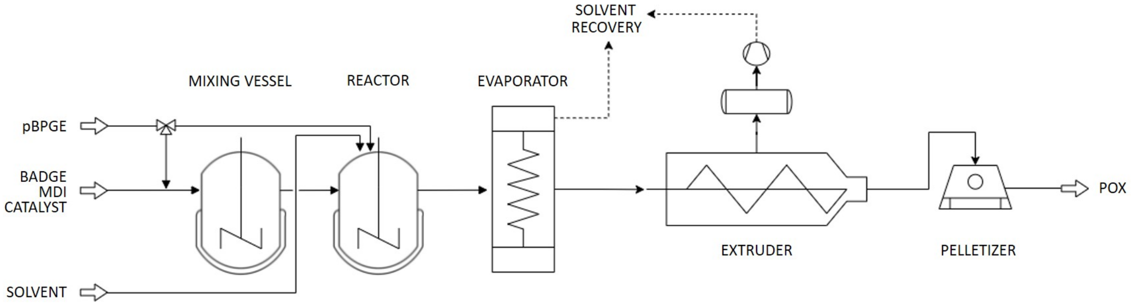

Figure 3.4: Simplified process flowsheet of the polyoxazolidinone (POX) synthesis and the extrusion-based downstream processing.

mental impact of their bio-based production. We considered the following bio-based chemicals since they are applicable in the HPT supply chain and sufficient data for modeling was available: Aniline, methanol, carbon monoxide, glycerol, and ethanol.

Aniline, methanol, and carbon monoxide are used to produce MDI.[210] For aniline, a bio-based process was recently developed.[211] Bio-based methanol is produced via the gasification of wood chips and the subsequent conversion to methanol. We choose wood chips as a feedstock as they are widely available and relatively inexpensive compared to other biomass feedstocks.[212] Methanol can be integrated into the POX supply chain by the methanol-to-olefins and methanol-to-aromatics processes to produce propylene and benzene, respectively. Propylene and benzene are used as feedstocks in the Hock process to produce phenol and acetone, the feedstocks for Bisphenol A. Bisphenol A, in turn, is the primary feedstock for BADGE. Furthermore, the product gas from the biomass gasification can be separated into carbon monoxide and H_2. The carbon monoxide can be used in MDI production.

The second feedstock necessary for producing BADGE is epichlorohydrin.[213,214] For bio-based production, we considered epichlorohydrin from glycerol. Bio-based production of epichlorohydrin has increased since glycerol became a cheap feedstock alternative as a by-product of biodiesel production.[213,215] Furthermore, bio-based ethanol is used in the PEI supply chain. Since ethanol is nowadays mainly produced bio-based, we did not assess fossil-based ethanol.

More information on the reference products, the supply chain modeling, and a list of all LCA datasets can be found in Appendix A.1, Appendix A.3, and Appendix A.4. Furthermore, we added a list of process yields for the most important chemical intermediates to Appendix A.1.

3.4 Environmental impacts of high-performance thermoplastics

In the following section, we first quantify the climate change impacts of POX in comparison to the reference HPTs. Here, we assess four scenarios differing in feedstock type and the supply of electricity, process steam, and fuel gas (*cf.* Table 3.1). To analyze potential burden-shifting, we additionally show acidification and eutrophication in this section. All other environmental impacts are shown in Appendix A.7.

Climate change. In the conventional scenario, the fossil-based production leads to 9.3 kgCO_2-eq/kg for POX and 14.4 - 16.8 kgCO_2-eq/kg for reference HPTs (Figure 3.5). For POX production, 51 % of GHG emissions result from feedstock supply, 17 % from energy supply, and 3 % from chain terminator and solvent supply and disposal. The end-of-life (EoL) treatment emits the remaining 30 %.

Compared to the reference HPTs, POX production achieves an 11 - 45 % reduction in GHG emissions from feedstock supply and 64 - 72 % savings in energy supply. Savings in energy supply mainly result from POX's lower process steam demand compared to the reference HPTs. For PEI, the higher process steam demand results from the more complex production requiring four process steps compared to the 1-step polyaddition in POX production. For PES and PSU, the production complexity is lower than for PEI, but the supply of the reactants already emits 31 - 45 % more GHGs than the supply of MDI and BADGE. The high GHG emissions from the PES and PSU supply chain arise from producing the organosulfur compounds Bisphenol S and DCDPS.

To investigate the impact of process yields, we added a sensitivity analysis to Appendix A.6, elaborating on the influence of key chemical intermediates and utilities on the climate change impacts of HPT. The sensitivity analysis shows that especially increased process steam demands and decreasing process yields can have a significant influence of up to 23 % on the GHG emissions of HPT. Still, POX remains climate beneficial compared to its reference HPT, even under unfavorable process conditions.

Due to the solvent-free downstream processing via extrusion, the direct emissions from waste treatment are 90 - 99 % lower for POX than for the reference HPTs. Direct emissions are particularly high for PEI due to the high amount of fuel gas burned in PEI production. The EoL emissions of the reference HPTs are 12 - 18 % lower for PES and PSU than for POX due to their lower carbon content. EoL treatment of PEI emits equal amounts of GHGs as POX.

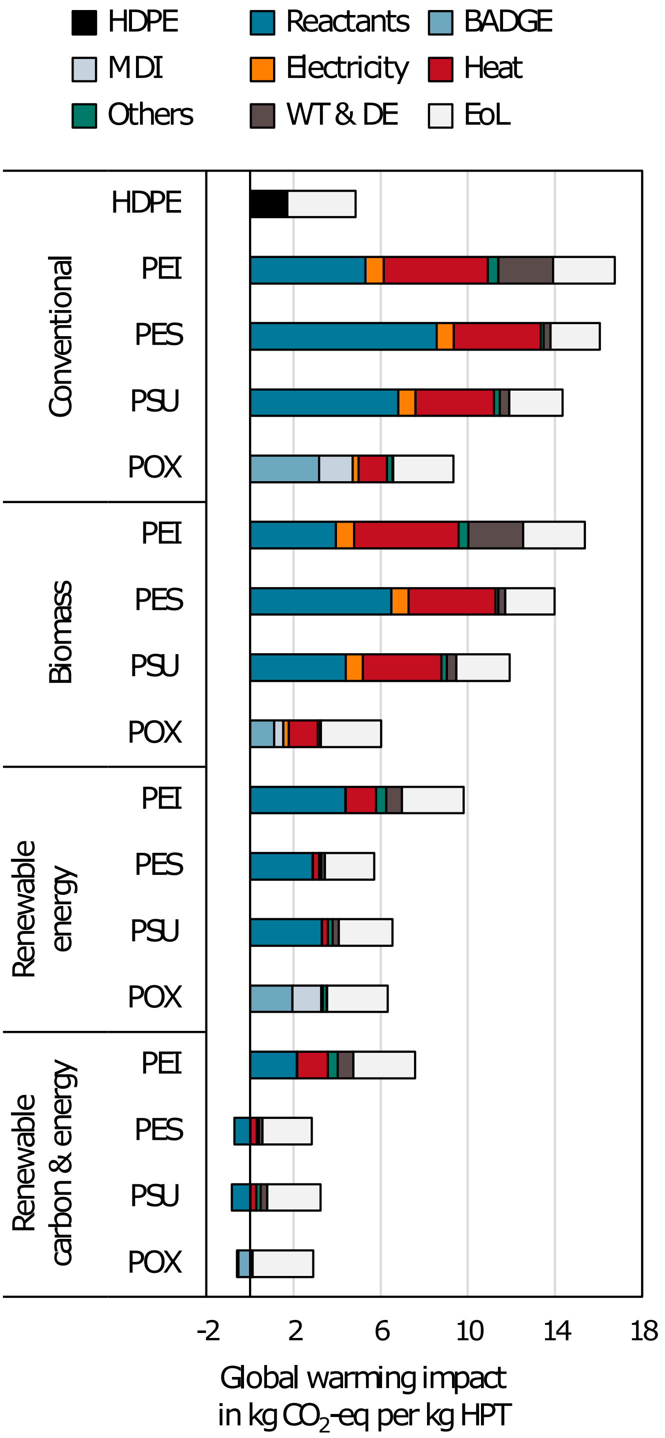

Figure 3.5: Global warming impact of 1 kg of high-performance thermoplastic polymers (HPT) under four scenarios: (1) fossil-based feedstock with fossil energy (conventional), (2) bio-based feedstock with fossil energy (biomass), (3) fossil-based feedstock with renewable energy using wind power and biogas (renewable energy), and (4) bio-based feedstock with renewable energy using wind power and biogas (renewable carbon and energy). We additionally show high-density polyethylene (HDPE) as a reference.[216] Further abbreviations: BADGE = bisphenol A diglycidyl ether, MDI = methylene diphenyl diisocyanate, WT & DE = waste treatment and direct emissions, EoL = End-of-life treatment.

The EoL emissions of HPTs are quantified assuming complete combustion. Recycling HPTs would reduce EoL emissions and substitute virgin production. However, as mentioned above, HPTs are applied in lower quantities compared to commodity plastics. Thus, HPT recycling would either require separate reverse logistics concepts or lead to high sorting efforts. Both approaches may outweigh the environmental benefits of HPT recycling compared to incineration.

Compared to commodity plastics like high-density polyethylene (HDPE), GHG emissions of HPTs are about 2 - 3 times higher from cradle-to-grave and even 4 - 8 times higher from cradle-to-gate.[216]

In the biomass scenario, POX production has GHG emissions of 6.0 kgCO$_2$-eq/kg, thus 35 % less compared to fossil-based production. These reductions are due to the reduced impact of bio-based BADGE and MDI. Bio-based BADGE reduces 65 % and MDI 73 % of their GHG emissions compared to their fossil counterparts.

The bio-based production of reference HPTs reduces GHG emissions by 8 - 17 %. Savings result mainly from bio-based bisphenol A for PEI and PSU and bio-based phenol in bisphenol S production for PES. For PEI, in particular, GHG emissions could be reduced further by using bio-based xylene to produce phthalic anhydride in the supply chain. However, no data of sufficient quality were available for modeling bio-based xylene. LUC emissions only increase GHG emissions from bio-based production to a minor extent of 1 - 8 % (see Appendix A.5).

The utilization of wind power and biogas in the renewable energy scenario saves about 96 % of GHG emissions from the energy supply in POX production. Additionally, 31 % GHG savings from feedstock supply can be achieved due to reduced GHG emissions in the supply chain. For the reference HPTs, using renewable energy in HPT production reduces 75 - 93 % of GHG emissions from energy supply. An additional 17 - 67 % of GHG emissions from feedstock supply can be reduced by using renewable energy in the HPT supply chain. The higher savings from feedstock supply for PES and PSU results from the energy-intensive production of DCDPS and bisphenol S. For DCDPS and bisphenol S, GHG emissions are reduced by 53 % and 85 %, respectively. Overall, using renewable energy results in PES having the lowest GHG emissions of all HPTs, followed by POX and PSU.

In the renewable carbon and energy scenario, POX production emits 2.3 kgCO$_2$-eq/kg GHGs, corresponding to a saving of 75 % compared to fossil-based production. POX's cradle-to-gate impact is even negative, meaning that more bio-based carbon is stored in POX than fossil-based carbon is emitted in production.

Bio-based production with renewable energy reduces GHG emissions of reference HPTs to 2.1 - 7.6 kgCO_2-eq/kg. The remaining GHG emissions of PEI are mainly related to the supply of m-phenylenediamine and phthalic anhydride. For m-phenylenediamine, low-carbon ammonia could further reduce GHG emissions.

In general, producing HPTs based on bio-based feedstocks and renewable energies reduces 55 - 87 % GHG emissions compared to fossil-based production. In the renewable carbon and energy scenario, POX emits only slightly more (<10 %) GHGs than PES and PSU, even though best-case assumptions were made for the reference HPTs without considering solvent and catalyst consumption. Thus, POX is expected to substantially reduce GHG emissions compared to the benchmark HPTs for fossil- and bio-based production, while leading to similar climate impacts as the best benchmark HPTs in low-carbon energy scenarios. However, especially bio-based feedstocks bear the risk of burden-shifting from GHG emissions to other environmental impacts. Therefore, we assess these other environmental impacts in the following section.

Acidification. PEI has the highest impact on acidification in all scenarios, followed by PES, PSU, and POX (see Figure 3.6). The high impact of fossil-based PEI results from m-phenylenediamine production (25 %) and direct emissions of nitrogen-containing compounds from waste treatment (35 %). In the renewable energy scenarios, the incineration of biogas as a fuel gas substitute for natural gas further increases PEI's acidification potential due to higher nitrogen oxides and sulfur dioxide emissions.

For fossil-based PES and PSU, the highest impact on acidification results from the supply of organosulfur compounds (63 - 75 %). POX has the lowest impact on acidification in all scenarios, reducing impacts by 15 - 74 % compared to the best HPT. However, the bio-based production of POX increases acidification due to bio-based glycerol in epichlorohydrin production. The acidification from the aggregated glycerol process mainly results from direct ammonia emissions into the air.[98]

Eutrophication. Eutrophication is classified into terrestrial, marine, and freshwater eutrophication (Figure 3.6). For HPT production, terrestrial eutrophication follows the same trend as acidification since both impacts result mainly from inorganic, nitrogen-containing emissions to the air. Marine eutrophication also shows similar results to acidification and terrestrial eutrophication. Thus, POX has the lowest impact on marine eutrophication in all scenarios and reduces impacts by 12 - 61 % compared to the best HPT. However, only 64 - 76 % of PEI's marine eutrophication is related to nitrogen-containing emissions to air, and the other 30 % is caused by nitrate and ammonium emissions to freshwater. For the other HPTs, the share of marine eutrophication from freshwater emissions ranges between 10 - 17 % for POX and 6 - 31 % for PES and PSU.

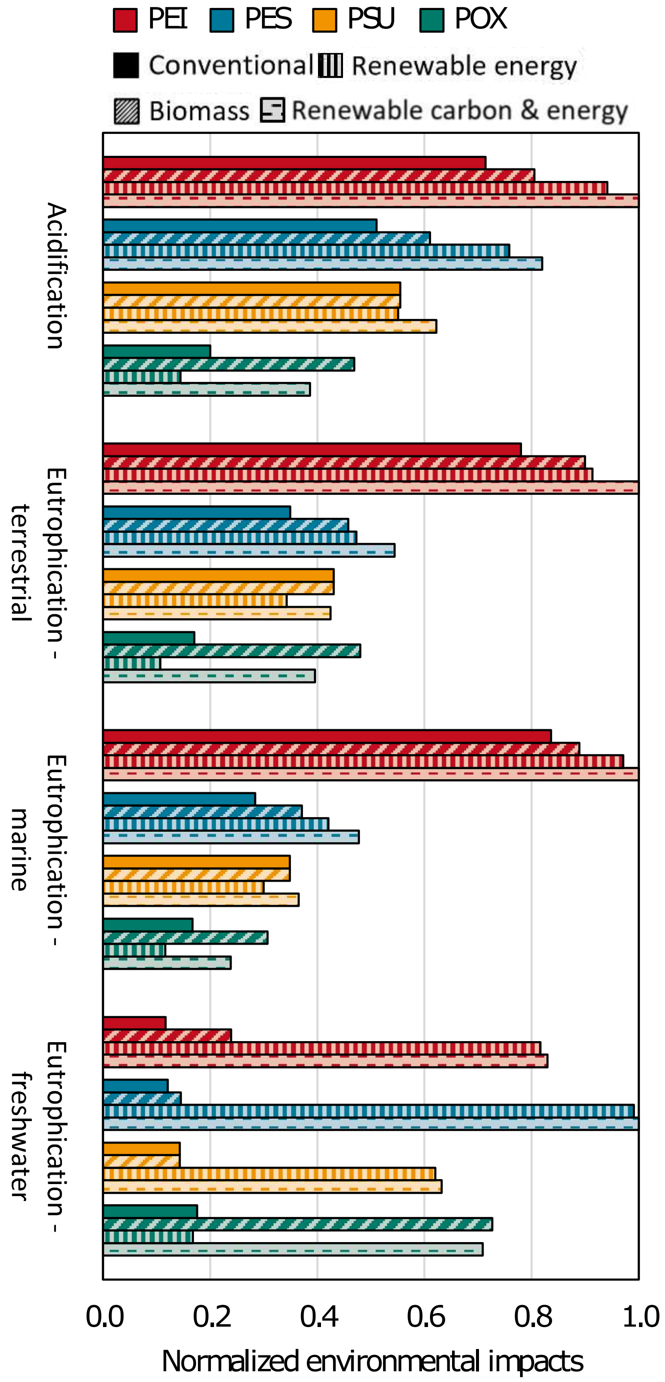

Figure 3.6: Environmental impacts of high-performance thermoplastic polymers normalized to the maximum environmental impact in each category. The scenarios are shown as patterns.

For freshwater eutrophication, fossil-based POX shows the highest impact compared to the fossil-based production of the reference HPTs. The higher impact results mainly from catalyst production. However, please note that catalyst production is not considered for the reference HPTs leading to a worst-case benchmarking study for POX (details in Appendix A.4). Thus, considering catalysts for reference HPTs might also increase freshwater eutrophication. Furthermore, switching to bio-based feedstocks and biogas increases freshwater eutrophication by up to 4 times for POX and up to 8 times for the reference HPTs.

Other environmental impacts. Considering the other environmental impact categories in the conventional scenario, POX reduces environmental impacts in 23 out of 25 categories compared to the reference HPTs (details in Appendix A.7). However, the catalyst in POX production increases ozone depletion. In the renewable energy scenarios, the supply of bio-based glycerol for POX production emits lead and mercury, which increases human toxicity. However, due to the high uncertainties, the Joint Research Center assigned the human toxicity categories with a recommendation level III ("recommended, but to be applied with caution"), and should therefore be interpreted with caution.

Overall, compared to the reference products, POX shows only minor shifting of environmental impacts from GHG emissions to other environmental impacts. Nevertheless, large-scale production of POX requires a detailed regional assessment of all environmental impacts.

3.5 Conclusions

High-performance thermoplastic polymers have become an essential building block for the industry due to their specialized property profile and high mechanical and thermal stability. However, the production of HPTs results in high environmental impacts, which were holistically investigated in this chapter. For this purpose, we conducted an LCA on the recently developed, amorphous HPT POX and its' reference products PEI, PES, and PSU.

For fossil-based production, POX reduces 35 - 45 % of GHG emissions compared to the reference HPTs. Please note that relative savings refer to the HPT production and the end-of-life treatment by incineration, whereas the use phase is not considered. POX reduces GHG emissions in the feedstock supply and by saving process energy. Savings in process energy result mainly from POX's simplified, extrusion-based downstreaming.

By switching to bio-based production with renewable energy, GHG emissions of POX decrease by 75 %, and for reference HPTs by 55 - 87 %. GHG emissions may decrease further by implementing circular production and disposal systems based on recycling. In particular, these systems are promising for larger volume applications such as battery cases for electric vehicles. In these applications, HPTs are easily accessible for reverse logistics, leading to only low environmental impacts from collection and sorting, provided they are not mixed or combined with other materials.

Other environmental impacts such as freshwater eutrophication increase by 4 - 8 times when bio-based products are used. Therefore, environmental trade-offs must be considered in detail before large-scale implementation.

We used conservative assumptions to evaluate POX environmental impacts compared to the reference HPTs, i.e., a mass-based functional unit, assessing catalyst consumption for POX and neglecting it for the reference HPTs, and an ideal solvent recovery rate of 100 % for the reference products. Furthermore, the sensitivity analyses of key process parameters for POX and reference HPT production show that POX is climate beneficial, even under unfavorable process conditions (see Appendix A.6 for details). Accordingly, we are confident that the environmental benefits of POX compared to reference HPTs can be achieved when POX is produced on an industrial scale. The presented study provides green light to advance TRL for POX. Overall, POX is a promising new HPT with environmental potential and thus provides the next step towards a decarbonized plastics industry.

The techno-economic assessment concluded that POX is highly cost-competitive against reference HPTs. The cost estimation suggests a 26 - 35 % price reduction compared to PEI, PES, and PSU. Furthermore, high profit margins of more than 100 % could be achieved on the market if POX is sold at similar prices to the reference products. However, the economic performance of POX is highly dependent on the fluctuations of the materials costs and the revenue that can be achieved on the market. Still, the presented study provides a green light to advance TRL for POX. POX is a promising new HPT with environmental and economic potential and thus provides the next step towards a decarbonized polymer industry.

Overall, the presented LCA case study reveals the environmental trade-offs caused by bio-based plastics production. Even for advanced applications such as HPT, bio-based production reduces GHG emissions while simultaneously increasing other environmental impacts. Accordingly, this chapter provided a motivating example for the use of biomass for GHG mitigation in the plastics industry. The following chapter elaborates on potential environmental synergies from combined production of biomass and CO_2.

Chapter 4

Environmental benefits from the synergetic use of biomass and CO_2

Chapter 3 has demonstrated the potential of biomass for GHG mitigation in the plastics industry. However, Chapter 3 also revealed that biomass utilization induces burden shifting, i.e., trade-offs between GHG emissions and other environmental impacts. In the following chapter,[a] we elaborate on potential environmental synergies from combining alternative carbon feedstocks. These synergies may decrease GHG emissions further and simultaneously mitigate burden shifting.

In particular, we quantify the environmental benefits from the synergetic use of biomass and CO_2 for plastics production. For this purpose, we study flexible polyurethane (PUR) foams as a representative example of plastics with high market values and volumes. PUR is particularly well suited for this study, as PUR production offers possibilities for both direct and indirect utilization of biomass and CO_2.[217] Furthermore, PUR can be used in a wide range of applications, making it the most versatile plastic among synthetic materials.[217]

To quantify potential synergies of biomass and CO_2 utilization, we build a bottom-up TCM of the PUR supply chain presented in Section 4.1. The model contains the conventional, fossil-based production of flexible PUR foams as well as bio-based and CCU-based production alternatives (Figure 4.1). In Section 4.2, we assess the technical potential of biomass and CO_2 for GHG reduction. For this purpose, we identify the optimal choice of technologies, depending on the availability and carbon footprint of biomass and renewable electricity. In Section 4.3 and 4.4, we then quantify potential benefits from the synergetic utilization of biomass and CO_2 regarding GHG reductions and other environmental impacts, respectively.

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[a] Major parts of this chapter are reproduced from:

Bachmann, M., Kätelhön, A., Winter, B., Meys, R., Müller, L.J., Bardow, A.. Renewable carbon feedstock for polymers: environmental benefits from synergistic use of biomass and CO_2. *Faraday Discussions*, 230, 227-246, 2021

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

4.1 The bottom-up model of polyurethane production

To quantify the environmental benefit from the synergetic use of biomass and CO_2, we build a bottom-up TCM of the fossil-based polyurethane supply chain. The model includes 47 production processes based on engineering-level data for a detailed accounting of the flows of mass and energy throughout the entire supply chain (Figure 4.1). Furthermore, we integrate bio- and CCU-based technologies into the model.

System boundaries. The model of the PUR supply chain uses cradle-to-grave system boundaries. A cradle-to-grave system boundary considers all life phases of a product, from resource extraction, through the manufacturing and use phase, to the final disposal. However, in a comparative LCA, identical life phases can be neglected.[218] In this study, we assume the same technical performance of all PUR products during the use phase. Therefore, we exclude the use phase from the LCA. However, different polyols in the PUR supply chain lead to different chemical compositions of PUR, which influences the final disposal. Therefore, we consider the end-of-life (EoL) treatment for which we assume incineration without energy recovery, representing a worst case for GHG emissions.

Furthermore, we divide the system boundary into the foreground and background systems (Figure 4.1): The foreground system is based on engineering-level data of 47 processes enabling a detailed analysis of the entire supply chain. Within the foreground system, we consider energy and material flows. However, we neglect the environmental impacts of plant construction in the foreground system since the environmental impacts of chemical plant construction are usually small and similar for conventional and alternative production pathways.[201] The background system is based on aggregated datasets from the LCA database ecoinvent.[99] For the aggregated datasets, we have used global markets as the default. If no data for global markets were available, we used the European counterparts. A list of all processes and data sources is provided in Appendix B.1.1.

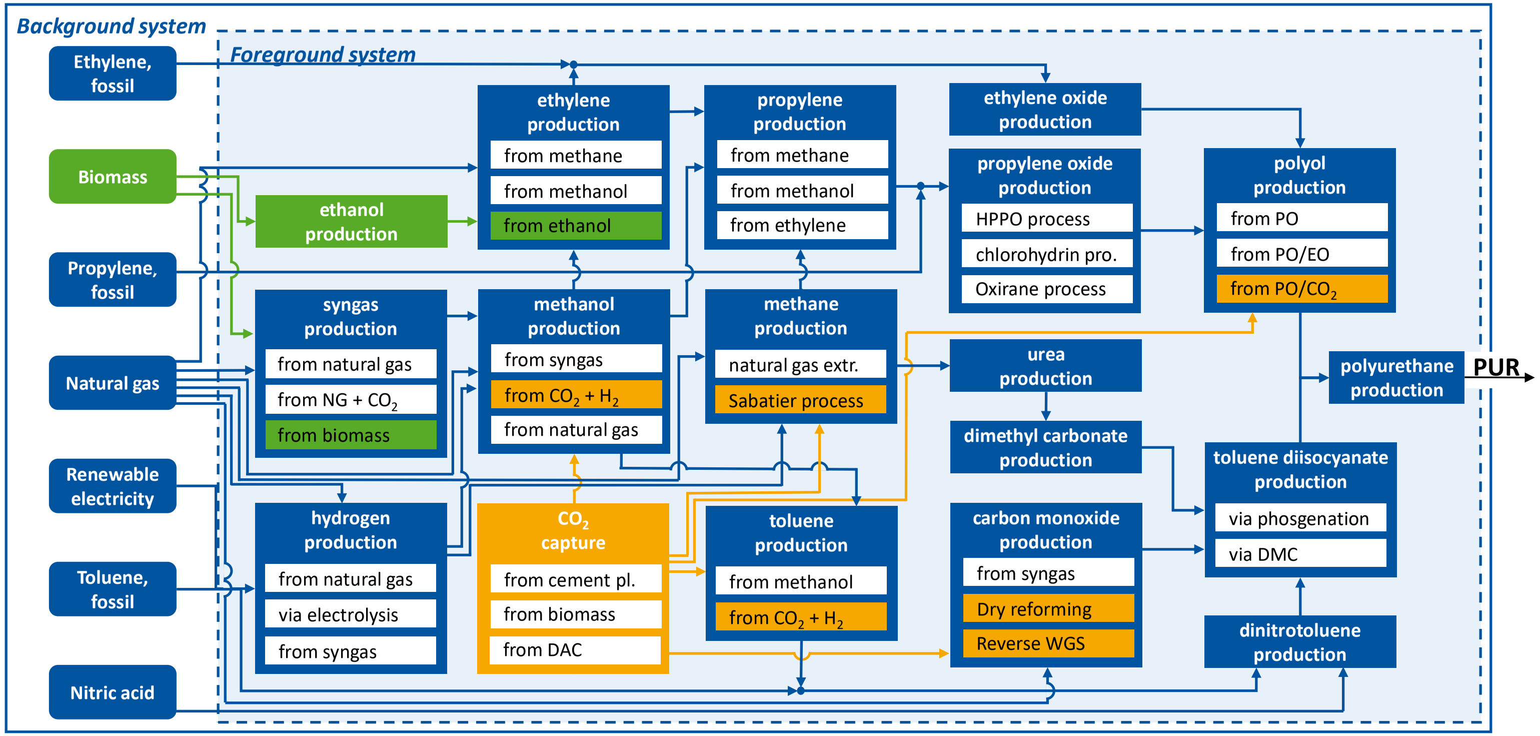

Figure 4.1: Simplified representation of the polyurethane (PUR) production system. The foreground system is based on engineering-level data of 47 processes. Data for the background system is taken from ecoinvent and includes all other raw material and energy flows needed for production. For better readability, only the most important processes and material flows are shown. Bio-based processes are highlighted in green and CCU technologies in orange. A detailed list of all processes is provided in Appendix B.1.1.

Polyurethane production. The considered flexible PUR foams can be used for various applications, such as mattresses or other furniture applications. Flexible PUR foams are produced by polyaddition of polyether polyols and isocyanates. As polyether polyols, we consider three variants: First, 100 % from propylene oxide (PO), second, 85 % from PO and 15 % from ethylene oxide (EO), and third, 80 % from PO and 20 % from CO_2. These variants correspond to compositions currently used on the industrial scale.[79] As the isocyanate, we consider toluene diisocyanate (TDI). The supply chain integrates all technologies required to convert the carbon feedstocks into PUR. The carbon feedstocks from the fossil supply chain are ethylene and propylene, toluene, and natural gas. As renewable carbon feedstocks, we consider CO_2 and biomass. We integrate all technologies that are already used on the industrial scale.[219] In addition, we include alternative technologies if sufficient data are available.

CO_2 supply and CCU technologies. For CO_2 supply, this case considers cement plants as an unavoidable industrial point source.[75] As further sources for CO_2 supply, we consider ambient air by direct air capture[75] and model endogenous CO_2 supply from biomass utilization technologies. We calculate the environmental impacts of CO_2 following Müller et al., as detailed in Section 2.3.1.[161] Through CCU, CO_2 substitutes epoxides in polyol production directly or via methanol, methane, or toluene. The latter routes require hydrogen as a co-reactant to activate the CO_2. Additionally, carbon monoxide can be produced by reverse water-gas shift (WGS) or dry reforming of CO_2 using hydrogen or methane, respectively.

It should be noted that the CO_2-to-toluene process is currently at an early development stage, with a technology-readiness level (TRL) far below 7.[17] Therefore, data availability for the toluene process is limited, resulting in high uncertainties in the life cycle inventory. The methodology used to generate the life cycle inventory for the toluene process is adapted from Kätelhön et al. (see Appendix B.1.1).[17]

Electricity supply. Since the environmental benefits of CCU technologies mainly depend on the supply of renewable electricity for hydrogen electrolysis,[27] we vary the availability and carbon intensity of electricity. These sensitivity analysis allow us to determine the tipping points at which conventional production switches to CCU-based production from an environmental perspective. As a base case, we use data for the European grid mix from Müller et al.[159] As further reference values, we use the inventory datasets for the low decarbonized, high decarbonized, and full decarbonized scenarios of the LCA guidelines for CCU.[159] The full decarbonized scenario is equivalent to wind electricity and is used as a best-case assumption for the carbon intensity of electricity in the sensitivity analysis. To analyze the specific impact of CO_2 utilization in PUR production, renewable electricity can only be used in hydrogen electrolysis. All other consumers use the European grid mix. Hydrogen from electrolysis is available to the CCU technologies and all other technologies in the foreground system.

Biomass supply and utilization technologies. For biomass supply, we consider perennial energy crops to represent second-generation biomass. Perennial energy crops have high crop yields and can be cultivated on marginal land due to low nutrient requirements.[220] Since food crops, in general, have higher nutrient requirements, perennial energy crops do not directly compete with food production.[221] Furthermore, the cultivation of perennial energy crops sequesters additional organic carbon in soil and, thus, further reduces GHG emissions by long-term storage of carbon in soil.[222] The amount of sequestered carbon depends on the land on which perennial energy crops are cultivated. We account for this effect by considering land-use change (LUC) emissions.[222,223]

In this study, we use miscanthus as a perennial energy crop. The environmental impacts of miscanthus depend on the carbon content of miscanthus, LUC, and additional cultivation efforts, e.g., harvesting methods or application of fertilizers and pesticides (see Section 2.3.1 for details). We account for the biomass carbon uptake by giving a credit of 1 kg CO_2-eq per kg of absorbed CO_2 as negative GHG emissions. We assume an average carbon content of 48 %[224] and a moisture content of 14 %,[99] resulting in a credit of 1.5 kg CO_2-eq per kilogram miscanthus. We consider GHG emissions from additional cultivation efforts by using data from ecoinvent. Regarding the LUC emission, Qin et al. assumed a range of -151 to 44 g CO_2-eq per kilogram of energy crops.[223] However, since quantifying LUC emissions is highly uncertain, we evaluate the impact of LUC emissions in a sensitivity analysis. To account for the high uncertainty, we choose a more conservative range of potential LUC emissions for the sensitivity analysis. In total, we vary the carbon footprint of miscanthus cultivation between -1.7 and -1.0 kg CO_2-eq per kg biomass. Through this variation, we identify tipping points for which bio-based production is more environmentally friendly than conventional production.

To consider the decentralized production and seasonality of biomass, our model includes transportation and storage. Following Styles et al., we assumed an average transportation distance of 150 km.[225] As the storage technique for biomass, we assume ambient storage with a material loss of 1 % per month and an average storage duration of 6 months.[226] For the conversion of perennial energy crops into chemicals, the model contains gasification[227–232] and fermentation[233–236] processes. The gasification processes convert miscanthus into syngas with a molar hydrogen-to-carbon monoxide ratio of 2:1. This syngas can be further processed into methanol. Alternatively, miscanthus can be fermented to ethanol, which can, in turn, be oxidized to ethylene.

Details of the alternative biomass to miscanthus and the considered processes can be found in Appendix B.1.1.

Environmental impact categories. For the characterization of elementary flows, we use the methods from the ILCD recommendations (V.2.0 2018).[101] We use all methods with good robustness (recommendation levels 1 and 2). However, at recommendation level 3 (recommended to use with caution), we include the following methods that are particularly important for this study: (1) land use, due to its importance for bio-based feedstocks, and (2) resource depletion, as an important indicator for fossil- and CCU-based technologies. Thereby, resource depletion considers energy carriers and minerals and metals separately.

4.2 Climate change mitigation through the utilization of either biomass or CO_2

In the following section, we first quantify the GHG reduction potentials for using either biomass or CO_2 in PUR production. The individual assessments of biomass and CO_2 provide a basis for assessing potential benefits through the combined utilization of biomass and CO_2 in Section 4.3.

Fossil-based production. Fossil-based production leads to GHG emissions of about 7.6 kg CO_2-eq per kg PUR from cradle to grave. GHG emissions result from the supply of raw materials (38 %) and utilities (22 %), direct emissions (12 %), and EoL treatment (28 %). The supply of grid electricity and process steam account for 7 % and 15 % of GHG emissions, respectively. Our results correspond well with the GHG emissions of fossil-based PUR production in ecoinvent.[99] PUR is produced by reacting a PO/EO polyether polyol with TDI. EO is produced by oxidation of ethylene, and PO is produced from propylene by the HPPO process. Both olefins are produced by standard fossil production pathways. TDI is produced by phosgenation of dinitrotoluene using hydrogen and carbon monoxide, and dinitrotoluene is produced from toluene and nitric acid, both taken from fossil production pathways. Hydrogen for phosgenation and the HPPO process is produced by steam reforming of natural gas, and carbon monoxide is produced by dry reforming of CO_2 captured from a cement plant. Fossil-based production consumes about 5 MJ of grid electricity and about 4 kg of process steam. For producing diluted hydrochloric acid in TDI production, we give a credit of 0.7 kg CO_2-eq per kg PUR. The credit remains the same in all scenarios in this study, as TDI is always produced via phosgenation.

GHG mitigation potential of CCU technologies. CCU technologies can reduce the global warming impact (GWI) of PUR by 45 % to 4.2 kg CO_2-eq per kg PUR. Here, we can distinguish between the direct and indirect utilization of CO_2. The direct substitution of PO and EO in the polyol with 20 % CO_2 can reduce the GWI of PUR to 7.0 kg CO_2-eq per kg PUR without requiring any renewable electricity. When renewable electricity is available in the full decarbonized scenario, CCU can further reduce the GWI to 4.2 kg CO_2-eq per kg PUR. The extent of the reduction depends on the availability and the carbon footprint of electricity (Figure 4.2). For carbon footprints of electricity greater than 54 g CO_2-eq per MJ electricity, no renewable electricity is used. Thus, CCU technologies reduce the carbon footprint of PUR only when using electricity with a sufficiently low carbon footprint.

The best-case CCU-based production is achieved in the full decarbonized scenario with a carbon footprint of renewable electricity of 3 g CO_2-eq per MJ electricity. Best-case CCU-based production uses a PO/CO_2 polyether polyol with TDI to form PUR. PO is produced by the HPPO process, and the required propylene is produced from ethylene by the Olefins Conversion Technology (OCT). Ethylene is produced by oxidative coupling of methane, which is produced by the Sabatier process using hydrogen from water electrolysis and CO_2. TDI is produced in the same way as in the fossil scenario, but with toluene from CO_2. The required CO_2 is captured from a cement plant. The remaining emissions for CCU-based production result from the supply of nitric acid and a higher demand for process steam and electricity compared to fossil-based production. About 50 % more process steam is required to perform the oxidative coupling process, and about 33 times as much electricity is used for water electrolysis compared to fossil-based production. Furthermore, about 100 % more grid electricity is required to carry out the OCT, the Sabatier process, the oxidative coupling process, and the CO_2 capture.

Ethylene production via the Sabatier process combined with oxidative coupling consumes about three times as much hydrogen and about two times as much steam per kilogram of olefin than the combination of CO_2-based methanol and the methanol-to-olefins process. Furthermore, oxidative coupling is less selective and produces several alkanes and other hydrocarbons as by-products. The by-products, however, lead to a total credit of only 0.3 kg CO_2-eq per kg PUR. While using less steam and hydrogen, production via methanol requires about three times as much grid electricity. Therefore, the cleaner the renewable electricity and, thus, the hydrogen from the water electrolysis, the more competitive becomes production via oxidative coupling in terms of GHG emissions. However, ethylene production via oxidative coupling only emits less GHG emissions than production via methanol in the full decarbonized scenario.

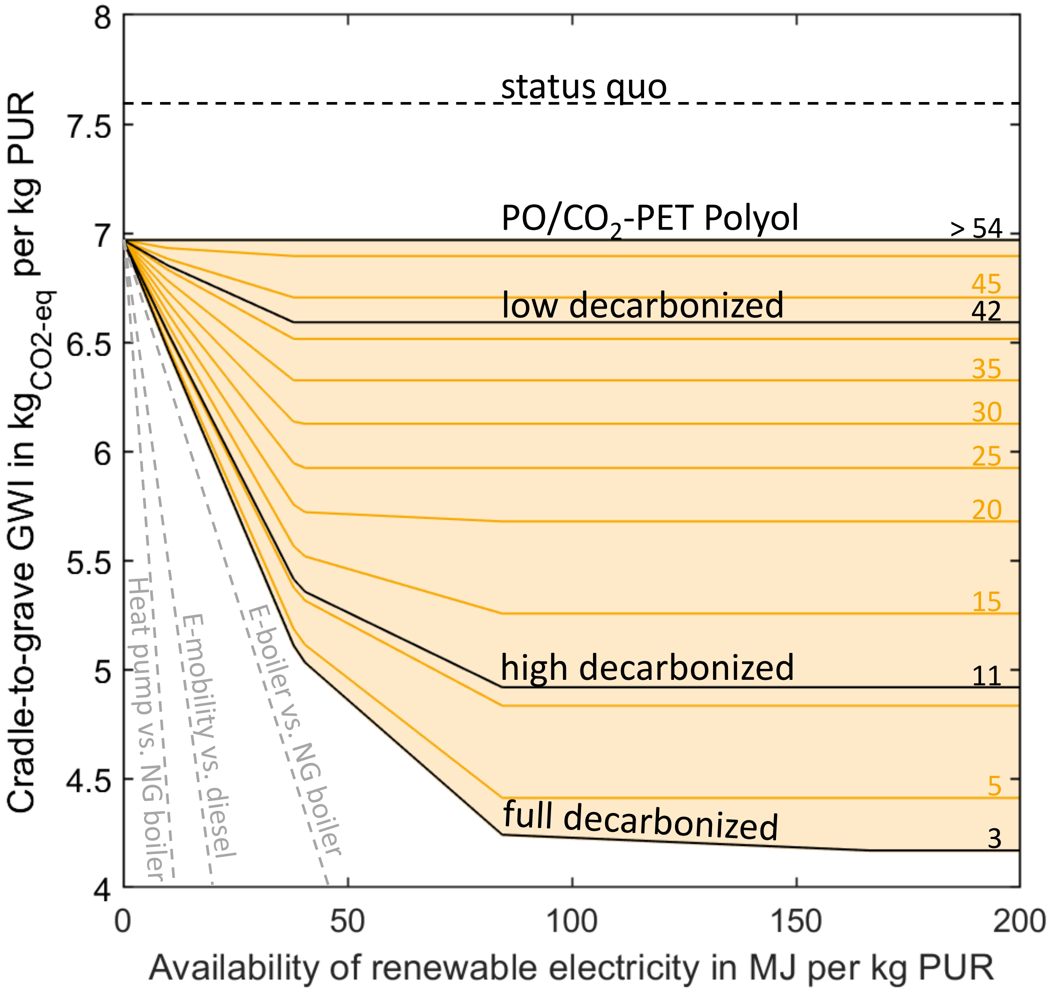

Figure 4.2: Cradle-to-grave global warming impact (GWI) of 1 kg PUR as a function of the availability (x-axis) for different carbon footprints of renewable electricity (lines). The carbon footprints of renewable energy are expressed in g CO_2-eq per MJ electricity above the lines. Cradle-to-grave emissions cover the production stage, including the supply of all raw materials and energy needed for production, as well as emissions from EoL treatment. Scenarios for the carbon footprint of renewable electricity were taken from Müller et al. (low decarbonized = 42 g CO_2-eq per MJ electricity, high decarbonized = 11 g CO_2-eq per MJ electricity, full decarbonized = 3 g CO_2-eq per MJ electricity).[159] The dashed gray lines indicate the GHG mitigation efficiency of other power-to-X technologies adapted from Sternberg et al.[237]

In this case, both technologies are quite similar and we believe that the differences are not significant given the current uncertainties in the energy demand.

In total, the best-case CCU production consumes about 167 MJ renewable electricity for water electrolysis and about 10 MJ of grid electricity per kilogram PUR. Due to the large demand and limited supply, we varied the amount of renewable electricity available (Table 4.1). With less renewable electricity available, production gradually switches from CCU-based production to fossil-based production. Furthermore, CCU technologies are not equally efficient in using renewable electricity to avoid GHG emissions. Therefore, the GHG emission reduction depends non-linearly on the availability of renewable electricity. It should be noted that all CCU technologies except the direct substitution of PO avoid less GHG emissions per MJ renewable electricity used than other power-to-X technologies such as e-mobility or power-to-heat (grey lines in Figure 4.2). Consequently, CCU technologies should only be used for PUR production if sufficient renewable electricity is available to supply also the more efficient power-to-X technologies.

Table 4.1: Tipping points leading to technology changes in the CCU-based production based on the availability of renewable electricity in the fully decarbonized scenario.

Available renewable electricity per kg PUR	**Chemical**	**From technology**	**To technology**
10 MJ	Hydrogen	Hydrogen from natural gas	Hydrogen from electrolysis
38 MJ	Toluene	Fossil toluene	Toluene from CO_2
41 MJ	Carbon monoxide	Dry reforming	Reverse WGS
84 MJ	Propylene	Fossil propylene	Methanol from CO_2 and H_2, methanol-to-olefins, and ethylene dimerization by OCT
167 MJ	Ethylene	Methanol from CO_2 and H_2, methanol-to-olefins	Sabatier process and oxidative coupling of methane

GHG mitigation potential of biomass. Biomass utilization can reduce the GWI of PUR by 46 % to 4.1 kg CO_2-eq per kg PUR (Figure 4.3). Again, the first reduction step is the direct substitution of PO and EO in the polyol with CO_2, which reduces the GWI from 7.6 kg CO_2-eq to 7.0 kg CO_2-eq per kg PUR. Although this effect is actually a CCU technology, we include it in the assessment since no renewable electricity is necessary to achieve the reduction. An additional reduction of 38 % can be achieved by using miscanthus with the lowest carbon footprint.

Here, PUR is also produced by using the PO/CO_2 polyether polyol and TDI. The PO required for polyol production is produced from propylene by the HPPO process. Propylene is partially produced by the methanol-to-olefins process and partially produced from ethylene by the OCT. Ethylene is a co-product of the methanol-to-olefins process. Methanol is produced by the conversion of syngas from biomass gasification plants and about 1 % of the excess CO_2 from the gasification plants is used in polyol production. The remaining CO_2 is emitted into the atmosphere. TDI is produced in the same way as in the conventional scenario, but with toluene from the methanol-to-toluene process and carbon monoxide from separation of bio-bassed syngas. Syngas separation provides some of the hydrogen required for the HPPO process and the phosgenation of dinitrotoluene. The remaining hydrogen is produced by steam reforming of natural gas.

The remaining emissions are caused by the supply of nitric acid and a higher demand for process steam and grid electricity compared to the fossil benchmark. About 50 % more process steam is used in the methanol-to-olefins and methanol-to-toluene processes, and 80 % more grid electricity is needed to operate the biomass gasifier. The demand for process steam could be reduced by integrating excess heat from gasification. However, we currently give a credit of 1.2 kg CO_2-eq per kg PUR for excess heat, which substitutes heat from natural gas in other district or industrial applications. Since both options substitute natural gas, heat integration does not reduce total GHG emissions.

The GHG reduction depends on the availability and the carbon footprint of miscanthus. GHG emissions are reduced the most by using biomass with the lowest carbon footprint of -1.7 kg CO_2-eq per kg biomass, resulting in a GWI of PUR of 4.1 kg CO_2-eq per kg PUR. However, our results indicate that even for a worst-case assumption of -1.0 kg CO_2-eq per kg biomass, GHG emissions can be reduced slightly by 0.2 kg CO_2-eq to 6.8 kg CO_2-eq per kg PUR.

To reach the maximum GHG reduction, 5.6 kg biomass is required per kg PUR. If the availability of biomass decreases, PUR production gradually switches from bio-based to fossil-based production (Table 4.2). The GHG reductions depend non-linearly

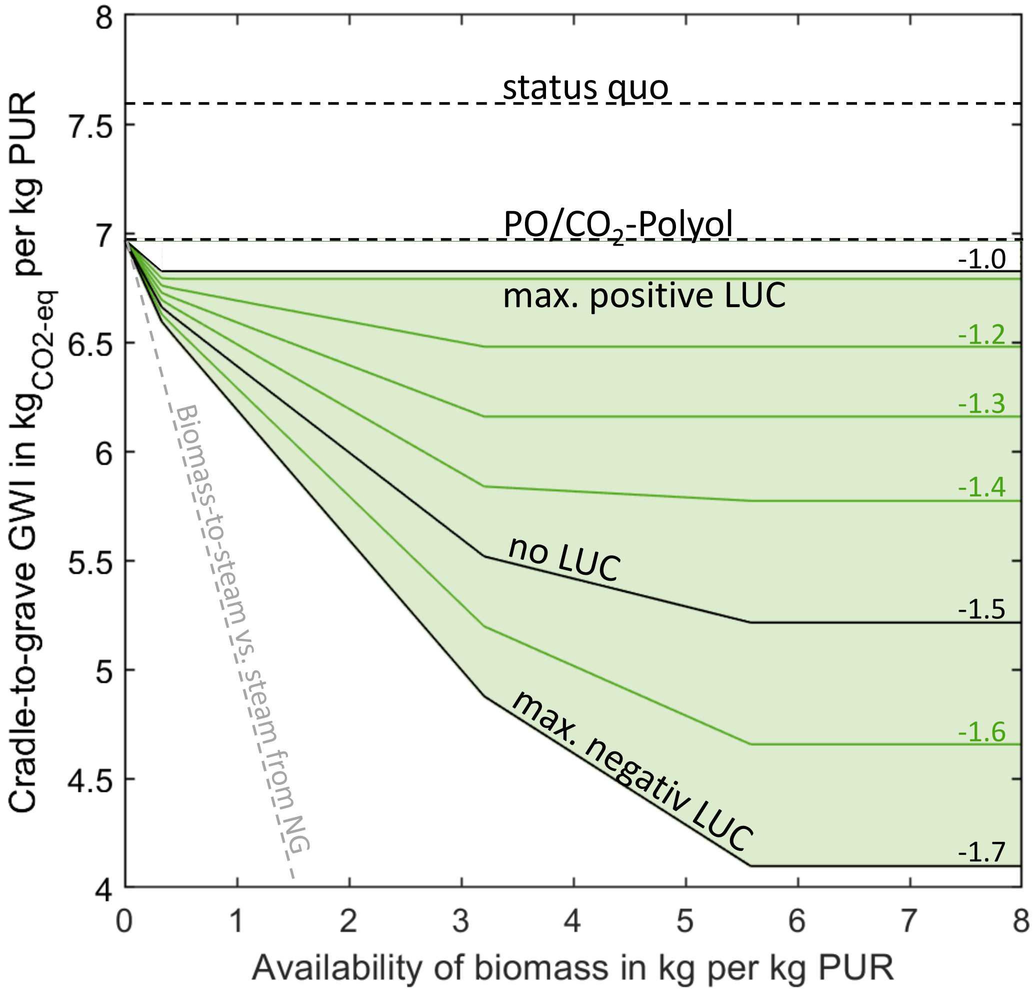

Figure 4.3: Cradle-to-grave global warming impact (GWI) of 1 kg PUR (y-axis) as a function of the availability of biomass (x-axis) with different carbon footprints (lines). The carbon footprints of biomass are expressed in kg CO_2-eq per kg biomass above the lines. Cradle-to-grave emissions cover the production stage, including the supply of all raw materials and energy needed for production, as well as emissions from EoL treatment. The gray line indicates the GHG mitigation efficiency when using biomass for process steam production to substitute process steam from natural gas.

on the availability of biomass since individual biomass utilization technologies have different efficiencies in using biomass to avoid GHG emissions. However, similar to CCU-based production, all biomass utilization technologies are less efficient at reducing GHG emissions per unit of biomass than bio-based process steam generation (grey line in Figure 4.2, details in Appendix B.1.7). Accordingly, bio-based PUR production should only be implemented in regions where more efficient biomass utilization technologies are either unavailable or already exhausted.

Overall, utilization of either biomass or CO_2 can significantly reduce the GHG emissions of PUR production. However, according to our analysis, substantial quantities of renewable resources are required, which would save more GHG emissions in other sectors. In the following section, we therefore look at combined utilization to determine whether synergies in production may save renewable resources.

4.3 Climate benefits from the synergetic utilization of biomass and CO_2

The combined utilization of biomass and CO_2 can reduce the GHG emissions of PUR by 59 % to 3.1 kg CO_2-eq per kg PUR, which corresponds to a 13 % higher reduction compared to the utilization of either biomass or CO_2 (Figure 4.4). Again, the basis is the PO/CO_2 polyether polyol, which needs neither biomass nor renewable electricity. As a result, Figure 4.4 already contains the 0.6 kg CO_2-eq per kg PUR savings through the direct utilization of CO_2 in the polyol. Combined utilization avoids more GHG emissions due to synergies in production. At the point of maximum reduction,

Table 4.2: Tipping points leading to technology changes in bio-based production based on the availability of biomass for a carbon footprint of -1.7 kgCO_2-eq/kg$_{\text{biomass}}$.

Available biomass per kg PUR	**Chemical**	**From technology**	**To technology**
0.4 kg	Carbon monoxide and hydrogen	Dry reforming and hydrogen from natural gas	Separation of syngas from biomass gasification
3.2 kg	Propylene	Fossil propylene	Methanol-to-olefins and ethylene dimerization by OCT
5.6 kg	Toluene	Fossil toluene	Methanol-to-toluene

PUR production is similar to the bio-based optimum, but less biomass is converted to syngas for methanol production. Instead, CO_2 from biomass gasification is captured and directly converted to toluene. Thus, bio-based CO_2 substitutes the bio-based methanol used in the methanol-to-toluene process. The additional hydrogen required for the CO_2 based toluene is produced by water electrolysis. For the maximum reduction, the combined utilization requires 79 % less renewable electricity and 43 % less biomass than the utilization of either biomass or CO_2, while the GHG savings increase. Additionally, combined utilization uses about 20 % less process steam than the utilization of either biomass or CO_2 since neither oxidative coupling of methane nor the methanol-to-toluene process is used. Excess heat from gasification leads to a credit of 0.7 kg CO_2-eq per kg PUR. Again, integrating excess heat could reduce process steam demand but would not reduce total GHG emissions (see discussion above).

However, synergies are not only present at the point of maximum reduction but can help to save renewable resources and lower GHG emissions in scenarios where less biomass or renewable electricity is available. When biomass and CO_2 are used in separate production facilities, the GHG emissions correspond to a linear combination of the GHG emissions of the separate production facilities. In contrast, Figure 4.4 shows that curves with constant GWI (iso-GWI curves) are flattened in combined production. The difference between the linear combination and the iso-GWI curves in Figure 4.4 corresponds to the saving of renewable resources. The following example illustrates this effect: by using biomass and CO_2 in separate production facilities, GHG emissions can, for instance, be reduced to 4.5 kg CO_2-eq per kg PUR. The GHG reduction requires 2 kg of biomass and about 45 MJ of renewable electricity per kilogram PUR. Combined utilization could achieve the same GHG reduction while using only 1.6 kg of biomass and about 33 MJ of renewable electricity. Thus, combined utilization saves about 25 % of renewable resources. A more detailed analysis can be found in Appendix B.2.

Synergies in production depend on the carbon footprint of biomass and renewable electricity. A sensitivity analysis of the effect of the carbon footprint of biomass and renewable electricity on the synergies is available in Appendix B.3. Overall, our results indicate that the utilization of integrated facilities that combine biomass and CO_2 utilization can save GHG emissions and limited resources compared to individual utilization.

However, even in the optimal scenario, the carbon footprint of PUR is not zero. The remaining emissions are due to the use of process steam (35 %), grid electricity (25 %), and remaining fossil feedstocks (40 %), in particular, nitric acid, oxygen, and

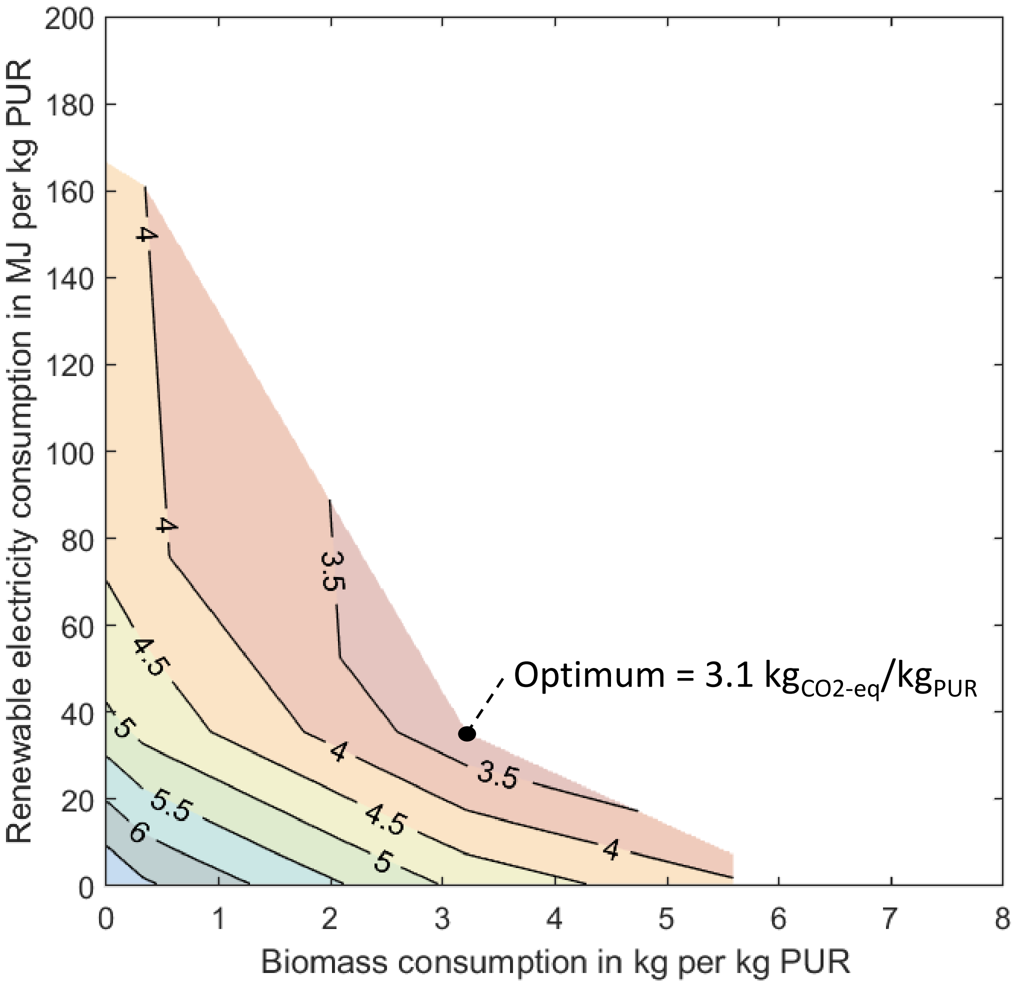

Figure 4.4: Pareto frontiers of the global warming impact of 1 kg PUR as a function of biomass and renewable electricity consumption. The biomass supply has a global warming impact of -1.7 kg CO_2-eq per kg biomass (best case). The electricity supply has a global warming impact of 3 g CO_2-eq per MJ electricity (best case). The black curves show combinations of bio-based and CCU-based production with constant global warming impacts (iso-GWI curves).

chlorine. In particular, the oxygen demand could be reduced by integrating the oxygen by-product from water electrolysis in the production. However, water electrolysis is likely to be used in places with large amounts of renewable electricity. In this case, not only the hydrogen but also the oxygen would have to be transported to the production facility. The remaining emissions from process steam and grid electricity supply could be reduced by renewable electricity. For the remaining fossil feedstocks, alternative production routes are under development. Nitric acid, for example, could be produced using ammonia from nitrogen and hydrogen from water electrolysis or biomass.[238] Thus, further reducing the carbon footprint of PUR would again increase the demand for renewables.

4.4 Effects on other environmental impacts

To assess the full potential of biomass and CO_2 as renewable carbon feedstocks, it is important to consider all environmental impacts and analyze potential burden shifting. Thus, we investigate eleven additional impact categories from the ILCD recommendations (V.2.0 2018, Figure 4.5). Our results show that environmental impacts increase in nine out of eleven categories for bio- and CCU-based production compared to fossil-based production.

For the best case of CCU-based production, the highest increase can be seen in the category mineral and metal depletion, where environmental impacts are about 28 times higher due to the high use of metals for wind electricity. However, it should be noted that the construction of electrolyzers, which is not considered in this analysis, would further increase mineral and metal depletion compared to fossil production. The high use of wind electricity and the higher demand for process steam increase acidification, eutrophication, and respiratory effects by between 60 and 250 %. Acidification, freshwater eutrophication, and terrestrial eutrophication mainly increase due to copper production for wind turbines, while marine eutrophication and respiratory effects increase due to the high demand for copper and reinforcing steel. Increases in ionizing radiation, however, mainly result from higher use of grid electricity and could be avoided by using renewable electricity instead.

The best-case bio-based production increases land use by a factor of about 37 due to the land requirements for miscanthus cultivation. Furthermore, both the cultivation and gasification of miscanthus increase eutrophication by 70 to 160 % due to the application of fertilizer and nitrate emissions from gasification. The increase in ionizing radiation results from the high demand for oxygen for gasification. Since the environmental impacts of oxygen result mainly from electricity consumption for

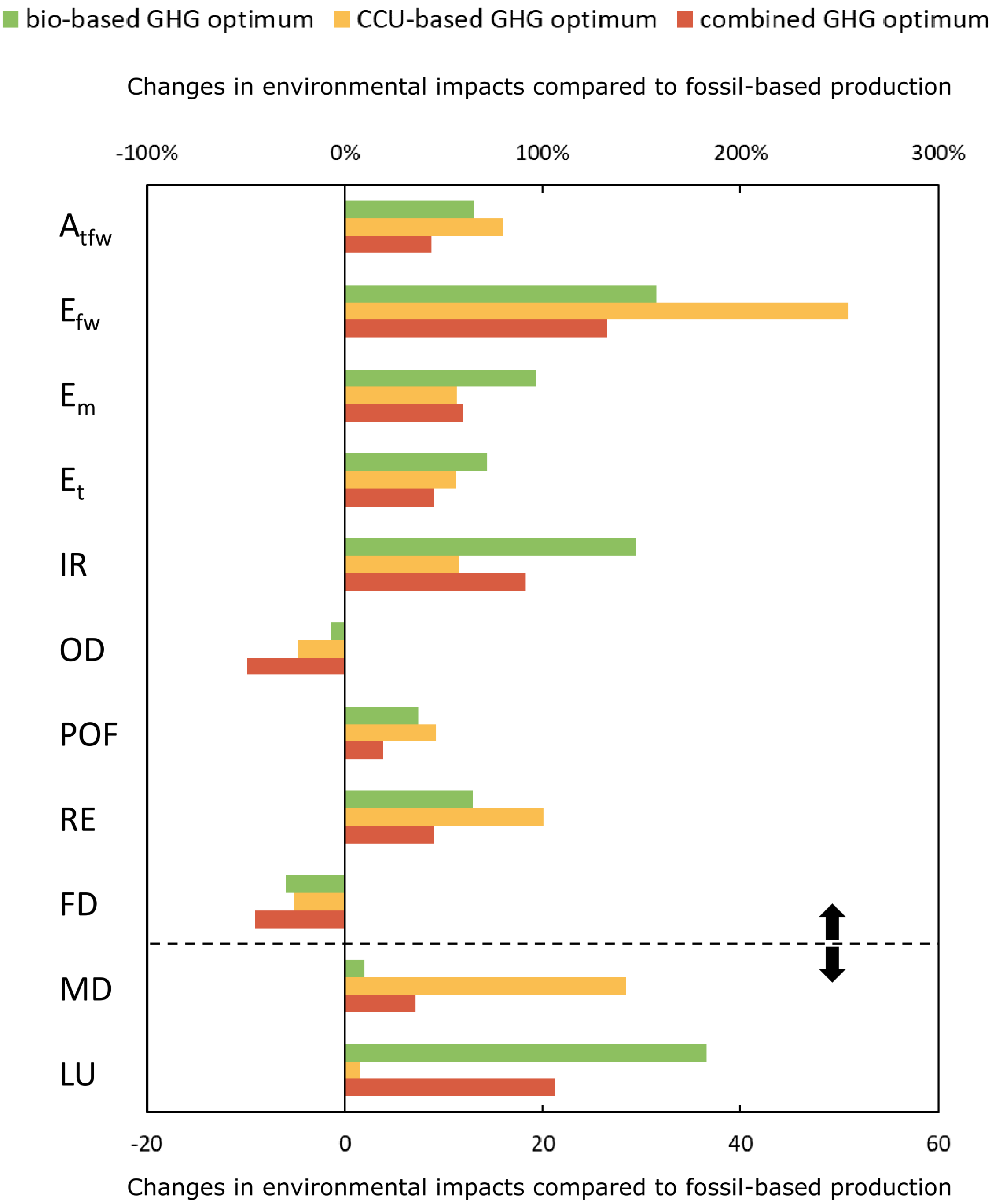

Figure 4.5: Changes in environmental impacts for bio-based, CCU-based, and combined production normalized to the environmental impacts of fossil-based production with PO/CO_2 polyether polyol. Impact categories: A_{tfw} = freshwater and terrestrial acidification, E_{fw} = freshwater eutrophication, E_m = marine eutrophication, E_t = terrestrial eutrophication, IR = ionizing radiation, OD = ozone layer depletion, POF = photochemical ozone formation, RE = respiratory effects, FD = fossil depletion, MD = mineral and metal depletion, LU = land use. Please note that mineral and metal depletion and land use are shown on the lower x-axis, and all other environmental impacts are shown on the upper x-axis (black arrows).

cryogenic air separation, the increased environmental impacts could also be avoided by using renewable electricity. However, oxygen supply is part of the background system and therefore not modeled in this study. Furthermore, environmental impacts from oxygen supply could also be reduced by integrating the oxygen by-product from water electrolysis, as mentioned in Section 4.3. In addition, acidification and respiratory effects increase due to the higher use of grid electricity. However, both bio- and CCU-based production reduce ozone layer depletion and fossil depletion due to the reduced demand for natural gas, fossil-based ethylene, and propylene.

Combined utilization always lowers environmental impacts compared to either biomass or CCU. In seven out of eleven categories, combined use leads to the lowest impacts, reducing impacts by 10 to 46 % compared to the best utilization of either biomass or CO_2. These savings result from reduced demand for process steam, grid electricity, and biomass. However, the environmental impacts of combined production are still higher than those of fossil-based production in nine out of eleven categories. These impacts could potentially be reduced by already taking the other environmental impacts into account during optimization. The analysis shows that the optimization of the PUR supply chain leads to environmental trade-offs.

4.5 Conclusions

The global warming impact of PUR can be reduced by the utilization of both bio and CCU-based technologies. CCU technologies can reduce the GWI by up to 45 %. Biomass utilization, on the other hand, can reduce the GWI of PUR by up to 46 %. However, large amounts of biomass and renewable electricity with a low carbon footprint are necessary to achieve GHG reductions. Therefore, the availability of limited renewable resources determines the GHG reductions.

We identified synergies from the combined utilization of bio- and CCU-based technologies that reduce GHG emissions by an additional 13 %. At the same time, we found that combined utilization reduces the demand for limited renewable resources compared to the utilization of either biomass or CO_2: demand decreases by about 25 % for biomass and renewable electricity. Synergies result from the more efficient use of bio-based carbon. Bio-based carbon is usually partially converted into CO_2 during gasification and fermentation and released into the atmosphere. In the combined utilization, the CO_2 is captured and reused in production, thus saving GHG emissions, raw materials, and process steam. Still, even the combined production of PUR remains carbon-positive with a carbon footprint of 3.1 kg CO_2-eq per kg PUR.

Further GHG reductions in energy and feedstock supply are necessary to achieve carbon-neutral PUR.

Our results show that by using renewable resources, burdens are shifted from climate impact to other environmental impact categories: nine out of eleven environmental impact categories increase compared to fossil production. In particular, land use and metal depletion increase significantly. Although the uncertainties are particularly high in these categories, the trend towards higher environmental impacts should not be ignored. Combined utilization of renewable resources can again reduce environmental impacts. In seven of the eleven categories, lower consumption of process steam, grid electricity, and biomass reduces environmental impacts by at least 10 to 46 % compared to the individual utilization of biomass and CO_2. However, most impacts remain higher compared to the fossil benchmark. It is therefore important to note that focusing only on GHG emissions when assessing mitigation strategies can lead to increases in other environmental impacts. Accordingly, a holistic assessment of all environmental impacts is necessary to avoid burden shifting between GHG emissions and other environmental impacts.

The PUR supply chain uses high-volume chemicals such as ethylene, propylene, and toluene. These chemicals are also used to produce other large-volume plastics. Due to the similar resource basis, the results of this study can therefore inform other plastics and chemical production systems. In particular, combined utilization of renewable resources is promising for a methanol-based industry since both bio-based syngas production and CCU-based methanol production are already at high TRL.[239] Combined utilization would increase resource flexibility and may help in adapting to local resource availability in different regions. Consequently, this study shows that synergies in production reduce the effort required to achieve high GHG reduction in the plastics industry.

In this chapter, we evaluated the environmental benefits and drawbacks of CCU and biomass utilization depending on the availability of renewable electricity and biomass. In doing so, we assumed that renewable electricity and biomass were generated or cultivated to be used exclusively for material purposes in the plastics supply chain. In contrast, Chapter 5 investigates the environmental impacts of alternative carbon feedstocks with limited availability already used in other applications.

Chapter 5

Syngas-from-what - comparative life cycle assessment of syngas from alternative carbon feedstocks

In the following chapter,[a] we identify environmentally optimal pathways for syngas production based on alternative carbon feedstocks. These alternative carbon feedstocks, however, are generally limited and already used for other purposes. Accordingly, we assess the system-wide environmental consequences of using these limited feedstocks by considering their conventional use. Considering system-wide effects is essential for a sound environmental assessment, as these effects may lead to undesirable environmental impacts.[154,240] For this purpose, we provide a consistent comparative LCA of syngas from fossil and alternative carbon feedstocks. We incorporate the various possibilities for combining alternative carbon feedstocks for syngas production by building a bottom-up TCM of value chains leading to syngas.

Section 5.1 provides a brief introduction to the future role of syngas. Next, Section 5.2 introduces the TCM consisting of 59 production processes based on engineering-level data for a detailed comparison between fossil-, bio-, CO_2-, and mill gas-based production. Please note that we also assess syngas from plastic gasification based on simplified assumptions in Appendix C.9. In Section 5.3, we investigate the technical potential of alternative syngas pathways for GHG reduction and identify the climate-optimal production pathways depending on the carbon footprint of electricity. We consider both the direct environmental impacts and the indirect system-wide environmental consequences of alternative syngas production by employing system expansion. Additionally, we discuss eleven impact categories of alternative syngas production and highlight their trade-offs in Section 5.4 before we draw conclusions in Section 5.5.

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[a] Major parts of this chapter are reproduced from:

Bachmann, M., Völker, S., Kleinekorte, J., Bardow, A. Syngas from what? Comparative life cycle assessment for syngas production from biomass, CO_2, and steel mill off-gases. *ACS Sustainable Chemistry and Engineering*, 2023.

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript.

5.1 The future role of syngas

Syngas is already a key intermediate in the chemical industry today, and its market is expected to grow as a precursor to bulk chemicals such as methanol and synthetic fuels from the Fischer-Tropsch process.[241,242] Methanol is a central component of the envisioned future chemical industry as a platform chemical to produce olefins and aromatics for plastics (see Section 2.2). Considering the increasing plastics demand described in Section 2.1, methanol demand is also expected to increase significantly.[4] Synthetic fuels could experience even greater growth in the coming decades as an enabler for GHG mitigation in the aviation and shipping sectors.[243] As a consequence, the global syngas demand is expected to grow with a high compound annual growth rate of 6 %.[244]

Today's syngas is mainly produced by coal gasification or steam reforming of natural gas. This fossil-based syngas production emits large amounts of GHG.[245] Furthermore, the fossil-based carbon stored in the products is usually emitted during disposal at the end of the life cycle leading to additional GHG emissions. Accordingly, achieving substantial reductions in GHG emissions requires syngas based on alternative feedstock.

Although a large proportion of syngas is used chemically[246], current studies mainly evaluate alternative syngas pathways for power generation.[62,247,248] Only a few studies have been published that assess syngas production based on alternative carbon feedstocks. Furthermore, these studies do not assess syngas directly but its material use in methanol, dimethyl ether, or Fischer-Tropsch processes.[164,245,249–252] In a pioneering study comparing alternative syngas production, Maggi et al. combined bio-based and CO_2-based syngas via superstructure optimization.[253] Maggi et al. use energy consumption as the objective function, which is known to be an important metric but does not allow for assessing environmental impacts.[254,255]

5.2 The bottom-up model of alternative syngas production

This study aims to compare the system-wide environmental consequences of syngas production from alternative carbon feedstocks. For this purpose, we conduct a comparative LCA according to the ISO standards.[23,24] This section describes the scope of the syngas production system, followed by the functional unit and the impact assessment methods. A list of all processes and data sources is provided in Appendix C.1.

Scope. The syngas model comprises a cradle-to-grave system boundary (Figure 5.1). However, in a comparative LCA, identical life phases can be neglected. Accordingly, we exclude the syngas use phase from the assessment. For syngas end-of-life treatment, we account for the carbon content of syngas converted to CO_2. Please note that this is a worst-case assumption for GHG emissions as syngas' carbon content may not be released to the atmosphere for a long time, e.g., when used to produce durable products. However, the end-of-life treatment does not compromise the comparability of the results and is only applied to avoid potentially misleading negative carbon footprints.

We use the system expansion approach recommended by the ISO standards to account for the system-wide environmental consequences of alternative syngas production.[23,24] These consequences arise from producing syngas from limited feedstocks already used for other purposes. Thus, as detailed below, the functional unit includes syngas and all products and services from the system expansion.

The system boundary consists of a foreground and a background system. The foreground system is based on engineering-level data of 59 processes enabling a detailed analysis of energy and material flows. Missing elementary flows are determined by mass and energy balances, according to Meys et al. We neglect the environmental impacts of plant construction in the foreground system since the environmental impacts of chemical plants are usually similar for conventional and alternative production pathways.[201] The background system is based on aggregated datasets from the LCA database ecoinvent 3.5 (see Appendix C.1 for details).[202]

Syngas requirements ($\mathbf{H_2/CO}$ ratio). We assume an average molar H_2/CO ratio of 2:1, suitable for methanol production (∼2.15:1) and Fischer-Tropsch synthesis (∼1.95:1), both representing large-scale syngas consumers.[253] The H_2/CO ratio is a simplified representation of the stoichiometry number, which also considers the amount of CO_2 in the syngas. If alternative technologies do not meet the required H_2/CO ratio, the superstructure model allows additional H_2 or CO mixing. We neglect feed or product gas impurities in the assessment (details in Appendix C.3).

Both methanol production and Fischer-Tropsch synthesis require high-pressure syngas of 30 bar or higher.[253] In contrast, the operating pressures of syngas technologies range from 5 bar (dry reforming of methane, short DRM) to 30 bar (steam reforming).[253] Thus, applying syngas in methanol production and Fischer-Tropsch requires additional electricity for compression that we account for using a multi-stage compressor model (details in Appendix C.2). The required syngas temperature for methanol production and Fischer-Tropsch synthesis is 200 °C.[253] We do not consider any temperature requirements since both methanol production and Fischer-Tropsch synthesis

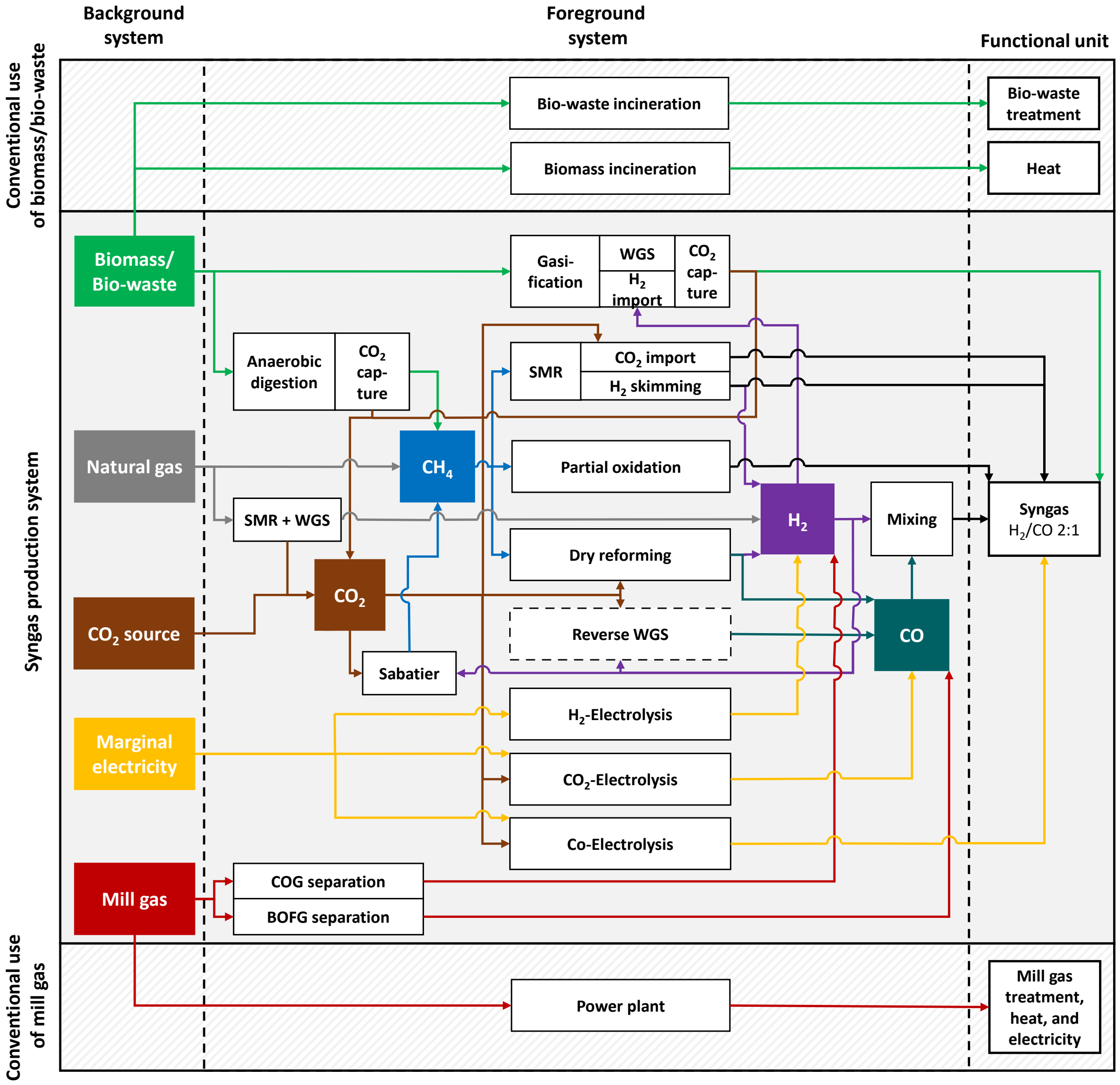

Figure 5.1: Simplified representation of the syngas production system and the conventional use of biomass, bio-waste, and mill gas. The foreground system (center area enclosed by dashed lines) is based on engineering-level data of 59 processes, and data for the background system (left) is taken from ecoinvent.[202] The functional unit is shown on the right. For better readability, only the most important processes and energy and material flows are shown. Furthermore, the syngas' use phase and end-of-life treatment are not shown.

are exothermic processes. Accordingly, the required heat for preheating syngas can be supplied via process integration.

Fossil-based production of syngas. Syngas can be produced from solid, liquid, and gaseous feedstock, with coal (48 %) and natural gas (47 %) being the predominant feedstocks used.[246] For fossil-based production, we consider steam reforming and partial oxidation of natural gas as the best available technologies in terms of GHG emissions.[256] Both partial oxidation and steam reforming operate at 30 bar.[253] Since steam reforming of natural gas leads to an H_2/CO ratio of 3:1, H_2 skimming or CO_2 import adjusts the H_2/CO ratio. H_2 skimming separates additional H_2 for energy or material purposes within the system boundaries. For CO_2 import, additional CO_2 is fed into the reactor to adjust the H_2/CO ratio by the water-gas shift (WGS) reaction. The datasets for fossil-based syngas were derived from the process database IHS Process Economics Program following the procedure from Meys et al. (details in Appendix C.1).[5,257]

Bio-based production of syngas. This study considers lignocellulosic biomass and bio-waste as renewable and low-cost feedstock.[62] We do not consider first-generation biomass to avoid competition with the food industry. Current studies often assume that both lignocellulosic biomass and bio-waste are abundantly available such that their use results in no additional environmental impact.[5,62,247] This assumption may not be justified. As an example, we consider the wood industry: Here, waste products are often used to generate heat, substituting heat from fossil resources.[258] If these waste products are used for syngas production, they are no longer available for heat generation. Accordingly, fossil resources must instead supply the required heat. Therefore, the overall environmental impacts of bio-based production may increase when system-wide interactions are considered.

To examine these system-wide environmental impacts, we define a conservative and an optimistic scenario: The conservative scenario only considers biomass already used elsewhere to show the upper bound of system-wide environmental consequences. The optimistic scenario considers biomass that currently does not displace any other product and bio-waste that otherwise has to be treated. Thereby, we also show the lower bound of environmental burdens.

Conservative scenario for biomass. The conservative scenario considers biomass already used to provide heat through combustion. In particular, we consider wood chips as feedstock. We assume that wood chips are conventionally applied in high-temperature industrial heat processes with a required temperature of 1000 °C, a boiler efficiency of 90 %, and a lower heating value of 18 MJ/kg dry biomass. The demand for high-temperature industrial process heat from biomass is expected to rise significantly in the coming years.[259] To substitute bio-based heat, we use natural gas boilers or resistance heaters depending on the impact of electricity. Assuming high-temperature heat is a worst-case assumption for bio-based syngas since other high-temperature heat sources must supply the required heat.

In the conservative scenario, biomass gasification is used to produce syngas. In particular, we consider a pressurized direct oxygen-steam blown circulating fluidized bed (CFB) gasifier and an atmospheric indirect air-blown dual fluidized bed (DFB) gasifier. The gasification processes results in a pre-adjusted H_2:CO ratio between 1.2 and 1.7. We additionally account for syngas upgrading by WGS and H_2 import, CO_2 capture, and syngas compression to 30 bar (details in Appendix C.2). The required H_2 can be supplied by all other H_2 sources within the system boundaries. Additionally, the model considers biomass drying before gasification if required. The life cycle inventory of biomass gasification and more details can be found in Appendix C.4.

Optimistic scenario for biomass. In the optimistic scenario, we distinguish between marginal biomass and bio-waste. Marginal biomass is assumed to grow solely on marginal land. Thus, the feedstock for syngas production does not displace any other product and therefore leads neither to system-wide interactions nor to indirect LUC emissions. As marginal biomass, we use miscanthus as an example of a perennial energy crop. The marginal biomass is gasified using the same gasifier described in the conservative scenario.

Bio-waste is converted via anaerobic digestion into bio-methane, which substitutes natural gas in fossil-based pathways. The anaerobic digestion model is based on inventory data from Ardolino et al.[247,260] The authors assume the organic fraction of municipal solid waste as the bio-waste source and a treatment capacity of 100 t/day. Furthermore, Ardolino et al. assume landfilling as the conventional bio-waste treatment. Landfilling partially degrades biowaste over time, converting the sequestered carbon to CO_2 and methane. For instance, ecoinvent assumes a degradation rate of about 20 % for a 100-year time horizon.[99] The direct venting of methane, in particular, results in high GHG emissions owing to its high global warming potential. However, most of today's landfill sites are required to have landfill gas collection and flaring systems that oxidize methane to CO_2.[261]

Accordingly, direct GHG emissions from bio-waste incineration are higher than from landfilling since the entire bio-waste carbon content is converted to CO_2. Therefore, the superstructure model applies incineration without energy recovery as the conventional bio-waste treatment. Consequentially, bio-based syngas production avoids emissions from incineration, which is a more optimistic assumption for syngas from bio-waste.

CO_2-based production of syngas. For CO_2 supply, we consider model-intrinsic point sources, i.e., steam reforming for H_2 production, biomass gasification, and anaerobic digestion. The CO_2 is captured by the Rectisol process or by amine scrubbing, which are commonly applied in industry.[262,263]

In addition, and as a best-case assumption, we consider high-purity industrial point sources such as ethylene oxide or ammonia. At these point sources, CO_2 is currently released into the atmosphere. Following Müller et al., we credit capturing the CO_2 that is otherwise emitted into the atmosphere (see Section 2.3.1 for details).[161] For capturing 1 kg of CO_2, the credit is 1 kg CO_2-eq. However, capturing CO_2 requires heat and electricity leading to additional GHG emissions. Therefore, we also account for the electricity and heat demand for CO_2 capture[75] and CO_2 compression to 100 bar.[264]

CO_2 from high-purity point sources may be fully exploited or replaced in the future so that other sources have to be used for syngas production. Therefore, we show results for direct-air capture as a worst-case CO_2 source with the highest energy demand in Appendix C.7. For CCU technologies, we consider the following processes:

- DRM with CO_2 to CO and H_2 yielding an H_2/CO ratio of 1:1,[265]
- reverse WGS of H_2 and CO_2 to CO,[265]
- high-temperature co-electrolysis to CO and H_2 yielding an H_2/CO ratio of 2:1,[245]
- high-temperature CO_2-electrolysis to CO,[266]
- and the Sabatier process that converts CO_2 to methane using H_2 as co-reactant.[267]

The methane from the Sabatier process substitutes natural gas in fossil-based syngas pathways. The CO_2-electrolysis is modeled following Nabil et al. with an energy efficiency of 58 % based on the Haldor Topsoe's eCOsTM unit.[266,268] In contrast, the co-electrolysis has an energy efficiency of 75 % based on process simulations from Linde AG (the LCIs are provided in Appendix C.5).[245] Furthermore, DRM and reverse WGS operate at 5 bar, whereas CO_2-electrolysis and co-electrolysis supply products at 20 bar. We account for additional compression to 30 bar.

Separation of steel mill off-gases for syngas production. Mill gases are off-gases in steel mills from the blast furnace, the coke oven, and the basic oxygen furnace (see Section 2.1.2 for details).[15] This study assumes mill gas compositions from Uribe-Soto et al. (details in Appendix C.6).[14]

For syngas production, the superstructure model considers coke oven gas (COG) and basic oxygen furnace gas (BOFG) as suggested by Shin et al. and separate H_2 from COG and CO from BOFG.[173] Blast furnace gas could also be used as a CO source. However, we focus on the higher-concentrated BOFG as a CO source since common steel mills provide enough BOFG to fully utilize the H_2 from COG for syngas (details in Appendix C.6).[15] COG separation uses a pressure swing adsorption (PSA) as the leading technology for H_2 separation from COG.[15] The PSA achieves an H_2 recovery rate of 90 % with an H_2 purity higher than 99 %. The energy requirements for PSA are estimated using a multi-stage compression to 30 bar (details in Appendix C.2).

For CO separation from BOFG, we consider PSA following Kasuya et al.[269] The PSA accounts for the compression of BOFG to 3 bar for adsorption followed by vacuum desorption at 0.1 bar leading to a CO yield of 90 % and a CO purity of 99 %. Afterward, the CO is compressed to 30 bar to meet syngas requirements.

Due to the high uncertainty of the mill gas separation processes, we vary the electricity consumption of the PSA in a sensitivity analysis. Furthermore, industrial PSA processes usually require an intricate design of multiple beds with different adsorbent layers, which exceeds the scope of this study.[15] Therefore, considering adsorbent consumption is beyond the scope of this study.

Mill gas is conventionally treated by combustion to provide heat and electricity for the steel mill. If mill gas is used to produce syngas instead, heat and electricity must be provided by other means. Again, we use a natural gas boiler or a resistance heater to substitute heat from mill gas treatment. The electricity from mill gas treatment is alternatively supplied by the electricity grid. Furthermore, the remaining COG and BOFG after separation are mixed with natural gas and sent back to combustion for heat and electricity provision, thus reducing the amount of natural gas.

Additional processes. Some processes such as Sabatier and reverse WGS require large amounts of H_2 as co-reactant for CO_2 conversion. For fossil-based H_2, we use steam reforming of natural gas.[202] Alternatively, H_2 can be produced by water electrolysis, enabling a low-carbon pathway to syngas. For water electrolysis, we use data for a polymer electrolyte membrane electrolyzer from Bareißet al. (details in Appendix C.1.[270]

Electrolysis requires large amounts of electricity. Therefore, the implementation of CCU changes the electricity demand. As with the other feedstock, electricity is already used today. Thus, the assessment of CCU technologies should not consider the average regional impact of electricity but rather the marginal impact generated by the additional electricity consumption.[164] The marginal electricity impact is varied in a sensitivity analysis. As a reference, we show the electricity impacts of wind power, photovoltaics, and gas combined cycle power as modeled in ecoinvent 3.5 as well as the forecasted global average for 2030 and 2050.[202,271] To improve readability, we refer to the marginal impact of the electricity grid simply as the electricity impact.

Functional unit and impact assessment method. As a reminder, the functional unit is a means to compare alternative production systems on a common basis. In this chapter, the functional unit is composed of two parts to cover the system-wide environmental consequences of alternative syngas production: First, all syngas pathways must provide 1 kg syngas at 30 bar with an H_2:CO ratio of 2:1. Second, all alternative syngas pathways must provide all additional functions of the conventional production system resulting from the conventional use and treatment of alternative feedstocks. These additional functions include the provision of heat and electricity or the treatment of wastes. We determine the reference flows of these additional functions (Table 5.1) in the following:

In the conservative scenario, a maximum of 1.7 kg of wood chips is required to produce 1 kg of bio-based syngas. This amount of wood chips is conventionally used to provide 27.4 MJ of high-temperature heat. The maximum amount of mill gas per 1 kg syngas is 1.1 kg COG with a heating value of 38.5 MJ/kg and 1.9 kg BOFG with a heating value of 5.4 MJ/kg. We adopt the power plants' electric efficiency of 34 % and the thermal efficiency of 15 % from ecoinvent 3.5 (details in Appendix C.7), resulting in reference flows of 7.5 MJ heat and 17.7 MJ electricity.[202,272]

In the optimistic scenario, 14.4 kg of bio-waste is needed to produce 1 kg of syngas by anaerobic digestion.

We use the environmental footprint 3.0 methods with recommendation levels 1 and 2 (good robustness) to characterize elementary flows.[101,102] In environmental footprint 3.0, GHG emissions are characterized using IPCC characterization factors for

Table 5.1: Functional unit for the conservative and optimistic scenario.

Reference flow	**Unit**	**Conservative scenario**	**Optimistic scenario**
Syngas	kg	1	1
Heat from biomass	MJ	27.4	0
Heat from mill gas	MJ	7.5	7.5
Electricity from mill gas	MJ	17.7	17.7
COG treatment	kg	1.1	1.1
BOFG treatment	kg	1.9	1.9
Bio-waste treatment	kg	0	14.4

a 100-year time horizon as common practice in LCA.[102] At recommendation level 3 (recommended to use with caution), we include land use due to its importance for bio-based feedstocks and resource use as an important indicator for fossil- and CO_2-based technologies. Resource use considers energy carriers and minerals and metals separately.

5.3 The global warming impact of syngas

In the following section, we quantify syngas' GWI based on natural gas, biomass, mill gas, and CO_2 via CCU. As described above, the following two scenarios differ in their conventional biomass use.

Conservative scenario. In the conservative scenario, syngas is produced with the lowest GWI from mill gas, followed by bio-based syngas (see Figure 5.2). Bio-based syngas emits less GHG than fossil- and CCU-based syngas across a wide range of electricity impacts, while CCU-based production only emits less GHG than fossil-based production when low-carbon electricity is used.

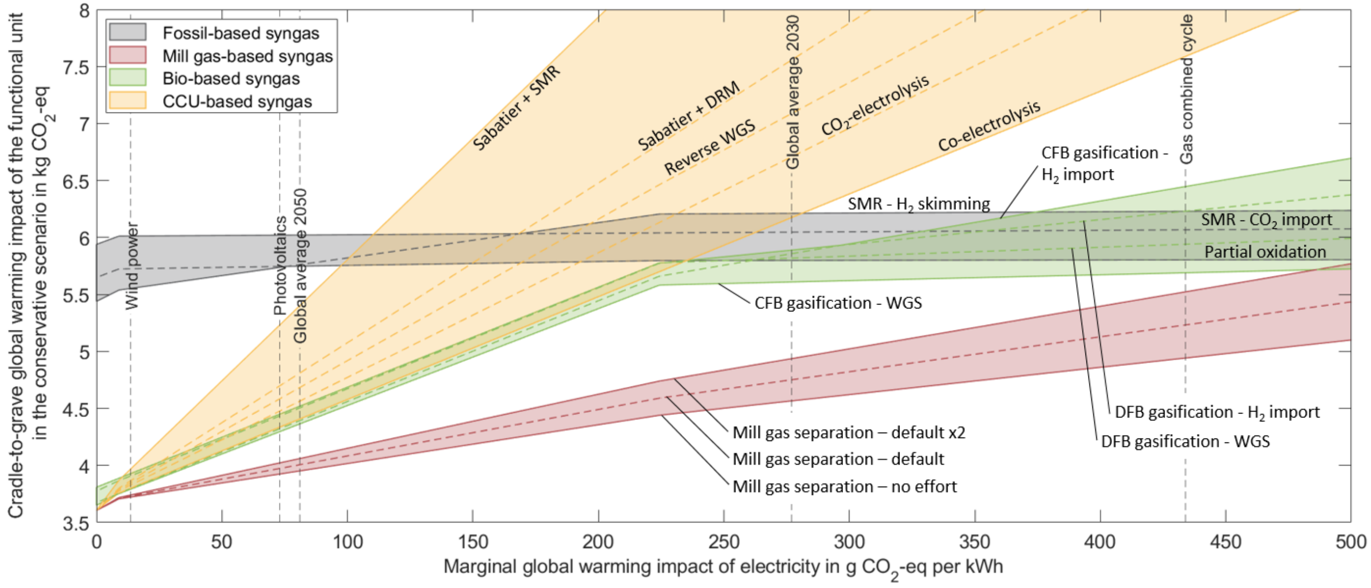

Figure 5.2: Cradle-to-grave global warming impact of the functional unit (Table 5.1) for the conservative scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO_2. The vertical dashed lines show the global warming impact of electricity from wind power, photovoltaics, and a gas combined cycle power plant, as well as the forecasted global average for 2030 and 2050.[202,271]

To obtain syngas from mill gas, H_2 is separated from COG and mixed with CO from BOFG. GWI savings of mill gas-based production result mainly from reducing the conventional BOFG treatment in the steel mill power plant (see Figure C.3 in Appendix C.7): The BOFG combustion emits about 2.1 kg CO_2-eq per kg syngas, which can be reduced to 0.7 kg CO_2-eq by separating 90 % of the CO from BOFG. However, the lower energy contents of the remaining mill gases reduce the electricity and heat output of the steel mill power plant. The missing electricity output is compensated by grid electricity. Accordingly, lower electricity impacts decrease the GWI of mill gas-based syngas. The missing heat output is compensated by natural gas combustion or electricity-driven resistance heaters. For electricity impacts lower than 220 g CO_2-eq/kWh, heat supply switches from natural gas to electricity-based heat. Such electricity impacts are lower than the predicted global average of about 280 g CO_2-eq/kWh in 2030.[271] However, even with carbon-free electricity, the GHG emissions of 3.6 kg CO_2-eq would remain from BOFG and COG combustion (0.7 and 1.5 kg CO_2-eq, respectively) and syngas end-of-life treatment (1.4 kg CO_2-eq). Please note that implementing electric resistance heating in practice can be challenging, both from a technical and economic perspective. Without electrical resistance heating, heat supply switches from natural gas to hydrogen-based heat using hydrogen from water electrolysis for electricity impacts lower than 130 g CO_2-eq/kWh. However, the analysis without electric resistance heating shows the same order of alternative syngas pathways. Furthermore, the sensitivity analysis on the electricity consumption of the PSA shows that mill gas-based production still performs best in GHG emissions for a 100 % higher electricity demand (details in Appendix C.7).

Bio-based production reduces the GWI of syngas compared to fossil-based production, although the functional unit (Table 5.1) ensures that all pathways use the same amount of biomass. Therefore, all pathways receive the same CO_2 credit for the carbon uptake from biomass growth phase (see Figure C.3 in Appendix C.7). Also, biomass gasification for syngas production emits more direct GHGs than fossil-based steam methane reforming or partial oxidation. In contrast, bio-based heat supply emits more direct GHG emissions than heat provision via natural gas or low-carbon electricity. Therefore, overall GHG emissions are reduced when using biomass for syngas production. With carbon-free electricity, bio-based production emits more GHG than all other alternative pathways due to GHG emissions from biomass cultivation. In contrast, all other pathways can switch from bio-based heat to heat from carbon-free electricity.

Bio-based production emits less GHG than mill gas-based syngas for electricity impacts higher than 580 g CO_2-eq/kWh (see Figure C.2 in Appendix C.7). Thus, for the current global average of about 700 g CO_2-eq/kWh[3], bio-based syngas is the best option regarding GHG emissions. For even higher electricity impacts, e.g., coal-based electricity, fossil-based production is the best GWI option since using the alternative feedstock for syngas would have to be compensated by high-impact electricity (see SI for details).

The GWI of CCU-based syngas largely depends on the CCU technology and the electricity impact. CCU-based syngas has the highest GWI of all pathways for electricity impacts higher than the global average in 2030. In 2050, electrochemical CO_2 reduction may achieve similar GHG emissions as bio-based production. However, electrochemical CO_2 reduction is currently at a low technology readiness level between 3-5.[85] Therefore, the environmental impacts are still uncertain for large-scale syngas plants based on electrochemical CO_2 reduction. Reverse WGS or the Sabatier process combined with dry or steam methane reforming require even lower electricity impacts to be environmentally beneficial compared to bio-based production. Especially the Sabatier process requires more steps, which lowers its efficiency. Overall, CCU-based syngas is only environmentally preferable if renewable electricity is used and neither mill gas nor biomass is available for syngas production.

Optimistic scenario. In the optimistic scenario, bio-based syngas production uses marginal biomass or bio-waste as feedstock, either grown solely for syngas production or conventionally treated by waste incineration. Therefore, bio-based production must cultivate the additional biomass or avoids emissions from incineration. However, in contrast to the conservative scenario, the syngas pathways do not provide heat for the functional unit (*cf.* Table 5.1).

Under these optimistic assumptions, bio-based production emits less GHG than any other syngas pathway (Figure 5.3). Biomass gasification performs better than anaerobic digestion for a wide range of electricity impacts since gasification requires less electricity. However, for renewable electricity from photovoltaics or wind power, anaerobic digestion has a lower GWI as it avoids biomass cultivation. All other pathways perform similarly as in the conservative scenario.

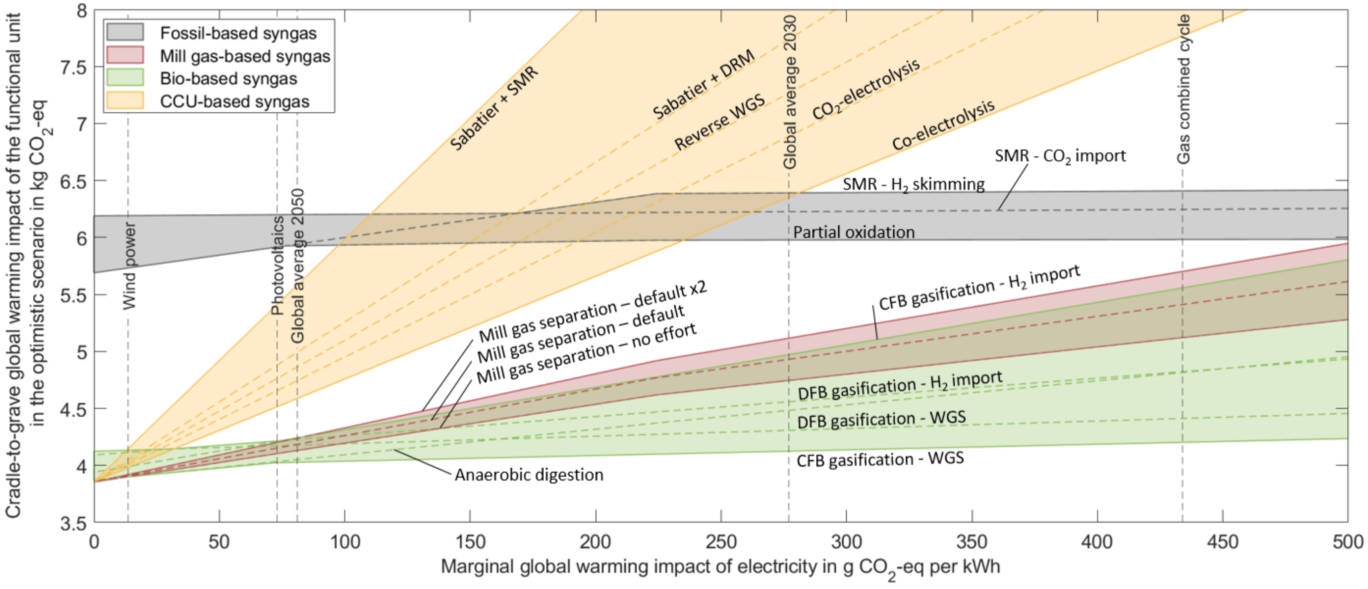

Figure 5.3: Cradle-to-grave global warming impact of the functional unit (Table 5.1) for the optimistic scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO_2. The vertical dashed lines show the global warming impact of electricity from wind power, photovoltaics, and a gas combined cycle power plant, as well as the forecasted global average for 2030 and 2050.[202,271]

5.4 Environmental impacts beyond climate change

Focusing on GHG reductions alone bears risks of increasing other environmental impacts. Thus, we investigate eleven additional impact categories of the environmental footprint 3.0 methods.[101,102] In this section, we focus on the impact categories that either indicate large environmental trade-offs or significant deviations between the conservative and optimistic scenarios. The impact categories are freshwater eutrophication, land use, metal depletion, and ozone depletion (see other impact categories in Appendix C.10). Fossil depletion is not shown as it follows the same trend as ozone depletion since both categories correlate directly with natural gas consumption (see details below). Furthermore, we focus on electricity supply from combined cycle power plants and wind power.

Mill gas-based syngas shows the least environmental trade-offs, with a maximum increase of about 140 % in metal depletion (Figure 5.4). Bio-based and CCU-based syngas indicate significantly higher trade-offs in freshwater eutrophication, land use, and metal depletion, which are discussed in the following.

Freshwater eutrophication results from phosphorus-containing emissions to water and soil. The conservative scenario indicates already significant increases of up to 100 % for bio- and 200 % for CCU-based syngas resulting from higher electricity demands. Biomass cultivation does not lead to trade-offs in freshwater eutrophication since all syngas pathways consume the same amount of biomass (Table 5.1). In contrast, in the optimistic scenario, freshwater eutrophication increases by up to 580 % for bio-based syngas, resulting from additional biomass cultivation.

The high impact of biomass cultivation can also be observed in the impact category of land use. In the conservative scenario, all syngas pathways require the same amount of land. Contrarily, in the optimistic scenario, the cultivation of energy crops increases land use by 66 times. However, land use only increases when biomass is required for gasification. For wind power, the optimal bio-based syngas production switches to anaerobic digestion of bio-waste, which does not require additional land. Therefore, land use can even be reduced by 20 % compared to fossil-based production. For CCU-based syngas, the higher electricity demand also increases land use by up to 260 %.

Higher electricity demands also lead to trade-offs in metal depletion. In the conservative scenario, the higher electricity demands increase metal depletion of CCU by up to 180 %. In the optimistic scenario, the cultivation of energy crops even increases metal depletion by 24 times due to agricultural machinery construction.

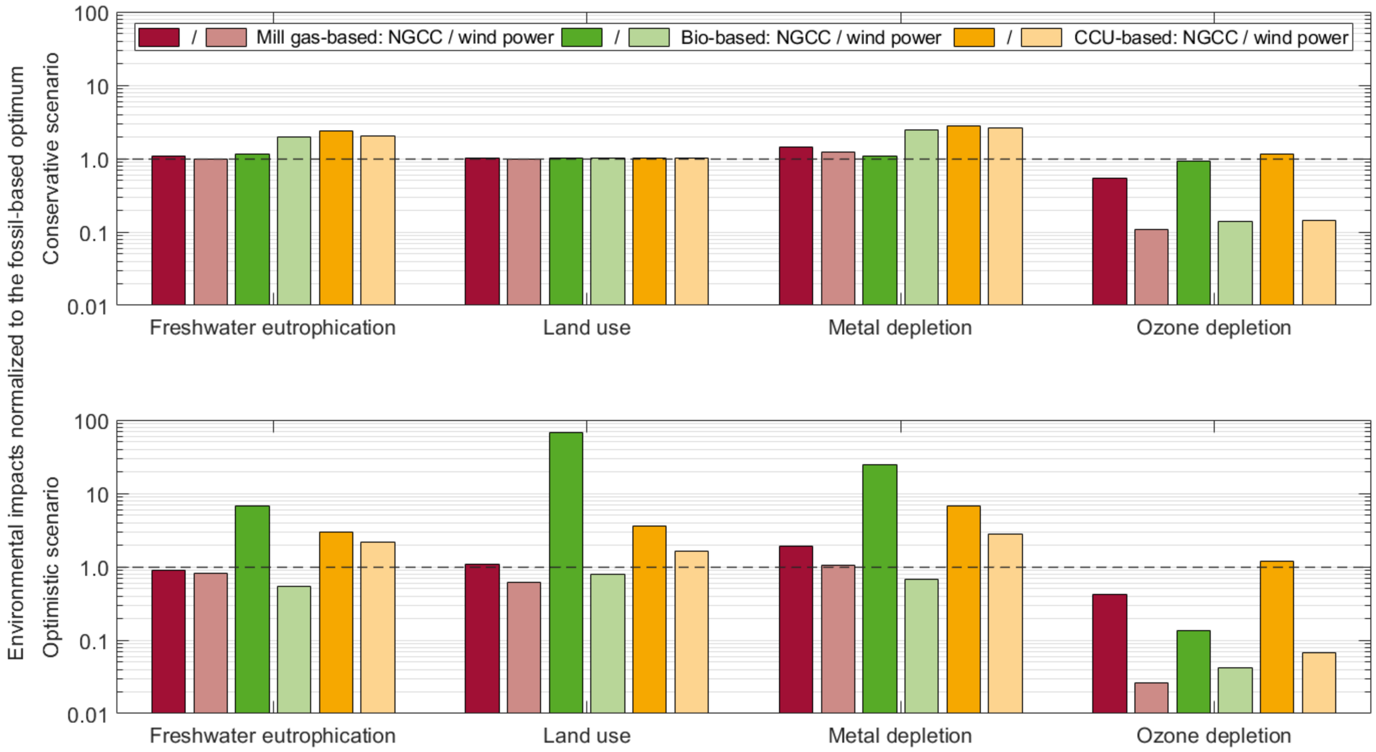

Figure 5.4: Environmental impacts of the optimal mill gas- (red), bio- (green), and CCU- based (orange) production normalized to the environmental impacts of the optimal fossil-based production (horizontal, dashed line). Filled bars represent the results calculated with electricity from a natural gas combined cycle (NGCC) power plant and dashed bars with wind power. For mill gas-based production, the results are shown for the default electricity demand (see Appendix C.6 for details). Please note that results are shown using a logarithmic scale.

Ozone depletion results from emissions of alkanes such as methane. Therefore, fugitive methane emissions from the natural gas supply of the fossil-based syngas pathways have a high impact on ozone depletion. Accordingly, most alternative syngas pathways decrease ozone depletion. However, CCU-based syngas increases ozone depletion by up to 20 %, depending on the electricity supply. Moreover, in the conservative scenario, bio-based production causes almost the same ozone depletion as fossil-based production. The comparable high impact results from substituting bio-based heat with natural gas. In contrast, using wind electricity to supply bio-based heat decreases ozone depletion by 80-90 %.

5.5 Conclusions

Syngas production based on fossil resources emits large amounts of GHG, which can be reduced by switching to biomass, mill gas, or CO_2 as feedstock. While each alternative feedstock has already been assessed individually, this study conducted a consistent environmental comparison between these alternatives. Furthermore, this study provides a sound understanding of the system-wide environmental impacts of using these alternative feedstocks by expanding the system boundaries to the conventional feedstock use.

We found that biomass solely cultivated for syngas production reduces the GWI of syngas most but leads to trade-offs in other environmental impacts, e.g., freshwater eutrophication and land use. These higher environmental impacts result mainly from biomass cultivation and can be avoided by switching to bio-waste as feedstock. In particular, anaerobic digestion of bio-waste combined with low-carbon electricity reduces GHG emissions and also other environmental impacts compared to fossil-based production. Even producing syngas from biomass already used in other applications such as heating does not indicate major environmental trade-offs. However, its potential to reduce syngas GWI is limited by the conventional feedstock use, highlighting the need to consider the conventional use of limited feedstocks in life cycle assessment.

To maximize the reduction of climate impacts, mill gas-based production of syngas seems preferable and has only moderate trade-offs in other environmental impacts. GHG emissions are mainly reduced by avoiding the conventional treatment of mill gases. However, mill gas-based syngas may only be a short-term solution for GHG mitigation due to other mitigation efforts in steel production (details in Appendix C.6).

CO_2-based syngas production reduces climate impacts compared to fossil-based production if low-carbon electricity is used. However, CCU's high electricity demand increases GHG emissions and other environmental impacts compared to bio- and mill gas-based syngas. Accordingly, CCU-based syngas is a viable alternative if CO_2 is the only available carbon source and low-carbon electricity is abundantly available.

This study applies linear optimization to identify climate-optimal syngas production pathways. However, focusing only on climate-optimal solutions may lead to overlooking near-optimal solutions with better performance in economic, social, or even other environmental indicators. Furthermore, model uncertainties, market imperfections, and information asymmetry may also lead to suboptimal decision-making. To address these limitations, future research should apply multi-objective optimization or uncertainty analysis, e.g., by Monte Carlo simulation.[28]

Overall, this study compares the environmental impacts of alternative syngas pathways. The results of this study should encourage further assessments on alternative syngas pathways considering, e.g., economic or regional aspects. Furthermore, the results should guide decision-making and allow industry and policymakers to make informed decisions to decarbonize syngas as a platform chemical of growing importance.

CHAPTER 6

Towards circular plastics within planetary boundaries

Section 2.1 has shown that plastics demand has risen sharply in the last 20 years and is expected to continue to rise through 2050.[1,48] Unfortunately, the increasing demand will intensify the global challenge of plastic pollution.[273–275] Therefore, the United Nations Environment Programme recently pledged to tackle the triple planetary crisis of habitat loss, environmental pollution due to plastic waste, and GHG emissions from plastics production and end-of-life treatment.[2] In particular, mitigating life-cycle GHG emissions of plastics is crucial to cap the global mean temperature rise to 1.5 °C relative to the pre-industrial era.

The previous chapters highlighted the potential for mitigating GHG when using alternative carbon feedstocks in plastics production. Chapter 5 has shown that all alternative carbon feedstocks considered in this thesis can reduce GHG emissions, and Chapter 4 has proven that synergies from combined production can even increase climate benefits. Furthermore, bio- and CCU-based processes have been shown to achieve net-zero GHG emission plastics when combined with recycling rates of 94 % (details in Section 2.3.1).[5] For this purpose, global recycling rates need to substantially increase from their current values, which are estimated to be around 23 %,[37] but might actually be even lower.[155] Even then, achieving net-zero GHG emission plastics still requires large amounts of renewable electricity and biomass.[5,17]

However, the previous chapters have also indicated that utilizing alternative carbon feedstocks shifts environmental burdens from climate change to other environmental impacts. In particular, Chapter 4 has shown that using alternative carbon feedstocks for plastics leads to burden shifting, even when environmental synergies from combined production are fully exploited. Still, previous literature did not quantify whether this burden shifting would compromise plastics' absolute environmental sustainability, i.e., exceed nature's carrying capacities (hereafter referred to as sustainability).[118] Therefore, we address this critical knowledge gap in the following.

In this chapter,[a] we quantify the environmental impacts of circular plastics relative to their ecological budget. In particular, we evaluate the sustainability implications of GHG mitigation strategies for plastics and the role of plastic recycling as a potential enabler for sustainable plastics (Figure 6.1). For this purpose, we first define the goal and scope of this study (Section 6.1), followed by an introduction to the bottom-up model of global plastics production and waste treatment (Section 6.2). The model represents the life cycle of over 90 % of global plastics.[5] In Section 6.3, we detail our assumptions regarding the absolute environmental sustainability assessment and apply economic downscaling principles to define the ecological budget for sustainable plastics, i.e., the plastics industry's share of the safe operating space (SOS). Section 6.4.1 determines the life cycle planetary footprints of plastics for 2030 to highlight the need for a fast transition and for 2050 to assess the challenge of growing plastics demand. In Section 6.4.2, we determine minimum recycling rates to achieve sustainable plastics before we conclude the results of this study in Section 6.5.

6.1 Goal and scope definition

The goal of this study is to assess the planetary footprints of GHG mitigation strategies for the global production of plastics. To calculate planetary footprints, we apply LCA in combination with the planetary boundaries framework as proposed by Ryberg et al.[114] As GHG mitigation strategies, we consider recycling, bio-based production, and production via CCU and compare their planetary footprints to the planetary footprints of fossil-based plastics. We use a bottom-up model covering >90 % of global plastics production for 2030 (and 2050, see Appendix D.3.6). The bottom-up model builds on the plastics production system from Meys et al. and includes plastics production, the supply chain, and the disposal of plastics at the end of life.[5] Please note that we assume that alternative carbon feedstocks are generated or cultivated specifically for use in the plastics industry. Accordingly, we do not consider system-wide environmental impacts of using feedstocks already used in other applications (see

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[a] Major parts of this chapter are reproduced from:

Bachmann, M., Zibunas, C., Hartmann, J., Tulus, V., Suh, S., Guillén-Gosálbez, G., Bardow, A. Towards circular plastics within planetary boundaries. *Nature Sustainability*, 1-12, 2023.

Contribution report: M.B. worked on conceptualization, methodology, data curation, and validation and wrote the original draft and the manuscript. M.B. led the implementation and enhancement of the planetary boundary framework, as well as the application of the downscaling principles to the plastics industry. All work has been conducted in close collaboration to Christian Zibunas, who contributed equally to this publication.

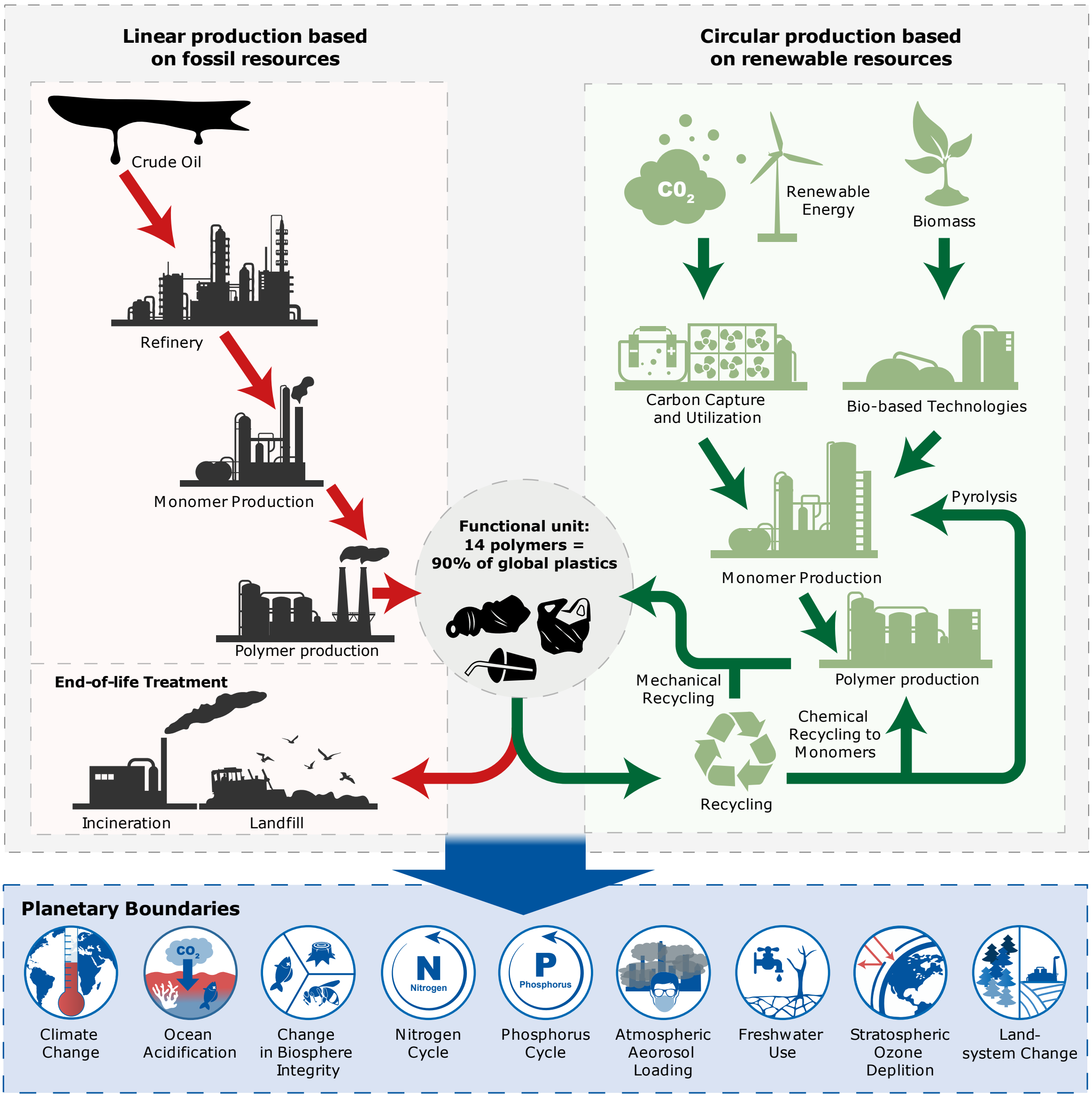

Figure 6.1: Conceptual framework of replacing current fossil-based plastics (left) with renewable plastics (right) based on biomass, CO_2 via carbon capture and utilization, and recycling, and assessing their planetary footprints (bottom)

Chapter 5 for details). Accordingly, determining the planetary footprints of plastics based on limited feedstocks is a task for future research.

In the following, we define the scope, the methodological framework, and the data sources for this analysis.

Functional unit. In this study, the function of the product system is the production and disposal of >90 % of global plastics. To cover >90 % of global plastics, we define the functional unit as the yearly global production and disposal of 14 large-volume plastics summarized in Table 6.1. We estimated the yearly production volumes for 2030 and 2050 based on the production volumes in 2015 and the annual growth rates shown in Table 6.1.

Our assessment includes plastic disposal. However, the production and disposal of plastics do not necessarily occur in the same year. For instance, while polyolefins used for plastic packaging have an average lifetime of six months, the average lifetime of polyurethane used in construction is 35 years (see Section 2.1.2 for details).[37] Including the lifetime of plastics, and thus, the temporal difference between production and disposal would lead to an increasing plastic stock. An increasing stock, in turn, represents a carbon sink during the production year that appears to enable the production of net-negative GHG emission plastics based on biomass or CCU. However, the plastic stock is not a permanent carbon sink, which would be required for producing net-negative GHG emission plastics.[162] To avoid misleading conclusions about net-negative bio- and CCU-based plastics, we assign the planetary footprints from disposal to the year of plastics production. Thereby, we conservatively assess the planetary footprints of plastics.

In addition, we address the challenge highlighted by Guinée et al. that the increasing demand for plastics renders determining plastics' absolute sustainability difficult.[276] We meet this challenge by assuming a steady-state production system with a recurring functional unit in the same amount every year. Thereby, we analyze discrete scenarios with constant consumption levels for plastics. Accordingly, our conclusions depend on the accuracy of the demand forecasts and apply only to the production volumes considered.

System boundaries. We use cradle-to-grave system boundaries, including plastics production and supply chain, potential recycling, and the final disposal at the end of life. Assessing the use phase of plastics is not possible due to a lack of data. The versatile properties of plastics result in a wide range of applications that cannot be represented in a single study. Furthermore, not only the emissions of the use phase would have to be considered (probably being relatively small) but also the system-wide environmental consequences of using plastics in each application compared to other

Table 6.1: Estimated production volumes and growth rates per plastics type. Production volumes for 2030 and 2050 are estimated based on production volumes from 2015.[4,37,87,277,278].

Plastics	**Estimated production volume** in Mt/a 2030	2050	**Annual growth rate** in %
PET pellets (fiber-grade)	151.8	327.5	3.9
Polypropylene	125.7	285.0	4.2
Polyethylene, HD	87.4	174.7	3.5
Polyethylene, LLD	72.6	181.1	4.7
PET pellets (bottle-grade)	66.7	170.5	4.8
Polyvinyl chloride	60.6	113.0	3.2
Polyethylene, LD	34.2	45.9	1.5
Polyurethane, flexible	21.4	33.9	2.4
Polyurethane, rigid	17.1	27.2	2.4
Polystyrene, GP	15.0	19.1	1.2
Polystyrene, HI	15.0	19.1	1.2
Polyamide 66	4.3	11.3	5.0
Polyamide 6	3.5	5.1	1.9
Polyacrylonitrile fiber	2.9	4.7	2.4

materials. Thus, a consequential assessment of the plastics' use phase is desirable but out of the scope of this study.

The plastics supply chain includes several intermediate chemicals such as monomers, solvents, or other reactants. The bottom-up model covers the production of all intermediate chemicals in the foreground system. As a background system, we use aggregated datasets from the LCA database ecoinvent. A list of all intermediate chemicals and all aggregated datasets can be found in Appendix D.1. In addition, the foreground system of the bottom-up model does not include environmental impacts from infrastructure and transportation due to a lack of data. However, we consider the environmental impacts of infrastructure and transportation from other industrial sectors by aggregated datasets, e.g., from electricity generation and biomass cultivation.

6.2 The bottom-up model of the plastics industry

The bottom-up model of the global plastics industry provides production pathways for the 14 largest-volume plastics in 2030 and 2050. The model includes the best available fossil-based technologies in terms of GHG emissions and the following technologies for plastic disposal and virgin production based on biomass and CCU.[279,280]

Plastic waste disposal. The bottom-up model includes three options for plastic waste disposal: landfilling, incineration with energy recovery, and recycling. Plastic waste can occur in several forms: As sorted fraction of municipal solid waste, as mixed plastics and residues from sorting, and as residues from mechanical recycling. For all fractions, we include waste incineration with energy recovery and landfilling.

Landfilled plastic waste is assumed to degrade by approximately 1 % of the contained carbon, which is in line with the ecoinvent database.[202] Mechanical recycling is only modeled for sorted fractions of packaging waste due to impurities of mixed and non-packaging wastes. In contrast, chemical recycling can be applied to all plastic fractions. In this study, we model chemical recycling as pyrolysis to refinery feedstock, i.e., naphtha. The pyrolysis has yields of 29 to 69 % depending on the type of plastic (details in Appendix D.1). Furthermore, we include chemical recycling options to monomers, which are still early stage technologies. To derive the minimal required recycling rate in Section 6.4.2, we apply an optimistic scenario with a 95 % yield of chemical recycling processes following common modeling in life-cycle inventories of chemicals (details in Appendix D.3.3).[281] All calculations are constrained to maximum recycling rates of 94 % since the remaining 6 % are assumed to be the minimal landfilling rate till mid-century.[37] The assumption is based on historical trends in end-of-life treatment.

Bio-based production. Bio-based GHG mitigation is frequently discussed in the literature and is often associated with competition to the food industry.[60] To avoid competition with the food industry, the bottom-up model is restricted to lignocellulosic biomass as feedstock, i.e., energy crops, forest residues, and by-products from other industrial biomass processes, e.g., bagasse. In this study, if not mentioned otherwise, we model biomass as energy crops due to their potential for large-scale application (details in Appendix D.3.4). However, we conduct a sensitivity analysis for other lignocellulosic biomass sources to assess the sustainability of bio-based plastics in more detail.

For each biomass type, we account for the carbon uptake during the biomass growth phase by giving a credit corresponding to the biomass carbon content. We do not consider land-use change emissions since current literature lacks an assessment of land-use change effects on other Earth-system processes besides climate change.

For biomass processing, we include the following high-maturity processes with TRL higher than 7: gasification to syngas and fermentation to ethanol, and the subsequent conversion to methanol and ethylene (Table D.1 in Appendix D.1.2). Methanol and ethylene can be further converted to propylene and aromatics, which all together represent the building blocks for all plastics in this study.

CCU-based production. CCU-based plastics production particularly requires CO_2 and hydrogen. For CO_2 supply, we consider CO_2 capture from highly concentrated point sources within the plastics supply chain. Highly concentrated point sources include the conventional fossil-based processes, ammonia production, steam methane reforming, ethylene oxide production, the bio-based processes, and plastic waste incineration. Capturing from processes within the plastics supply chain is limited by the amount of CO_2 emitted by these processes and avoids the corresponding emissions. For these processes, we considered the energy demand for compressing the CO_2 with 0.4 MJ of electricity.[264] For waste incineration, we consider a decrease in energy output when capturing CO_2. All further CO_2 sources are conservatively approximated by direct air capture (DAC). For 1 kg CO_2 captured via DAC, we include an uptake of 1 kg of CO_2-eq while considering the energy demand of 1.29 MJ electricity and 4.19 MJ heat.[161,271]

Hydrogen for CCU is produced via water electrolysis with an overall efficiency of 67 %.[282] Previous studies have already shown that renewable electricity is required for CCU to be environmentally beneficial (see Section 2.3.1).[17] Thus, we conduct a sensitivity analysis for multiple electricity technologies to assess their influence on the sustainability of CCU-based plastics in Appendix D.3.5.

For CCU-based production, we include high-maturity technologies with TRL higher than 7, such as CO_2-based methanol and methane, as well as subsequent production of olefins and aromatics (Table D.1 in Appendix D.1.2). We do not consider CCS as an additional scenario since fossil resources and storage capacities are ultimately limited. Therefore, CCS may serve as an interim solution for GHG mitigation but stands in contrast to long-term sustainability as the goal of this study.

Pathway definition. In the following sections, we assess nine pathways for the plastics industry towards sustainability: (1) Fossil-based plastics production with the current recycling rate of 23 % serves as a reference. The recycling rate refers to the available plastic waste, i.e., production wastes and post-consumer plastics. Furthermore, we include two pathways combining all circular technologies: Pathway (2) minimizes the climate change impact (climate-optimal), while pathway (3) minimizes the maximal transgression of the plastics industry's share of safe operating space (balanced, Figure 6.2). To assess the impact of switching from fossil to renewable feedstocks, we introduce a (4) bio-based and (5) CCU-based pathway (Figure 6.3). Both pathways include the current recycling rate of 23 %. In addition, we introduce three pathways with the maximum recycling rates of 94 %, where the remaining virgin production is based on (6) fossil resources, (7) biomass, and (8) CO_2 (Figure 6.3). Ultimately, pathway (9) combines biomass, CCU, and recycling and additionally includes chemical recycling to monomers to calculate the minimal recycling rate to achieve sustainable plastics (Figure 6.5).

6.3 Framework for assessing plastics' absolute environmental sustainability

The Planetary Boundaries. We follow the recommendations for absolute environmental sustainability assessment from Bjørn et al. and choose the planetary boundaries framework for the assessment.[118] The planetary boundaries framework suits the study's goal best due to its precautionary definition of environmental thresholds, defining the safe operating space (SOS). We assess eight of the nine Earth-system processes suggested by Steffen et al., namely climate change, ocean acidification, changes in biosphere integrity, the biogeochemical flow of nitrogen and phosphorus (referred to as N-cycle and P-cycle), aerosol loading, freshwater use, stratospheric ozone depletion, and land-system change.[111] We do not assess the Earth-system process of novel entities since neither control variables nor the boundary itself is yet adequately defined.[113,114] We consider the global boundaries for the Earth-system processes in line with the scope of this study.

For the two subprocesses for climate change, namely atmospheric CO_2 concentration and energy imbalance at the top-of-atmosphere, we only consider the energy imbalance at the top-of-atmosphere quantified by radiative forcing. We focus on radiative forcing since the control variable is more inclusive and fundamental, and the global limits are stricter than for atmospheric CO_2 concentration.[111] Thereby, we conservatively assess climate change.

Biosphere integrity is divided into functional and genetic diversity of species. Preserving functional diversity ensures a stable ecosystem by maintaining all ecosystem services. We assess the functional diversity of species as proposed by Galán-Martín et al.[115] The method covers the mean species abundance loss caused by the two main stressors, direct land use and GHG emissions, as a proxy for the biodiversity intactness index. Genetic diversity provides the long-term ability of the biosphere to persist under and adapt to gradual changes of the environment.[111] Genetic diversity is often approximated by the global extinction rate. However, using the global extinction rate does not fully cover variation of genetic composition, resulting in high uncertainties when quantifying genetic diversity.[115] Thus, we focus on functional diversity.

Downscaling of the safe operating space. As the plastics industry accounts for only a fraction of all human activities, we assign a share of the safe operating space (SOS) to plastics. We consider the plastics industry sustainable if it operates within its assigned share of the SOS in all Earth-system processes. To assign a share of SOS to the plastics industry, we apply utilitarian downscaling principles. Utilitarian downscaling principles are tailored to maximize welfare in society.[118] We approximate welfare by consumption expenditure on plastics as an economic indicator for consumer preferences and human needs.[137] An extensive discussion on the other downscaling principles and their implications can be found in Section 2.2.2 and Appendix D.2.3.

While the final consumption expenditures on plastics are negligible, the industry consumes plastics to produce other goods. Accordingly, plastics are produced mostly in the upstream supply chain to support the final consumption of other goods. Thus, consuming other goods induces plastic production. To account for this inducement of plastic production, we used the total global plastics production $x_{plastics}$ to represent the global intermediate and final consumption expenditure on plastics. For this purpose, we use the gross output vector x of the EXIOBASE's product-by-product input-output table of the year 2020.[283] To calculate the share of safe operating space of the plastics industry, we divide the total global plastics production $x_{plastics}$ by the gross world product. The gross world product equals the total global final consumption expenditure. Analogously, we also consider plastics' end-of-life treatment to be consistent with the system boundaries of the environmental assessment. Accordingly, we conservatively assign the entire life cycle emissions of plastics to the production year, although plastics produced in a year may partially be disposed of in later years. By following this procedure, we assign 1.1 % of the global SOS to plastics.

We estimate the share of SOS for the plastics industry for 2030 and 2050 based on data for the year 2020. Accordingly, we assume that the plastics industry's market share and, thus, its share of SOS does not change in the coming years despite the increasing production volume of plastics. Thereby, we implicitly assume that all industries grow equally economically. Alternatively, economic forecasting models could estimate future market shares of plastics. However, applying economic forecasting models is complex, and the results would still be highly uncertain, especially if industry pursues low-carbon technology pathways. Therefore, estimating future market shares is beyond the scope of this study.

6.4 Reducing plastics' planetary footprints

In the following sections, we quantify the planetary footprints for fossil-based plastic and plastics based on renewable carbon feedstocks. As alternative carbon feedstocks, we use biomass, CO_2, and plastic waste. In Section 6.4.1, plastic waste can only be treated by mature recycling technologies, i.e., mechanical recycling and chemical recycling via pyrolysis. In Section 6.4.2, we additionally assess the potential of emerging chemical recycling to monomers.

6.4.1 The planetary boundary footprints of plastics

If plastics production remains fossil-based, the plastics industry strongly exceeds its assigned share of SOS, even using best available fossil technology and the current recycling rate of 23 % (grey bars in Figure 6.2). In particular, the share of SOS is exceeded by 38 times in climate change (42 % of the global SOS), 12 times in ocean acidification (14 %), two times in biosphere integrity (3.8 %), and one time in aerosol loading (2.5 %). Notably, a high share of today's plastics production is coal-based, additionally worsening environmental impacts compared to the assumed best available fossil technologies.[42] The other planetary footprints remain within the allocated share of SOS (for the excluded category of novel entities, see discussion). The high impacts on climate change, ocean acidification, and biosphere integrity result mainly from CO_2 emissions from plastic waste treatment (60-62 %), whereas aerosol loading is primarily due to naphtha production (92 %) and its particulate matter emissions. The drastic overshoot of the assigned share of the CO_2-related Earth-system processes renders fossil-based plastics highly unsustainable and emphasizes the urgency for GHG mitigation in plastics production and end-of-life treatment.

A climate-optimal plastics production would employ biomass and recycling: Biomass is primarily converted to methanol as a precursor for plastic monomers, while mechanical recycling treats packaging waste and chemical recycling via pyrolysis converts non-packaging into refinery feedstock (details in Appendix D.3.1). This climate-optimal pathway remains within its share of SOS in climate change, ocean acidification, and aerosol loading. However, the high share of bio-based plastics worsens biosphere integrity and the biogeochemical flows of nitrogen (N-cycle) to about 5-6 % of the global SOS, exceeding the share of SOS assigned to the plastics industry by about four times (yellow bars in Figure 6.2). Biosphere integrity deteriorates mainly due to biomass cultivation requiring land occupation, which causes habitat loss and corresponding loss of biosphere integrity. The impacts on the N-cycle footprint result from nitrogen-containing fertilizers for biomass cultivation. The climate-optimal production mini-

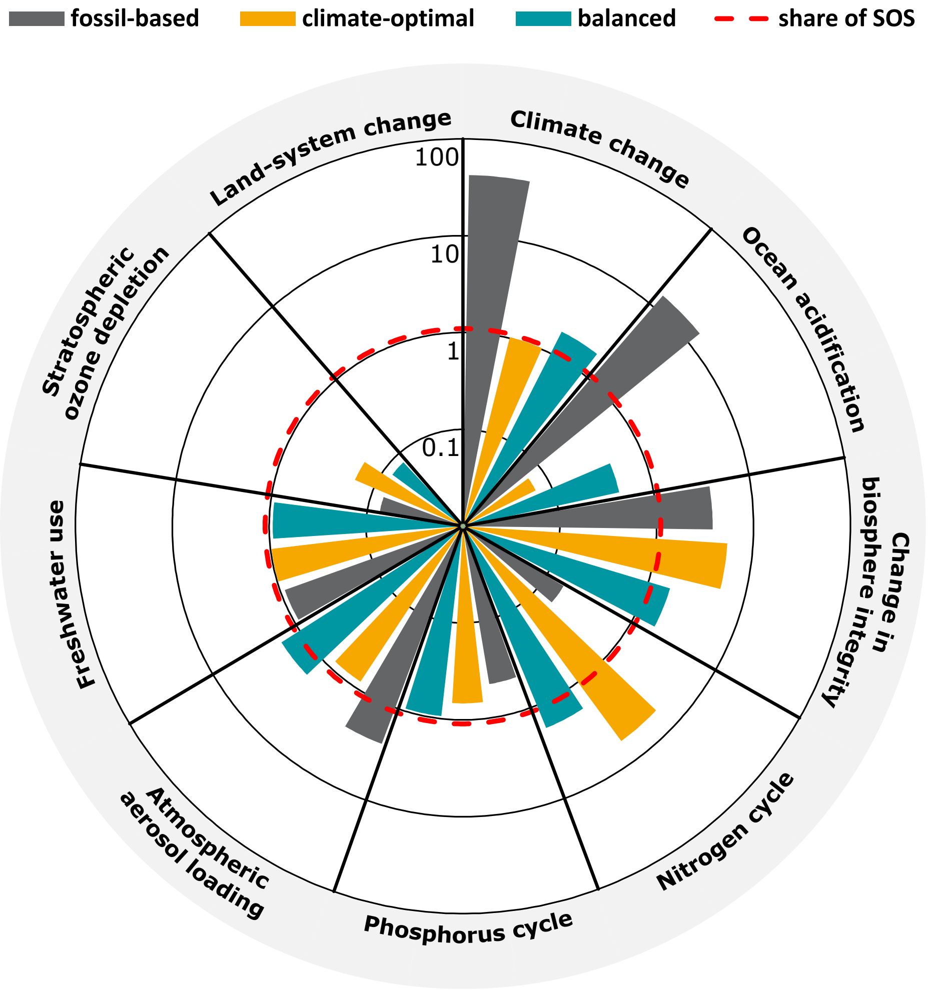

Figure 6.2: The planetary footprint of the plastics industry for three pathways. The pathways comprise a fossil reference (fossil-based), the optimal combination of circular technologies that minimizes plastics industry's global warming impact (climate-optimal), and the optimal combination of circular technologies to minimize the maximal transgression of the plastics industry's share of safe operating space (balanced). The planetary footprints are calculated for production volumes in 2030. The planetary footprints are shown as % of global SOS. The share of safe operating space assigned to the plastics industry (1.1 %) is highlighted in red (share of SOS).

mizes biomass consumption by maximizing recycling rates up to the limit imposed by assuming 6 % of residual landfilling (details in Section 6.2).[37] Still, a climate-optimal plastics industry is unsustainable when assuming an economically-assigned share of SOS.

Focusing on climate change while assessing multiple objectives introduces an unnecessary bias. Accordingly, we assess a balanced solution that minimizes the maximum transgression across all Earth-system processes (turquoise bars in Figure 6.2). The balanced solution combines bio- and CCU-based production with maximum recycling rates. Compared to the climate-optimal solution, 72 % of methanol production switches from biomass utilization to CCU. The CCU route uses hydrogen from water electrolysis and CO_2 from the remaining biomass gasification and incineration processes (details in Appendix D.3.1). However, even the balanced solution transgresses the assigned share of SOS for climate change and the N-cycle footprint by 66 % and biosphere integrity and aerosol loading by about 55 %. Additionally, the biogeochemical flows of phosphorus (P-cycle) increase to 87 % of the assigned share of SOS due to emissions of phosphorus and phosphorus-containing substances from biomass cultivation and electricity generation. Accordingly, even the balanced solution does not lead to sustainable plastics within the environmental thresholds.

In the following, we, therefore, analyze the contributors to the overall planetary footprints of the balanced solution (recycling, biomass utilization, and CCU) in more detail to identify potential levers for additional improvement towards sustainable plastics.

Recycling enhances the sustainability of plastics. Maximizing recycling rates from currently 23 to 94 % reduces all planetary footprints by 10 - 49 % for fossil-based plastics, 33 - 83 % for bio-based plastics, and 8 - 58 % for CCU-based plastics (grey, green, and blue bars in Figure 6.3). Thus, recycling does not trigger any significant burden shifting in any scenario. However, even the maximum recycling rates are insufficient to achieve sustainability due to material losses of current mature technologies (Figure 6.3), which must be compensated by virgin production and ultimately lead to the transgression of the planetary boundaries.

The maximum recycling rate of 94 % includes 39 % mechanical recycling of pure plastic mono-streams and 55 % chemical recycling of mixed plastics via pyrolysis. Chemical recycling treats plastics not suitable for mechanical recycling due to contaminants, additives, or their inability to be reprocessed.[11] Material losses result from chain degradation in the mechanical recycling[8] and moderate yields of the pyrolysis-based chemical recycling of mixed plastics.[284,285] Due to the material losses, recycling 94 % of all plastic waste corresponds to an effective recycling rate of 70 %, i.e., 70 %

of the waste is reused in plastics production. The chemical recycling of polymers such as polyethylene or polyvinylchloride is particularly challenging due to the strong carbon-carbon bonds in the polymer backbone. Furthermore, deconstructing plastic waste to pyrolysis oil and other hydrocarbons requires the re-production of monomers, resulting in increased impacts. Overall, the plastics' planetary footprints could be further reduced if recycling yields increase, either by improving the considered mature recycling technologies or by applying highly selective emerging technologies such as solvolysis or enzymatic hydrolysis (Figure D.2 in Appendix D.3.3).[286]

Bio- and CCU-based plastics can reduce climate change. The inefficiencies of current plastic recycling and the residual landfilling require the virgin production of plastics. Switching the remaining virgin production from fossil resources to biomass or CO_2 as feedstock reduces climate change to 1.0 and 2.3 % of the SOS, respectively (green and blue bars in Figure 6.3). The bio-based production, which corresponds to the climate-optimal solution from Figure 6.2, complies with the assigned share of SOS for climate change, since the carbon uptake during biomass growth offsets CO_2 emissions from plastics production and waste treatment. The remaining footprint results from fossil resource use in biomass cultivation (see Appendix D.3.2).

The CCU-based production still exceeds its assigned SOS for climate change due to the large amounts of electricity needed for hydrogen generation through water electrolysis.[282] Accordingly, previous studies found the carbon footprint of the electricity mix to be crucial for GHG mitigation.[7,17] Even the electricity mix in 2030 from the IEA Net-zero 2050 scenario[63] leads to a climate-impact of CCU-based production that is 47 % higher than fossil-based production (dark blue bar in Figure 6.3). Thus, in the following, we assume wind power representing a best-case renewable energy mix for GHG emissions and thereby assess CCU's maximum potential to reduce plastics' planetary footprints (light blue bar in Figure 6.3).

Mitigating burden shifting from bio-based plastics. Using biomass for the remaining virgin plastics production leads to an unsustainable burden shifting from climate change to other Earth-system processes if energy crops are used (green bars in Figure 6.3). Impacts on biosphere integrity increase due to higher land occupation. Furthermore, the N-cycle footprints results from fertilizers for biomass cultivation, stressing the importance of fertilizer management to reduce nitrogen surpluses.[287] Similarly, 70 % of the P-cycle footprint results from phosphorus-containing fertilizers for biomass cultivation. Biomass cultivation also causes 80 % of aerosol loading (Figure 6.4), of which 52 % originates from agricultural machinery (see Appendix D.3.4 for details).

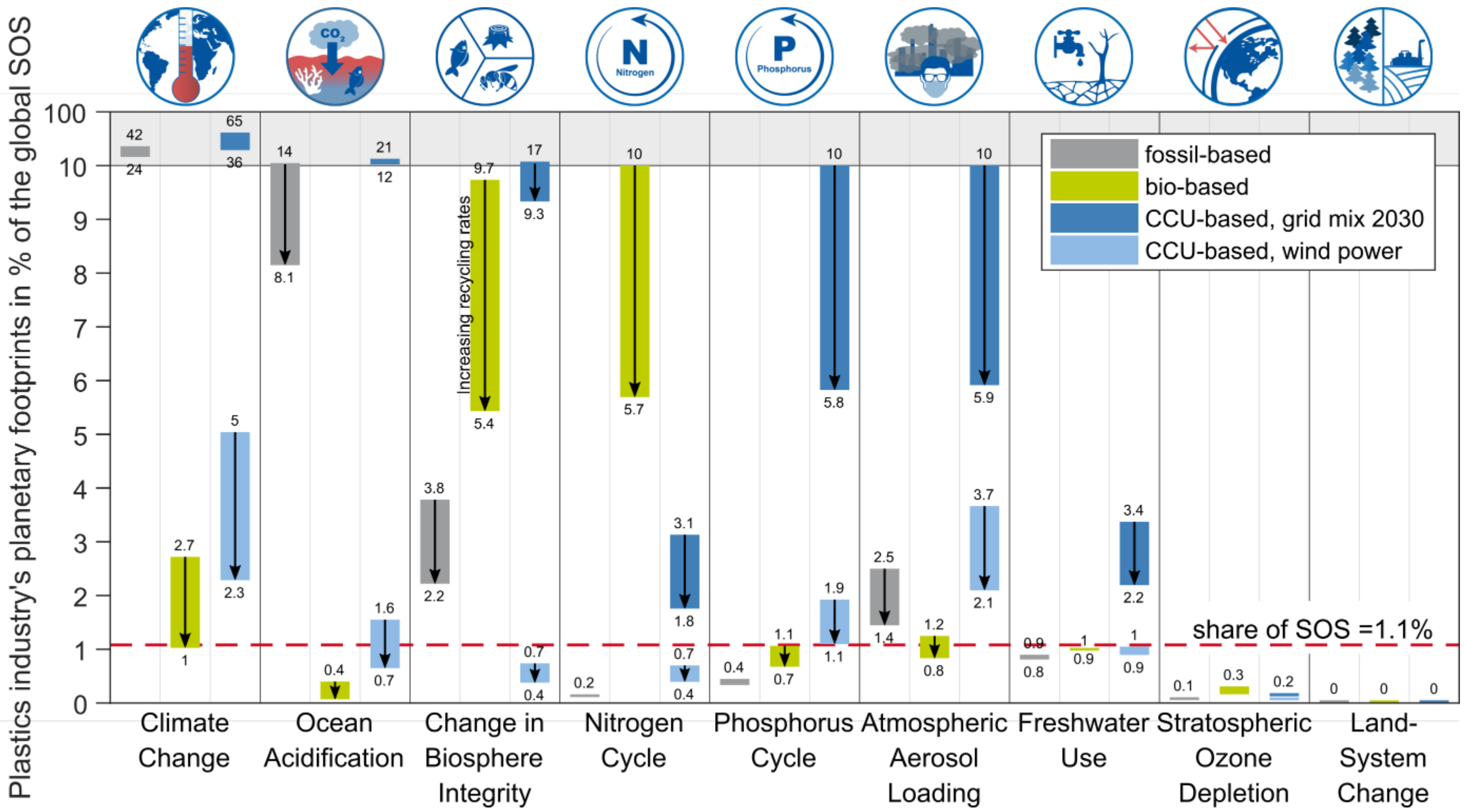

Figure 6.3: **The planetary footprint of the plastics industry for three pathways.** The planetary footprints are calculated by minimizing the environmental impact of climate change for production volumes in 2030. The pathways include fossil-based (grey), bio-based (green), and CCU-based (light and dark blue) plastics, with recycling rates corresponding to the current value (upper value) and the maximum of 94 % (lower value). The only exception is the freshwater use of bio-based plastics, where the lower value represents the current recycling rate. Arrows indicate increasing recycling rates. The dark blue bars for CCU-based plastics show planetary footprints when applying the grid mix in 2030 from the International Energy Agency's Net-zero 2050 scenario, and the light blue bars assume wind power to represent a decarbonized grid mix.[63]

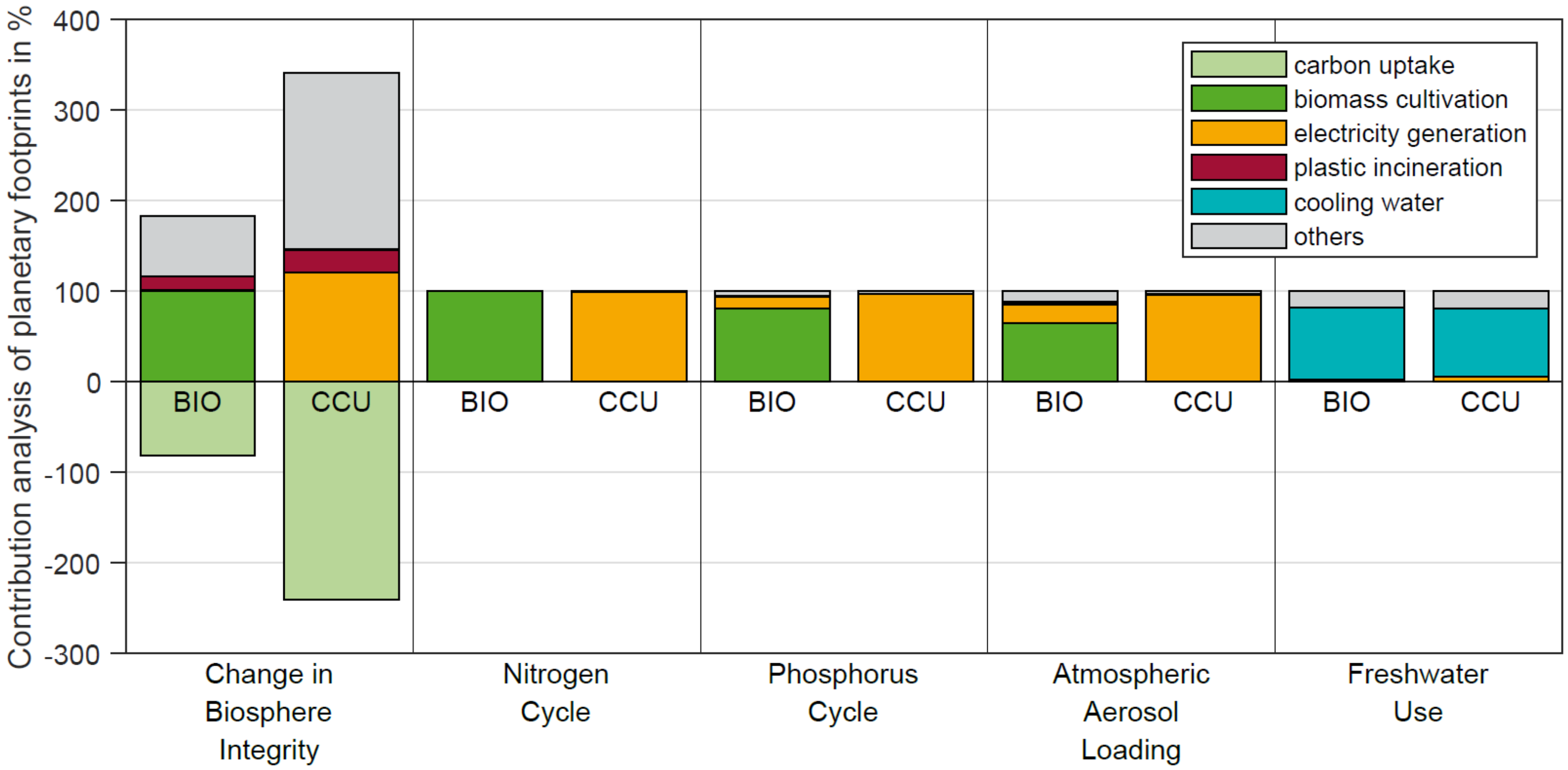

Figure 6.4: **Contribution analysis of the planetary footprints of the plastics industry.** The figure shows the process contribution to the planetary footprints in biosphere integrity, nitrogen cycle, phosphorus cycle, atmospheric aerosol loading, and freshwater use. For all other planetary footprints, see Figure D.1 in Appendix D.3.3. The left of each pair shows the pathways based on biomass (BIO), and the right shows the pathway based on CCU, both employing maximum recycling rates. The net footprints correspond to the lower value of the green and light blue bars in Figure 6.3.

Freshwater use considers the consumption of blue water, i.e., water sourced from surface or groundwater resources. Evaporated cooling water for heat removal in chemical processes contributes to 80 % of freshwater use. In contrast, process water and irrigation of biomass only have a minor impact (Figure 6.4). Furthermore, the planetary footprints of ozone depletion and land-system change are low and within the share of SOS for all production pathways (Figure 6.3). The footprint in land-system change is low despite the land use for biomass cultivation of 1.15 m^2 per kg of plastics. This land is assumed to be cropland for the considered energy crops, which thus do not require the transformation of forested land (see Appendix D.3.4 for details). However, the control variable of the land-system change planetary boundary only considers the transformation of forested land, while the literature suggests to assess land-system changes beyond forested land in the future.[288] Still, the observed land-use requirements from bio-based plastics already contribute to the biosphere integrity impact (Figure 6.4).

Overall, the planetary footprints of bio-based plastics mainly result from biomass cultivation (Figure 6.4). A sensitivity analysis for multiple biomass sources shows environmental trade-offs. (Figure D.3 in Appendix D.3.4): Lignocellulosic feedstocks from forestry reduce fertilizer demand, decreasing the N-cycle footprint (<0.6 % of the SOS), while their lower yields increase land occupation and, thus, losses in biosphere integrity (4 - 20 % of the SOS). Furthermore, certain biomass feedstocks might not be suitable for large-scale plastics production due to limited availability. Accordingly, using multiple biomass feedstocks could help to ensure sufficient availability while keeping negative trade-offs at a minimum.

Mitigating burden shifting from CCU-based plastics. CCU-based plastics production increases aerosol loading to 2.1 % and P-cycle to 1.1 % of the global SOS even when assuming wind power (light blue bars in Figure 6.3). Thus, basing the remaining virgin production solely on CCU is unsustainable regarding the assigned share of SOS. Aerosol loading originates 95 % from electricity generation primarily due to coal-based steel production for wind turbines. Electricity generation also causes 96 % of the P-cycle footprint (Figure 6.3). The emissions of phosphorus-containing substances originate from the construction of wind turbines. The wind turbines' P-cycle footprint is linked to copper mine tailings (26 %) and coal-based steel production (48 %). However, wind turbines will not be the only large-scale renewable energy source globally. A sensitivity analysis showed that photovoltaics and geothermal power would increase the planetary footprints of climate change to 21 % and 10 % of the global SOS and the P-Cycle footprints to 7.7 and 3.0 % of the global SOS, respectively (Figure D.4 in Appendix D.3.5). In contrast, hydro, nuclear, and wind power are more promising technologies towards the sustainable production of CCU-based plastics, all having similar planetary footprints. The analysis shows that improving sustainability requires reducing environmental impacts from the construction of electricity-generation technologies.

6.4.2 Towards sustainability by improving recycling processes

The plastics industry can significantly reduce its planetary footprint by switching the feedstock from fossil resources to a combination of plastic waste and renewable resources. Recycling reduces the demand for renewable resources and thus is the key enabler to mitigate burden shifting. Therefore, increasing circularity via recycling technologies is currently the most promising approach to mitigate GHG emissions and simultaneously improve sustainability (Figure 6.3). Yet, current recycling technologies fail to achieve sustainability in the plastics industry.

We, therefore, explore the potential of increasing recycling process yields to improve the sustainability of plastics. For this purpose, we define an optimistic scenario to assess emerging chemical recycling technologies by assuming a yield of 95 %. Such high yields are optimistic, given that the highest reported yields range from 70 - 90 %.[5,289–291] However, the 95 % yield complies with the default assumption for chemical processes in the well-established LCA-database ecoinvent.[202] Moreover, incumbent chemical processes achieve even higher yields, e.g., up to 99 % for conventional methanol and acetic acid production.[292] In addition to the 95 % yield, the optimistic scenario considers wind power as the source of electricity, while energy crops represent biomass due to their ability for large-scale application.[293]

This optimistic scenario indicates a potential for producing sustainable plastics in 2030 (Figure 6.5): The minimum recycling rate that achieves sustainability is about 75 %, with 39 % of the plastics being recycled mechanically and 35 % chemically. Lower recycling rates increase the demand for renewable resources to the extent that the assigned share of SOS would be transgressed due to aerosol loading from electricity supply or the N-cycle footprint from biomass supply. Under the minimum recycling rate, the plastic industry consumes 14.3 EJ of wind power and 3.5 EJ of biomass compared to the 21.6 EJ of naphtha for the fossil-based plastics industry under current recycling rates and 10.5 EJ for maximum recycling.

Without biomass, a sustainable plastics industry requires a minimum recycling rate of 82 %, consuming 15.3 EJ of wind power. Accordingly, the optimistic scenario allows producing circular CCU-based plastics with-in planetary boundaries in 2030. The demand for wind power can be decreased to 8.6 EJ by maximizing recycling rates to 94 %. However, reducing the demand for wind power even further while complying with the assigned share of SOS requires biomass. Ultimately, reducing wind power is limited to about 2.8 EJ at the maximum recycling rate and a biomass demand of 3.9 EJ. Requiring more than 3.9 EJ of biomass exceeds plastics' share of SOS in biosphere integrity. Thus, circular bio-plastics cannot achieve sustainability.

In summary, high recycling yields enable multiple sustainable pathways for 2030 when assigning the plastics industry's share of SOS based on economic indicators. However, the development and scale-up of such recycling technologies require time. Thus, reaching market readiness by 2030 is hardly achievable. In addition, covering a major share of end-of-life treatment seems unrealistic. Therefore, we extend our assessment to a scenario for 2050 (Figure D.5 in Appendix D.3.6).[37] In the 2050 scenario, the plastics industry's planetary footprints increase due to higher demand for plastics. Thereby, the plastics industry exceeds its assigned share of SOS even with high recycling yields. This finding suggests that the remaining virgin production needs to reduce its environmental impacts. Otherwise, 2050's demand will compromise plastics' sustainability. Still, recycling is the key towards environmentally sustainable plastics as it keeps virgin production to a minimum.

Together, the assessments for 2030 and 2050 emphasize the potential of high recycling yields and the challenge of growing plastics demand for achieving sustainable plastics. However, the growing plastics market is not only a challenge but may also alter the allocation of the SOS. If the plastics market grows faster than the average economy, its contribution to the economy will grow. Consequently, plastics industry's share of SOS would increase if economic indicators were used for downscaling. However, using economic indicators for downscaling is controversial (see the following discussion, Section 6.5). Nevertheless, a growing recycling market could additionally increase the value of the plastics market by making plastic waste a valuable resource.

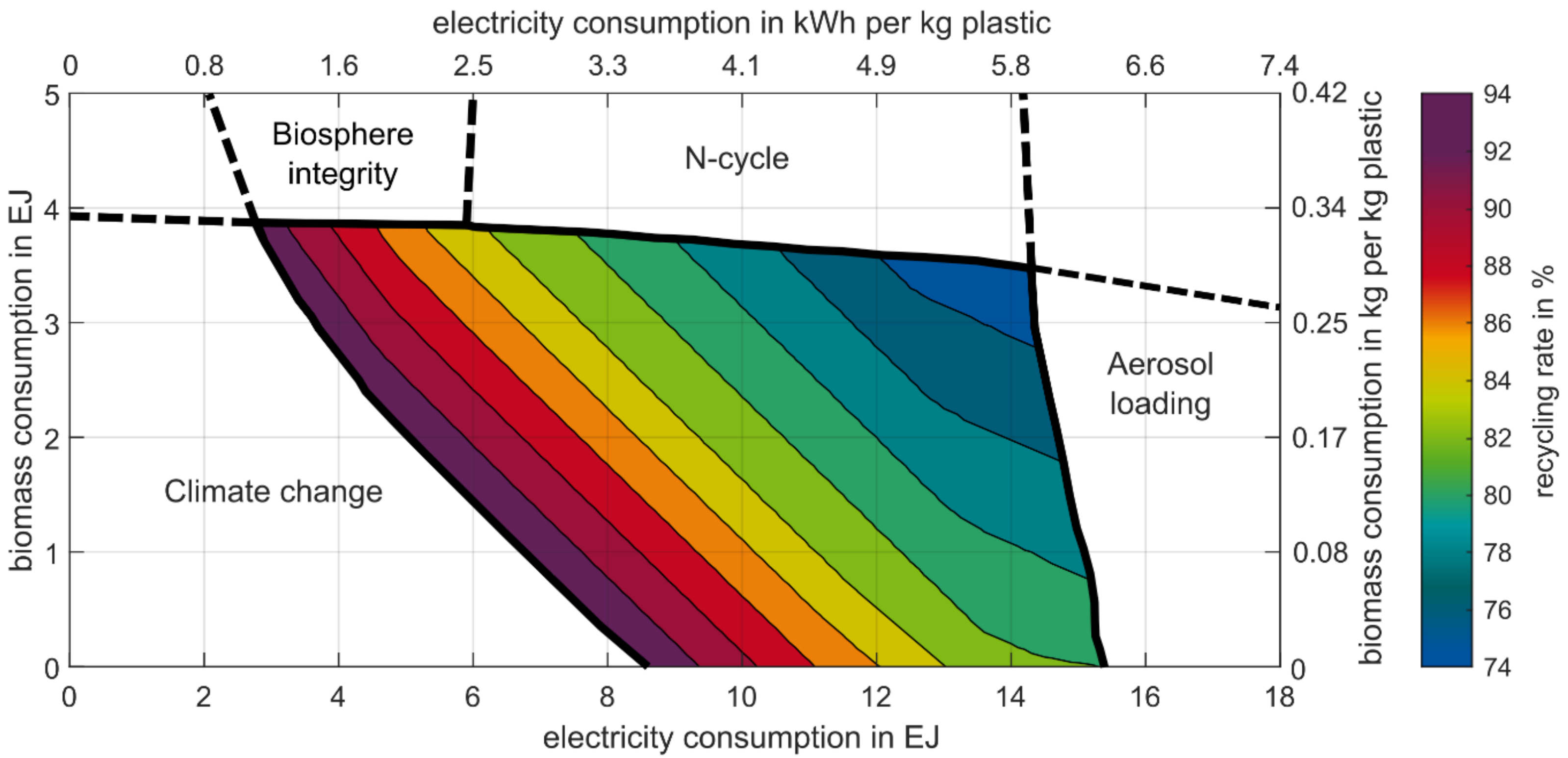

Figure 6.5: **Absolute environmental sustainability of plastics as a function of renewable resource consumption and recycling rates.** The planetary footprints are calculated for production volumes in 2030. The plastics industry's assigned share of the safe operating space (SOS) is limited to 1.1 % for all Earth-system processes. The colored area represents the zone of sustainable plastics where all planetary footprints are below the assigned share of SOS. Each point in the colored zone represents a plastics industry that consumes wind power (x-axis) and biomass (y-axis) at various recycling rates (color gradient). In contrast, plastics are considered unsustainable in white areas. Labels of the lines surrounding the solution space refer to the planetary footprint exceeded first when leaving the solution space. Chemical monomer recycling technologies are assumed to have a 95 % yield (see Appendix D.3.3 for details).

6.5 Conclusions

This study determines the absolute environmental sustainability of GHG mitigation strategies for plastics by combining a bottom-up model of the plastic industries with the planetary boundary framework. Key assumptions for the assessment concern the yield of recycling processes, biomass feedstocks, and renewable electricity generation. Furthermore, the share of SOS of the plastics industry, and thus the sustainability threshold for plastics, is assigned based on consumption expenditure.

Our results show that combining high recycling rates with renewable feedstocks improves plastics' absolute sustainability. If the plastics industry achieves a 74 % recycling rate with advanced recycling technologies in 2030, plastics can comply with their assigned share of the SOS and be considered absolute environmentally sustainable regarding the considered eight planetary boundaries. The remaining virgin plastics production would predominantly rely on CO_2 and renewable electricity from wind, hydro, or nuclear power. A smaller portion of plastics would come from biomass.

The required recycling rate contrasts with today's recycling rates of less than 23 %, highlighting the need to foster recycling through efficient policies. For instance, a barrier to increasing recycling rates is the mismanagement of plastic waste. Mismanagement of plastic waste often occurs in low- and middle-income countries, e.g., by open burning, which is additionally associated with human health issues.[1,294] As stated by OECD, fostering recycling and reducing mismanagement requires the development of recycled plastic markets promoted by push-and-pull strategies.[1] A suitable push strategy could extend plastics producer responsibility beyond the factory gate, whereas pull strategies could set design requirements or targets for recycled plastic content in new products. The design of plastic products already determines their current recycling ability and, thus, their sustainability. Products made of pure plastics can already be treated efficiently by mature mechanical recycling, while mixed plastics must be treated by less efficient pyrolysis. However, the high recycling rates, technological developments, and favorable policies will hardly be achievable by 2030. In contrast, these requirements might be achievable by 2050 but will still be insufficient to cope with the expected growth of the plastics market, as shown by the scenario for 2050 (see Figure D.5 in Appendix D.3.6).

High recycling rates reduce renewable feedstock consumption and the corresponding environmental impacts. The remaining feedstock has to be supplied by renewable resources, i.e., biomass or CO_2 via carbon capture and utilization. However, current farming practices limit the share of bio-based production for sustainable plastics. Increasing the share of bio-based plastics requires promoting practices that close nutrient cycles and push the sustainable intensification of agriculture (details in Appendix D.3.4.[287]

CCU-based plastics rely heavily on renewable electricity. In this study, environmental sustainability could only be achieved using wind, hydro, or nuclear power, whereas even optimistic scenarios for future grids fail to achieve sustainability. Using nuclear power raises social and political concerns[295], regional topography limits the large-scale application of hydropower (see Appendix D.3.5), and wind power is intermittent, challenging the mostly continuous production of plastics. However, the analysis shows the potential to combine several low-carbon electricity sources. If required, the dependence on renewable electricity can be reduced by combining CCU- and bio-based production, which also increases feedstock flexibility.

The availability and environmental impact of biomass and renewable electricity vary by region. In addition, waste management systems show large regional variations in recycling efficiencies and emissions from waste incineration.[1] Therefore, future studies should focus on regionalized assessments that address regional boundaries and deviations in ecosystem functions and species richness.[296]

Assessing regional boundaries requires further downscaling. In this study, the globally-averaged economic indicator of consumption expenditure was chosen to assign a share of the SOS (1.1 %) to the plastics industry. However, economic indicators differ widely by region. In particular, low-income countries show other consumption behaviors by spending a higher share of their expenditures on fundamental needs such as food or healthcare. Since the purchasing power of these countries is low, their fundamental needs are underrepresented by a global average. A regionally-adapted indicator of consumption expenditure results in a lower share of SOS from initially 1.1 to 1.0 % (see Appendix D.2.3), which would add to the pressure on the plastics industry to reduce its planetary footprint. In addition, applying economic indicators themselves to represent human needs is widely discussed:[118,297] Even regionally-adapted economic indicators assign a high share of the SOS to upmarket goods and poorly represent some fundamental needs that a sustainable society must secure, e.g., access to water. It is argued that these fundamental needs should be given a higher weight, which may even increase the challenge for the plastics industry.[118,297]

At the same time, plastics represent a crucial element in essential sectors such as healthcare, where they are indispensable in daily business. Thus, the utility of plastics may exceed its relatively low economic value, which has to be considered for a sound assignment of the SOS. Furthermore, economic downscaling does not give room for emerging industries that society does not spend money on today but might be essential for a future sustainable economy. Overall, there is currently no scientific consensus on how to assign a share of the SOS to an industrial sector yet economic indicators are often used for downscaling.

Therefore, we also discuss non-economic downscaling principles in Appendix D.2.3. For instance, downscaling based on a capability to reduce approach may increase the share of SOS for plastics. However, these other approaches are currently not quantifiable. Thus, downscaling should be further explored, e.g., by applying science-based target methods such as the sectoral decarbonization approach.[298–300]

The planetary boundaries framework has been defined for nine Earth-system processes.[111] Our analysis covers the eight systems for which quantitative methods are available. Only quantifying novel entities is not yet possible since neither control variables nor a SOS have been defined.[113,301] The process of novel entities refers to the release of substances and modified life forms with unwanted geophysical or biological effects on the environment.[111]

To be of concern at the global level, novel entities need to exhibit persistence, a widespread distribution, and potential impacts threatening the integrity of other vital Earth-system processes.[111] Plastics certainly possess these characteristics, and recent literature indicates that plastic pollution has already exceeded the planetary boundary of novel entities.[113] However, the indication is solely based on the fact that the annual production and release of plastics exceeds the capacity for safety assessments and monitoring. A quantifiable control variable that meets the criteria of feasibility, relevance, and comprehensiveness has not yet been identified. Overall, plastics certainly provide a major concern regarding the planetary boundary of novel entities. However, despite the ongoing efforts to quantify novel entities, quantifying plastics' planetary footprint in novel entities is not yet possible. Still, Meng et al. discuss that increasing plastic recycling, as suggested in this study, would reduce the amount of plastics entering the environment, thereby reducing plastic pollution and the pressure on novel entities.[183]

Increasing recycling rates tackle all pillars of the triple planetary crisis addressed by the United Nations Environment Programme.[2] Therefore, fostering recycling could become a win-win-win situation, avoiding pollution, habitat loss, and other environmental impacts while conserving valuable resources and increasing the value of plastic waste at the same time. However, the 36 – 51 % higher capital expenditures determined by Zibunas et al. provide an implementation barrier for circular technologies, albeit total annualized costs are similar to fossil-based production.[302] Thus, additional investment incentives are required, which may come from governments or other stakeholders interested in increasing plastics sustainability. Overall, reducing plastic consumption while treating plastic waste as a valuable resource will be essential for reducing the planetary footprint of plastics. Accordingly, society needs to decide whether to stop considering plastics as cheap and disposable and to start placing a higher value on this versatile and durable product.

Chapter 7

Summary, conclusions, and future perspectives

In this final chapter, we summarize the main conclusions of this thesis (Section 7.1) and provide an outlook for potential future research perspectives (Section 7.2).

7.1 Summary and conclusions

The rapid growth of plastics demand exacerbated the triple planetary crisis of habitat loss, plastic pollution, and greenhouse gas (GHG) emissions. To reduce GHG emissions, the plastics industry needs to shift towards alternative carbon feedstocks. Alternative carbon feedstocks include plastic waste, biomass, CO_2, and steel mill off-gases. Based on an exemplary literature review in Section 2.3.1, we found that all of these feedstocks have been shown to reduce life-cycle GHG emissions of plastics, however, often at the expense of increased utilization of limited resources and associated burden shifting from climate change to other environmental impacts.

In particular, we have identified five critical research gaps in the current environmental assessment practice of these alternative carbon feedstocks: (1) a lack of comparability due to deviating assumptions and methodological variations, (2) unexplored environmental synergies between alternative carbon feedstocks, (3) disregarded availability of limited feedstocks that potentially increase system-wide environmental impacts, (4) a climate change bias that may unintentionally foster burden shifting, and (5) insufficient handling of burden shifting.

In this thesis, we evaluated, compared, and combined the four aforementioned feedstock alternatives in consistent LCAs using the Technology Choice Model (TCM). Thus, we aimed to improve the lack of comparability between alternative carbon feedstocks for plastics production. By using the TCM, we could apply optimization to identify the most promising technologies for GHG mitigation and simultaneously determine other environmental impacts. Furthermore, the bottom-up structure of the

TCM allowed for a fair comparison between technology alternatives under the same assumptions, e.g., electricity impacts or limited feedstock availabilities.

To motivate this thesis, we first conducted an LCA on high-performance thermoplastic polymers (HPTs). HPTs represent a group of plastics with superior chemical and mechanical properties at elevated temperatures. However, producing HPTs is resource- and energy-intensive, resulting in high environmental impacts that have hardly been studied in previous LCA literature on plastics. In particular, we assessed the environmental performance of polyoxazolidinone (POX). POX has been proposed as a novel HPT with potential environmental benefits compared to reference HPTs by increased process efficiency and readily available inputs. Furthermore, these inputs can be produced largely from bio-based feedstocks, which makes this case study particularly interesting for this thesis, as it demonstrates potential GHG reductions and burden shifts from using alternative carbon feedstocks. We found that POX reduces environmental impacts compared to its reference HPTs polyetherimide, polyethersulfone, and polysulfone. For fossil-based production, POX reduces GHG emissions by 34 - 45 %. Bio-based production combined with renewable energy further reduces GHG emissions of HPTs by 55 - 78 % but leads to environmental trade-offs, e.g., in eutrophication and human toxicity.

We expanded the scope from biomass utilization to potential environmental synergies between biomass and CO_2 utilization to reduce both GHG emissions and other environmental impacts. For this purpose, we quantified the environmental benefits of the combined utilization of biomass and CO_2 in the polyurethane supply chain. Polyurethane was particularly well suited for this purpose as its supply chain offers possibilities for both direct and indirect utilization of biomass and CO_2.

Our results show that the combined utilization reduces GHG emissions by 13 % more than the individual utilization of either biomass or CO_2. In addition, the synergies between bio- and CO_2-based production save about 25 % of the limited resources and mitigate burden shifting from climate change to other environmental impacts, e.g., metal depletion or land use. This finding is particularly significant for the plastics industry, as other sectors are more efficient at avoiding GHG emissions by using limited resources. Our results show how the combined utilization of alternative carbon feedstocks in the plastics supply chains reduces both GHG emissions and other environmental impacts by exploiting synergies between feedstocks. Still, using alternative carbon feedstocks for plastics production leads to burden shifting, even when environmental synergies from combined production are fully exploited.

Next, we address the third gap regarding system-wide environmental impacts from limited feedstock availability. For this purpose, we conducted a comparative LCA of alternative syngas pathways. We show that bio- and mill gas-based syngas reduce GHG emissions the most, although the results strongly depend on the conventional feedstock use: If the feedstock is limited and already used elsewhere, its climate benefits strongly decrease.

Furthermore, producing syngas from mill gas or bio-waste leads to moderate environmental trade-offs, while other bio-feedstocks and CO_2 can significantly increase other environmental impacts than climate change. CO_2-based syngas is a viable alternative to replace fossil syngas if abundant low-carbon electricity and no other carbon source is available. Our results demonstrate that a consistent assessment of alternative pathways is required to make informed decisions on syngas decarbonization and highlight the importance of considering the conventional use of limited feedstocks in life cycle assessments.

Finally, we assessed the absolute environmental sustainability of plastics from alternative carbon feedstocks as an approach to improve the currently insufficient handling of burden shifting. In particular, we determined the planetary footprints of plastics from fossil and alternative carbon feedstocks. Under the assumption of economic downscaling, we found that a fossil-based plastics industry transgresses sustainability thresholds by up to 42 times by 2030. This drastic overshoot renders fossil-based plastics highly unsustainable. However, a climate-optimal plastics industry that combines mature recycling technologies with biomass utilization still transgresses sustainability thresholds by 4 times. Accordingly, switching from fossil to alternative carbon feedstocks while focusing on climate change can significantly reduce environmental impact. However, this climate change bias threatens other vital Earth-system processes.

In contrast, a scenario for 2030 with improved recycling technologies, biomass utilization, and carbon capture and utilization indicates potential for sustainable plastics, provided proper accounting of the effect of novel entities onto the biosphere and recycling rates of at least 75 %. Accordingly, our findings provide sound quantitative evidence of the need to foster recycling globally to achieve environmentally sustainable plastics in the future. While being the key towards sustainability, even enhanced recycling cannot cope with the growth in plastics demand predicted until 2050. Thus, achieving absolute sustainability of plastics requires a fundamental change in our way of both producing and using plastics.

7.2 Perspectives for future research

The following section discusses perspectives on future research that may further improve the current environmental assessment practice of alternative carbon feedstocks, potentially enhancing the absolute environmental sustainability of the plastics industry.

Enhancing data availability

High-quality data are essential for the environmental assessment of industrial processes. However, this thesis has shown that high-quality and standardized data on the plastics industry are scarce. The plastics industry disclosed its data only in rare exceptions, as demonstrated for polyoxazolidinone in Chapter 3. Therefore, the literature often uses stoichiometric estimates to determine material demands and generic factors for energy requirements. However, these estimates only inaccurately depict the production of plastics, resulting in a high uncertainty of LCA results.[203]

In some cases, we had to rely on such stoichiometric estimates in this thesis. In other cases, we used economic databases such as NexantECA or IHS Markit.[257,303] While these databases provide high-quality data, the data cannot be publicly disclosed since access requires a user license. In addition, we have used aggregate datasets to model LCI background systems. However, these aggregated processes provide little insight into the underlying modeling, making it difficult to draw conclusions and provide recommendations from LCA results. In contrast, a standardized, publicly available database of high-quality data on plastics production is desirable to promote research on a decarbonized plastics industry. Artificial intelligence could provide a solution by harvesting data from publicly available simulation models and standardizing them in an open-access database.[304]

Promoting integrated assessments of limited feedstocks

The availability of alternative feedstocks for plastics, such as biomass or hydrogen from renewable electricity, is limited. Still, our literature review has revealed that most LCA studies on plastics production do not consider the limited availability of alternative carbon feedstocks. However, this thesis has shown that the limited availability can strongly reduce the environmental benefits of alternative carbon feedstocks. Accordingly, limited resource availability must be given greater consideration in future LCA studies. Integrated assessment models (IAM) provide a promising tool to account for resource limitations.[305–307] For instance, an IAM of the manufacturing industry could determine the demand for alternative carbon feedstocks to decarbonize multiple industrial sectors.

Furthermore, integrating the power sector is crucial to represent the environmental impacts of renewable electricity from energy systems rather than conducting sensitivity analyses of individual electricity generation technologies.[308] Combining multiple industrial sectors in one IAM may also reveal additional environmental synergies that could reduce feedstock demands. In addition, the absolute environmental sustainability of plastics will also strongly depend on the availability of alternative carbon feedstocks. Accordingly, future studies should combine the approaches of determining system-wide environmental impacts from alternative carbon feedstocks (Chapter 5) and plastics' absolute environmental sustainability (Chapter 6).

Bringing environmental thresholds into decision-making

Politics and industry increasingly consider environmental indicators in decision-making. LCA represents a valuable tool to provide these environmental indicators and demonstrate environmental benefits and trade-offs. However, even if a novel product or technology offers environmental benefits compared to the benchmark, decision-making requires absolute thresholds to determine whether these benefits are sufficient in terms of environmental sustainability.

In this thesis, we applied economic downscaling factors to determine environmental thresholds for the plastics industry. However, using economic indicators to assign environmental thresholds is controversial, especially in regionalized assessments (see Section 6.5). However, other indicators are either also controversially discussed or cannot be determined due to a lack of data. Accordingly, there is a growing need for scientific consensus and standardization on how to allocate ecological budgets on a regional, industrial, and product level. Allocating ecological budgets for products and industries will define upper bounds for human development, which may increase pressure for innovation. In turn, pressure for innovation can amplify efforts in research and development, potentially leading to novel products such as polyoxazolidinone that contribute to decarbonizing the plastics industry.

Advancing regionalized assessments of absolute environmental sustainability

In this thesis, we assessed the environmental sustainability of the global plastics industry. Consequentially, we considered globally-defined planetary boundaries. However, defining ecological budgets on a sub-global level also requires accounting for regional heterogeneity in the biosphere. Accounting for this regional heterogeneity is particularly important for planetary boundaries not connected to a well-mixed global indicator. For instance, freshwater use may affect aquatic ecosystems differently depending on the location and other factors such as consumption rates and sequencing of processes.[309] Accordingly, Steffen et al. also defined regional boundaries, which should be considered in regionalized assessments of the plastics industry.[111]

Including social and economic aspects

This thesis focused exclusively on the environmental impacts of the plastics industry. The thesis has shown that transforming the plastics industry from fossil resources to alternative carbon sources offers environmental benefits. However, social and economic factors also play decisive roles in transformation processes. Social aspects include issues such as child and forced labor, discrimination, and fair salary. For instance, Spierling et al. show that bio-based plastics have a high social risk potential since bio-based feedstocks are often cultivated in countries with low social standards and weak legal conditions.[6] Accordingly, assessing social aspects is crucial to holistically determine the sustainability of plastics from alternative carbon feedstocks.

Furthermore, a plastics industry based on alternative carbon feedstocks needs to be cost-competitive to actually achieve environmental benefits. While previous literature has shown that operational costs are in the same range as those of fossil-based plastics, up to about 50 % higher capital expenditures are expected when using alternative carbon feedstocks in production.[5,302] Accordingly, additional measures such as carbon pricing are needed to incentivize the transition towards a sustainable plastics industry based on alternative carbon feedstocks.

Appendices

Appendix A

Supplementary information on high-performance plastics (HPTs)

A.1 Data sources for the life cycle inventory of HPTs

Data sources of all chemicals used in high-performance thermoplastic polymer (HPT) production are summarized in Table A.1. For the background system, we used aggregated datasets from the LCA database GaBi.[98] If no aggregated dataset was available, we expanded the foreground system until all inputs were available. For the foreground system, we choose the data sources based on the following hierarchy:

1. We modeled the processes based on unit process data from NexantECA. The datasets from NexantECA are based on process simulations verified by industrial experts. Thus, we assume a high data quality.
2. If no data from NexantECA was available, we modeled the process based on unit process data from ecoinvent. The data quality differs between ecoinvent datasets since some are modeled based on industry data and others on stoichiometry.
3. If no process data was available in ecoinvent, we used stoichiometry to calculate the demand for raw materials assuming 100 % conversion. Furthermore, following the procedure from ecoinvent, the energy consumption of production is estimated based on data from a large chemical plant site in Gendorf, Germany.[202]

For process steam, we assumed medium-pressure steam with 13.8 bar (200 psig) according to the NexantECA reports.[303] The specific enthalpy of the medium-pressure steam is 2757 kJ/kg. We assumed a heating value of 50 MJ/kg for fuel gas demands and by-product credit, corresponding to methane. Furthermore, Table A.1 summarizes all chemicals and data sources and includes potential exceptions from the hierarchy.

Table A.1: Summary of chemicals, production technologies, locations, and data sources of the HPT production systems.

Name of chemical	**Production technology**	**Location**	**Source**	**Comment**
Acetic acid	Catalytic reaction of methanol and carbon monoxide	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Acetone	Hock process	N/A	NexantECA.[310]	Allocated by mass allocation, allocation factor = 0.3809
Allyl chloride	Chlorination of propylene	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Ammonia	Haber-Bosch process, without CO_2 recovery	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Aniline	Catalytic hydrogenation of nitrobenzene	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
	Fermentation and catalytic decarbonization	N/A	Winter et al. 2020[211]	Aggregated process
Benzene	Technology mix	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
	Methanol-to-aromatics	N/A	IHS Markit[257]	Methodology as described in Meys et al. 20216
Benzonitrile	Sohio process	N/A	Ullmann's Encyclopedia of Industrial Chemistry[219]	Process modeled based on stoichiometry
Bisphenol A	Sinopec/Lummus process	N/A	NexantECA.[311]	
Bisphenol A diglycidyl ether (BADGE)	Continuous Caustic Coupling Process of Epichlorohydrin and Bisphenol A	N/A	NexantECA.[214]	Modeled as liquid epoxy resin
p-tert-Butylphenyl glycidyl ether (PBPGE)	-	N/A	-	BADGE used as proxy

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Name of chemical	Production technology	Location	Source	Comment
Calcium chloride	Solvay process	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.5046
Calcium hydroxide	Technology mix	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Carbon dioxide	CO_2 capture from ammonia plant	N/A	Von der Assen el al.[75]	Modeled as monoethanolamine absorption
Carbon monoxide	Cryogenic air separation of synthesis gas	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
	Partial condensation of synthesis gas from biomass gasification	N/A	IHS Markit[257]	Methodology as described in Meys et al. 20216
Chlorine	Technology mix	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Chlorobenzene	Benzene chlorination	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.9105
Cooling water	Tap water from surface water	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
o-Dichlorobenzene	Benzene chlorination	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.0380
4,4’-Dichlorodiphenyl sulfone	Sulfonation of chlorobenzene using sulfur trioxide and thionyl chloride	N/A	NexantECA.[303] and patent[313]	For details see section 4

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Name of chemical	**Production technology**	**Location**	**Source**	**Comment**
Dihydroxydiphenyl sulfone (Bisphenol S)	Sulfonation of phenol using oleum (65 %)	N/A	NexantECA.[193] and patent[313]	For details see section 4
Electricity	Grid mix 2019	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
	From wind power	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Epichlorohydrin	Allyl chloride hypochlorination and alkaline epoxidation	N/A	NexantECA.[213]	
Glycerol	hypochlorination and alkaline epoxidation	N/A	NexantECA.[213]	
Ethanol	Fermentation, from sugar beet	EU-28	Sphera - GaBi Version 2021.2[98]	Aggregated process
Formaldehyde	Oxidation of methanol	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Glycerine	By product from rapeseed methyl ester via extraction, refining, transesterification	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process, 2014 price allocated
Hydrochloric acid (100 %)	Technology mix	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Hydrogen	Steam reforming of natural gas	DE	Sphera - GaBi Version 2021.2[98]	Aggregated process
Light fuel oil	From crude oil	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Methanol	Technology mix	EU-28	Sphera – GaBi Version 2021.2[98]	Aggregated process
	From synthesis gas	N/A	Andersson et al.[314]	For details see section 3

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Name of chemical	Production technology	Location	Source	Comment
Methyl chloride	Reaction of methane and chlorine	N/A	Ullmann's Encyclopedia of Industrial Chemistry[219]	Process modeled based on stoichiometry
Methylene diphenyl diisocyanate (MDI)	Chematur condensation of aniline	N/A	NexantECA.[210]	
Momomethylamine	Reaction of methanol and ammonia	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Natural gas	Consumption mix	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Nitric acid, dilute (60 %)	Oxidation of ammonia	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Nitric acid (100 %)	Oxidation of ammonia	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Nitrogen	Cryogenic air separation	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Nitrous dioxide	Ostwald process	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Nitrous oxide	Ostwald process	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Oleum (65 %)	Mixing of sulfuric acid and sulfur trioxide	N/A	Ullmann's Encyclopedia of Industrial Chemistry[219]	Process modeled based on stoichiometry
Phenol	Hock process	N/A	NexantECA.[310]	Allocated by mass allocation, allocation factor = 0.6191
m-Phenylenediamine	Diazotization and hydrogenation of aniline	N/A	NexantECA.[315]	p-Phenylenediamine used as proxy

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Name of chemical	Production technology	Location	Source	Comment
Phthalic anhydride	Oxidation of xylene	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
N-methyl Phthalimide	Reaction of phthalic anhydride with momomethylamine	RER	ecoinvent 3.7 - undefined[312]	Process modeled based on stoichiometry
Polyethersulfone	Polymerization of DCDPS, Bisphenol S, and potassium carbonate	N/A	NexantECA.[303]	For details see section 4
Polyetherimide	Polymerization of Bisphenol A, phthalic acid, n-methyl phthalimide, and m-phenylenediamine	N/A	NexantECA.[303]	For details see section 4
Polysulfone	Polymerization of DCDPS and Bisphenol A	N/A	NexantECA.[303]	For details see section 4
Polyoxazolidinone	Polymerization of BADGE and MDI	N/A	Covestro Deutschland AG[199]	Details see paper
Potassium carbonate	Reaction of potassium hydroxide and carbon dioxide	GLO	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Potassium chloride	Shaft mining and beneficiation	EU-28	Sphera – GaBi Version 2021.2[98]	Aggregated process
Potassium hydroxide	Electrolysis of potassium chloride brine	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Process steam	From natural gas (95 % efficiency)	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
	From electricity (95 % efficiency)	N/A	-	An electric boiler efficiency of 95 % is assumed
Process water	From groundwater	EU-28	Sphera – GaBi Version 2021.2[98]	Aggregated process

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Name of chemical	Production technology	Location	Source	Comment
Propylene	Steam cracker	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
	Methanol-to-Olefins by the Lurgi process	N/A	IHS Markit[257]	Methodology as described in Meys et al. 20216
Sodium hydroxide (caustic soda)	Technology mix	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Sodium nitrite	Reaction of nitrogen oxides with sodium carbonate	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Sulfuric acid (96 %)	Technology mix	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Sulfur (elemental)	From crude oil	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process
Sulfur dichloride	Reaction of sulfur and chloride	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Sulfur dioxide	Liquid SO_2 production via sulfur combustion	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Sulfur trioxide	From sulfuric acid	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Synthesis gas	Biomass gasification	N/A	-	For details see section 3
Thionyl chloride	Reaction of sulfur dioxide, sulfur dichloride, and chlorine	RER	ecoinvent 3.7 - undefined[312]	Modeled using unit process data from ecoinvent
Toluene	BTX from reformate	DE	Sphera – GaBi Version 2021.2[98]	Aggregated process

End of table

Table A.2: Process yields for the production of HPT monomers and other important chemical intermediates. Process yields for aggregated processes could not be provided since they were not stated by the GaBi database. The process yield for bio-based aniline is confidential. *For the other bio-based processes, the process yield refers to the carbon efficiency of the process. The carbon efficiency of bio-based processes is usually lower than that of fossil-based processes due to the partially oxidized nature of biomass.

Name of chemical	**Production technology**	**Limiting compound**	**Process yield in %**
Bisphenol A diglycidyl ether (BADGE)	Continuous Caustic Coupling Process of epichlorohydrin and bisphenol A	Bisphenol A	99.9
Bisphenol A	Sinopec/Lummus process	Phenol	98.6
Phenol and Acetone	Hock process	Benzene	96.6
Benzene	Technology mix - aggregated process	Not provided	-
	Methanol-to-aromatics	Methanol	71.5
Propylene	Steam cracker - aggregated process	Not provided	-
	Methanol-to-olefins	Methanol	66.0
Methanol	Technology mix – aggregated process	Not provided	-
	From biomass gasification	Biomass	40.1*
Epichlorohydrin	Allyl chloride hypochlorination and alkaline epoxidation	Allyl chloride	95.0
	Glycerol hypochlorination and alkaline epoxidation	Glycerine	90.0
Allyl chloride	Chlorination of propylene – aggregated process	Not provided	-
Glycerine	By product from rapeseed methyl ester via extraction, refining, transesterification – aggregated process	Not provided	-
Methylene diphenyl diisocyanate (MDI)	Chematur condensation of aniline	Aniline	99.6
Aniline	Catalytic hydrogenation of nitrobenzene – aggregated process	Not provided	-
	Fermentation and catalytic decarbonization	Sugar beet	confidential
Formaldehyde	Oxidation of methanol	Methanol	83.3
Carbon monoxide	Cryogenic air separation of synthesis gas – aggregated process	Not provided	-

Continued on next page

Name of chemical	Production technology	Limiting compound	Process yield in %
	Partial condensation of synthesis gas from biomass gasification	Biomass	46.9*
N-methyl phthalimide	Reaction of phthalic anhydride with momomethylamine	Stoichiometry	100
m-Phenylenediamine	Diazotization and hydrogenation of aniline	Aniline	75.9
Dihydroxydiphenyl sulfone (Bisphenol S)	Sulfonation of phenol using oleum (65 %)	Phenol	93.7
4,4‘-Dichlorodiphenyl sulfone	Sulfonation of chlorobenzene using sulfur trioxide and thionyl chloride	Chlorobenzene	75.0
Chlorobenzene	Benzene chlorination	Chlorine	79.2

End of table

A.2 Material properties of HPTs

Table A.3: Material properties of typical high-performance thermoplastic polymers and polyethylene (PE) 100 as a reference for commodity plastics. Material properties of polyoxyzolidinone (POX), polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU) were measured by the Kunststoffzentrum Leipzig and reflect typical values. However, the material properties should not be considered absolute or warranted values.

Material property	POX	PEI	PES	PSU	PE
		Ultem 1000	Ultrason E2010	Ultrason S3010	100
Tensile modulus [MPa]	2740	3236	2656	2516	1100[316]
Stress at yield [MPa]	80	115	90	75	25[316,317]
Strain at yield [%]	6	7	7	6	9[316] - 10[317]
Stress at break [MPa]	84	90	62	64	40[317]
Strain at break [%]	92	80	82	118	1500[317]
Flexural modulus [MPa]	2623	3437	2704	2767	1090[317] - 1150[318]
Flexural strength [MPa]	121	162	125	113	24[316]
Ball indentation hardness HB [MPa]	165	202	154	136	46[316]
Vicat B [°C]	159	211	214	182	77[316] - 125[317]

A.3 Life cycle inventory for the polyoxazolidinone supply chain

The following section summarizes the modeling of the reactants and auxiliaries of POX production.

Bisphenol A diglycidyl ether

We modeled bisphenol A digylcidyl ether (BADGE) production based on process data for the continuous caustic coupling of epichlorohydrin and bisphenol A.[214] Epichlorohydrin is produced conventionally by chlorohydrination of allyl chloride with chlorine.[219] Alternatively, epichlorohydrin can be produced from glycerol and hydrochloric acid.[215] Since glycerol is a by-product of biodiesel production, the availability of glycerol has increased, and the price has decreased sharply in recent years.[215] Thus, production via bio-based glycerol may offer a low-cost and environmentally beneficial pathway to epichlorohydrin.

We modeled the production of epichlorohydrin by using process data for the conventional and alternative pathways from NexantECA.[213] The conventional production via allyl chloride produces calcium chloride as a by-product. We give a credit for avoiding the conventional production of calcium chloride from the Solvay process. Process data for the Solvay process were taken from ecoinvent. Since the Solvay process produced soda ash, calcium chloride, and sodium bicarbonate, we used mass allocation with an allocation factor of 0.51 to allocate the environmental impacts to calcium chloride. An economic allocation based on ecoinvent prices would result in an allocation factor of 0.57, leading to similar environmental impacts. The alternative production via bio-based glycerol produces sodium chloride and fuel residues as by-products. To give a credit for the avoided conventional production of sodium chloride, we used the aggregated dataset from the LCA database GaBi (GaBi).[98] For the fuel residues, we give a credit based on the “light fuel oil at refinery” process from GaBi. To account for the environmental impact of bio-based glycerol, we used the price-allocated dataset from GaBi since no mass-allocated dataset is available.

Bisphenol A is mainly produced by reacting acetone with phenol.[219] Therefore, bio-based phenol would enable the production of bio-based bisphenol A and, thus, increase the share of bio-based reactants for POX. However, a direct route to bio-based phenol is not yet commercialized.[319] Therefore, we only consider an indirect pathway to bio-based phenol and acetone via the Hock process using bio-based benzene and propylene.[310] Bio-based benzene and propylene, in turn, are produced via the methanol-to-aromatics and methanol-to-olefins processes using bio-based methanol from biomass gasification.[257] The gasification process uses wood pellets as feedstock. We adapted the LCI for wood pellet gasification from the syngas production system (see Appendix C for details) and integrated the production of methanol in the LCI.[314] The fossil-based production of phenol and acetone uses benzene and propylene from the aggregated GaBi datasets.

Methylene diphenyl diisocyanate

Methylene diphenyl diisocyanate (MDI) is commercially produced in a two-step synthesis using aniline, formaldehyde, and phosgene as feedstock. We modeled the production of MDI based on process data from NexantECA.[210] We considered two alternatives for the supply of aniline: First, fossil-based aniline based on an aggregated dataset from GaBi, and second, bio-based aniline from Winter et al.[211] For formaldehyde production, we included oxidation of methanol from ecoinvent. Methanol can either be taken from a biomass gasification plant or steam reforming of natural gas (aggregated GaBi dataset). We assume that phosgene is produced on-site, and thus, only carbon monoxide and chlorine are required as inputs in addition to aniline. Carbon monoxide is produced by separating either fossil- or bio-based synthesis gas.

p-tert-Butylphenyl glycidyl ether

No process data for the production of p-tert-butylphenyl glycidyl ether (pBPGE) are available. Therefore, the environmental impact of bBPGE cannot be determined. We use BADGE as a proxy for the environmental impacts of pBPGE since the chemical structures of both molecules contain the same building blocks. Thus, it is likely that both molecules are produced from the same reactants and that the production results in similar environmental impacts.

Catalyst

The catalyst system of POX production used by Covestro Deutschland AG is confidential and cannot be disclosed. We modeled the catalyst production based on stoichiometry. However, modeling one of the reactants was not possible due to a lack of data in GaBi. To account for the environmental impact of this reactant, we used an aggregated dataset from ecoinvent. This dataset is the only ecoinvent dataset used for the background system.

Benzonitrile

Benzonitrile is produced commercially by vapor-phase ammoxidation of toluene with ammonia and air.[219] Since no process data is available for benzonitrile production, we used stoichiometry to generate the LCI. The reaction is carried out with a ratio of ammonia to toluene of 4:1. The selectivity of toluene to benzonitrile is 87.4 %, and the conversion of toluene and ammonia is 97 % and 30 %, respectively.[219] We assumed that unreacted ammonia is neutralized with sulfuric acid (37 %), resulting in ammonium sulfate production. The assumption for ammonia neutralization is based on the acrylonitrile process, where acrylonitrile is produced by the ammoxidation of propylene.[320] We assume that all by-products from benzonitrile production are treated by incineration. For energy requirements of the benzonitrile process, we use data from a large chemical plant site in Gendorf, Germany.[321]

Benzonitrile is also produced commercially from benzoic acid and urea.[322] However, no process data for the benzoic acid-based production are available. Yet, the higher environmental impact of the reactants suggests that the benzoic acid pathway may also have higher environmental impacts.

A.4 Life cycle inventory for the reference HPTs production and supply chain

The following section explains the main steps in the production of the reference products polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU). Process data and energy requirements for production are taken from the Technoeconomics Report Amorphous High Temperature Engineering Thermoplastics from NexantECA.[303] The process data do not contain any information about the amounts of solvents or precipitation and washing agents used in the HPT production. Therefore, we neglect all solvents and other materials for the production of the reference HPTs. Neglecting all solvents and other materials corresponds to a 100 % solvent and material recovery rate, resulting in a best-case assumption for the reference HPT and a corresponding worst-case assumption for POX. Thus, we conduct a conservative assessment for POX.

Furthermore, the amount of chain stopper for polymerization is not included in the NexantECA process data. Thus, we calculate the minimum amount of chain stopper to set the active chain ends of the reaction to zero using the Carothers equation.[323] To calculate the active chain ends, we assumed a polymer molecular weight of 15000 g/mol resulting in a stoichiometric monomer ratio of about 0.97. Calculating the minimum amount of chain stopper also corresponds to a conservative assessment for POX.

Polyetherimide

Polyetherimide (PEI) is produced in a four-step synthesis based on bisphenol A, phthalic acid, n-methyl phthalimide, and m-phenylenediamine (see Figure A.1).[303]

First, bisphenol A reacts with sodium hydroxide to form a di-sodium salt in o-dichlorobenzene. After water removal, the anhydrous di-sodium salt reacts with N-methyl nitrophthalimide to bis-ether phthalimide using o-dichlorobenzene as reaction solvent.

In the second step, sodium nitrate by-product and o-dichlorobenzene are removed from bis-ether phthalimide by extraction and evaporation, respectively. Water with 1 % sodium hydroxide is used as extraction solvent. The bis-ether phthalimide is mixed with aqueous phthalic acid and dehydrated to form bis(ether phthalic dianhydride). As a catalyst, an imide-anhydride exchange catalyst such as triethylamine is used. However, the process data do not provide any information about the amount of catalyst used per unit of PEI. Therefore, we did not consider the catalyst in the assessment. The reactor effluent, containing bis(ether phthalic dianhydride), unreacted bis-ether phthalimide, catalyst, and N-methylphalimide by-product, is separated by extraction. For the extraction, o-dichlorobenzene is used as extraction solvent.

As a third step (not shown in Figure A.1), N-methylphthalimide is recovered from the organic extraction effluent and reacted with nitric acid to produce N-methyl nitrophthalimide. N-methyl nitrophthalimide is purified by precipitation and washing with methanol. The resulting N-methyl nitrophthalimide is recycled to the first reaction step.

In the fourth step, the phthalic dianhydride monomer is polymerized with m-phenylenediamine in a melt polymerization using triethylamine as a chain stopper in the presence of o-dichlorobenzene. We do not consider any catalyst for the polymerization since no data on the type and amount of catalyst is available. The resulting PEI is separated via extrusion.

During production, high amounts of dilute nitric acid are produced. Accordingly, we give a credit for the avoided conventional production of dilute nitric acid.

Furthermore, to the best of the author's knowledge, no datasets for n-methyl phthalimide and m-phenylenediamine are publically or commercially available. For n-methyl phthalimide, we used process data for phthalimide production from ecoinvent as a proxy. For m-phenylenediamine, the energy demand for production from ecoinvent seems unusually and unjustifiably high. Thus, we modeled the production of p-phenylenediamine as a proxy for m-phenylenediamine based on the process data from the Aromatic Polyamides (Polyaramids) PERP Report from NexantECA.[315] To model the production of trimethylamine, we used process data from ecoinvent.

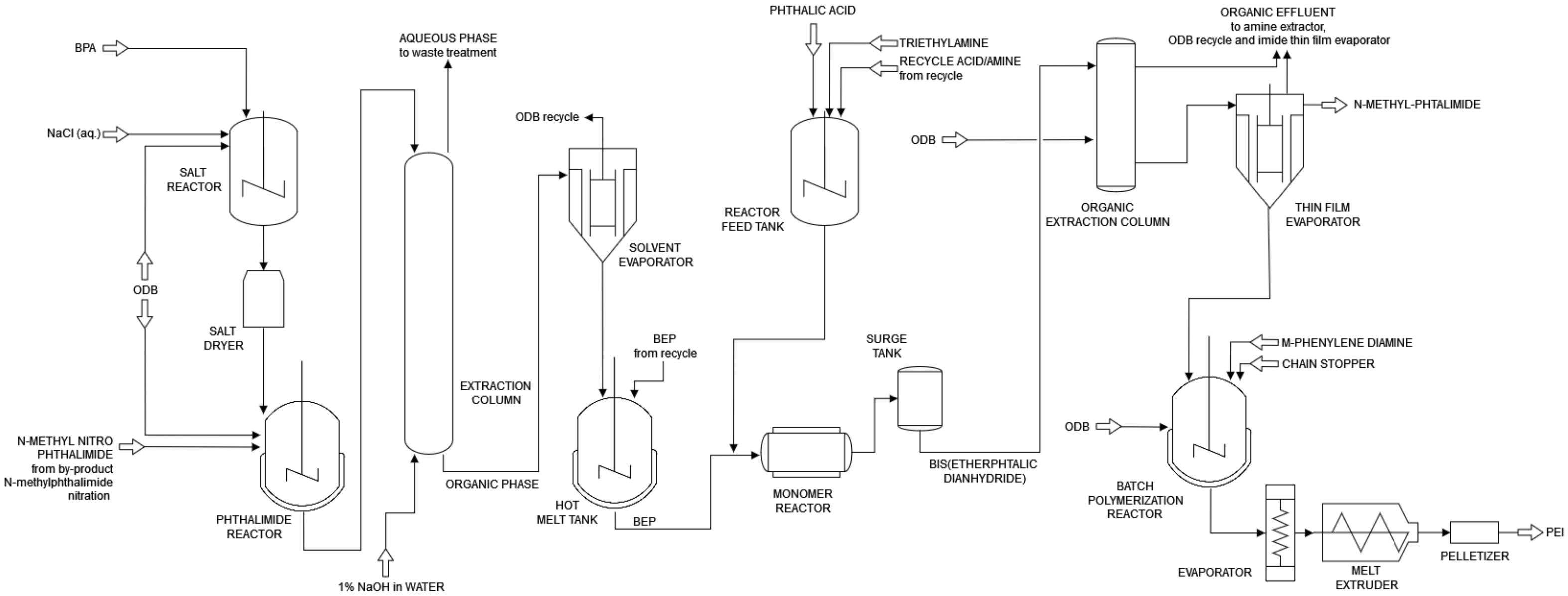

Figure A.1: Simplified process flowsheet of polyetherimide (PEI) production adapted from NexantECA. Not shown: Amine extractor for phtalic acid and amine recycle, solvent thin film evaporator for ODB recycle, imide thin film evaporator for BEP recycle and the separation of N-methylphtalimide for the nitration process to get nitric acid and methanol recovery, N-methylphthalimide nitration process for monomer production, solvent recycles. Abbreviations: BEP = Bis(ether phthalimide), BPA = Bisphenol A, NaCl (aq.) = sodium hydroxide, ODB = o-Dichlorobenzene.

Polyethersulfone

The production of polyethersulfone (PES) consists of polymerization, followed by polymer and solvent recovery (see Figure A.2). The typical production of PES is solely based on 4,4'-dichlorodiphenyl sulfone (DCDPS). However, we considered the alternative production based on DCDPS and 4,4'-dihydroxydiphenyl sulfone (bisphenol S) with faster reaction rates and lower temperature since the alternative production is more likely to be applied industrially.[303] For the polymerization, DCDPS, bisphenol S, and potassium carbonate are charged to the reactor with dimethyl sulfoxide (DMSO) as the reaction solvent.

Since no data for DCDPS, bisphenol S, or potassium carbonate are available, we modeled each production separately (see details below). As chain stopper, methyl chloride is fed to the reactor to end-cap the reactive chains. PES is recovered from the reaction slurry by precipitation with methanol and subsequent washing with methanol and water. We do not consider any catalyst for the reaction due to a lack of data.

4,4'-Dichlorodiphenyl sulfone and 4,4'-dihydroxydiphenyl sulfone

The Life Cycle Inventory for producing 4,4'-dichlorodiphenyl sulfone (DCDPS) was derived from the Process Evaluation/Research Planning (PERP) Report for Amorphous High Temperature Engineering Thermoplastics from NexantECA.[193] The PERP Report includes detailed information about energy and material requirements for DCDPS production. However, it does not include the amount of caustic soda needed for off-gas scrubbing of sulfur dioxide and hydrochloric acid. Consequentially, we calculated the amount of caustic soda based on stoichiometry as a conservative assumption.

Furthermore, the PERP Report does not include any process data for 4,4'-dihydroxy -diphenyl sulfone (bisphenol S production). Thus, we modeled the production based on the patent EP0489788B1, which proposes a procedure for producing bisphenol S.[313] We chose example 4 of the patent using phenol and oleum (65 %) as reactants and o-dichlorobenzene as reaction solvent. The bisphenol S yield from phenol is 93 %. Since the patent does not include any information about energy requirements for production, we used the energy requirements from DCDPS as a proxy for bisphenol S.

Potassium carbonate

We modeled the production of potassium carbonate based on process data from ecoinvent.

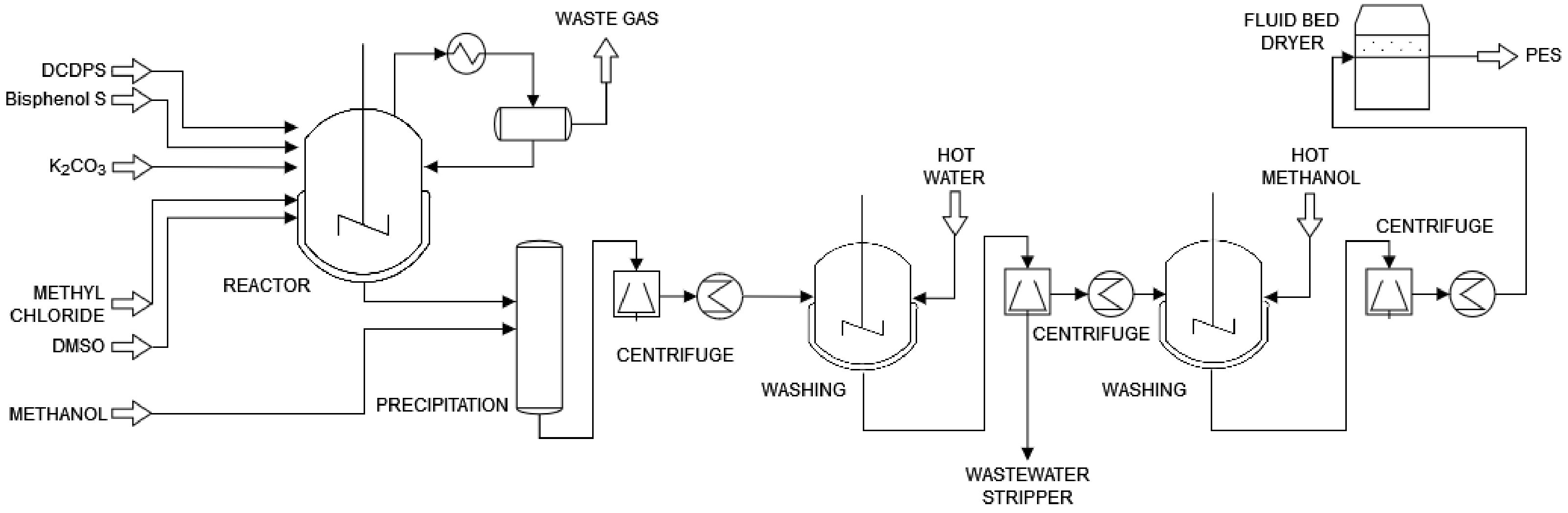

Figure A.2: Simplified process flowsheet of polyethersulfone (PES) production adapted from NexantECA. Abbreviations: DCDPS = 4,4'-Dichlorodiphenyl sulfone, DMSO = dimethyl sulfoxide, K_2CO_3 = potassium carbonate.

Polysulfone

The process design of polysulfone (PSU) is mainly based on patents from Solvay (formerly Union Carbide). The process design consists of a two-step polymerization reaction with subsequent solvent and polymer recovery. First, bisphenol A and a mixture of chlorobenzene and DMSO are fed to the polymerization reactor. Subsequently, a 50 wt-% caustic soda solution is added, forming a di-sodium salt of bisphenol A. Water and chlorobenzene form an azeotrope that is distilled off and separated in a decanter. The recovered chlorobenzene is recycled to the polymerization reactor.

In a second step, DCDPS is added to the reactor and polymerized with the bisphenol A salt to PSU. To end polymerization, methyl chloride is injected as a chain stopper. Afterward, the polymer slurry is diluted in chlorobenzene, and sodium chloride by-product is removed by centrifugation. Furthermore, DMSO is separated and recovered using extraction and subsequent distillation. Finally, PSU is obtained by coagulation using n-hexane, filtering, and drying.

Like in PEI production, melt polymerization may also be applied in POX, PES, and PSU production. Melt polymerization may reduce both energy and solvent requirements of HPT production.[323] However, as data for melt polymerization are not available for all HPTs, this study is limited to the conventional production of HPT.

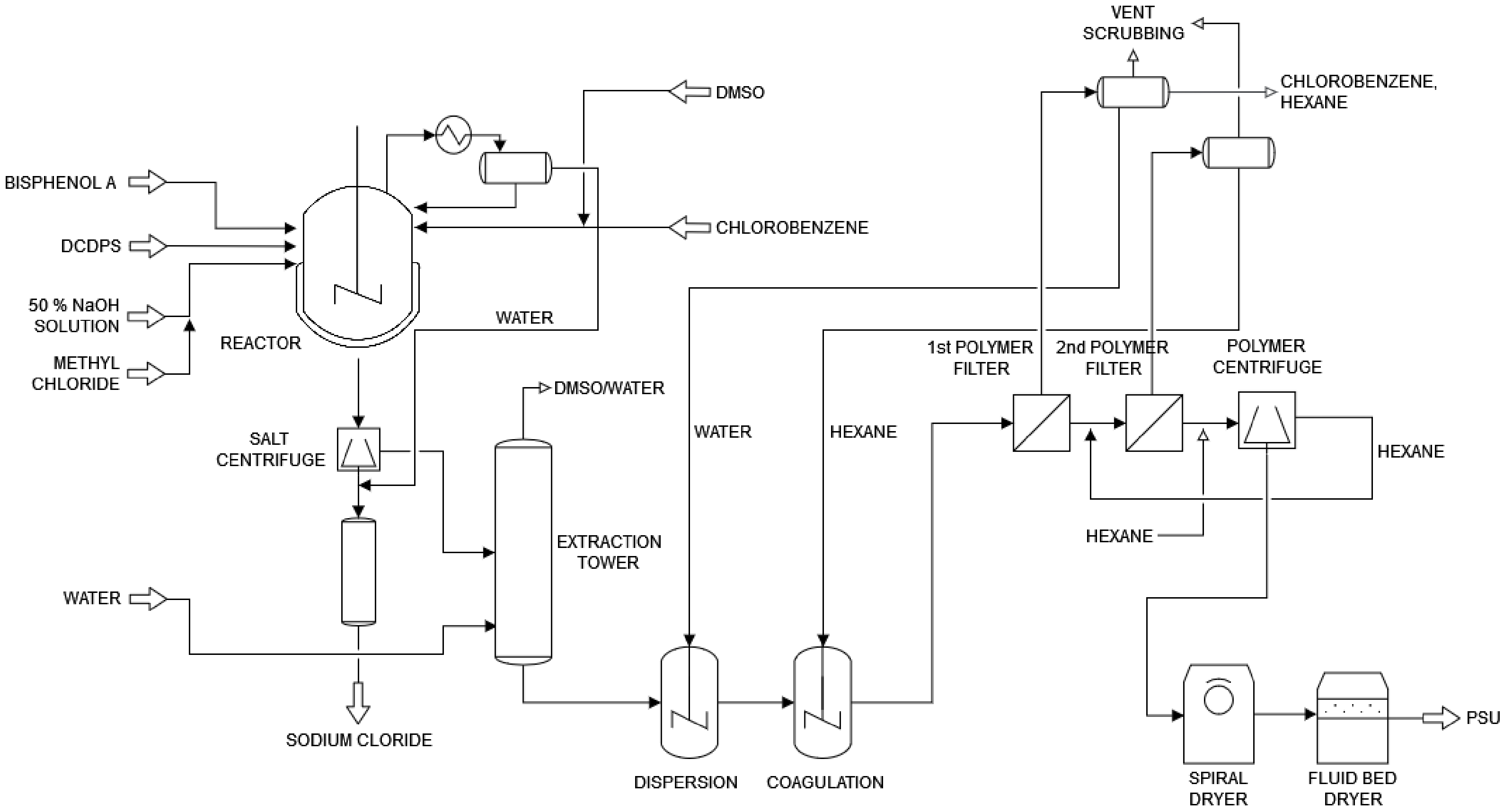

Figure A.3: Simplified process flowsheet of polysulfone (PSU) production adapted from NexantECA. Abbreviations: DCDPS = 4,4’-Dichlorodiphenyl sulfone, DMSO = dimethyl sulfoxide.

A.5 Land-use change emissions from bio-based HPTs

The cultivation of biomass can change the carbon content of the soil, resulting in so-called land-use change (LUC) emissions. We account for LUC emissions of bio-based products considered in this study, namely ethanol, aniline, glycerol, carbon monoxide, and methanol. The aggregated datasets from GaBi already include LUC emissions.[98] To validate the LUC emissions from GaBi, we compare them with literature data (see Figure A.4).

For ethanol and aniline, we used the worst-case assumptions for LUC emissions from Winter et al. corresponding to the values from Al-Riffai et al.[211,324] Glycerol is a by-product from biodiesel production that we modeled using an aggregated and economically allocated dataset from GaBi.[98] The aggregated dataset does not reveal any information about the amount of biomass consumed. Therefore, we used data on LUC emissions from biodiesel from Malca et al. to calculate the LUC emissions from glycerol.[325] We used the ratio of GHG emissions with and without LUC emissions from Marca et al. and applied it to the aggregated dataset from GaBi.

Carbon monoxide and methanol are produced from synthesis gas from wood pellet gasification. According to the literature, wood pellets are mainly produced from softwood pine, which has either no or even negative direct LUC emissions.[326–328] In addition, indirect LUC emissions from wood pellets are considered small.[329] Assuming no LUC emissions is consistent with the general assumption that second-generation biomass and biofuels have lower LUC emissions than first-generation biomass and biofuels.[330] Furthermore, wood pellets are often produced from waste materials such as forest residues or sawdust from sawmills, so that potential LUC emissions could also be allocated to the main product.[202] Overall, we assume that bio-based carbon monoxide and methanol from wood pellet gasification does not lead to LUC emission.

Overall, LUC emissions are small compared to the total product emissions of HPTs (see Figure A.4). POX has higher LUC emissions than the reference HPTs since more aniline and glycerol are used in POX production. In contrast, the reference products rely mainly on methanol (and PEI on ethanol) as a biogenic carbon source.

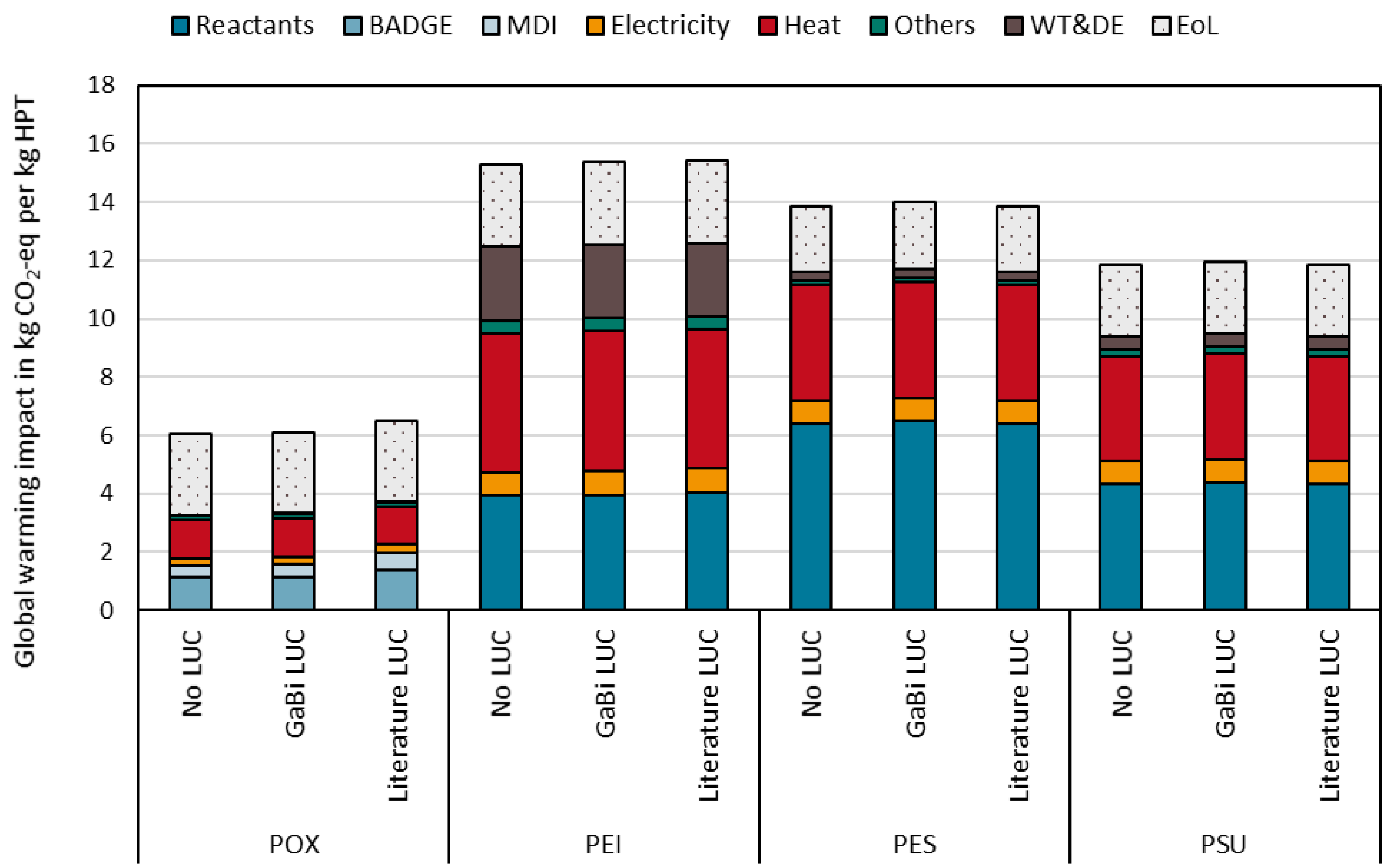

Figure A.4: Global warming impact of high-performance thermoplastic polymer excluding LUC emissions (No LUC) and including LUC emissions from GaBi (GaBi LUC) or literature values (Literature LUC).

A.6 Sensitivity analysis on the climate change impact of fossil-based HPTs

The analysis of HPT production incorporates uncertainties. To address these uncertainties, we vary the demands of electricity, steam, and fuel gas (only reference HPT) and the process yields for key chemical intermediates in reasonable ranges in a sensitivity analysis (Figure A.5 - Figure A.8). For POX, the process yield of BADGE production, which is set to 99.9 % and, thus, close to stoichiometric conditions, has the most significant influence on GHG emissions. Changing the process yield of BADGE production to 80 % results in about 1.2 kg CO_2-eq higher GHG emissions per kg POX, corresponding to an increase of about 13 %. The parameters with the next largest sensitivity for the GHG emissions of POX are the MDI process yield and the steam demand for POX production.

For the reference HPTs, steam demands in HPT production also strongly influence GHG emissions. Increasing or decreasing the steam demand by 50 % increases or decreases the GHG emissions of the reference HPTs by 1.8-2.2 kg CO_2-eq, respectively, which corresponds to a change of about 13 %. Furthermore, the process yield of DCDPS production, which is set to 75 %, can change the GHG emissions of PES and PSU by about -1.7-3.3 kg CO_2-eq (-10 % to 23 %).

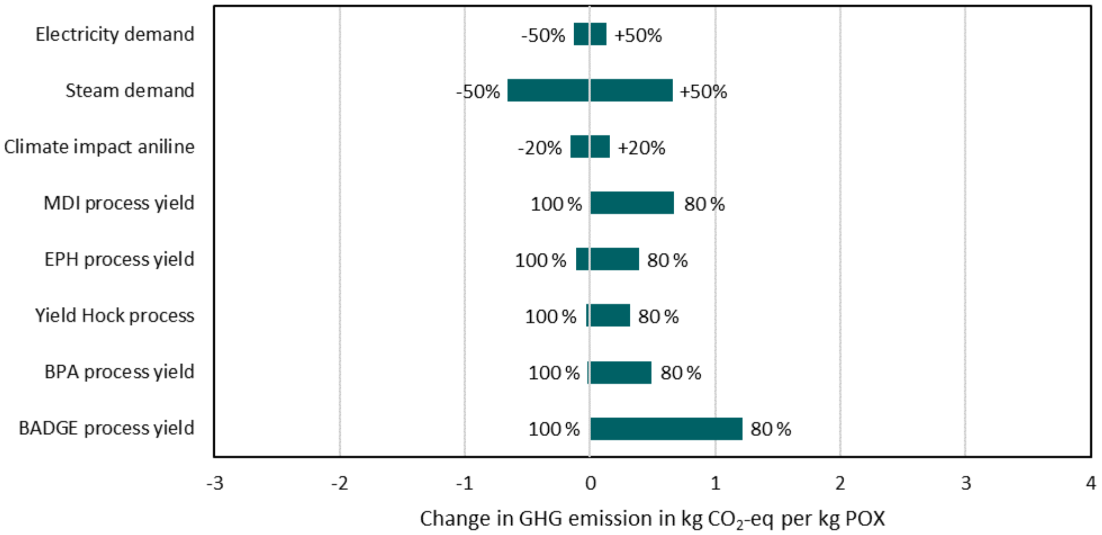

Figure A.5: Change in GHG emissions for polyoxazolidinone (POX) depending on utility demands, GHG emissions of the aggregated aniline process, and process yields in the POX supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in Section 3.4. The percentages next to the bars refer to the minimum and maximum values for the sensitivity analysis. The Hock process produces phenol and acetone. Abbrevaitions: MDI = methylene diphenyl diisocyanate, EPH = epichlorohydrin, BPA = bisphenol A, BADGE = bisphenol A diglycidyl ether.

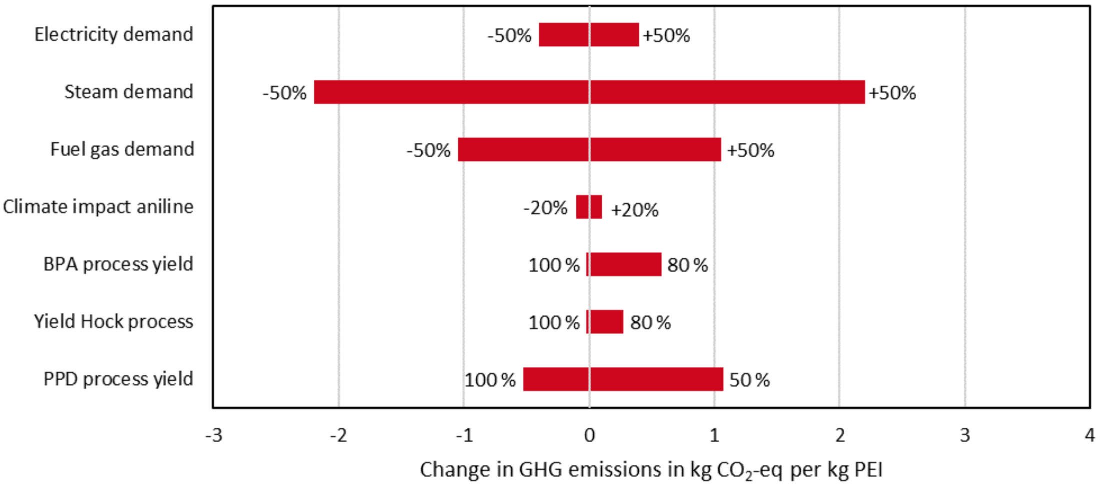

Figure A.6: Change in GHG emissions for polyetherimide (PEI) depending on utility demands, GHG emissions of the aggregated aniline process, and process yields in the PEI supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in Section 3.4. The percentages next to the bars refer to the minimum and maximum values for the sensitivity analysis. The Hock process produces phenol and acetone. Abbrevaitions: BPA = bisphenol A, PPD = m-Phenylenediamine.

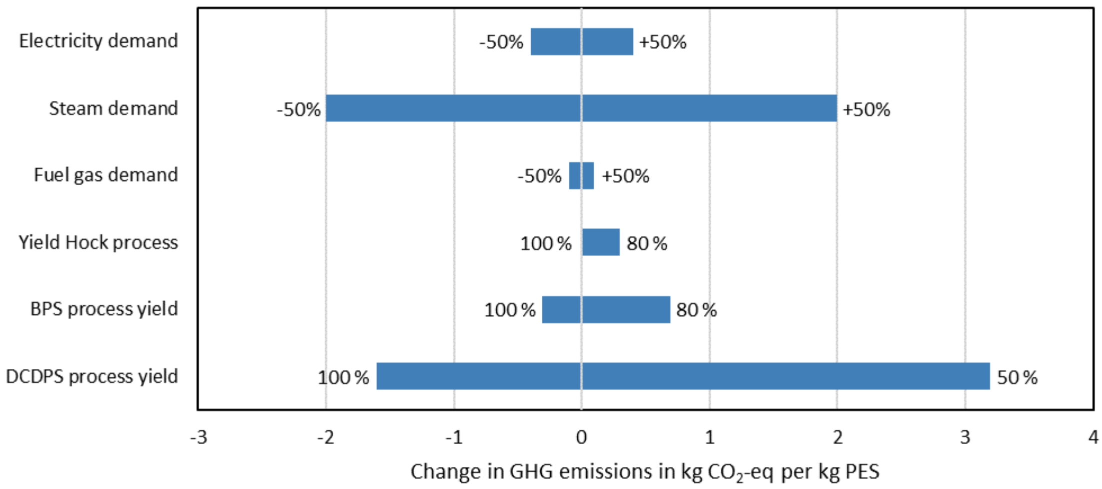

Figure A.7: Change in GHG emissions for polyethersulfone (PES) depending on utility demands and process yields in the PES supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in Section 3.4. The percentages next to the bars refer to the minimum and maximum values for the sensitivity analysis. The Hock process produces phenol and acetone. Abbrevaitions: BPS = dihydroxydiphenyl sulfone (bisphenol S), DCDPS = 4,4'-dichlorodiphenyl sulfone

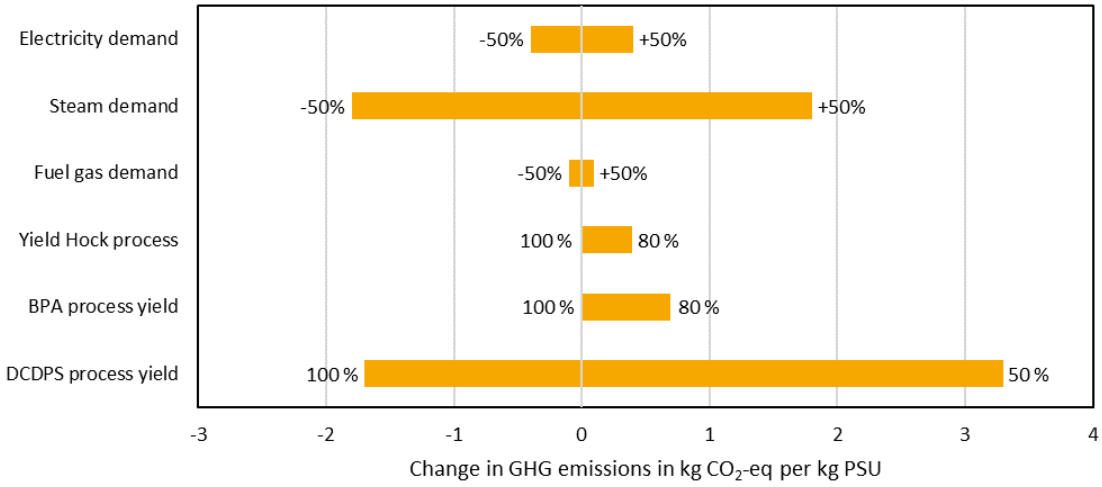

Figure A.8: Change in GHG emissions for polysulfone (PSU) depending on utility demands and process yields in the PSU supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in Section 3.4. The percentages next to the bars refer to the minimum and maximum values for the sensitivity analysis. The Hock process produces phenol and acetone. Abbrevaitions: BPA = bisphenol A, DCDPS = 4,4'-dichlorodiphenyl sulfone

A.7 Further environmental impacts of HPTs

Table A.4: Cradle-to-grave environmental impacts of HPTs for the conventional scenario.

Conventional scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0242	0.0173	0.0148	0.00679
EF 3.0 Climate Change [kg CO_2-eq.]	13.9	13.8	11.9	6.57
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	188	202	211	107
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	180	192	202	108
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	7.89	9.07	9.11	-1.44
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	0.355	0.374	0.37	0.283
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.0000261	0.0000269	0.0000257	0.0000391
EF 3.0 Eutrophication, marine [kg N eq.]	0.0143	0.00485	0.00425	0.00286
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.117	0.0524	0.0461	0.0255
EF 3.0 Human toxicity, cancer - total [CTUh]	2.61E-09	3.05E-09	2.63E-09	1.58E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	2.37E-19	1.59E-19	1.31E-19	8.7E-20
EF 3.0 Human toxicity, cancer metals [CTUh]	1.77E-09	1.87E-09	1.71E-09	1.06E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	8.43E-10	1.18E-09	9.16E-10	5.18E-10
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.83E-07	1.93E-07	1.71E-07	9.68E-08
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.63E-08	4.05E-08	4.09E-08	2.33E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.46E-07	1.53E-07	0.00000013	7.33E-08
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.34E-09	1.42E-09	1.2E-09	7.35E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.273	0.307	0.254	0.156
EF 3.0 Land Use [Pt]	16.1	21.7	18.1	10.7
EF 3.0 Ozone depletion [kg CFC-11 eq.]	8.05E-14	1.31E-13	1.02E-13	7.39E-10
EF 3.0 Particulate matter [Disease incidences]	1.25E-07	1.33E-07	1.19E-07	6.06E-08
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0281	0.02	0.0185	0.00829
EF 3.0 Resource use, fossils [MJ]	251	283	237	137
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000186	0.0000283	0.0000172	0.00000182
EF 3.0 Water use [m^3 world equiv.]	1.49	3.15	2.9	1.04

Table A.5: Cradle-to-grave environmental impacts of HPTs for the biomass scenario.

Biomass scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0273	0.0207	0.0188	0.0159
EF 3.0 Climate Change [kg CO_2-eq.]	12.5	11.7	9.47	3.32
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	165	175	181	77
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	161	164	169	75.2
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	5.27	11.1	11.4	2.68
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	-1.29	0.195	0.164	-0.877
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.0000533	0.0000324	0.000032	0.000162
EF 3.0 Eutrophication, marine [kg N eq.]	0.0152	0.00635	0.00596	0.00525
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.135	0.0687	0.0646	0.072
EF 3.0 Human toxicity, cancer - total [CTUh]	2.15E-09	2.8E-09	2.34E-09	2.13E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	7.55E-19	3.29E-19	3.26E-19	8.13E-19
EF 3.0 Human toxicity, cancer metals [CTUh]	1.19E-09	1.34E-09	1.1E-09	1.56E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	9.56E-10	1.46E-09	1.24E-09	5.62E-10
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.66E-07	1.81E-07	1.57E-07	2.98E-07
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.58E-08	4.02E-08	4.05E-08	1.99E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	0.00000013	1.41E-07	1.16E-07	2.78E-07
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.17E-09	1.33E-09	1.1E-09	4.09E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.364	0.488	0.46	0.222
EF 3.0 Land Use [Pt]	24.1	110	119	67.2
EF 3.0 Ozone depletion [kg CFC-11 eq.]	-1.59E-08	1.81E-13	1.59E-13	-2.31E-08
EF 3.0 Particulate matter [Disease incidences]	1.82E-07	2.55E-07	2.59E-07	1.59E-07
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0318	0.0237	0.0227	0.0121
EF 3.0 Resource use, fossils [MJ]	232	262	213	88.3
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	1.12E-07	0.0000288	0.0000177	-3.59E-07
EF 3.0 Water use [m^3 world equiv.]	0.179	3.49	3.3	-0.575

Table A.6: Cradle-to-grave environmental impacts of HPTs for the renewable energy scenario.

Renewable energy scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0319	0.0257	0.01867	0.00489
EF 3.0 Climate Change [kg CO_2-eq.]	6.98	3.45	4.09	3.55
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	249	276	254	105
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	242	269	246	107
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	6.76	6.44	7.27	-2.14
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	0.932	1.09	0.784	0.272
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.000182	0.000221	0.000138	0.0000374
EF 3.0 Eutrophication, marine [kg N eq.]	0.0166	0.00719	0.00512	0.00199
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.137	0.0709	0.0515	0.016
EF 3.0 Human toxicity, cancer - total [CTUh]	9.59E-09	1.31E-08	1.03E-08	4.54E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	1.97E-19	7.27E-20	7.13E-20	6.55E-20
EF 3.0 Human toxicity, cancer metals [CTUh]	1.89E-09	2.04E-09	1.85E-09	1.12E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	7.71E-09	1.11E-08	8.43E-09	3.42E-09
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.95E-07	2.09E-07	1.82E-07	9.96E-08
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	4.02E-08	4.38E-08	4.20E-08	2.18E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.54E-07	1.64E-07	1.39E-07	7.76E-08
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.5E-09	1.5E-09	1.10E-09	4.87E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.178	0.113	0.120	0.109
EF 3.0 Land Use [Pt]	194	242	145	7.43
EF 3.0 Ozone depletion [kg CFC-11 eq.]	2.42E-13	3.49E-13	2.82E-13	7.39E-10
EF 3.0 Particulate matter [Disease incidences]	1.91E-07	2.06E-07	1.56E-07	4.99E-08
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.03	0.0209	0.0176	0.00587
EF 3.0 Resource use, fossils [MJ]	118	90	94	85.2
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000876	0.0000379	2.42E-05	0.00000423
EF 3.0 Water use [m^3 world equiv.]	2.65	4.81	4.22	1.62

Table A.7: Cradle-to-grave environmental impacts of HPTs for the renewable carbon & energy scenario.

renewable carbon & energy scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0339	0.0278	0.0211	0.0131
EF 3.0 Climate Change [kg CO_2-eq.]	4.76	-0.137	-0.0453	-0.461
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	226	246	220	72.6
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	223	238	211	72.5
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	3.67	7.31	8.26	1.08
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	-0.727	0.897	0.562	-0.899
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.000185	0.000223	0.000141	0.000158
EF 3.0 Eutrophication, marine [kg N eq.]	0.0171	0.00817	0.00624	0.00408
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.15	0.0816	0.0637	0.0593
EF 3.0 Human toxicity, cancer - total [CTUh]	9.68E-09	1.41E-08	1.13E-08	5.59E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	6.93E-19	2.09E-19	2.27E-19	7.65E-19
EF 3.0 Human toxicity, cancer metals [CTUh]	1.32E-09	1.53E-09	1.25E-09	1.63E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	8.36E-09	1.25E-08	1.01E-08	3.96E-09
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.78E-07	1.96E-07	1.67E-07	0.0000003
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.85E-08	4.2E-08	3.99E-08	1.73E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.38E-07	1.53E-07	1.27E-07	2.83E-07
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.27E-09	1.3E-09	8.67E-10	1.02E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.222	0.222	0.245	0.12
EF 3.0 Land Use [Pt]	198	325	240	60.1
EF 3.0 Ozone depletion [kg CFC-11 eq.]	-1.6E-08	4.12E-13	3.54E-13	-2.31E-08
EF 3.0 Particulate matter [Disease incidences]	2.39E-07	0.00000032	2.86E-07	1.42E-07
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0328	0.0233	0.0203	0.00894
EF 3.0 Resource use, fossils [MJ]	86.2	45.4	42.4	25.3
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000855	0.0000392	0.0000257	0.0000023
EF 3.0 Water use [m^3 world equiv.]	1.42	5.34	4.84	0.064

Appendix B

Supplementary information on bio- and CO_2-based polyurethane

B.1 Details on the bottom-up model for polyurethane production

The following chapter first summarizes the data sources and assumption for compiling the bottom-up model for polyurethane production in Section B.1.1, followed by additional results of the LCA in Section B.2 and B.3.

B.1.1 Data sources for the life cycle inventory

Table B.1: Summary of flows, production technologies and data sources of the bottom-up model of the polyurethane production system.

Name of flow	Production technology	Source	Comment
Ammonia	European market for ammonia	ecoinvent 3.5[99] - cut-off	
Ash	European market for wood ash mixture, pure	ecoinvent 3.5[99] - cut-off	
Butane	Global market for butane	ecoinvent 3.5[99] - cut-off	
Calcium dioxide	European market for quicklime, milled, packed	ecoinvent 3.5[99] - cut-off	
Carbon dioxide	By direct air capture	von der Assen et al. (2016)[75]	Details see below
	From cement plant	von der Assen et al. (2016)[75]	Details see below
Carbon monoxide	Reverse water-gas shift	Sternberg et al. (2015)[237]	
	Dry reforming	CO2RRECT[331]	

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Name of flow	**Production technology**	**Source**	**Comment**
	Separation of syngas via partial condensation	IHS PEP Yearbook[257]	
Caustic soda	Global market for sodium hydroxide, without water, in 50 % solution state	ecoinvent 3.5[99] - cut-off	
Chlorine	European market for chlorine	ecoinvent 3.5[99] - cut-off	
Cooling water	global market for water, decarbonized, at user	ecoinvent 3.5[99] - cut-off	
Deionized water	European market for water, deionized, from tap water, at user	ecoinvent 3.5[99] - cut-off	
Diammonium phosphate	European diammonium phosphate production	ecoinvent 3.5[99] - cut-off	
Dinitrotoluene	From toluene by nitration	IHS PEP Yearbook[257]	
Dimethyl carbonate	From vapor-phase oxidative carbonylation	IHS PEP Yearbook[257]	
	From liquid-phase oxidative carbonylation	IHS PEP Yearbook[257]	
	From methanol and urea	IHS PEP Yearbook[257]	
Electricity	European grid mix	Müeller et al.[159]	
Ethanol	From fermentation of miscanthus, carbon dioxide from fermentation is captured, flue gas is released to environment		Details see below
	From fermentation of miscanthus, carbon dioxide from fermentation and flue gas is captured		Details see below
Ethylbenzene	European market for ethylene	ecoinvent 3.5[99] - cut-off	
Ethylene	Global market for ethylene	ecoinvent 3.5[99] - cut-off	
	From ethanol by adiabatic fixed-bed catalytic dehydration	IHS PEP Yearbook[257]	
	From methanol by MTO process	IHS PEP Yearbook[257]	Details see below
	From natural gas by oxidative coupling	IHS PEP Yearbook[257]	

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Name of flow	**Production technology**	**Source**	**Comment**
Ethylene oxide	From ethylene by oxidation	IHS PEP Yearbook[257]	
Ethylene glycol	Global market for ethylene glycol	ecoinvent 3.5[99] - cut-off	
Excess heat	European market for heat, district or industrial, natural gas	ecoinvent 3.5[99] - cut-off	
Fuel oil	European market for light fuel oil	ecoinvent 3.5[99] - cut-off	
Glucose	Global market for glucose	ecoinvent 3.5[99] - cut-off	
Glycerol	European market for glycerine	ecoinvent 3.5[99] - cut-off	
Hydrochloric acid	European market for hydrochloric acid, without water, in 30 % solution state	ecoinvent 3.5[99] - cut-off	
Hydrogen	From steam reforming of natural gas	IHS PEP Yearbook[257]	
	From electrolysis	U.S. Department of Energy[332]	
Inert gas	European market for nitrogen, liquid	ecoinvent 3.5[99] - cut-off	
Methane	German market for natural gas, high pressure	ecoinvent 3.5[99] - cut-off	no data for global or European market available
	from carbon dioxide (Sabatier reaction)	Müller et al. (2013)[333]	
Methanol	global market for methanol	ecoinvent 3.5[99] - cut-off	
	from syngas via JM/ICI/DPT technology	IHS PEP Yearbook[257]	
	from natural via JM/ICI/DPT technology	IHS PEP Yearbook[257]	
	from carbon dioxide and hydrogen (direct hydrogenation)	Rihko-Struckmann (2010)[334]	
Miscanthus, at farm gate	global market for miscanthus, chopped	ecoinvent 3.5[99] - cut-off	
Miscanthus, at refinery	miscanthus transportation, average of 300 km	Styles et al. (2008)[225]	

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Name of flow	**Production technology**	**Source**	**Comment**
Miscanthus, stored at refinery	miscanthus storage, ambient storage	Rentizelas et al. (2009)[226]	
Natural gas	German market for natural gas, high pressure	ecoinvent 3.5[99] - cut-off	no datat for global or European market available
Nitric acid	European market for nitric acid, without water, in 50 % solution state	ecoinvent 3.5[99] - cut-off	
Nitric oxide	Global market for nitric oxide	ecoinvent 3.5[99] - cut-off	
Nitrogen	European market for nitrogen, liquid	ecoinvent 3.5[99] - cut-off	
Oxygen	European market for oxygen, liquid	ecoinvent 3.5[99] - cut-off	
Pentane	Global market for pentane	ecoinvent 3.5[99] - cut-off	
Polyol (PO)	From propylene oxid, glycerol as starter	von der Assen et al. (2015)[335]	
Polyol (PO/CO_2)	From propylene oxide and carbon dioxide, glycerol as starter	Covestro Deutschland AG (2018)[80]	
Polyol (PO/EO)	From propylene oxide and ethylene oxide, glycerol as starter	Ionescu (2016)[79]	
Polyurethane, flexible foam	From polyol and TDI	ecoinvent 3.5[99] - UPR	
Process water	Global market for water, decarbonised, at user	ecoinvent 3.5[99] - cut-off	
Propane	Global market for propane	ecoinvent 3.5[99] - cut-off	
Propylene	European market for propylene	ecoinvent 3.5[99] - cut-off	
	from ethylene via dimerization and olefin conversion technology by Lummus Technology	IHS PEP Yearbook[257]	
Propylene dichloride	Technical chlorination of propane	stoichiometric calculation, hydrochloric acid as co-product	
Propylene oxide	From conventional chlorohydrin process	IHS PEP Yearbook[257]	
	From BASF-DOW HPPO process	IHS PEP Yearbook[257]	

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Name of flow	**Production technology**	**Source**	**Comment**
	From Lyondell Oxirane process with styrene as by-product	IHS PEP Yearbook[257]	Details see below
Rapeseed oil methyl ester	Global market for vegetable oil methyl ester	ecoinvent 3.5[99] - cut-off	
Steam	Global market for steam, in chemical industry	ecoinvent 3.5[99] - cut-off	
Styrene	Global market for styrene	ecoinvent 3.5[99] - cut-off	
Sulfuric acid	European market for sulfuric acid	ecoinvent 3.5[99] - cut-off	
Syngas (molar hydrogen-to-carbon monoxide ratio of 2:1	From natural gas by partial oxidation	IHS PEP Yearbook[257]	
	From natural gas by steam reforming with carbon dioxide import	IHS PEP Yearbook[257]	
	From gasification of miscanthus in pressurized direct oxygen-steam blown circulating fluidized bed gasifier		Details see below
	From gasification of miscanthus in dual fluidized bed gasifier		Details see below
Toluene	European market for toluene, liquid	ecoinvent 3.5[99] - cut-off	
	9 CO_2 + 26 H_2 –> C_7H_8 + 18 H_2O + 2 CH_4	Low-TRL CCU technology[17,336]	
	methanol-to-aromatics	High-TRL CCU technology[337]	
Toluene diisocyanate	From phosgenation	IHS PEP Yearbook[257]	
	From dinitrotoluene	IHS PEP Yearbook[257]	
Transportation of miscanthus	European market for transport, freight, lorry >32 metric ton, EURO5	ecoinvent 3.5[99] - cut-off	
Urea	From mitsui toatsu process	IHS PEP Yearbook[257]	

End of table

B.1.2 CO_2 capture and transportation

For CO_2 supply, we consider biomass utilization technologies, cement plants, and ambient air. In both biomass utilization technologies, namely fermentation and gasification, CO_2 is obtained in high concentrations at ambient pressure. In all cases, to use CO_2 as feedstock, it is compressed to 110 bar and then transported to the production site. We account for the energy demand for compression, according to Farla et al.[264], and neglected all other environmental impacts of compression and transportation. Excess CO_2 from biomass utilization technologies, which is not used in CCU processes, is released into the environment. For the supply of CO_2 from cement plants and ambient air by direct air capture, we use average values from von der Assen et al.[75]

B.1.3 Methanol-to-Olefins process

We consider two methanol-to-olefins (MtO) processes with different product ratios of ethylene to propylene. Data for the process with an ethylene to propylene molar ratio of 2:1 are based on a patent from Union Carbide and UOP. In contrast, data for a molar ratio of 1:1 are based on the DMTO-II technology. Despite the higher propylene yield, the Union Carbide and UOP process is selected in the optimization due to its lower heat and power demand.

B.1.4 Propylene oxide production

For propylene oxide production, we consider the chlorohydrin, HPPO, and the oxirane process. However, we only consider the oxirane process with styrol as by-product. The oxirane process with tert-butanol as a by-product is not considered, since no data are available that sufficiently describe the substitution of tert-butanol. However, the oxirane process with tert-butanol as a by-product may be environmentally beneficial if sufficient tert-butanol can be sold on the market.

B.1.5 Miscanthus gasification for syngas production

We consider two technologies for the gasification of miscanthus to syngas: a pressurized direct oxygen-steam blown circulating fluidized bed (CFB) gasifier and an atmospheric indirect air-blown dual fluidized bed (DFB) gasifier. Details on the gasification models can be found in Appendix C.

B.1.6 Miscanthus fermentation for ethanol production

The ethanol production from miscanthus is based on the 2011 design report by the National Renewable Energy Laboratory[338] and the associated aspen model. The aspen model only considers corn stover as feedstock for ethanol production. We modified the lignocellulosic feedstock's composition in the aspen model to reflect the composition of miscanthus. Miscanthus is used to supply both feedstock for fermentation and process heat. Excess heat is used to produce electricity, which can be used in other processes within the foreground system or substitutes grid electricity. The fermentation vents a high concentrated CO_2 stream that can be compressed and used in the foreground system.

In addition to CO_2 released during the fermentation, additional CO_2 is released as flue gas during lignin and other combustibles' incineration. However, the flue gas has a much lower CO_2 concentration than the fermentation CO_2 steam and is thus harder to purify. Therefore, we added another dataset for the fermentation process, where we added CO_2 capture from flue gas. For CO_2 capture from flue gas, we assumed the same heat and electricity requirements as for the CO_2 capture from cement plants,[75] since both flue gases have similar CO_2 concentrations. The heat required for CO_2 capture is supplied by excess heat of the fermentation process. The modified model, therefore, does not produce any excess electricity. The captured CO_2 can be compressed and used in the foreground system.

B.1.7 Biomass-to-heat efficiency

We calculated the biomass-to-steam efficiency with a steam boiler efficiency of 95 % and an energy content of steam of 2.75 MJ/kg. We used a carbon footprint of miscanthus of -1.5 kg CO_2-eq per kg of biomass for calculation and assumed an average heating value of 20 MJ/kg of biomass.[224] GHG emissions of fossil-based steam is taken from ecoinvent 3.5 - cut-off.[99] We neglect the transportation and storage of miscanthus in this calculation.

B.1.8 Miscanthus as a feedstock

With miscanthus as perennial energy crop, this study considers only one possible biomass feedstock for polymer production. Perennial energy crops have great potential to serve as a supplier of energy and carbon feedstock in the future.[339] However, the availability of perennial energy crops is still limited today. The actual potential varies greatly between studies[339,340] since it depends on many factors such as the availability and type of marginal land used for cultivation. Therefore, large-scale implementation of bio-based production should also consider other lignocellulosic biomass. Consequently, we discuss the potential use of other lignocellulosic biomass for the considered processes.

For gasification, various lignocellulosic biomass feedstocks are suitable.[341] The type of lignocellulosic biomass influences the characteristics of the gasification process, such as the operating conditions and the gasifying agent.[342] The syngas yield and quality depend on moisture content, particle size, and particle density of the biomass feedstock.[342] Furthermore, the heating value of the biomass feedstock ranges between 18 and 22 MJ/kg for most lignocellulosic biomass and has a significant impact on the syngas yield and process efficiency.[341]

For fermentation of lignocellulosic biomass to ethanol, various feedstocks can be used as well. Here, the biomass composition, which consists of cellulose, hemicellulose, and lignin, has a significant impact on the ethanol yield.[343] The higher the lignin content of the biomass, the lower the ethanol yield. Since the share of lignin is particularly high for lignocellulosic biomass, the conversion process requires efficient pretreatment processes to degrade the crystallinity of cellulose fibers and remove lignin from biomass.[343] However, the use of other lignocellulosic biomass feedstocks leads to product yields similar to those obtained with the technologies employed in this study.[344]

Thus, alternative lignocellulosic biomass could be employed. However, the choice of biomass feedstock determines the overall process design of the gasification and fermentation and thus, influences the environmental impacts of bio-based products. Furthermore, other lignocellulosic biomass feedstocks have to be analyzed comprehensively in terms of harvesting effort and LUC emissions.

B.2 Renewable resource savings from the synergetic use of biomass and CO_2

Synergies from combined utilization save renewable resources compared to the utilization of either biomass or CO_2. In the paper, we analyze the GHG reduction from 7.6 kg CO_2-eq/kg_{PUR} to 4.5 kg CO_2-eq/kg_{PUR} for the carbon footprint of -1.7 kg CO_2-eq per kg biomass and 3 g CO_2-eq per MJ renewable electricity. The reduction requires 2 kg of biomass and 45 MJ of renewable electricity used in separate production facilities (linear combination in Figure S1). In combined utilization, the same GHG reduction is achieved using only 1.6 kg of biomass and 33 MJ of renewable electricity.

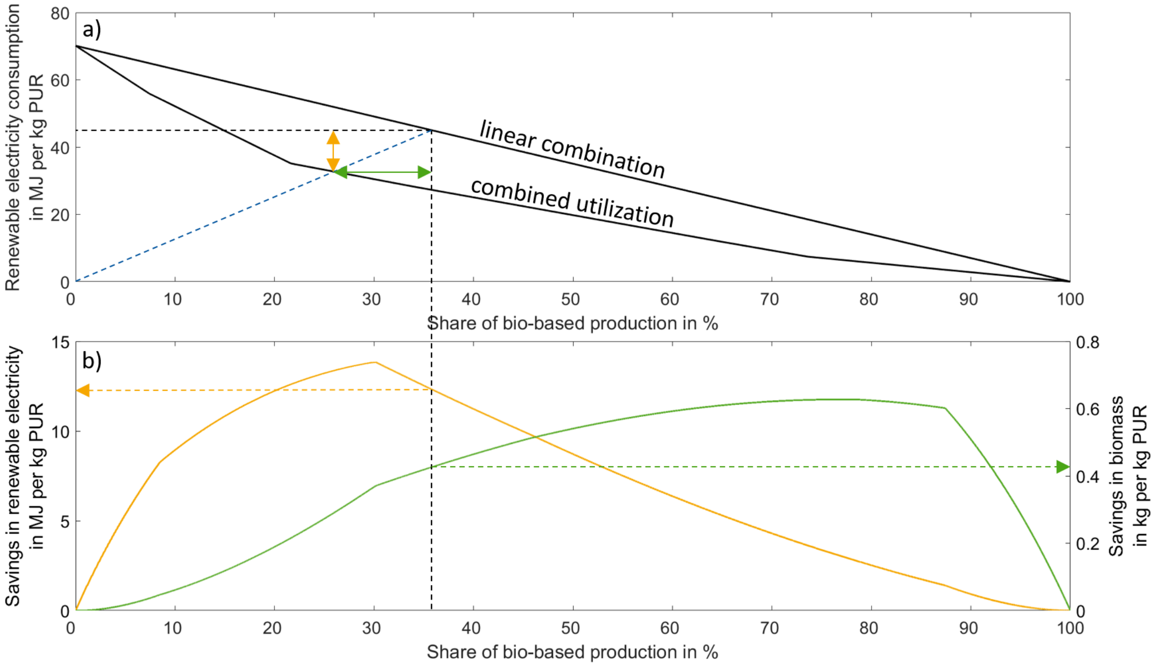

Figure B.1: Upper figure: Renewable electricity consumption for a linear combination of bio- and CCU-based production and combined utilization as a function of the share of the bio-based production for a global warming impact of 4.5 kg CO_2-eq/kg_{PUR}.

Lower figure: Savings of renewable electricity (left y-axis) and biomass (right y-axis) as a function of the share of bio-based production for a global warming impact of 4.5 kg CO_2-eq/kg_{PUR}. The savings equal the difference between the linear combination of bio- and CCU-based production and the combined utilization.

B.3 Sensitivity analysis for the carbon footprint of renewable resources

Synergies from combined utilization of biomass and CO_2 can reduce GHG emissions compared to the utilization of either biomass or CO_2. However, the extent of additional savings depends on the carbon footprints of biomass and electricity (Figure S2). We, therefore, vary the carbon footprint of biomass and electricity in a sensitivity analysis. Our results indicate that for high carbon footprints of either biomass or electricity, the respective other technology is selected.

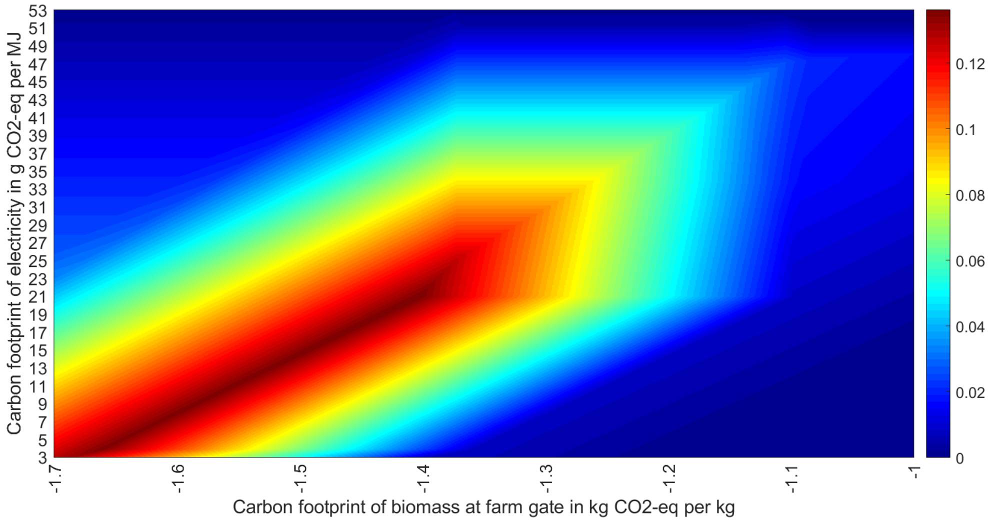

Figure B.2: Relative savings in GHG emissions of the combined utilization of biomass and CO_2 compared to individual utilization as a function of the carbon footprint of biomass and CO_2. The relative savings are expressed as the difference between the minimum GHG emissions of the individual utilization and the combined utilization of biomass and CO_2 divided by the minimum GHG emissions of the individual utilization.

APPENDIX C

Supplementary information on alternative syngas production

C.1 Data sources for life cycle inventory of syngas production

The bottom-up model of the syngas production system is divided into a background and a foreground system. The background system is based on aggregated datasets from the LCA database ecoinvent (see Table C.1). For the aggregated datasets, we use global markets as default. If no data for global markets are available, we use the European counterparts or ”rest of world” datasets.

Table C.1 also includes data sources for the foreground system. The data for the fossil-based syngas production (partial oxidation and steam methane reforming) and a few other datasets were taken from IHS Markit.[257] We followed the procedure from Meys et al. to generate life cycle inventories from IHS Markit data.[5] The data is publicly available, but access requires a user license. Accordingly, the life cycle inventory data can not be disclosed. For the bio- and CO_2-based production, the life cycle inventories are disclosed in Section C.4 and C.5.

Table C.1: Summary of flows, production technologies, and data sources of the bottom-up model of syngas production. The following numbers represent the scenarios in which the technology is available: 1: fossil-based production, 2: bio-based production - a = conservative – b = optimistic scenario, 3: CO_2-based production, 4: Millgas-based production. Locations: GLO = global, RER = Europe, RoW = rest of world.

Flows	**Technology**	**Source**	**Location**	**Scenarios**	**Comments**
Ash	Treatment of wood ash mixture, pure, sanitary landfill	ecoinvent v3.5[202]	RoW	[2]	
Basic oxygen furnace gas	By-product from the reduction of iron ore with coke in steel mills	Uribe-Soto et al.[14]	-	[1,2,3,4]	
Carbon dioxide (CO_2)	Capture from ammonia plant via Rectisol	Von der Aßen[75]	-	[1,2,3,4]	
	Capture from anaerobic digestion plant via membrane separation	Ardolino et al.[247,260]	-	[2b]	
	Capture from biomass gasification plant via Rectisol	*Cf.* Section C.3	-	[2]	
	Capture from steam methane reforming via Rectisol	IHS Markit[257]	-	[1,2,3,4]	
	Capture from water-gas shift via amine scrubbing	IHS Markit[257]	-	[1,2,3,4]	
	Compression of CO_2	Farla et al.[264]	-	[1,2,3,4]	If CO_2 is used as feedstock, compression to 100 bar is applied
	Direct-air capture	Deutz et al.[271]	-	Sensitivity analysis	
Carbon monoxide	CO_2-electrolysis	Nabil et al.[266]	-	[3]	
	Dry reforming of methane	CO_2RRECT[331], adapted from Sternberg[250]	-	[3]	
	Reverse water-gas shift	CO_2RRECT[331], adapted from Sternberg[250]	-	[3]	

Continued on next page

Flows	**Technology**	**Source**	**Location**	**Scenarios**	**Comments**
	Separation of basic oxygen furnace gas via pressure swing adsorption	Kasuya et al.[269]	-	[4]	
Coke oven gas	By-product from coke production in steel mills	Uribe-Soto et al.[14]	-	[1,2,3,4]	
Cooling water	Market for water, decarbonised, at user	ecoinvent v3.5[202]	GLO	[1,2,3,4]	
Diesel	Market for diesel	ecoinvent v3.5[202]	RoW	[1,2,3,4]	
Electricity	Conventional treatment of basic oxygen furnace gas in steel mill power plant	ecoinvent v3.5[202]	GLO	[1,2,3,4]	Power plant efficiencies adopted from treatment of blast furnace gas as a conservative assumption
	Conventional treatment of coke oven gas in steel mill power plant	ecoinvent v3.5[202]	GLO	[1,2,3,4]	Power plant efficiencies adopted from treatment of blast furnace gas as a conservative assumption
	Sensitivity analysis of the marginal global warming impact of the grid	-	-	[1,2,3,4]	
	Natural gas, combined cycle power plant	ecoinvent v3.5[202]	RoW	[1,2,3,4]	For the assessment of other environmental impacts besides GWI
	Wind power, 1-3 MW turbine onshore	ecoinvent v3.5[202]	RoW	[1,2,3,4]	For the assessment of other environmental impacts besides GWI
Heat, high-temperature	Biomass incineration for industrial process heat	-	-	[1,3,4]	90 % efficiency
	Conventional treatment of basic oxygen furnace gas in steel mill power plant	ecoinvent v3.5[202]	GLO	[1,2,3,4]	Power plant efficiencies adopted from treatment of blast furnace gas as a conservative assumption
	Conventional treatment of coke oven gas in steel mill power plant	ecoinvent v3.5[202]	GLO	[1,2,3,4]	Power plant efficiencies adopted from treatment of blast furnace gas as a conservative assumption
	Excess hydrogen incineration	-	-	[1,2,3,4]	90 % efficiency
	Natural gas boiler	-	-	[1,2,3,4]	95 % efficiency

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Flows	Technology	Source	Location	Scenarios	Comments
Heat, low-temperature	Resistance heater	Meys et al.[5]	-	[1,2,3,4]	95 % efficiency
	Excess heat from biomass gasification	*Cf.* Section C.3	-	[2]	
	Heat pump	Deutz et al.9	-	[1,2,3,4]	
Hydrogen	Dry reforming of methane	CO_2RRECT[331], adapted from Sternberg[250]	-	[3]	
	Polymer electrolyte membrane (PEM) electrolyzer	Bareiß et al.[270]	-	[1,2,3,4]	
	Separation of coke oven gas via pressure swing adsorption	Ramírez-Santos et al.[15]	-	[4]	
	Steam methane reforming and water-gas shift with CO_2 capture	IHS Markit[257]	-	[1,2,3,4]	
	Water-gas shift and amine separation of CO_2	IHS Markit[257]	-	[1,2,3,4]	
Methane	Anaerobic digestion of bio-waste	Ardolino et al.[247,260]	-	[2b]	
	From natural gas	ecoinvent v3.5[202]	RoW	[1]	
	Sabatier process	Perner et al.[267]	-	[3]	
Miscanthus	Market for miscanthus, chopped	ecoinvent v3.5[202]	GLO	[2b]	
Monoethanolamine	Market for monoethanolamine	ecoinvent v3.5[202]	GLO	[1,2,3,4]	
Natural gas	Market for natural gas, high pressure	ecoinvent v3.5[202]	RoW	[1,2,3,4]	
Oxygen	Cryogenic air separation	IHS Markit[257]	-	[1,2,3,4]	
Process water	Market for water, decarbonised, at user	ecoinvent v3.5[202]	GLO	[1,2,3,4]	
Rapeseed oil methyl ester	Market for vegetable oil methyl ester	ecoinvent v3.5[202]	GLO	[2]	
Silicon carbide	Market for silicon carbide	ecoinvent v3.5[202]	GLO	[1,2,3,4]	

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Flows	Technology	Source	Location	Scenarios	Comments
Solid digestate & solid residues	Incineration	-	-	[2b]	Complete combustion based on composition assumed
Bio-waste	Biodegradable municipal Waste	Ardolino et al.[247,260]	-	[1,2b,3,4]	
	Conventional treatment by solid waste incineration	-	-	[1,3,4]	Complete combustion based on composition assumed
Steam	Electric boiler	IHS Markit[257]	-	[1,2,3,4]	
	Excess steam from hydrogen production via steam methane reforming and water-gas shift with CO_2 capture	IHS Markit[257]	-	[1,2,3,4]	
	Packaged gas boiler, from low or high-temperature heat	ecoinvent v3.5[202]	-	[1,2,3,4]	specific enthalpy of steam = 2750 kJ/kg
Syngas 2:1	Biomass gasification via circulating fluidized bed gasifier	*Cf.* Section C.3	-	[2]	
	Biomass gasification via dual fluidized bed gasifier	*Cf.* Section C.3	-	[2]	
	Co-electrolysis	Schreiber et al.[245]	-	[3]	
	Mixing of carbon monoxide and hydrogen	-	-	[1,2,3,4]	Based on stoichiometry
	Partial oxidation of methane	IHS Markit[257]	-	[1,2,3,4]	
	Steam methane reforming with CO_2 import	IHS Markit[257]	-	[1,2,3,4]	We consider this technology in the fossil scenario, although it requires a CO_2 input.
	Steam methane reforming with hydrogen skimming	IHS Markit[257]	-	[1,2,3,4]	
Wood chips	Market for wood chips, wet, measured as dry mass	ecoinvent v3.5[202]	RER	[1,2a,3,4]	

End of table

C.2 Pressure adjustments in syngas production

The syngas production technologies in this study differ in pressure and temperature levels. To ensure a consistent comparison of technologies, we set the functional unit to 1 kg syngas at a pressure of 30 bar. If a technology does not meet the pressure requirements of either syngas or the intermediates CO and H_2, we included the additional electricity demand for compression. The electricity demand was estimated using a multi-stage compression in the process simulation software Aspen Plus®. The multi-stage compression was modeled with an isentropic compressor model and fixed discharge conditions from each stage. These discharge conditions correspond to a maximum gas temperature of 200 °C with intermediate cooling to 50 °C. The number of compressor stages corresponds to the minimum number required.

C.3 Handling of impurities in feed and product gas

Feed gases and syngas may contain impurities, e.g., nitrogen-containing compounds or hydrocarbons. These impurities typically show either inert or reversible poisoning character for the catalyst for methanol production.[345] Regarding the catalyst for Fischer-Tropsch synthesis, potential sulfur impurities show critical toxicity character and should be separated.[242] However, we neglect these impurities in the assessment due to a lack of data.

C.4 Bio-based syngas - details and life cycle inventory

This section provides additional information on marginal biomass and bio-waste, the biomass carbon footprints, and the life cycle inventory generation of the bio-based technologies.

Marginal Biomass

We define marginal biomass as biomass grown solely as a feedstock for syngas production. As an example of marginal biomass, we consider perennial energy crops. Perennial energy crops combine high crop yields with low pesticide and nutrient requirements.[220,346] Therefore, perennial energy crops can be cultivated on marginal land where they do not compete with conventional crops for land use.

Bio-waste

Bio-waste includes manure, sewage sludge, and the organic fraction from municipal, commercial and industrial waste.[247] We consider the organic fraction of municipal solid waste, called bio-waste hereafter, as feedstock for syngas production. Bio-waste can be treated by composting, biological treatment like anaerobic digestion, incineration, or landfilling.[347] The conventional treatment of bio-waste differs significantly by region. For instance, composting and incineration are the predominant waste management options in the European Union.[347] We assume incineration without energy recovery as the conventional bio-waste treatment, which is the most optimistic assumption for syngas production from bio-waste.

The carbon footprint of biomass and bio-waste

The carbon footprint of biomass and bio-waste depends on their carbon content and additional cultivation and logistical efforts, e.g., harvesting methods, gathering efforts, or fertilizer and pesticide application.[55] In addition, biomass absorbs CO_2 from the atmosphere during the growth phase. The amount of CO_2 absorbed depends on the carbon content of the biomass. We account for the carbon uptake from biomass and bio-waste by giving a credit corresponding to the carbon content. The carbon content of wood chips is about 50 wt-% per kg of dry biomass, and the moisture content is also 50 %.[348] For miscanthus, the carbon content is 48 wt- %, and the moisture content is 14 %.[202,224] The wet bio-waste has a carbon content of 15.5 wt- % per kg.[260] Furthermore, we consider GHG emissions from cultivation and logistical efforts using the LCA database ecoinvent.[202] In addition, biomass cultivation affects the carbon content of the soil, which may lead to additional LUC emissions from soil-bound carbon.

However, LUC emissions from woody biomass such as pine are considered to be small.[328] Furthermore, the conservative scenario in Chapter 5 requires all syngas pathways to use the same amount of wood chips, either for gasification or to provide bio-based heat (*cf.* Table 5.1 in Chapter 5). Therefore, LUC emissions from wood chips would only be a GWI offset for all syngas pathways.

In the optimistic scenario, bio-waste and marginal biomass are used for syngas production. Again, LUC emissions from bio-waste would only be a GWI offset since all pathways treat the same amount of bio-waste. In addition, LUC emissions from bio-waste are assumed to be small since potential LUC emissions can be allocated to the bio-waste main product.

To assess the LUC emissions from marginal biomass, one has to differentiate between direct and indirect LUC emissions. Direct LUC emissions occur when biomass cultivation alters the carbon content of the soil. Since cultivating energy crops remains or increases the soil's carbon content, direct LUC emissions are small or even negative.[222] Indirect LUC emissions occur when biomass cultivation displaces other crops since these crops must be cultivated elsewhere to meet their demand. This displaced cultivation may change the soil carbon content, resulting in indirect LUC emissions. However, marginal biomass, per definition, is grown on marginal land where they do not compete with other crops. Therefore, cultivating marginal biomass does not lead to indirect LUC emissions. Thus, overall, we do not consider LUC emissions in Chapter 5.

Biomass gasification technologies

For biomass gasification, four types of gasifiers exist: Fixed bed, bubbling fluidized bed, circulating fluidized bed, and entrained flow gasifiers.[229] Entrained flow gasifiers require biomass pretreatment, such as extensive milling, leading to feeding issues in large-scale applications.[349] Fixed bed and bubbling fluidized bed gasifiers have lower capacities and biomass conversion rates than circulating fluidized bed gasifiers.[350] Thus, we consider circulating fluidized bed gasifiers in Chapter 5.

Circulating fluidized bed gasifiers can be divided into directly and indirectly heated, so-called dual-bed systems.[229] Directly heated systems obtain the required heat for gasification by partially combusting biomass within the reactor. Directly heated systems require oxygen instead of ambient air as an oxidizing agent to keep nitrogen content in the syngas low. In contrast, indirectly heated systems supply the heat by circulating the biomass between the reactor and a separate combustion chamber. Accordingly, the indirectly heated system can use ambient air as the oxidizing agent in the combustion chamber. Furthermore, gasification requires a biomass moisture content of less than 10-15 %, which can be adjusted by a previous drying step.[351]

The life cycle inventories for the directly heated circulating fluidized bed (CFB) and the indirectly heated dual-fluidized bed (DFB) gasifier were generated using Aspen Plus® (see Figure C.1). The CFB gasifier model is based on a concept by Hannula et al.[227,228] and the associated process layout by Isaksson et al.[229] The dryer and the gasifier models are taken from Arvidsson et al.[231] The reformer model is based on data published by the National Renewable Energy Laboratory.[232] LCI data for the DFB gasifier were generated using a model developed by Arvidsson et al., based on the technology used in the Gothenburg Biomass Gasification project.[230]

Both gasification models are modified to account for miscanthus' higher ash content compared to wood chips and wood pellets conventionally used for gasification. The produced syngas has a hydrogen to carbon monoxide ratio of 2:1. Additional CO_2 from syngas upgrading is captured and can be used in the foreground system. In the syngas study, the bio-based CO_2 from the gasification plant can only be used as feedstock for CCU in the combined scenario in Section C.7 and C.8. We modeled a simplified heat integration using a Grand Composite Curve. The low-temperature excess heat can be used to generate steam or substitute district or industrial heat. Matthias Hermesmann performed the modeling of the gasification process under the supervision of Johan Ahlström, Stavros Papadokonstantakis, and Harvey Simon at the Chalmers University of Technology. The inventory data (see Table C.2) has not yet been disclosed but has already been used in a publication by Meys et al.[5]

Anaerobic digestion of bio-waste

Bio-waste treatment offers considerable resource and energy recovery potential through anaerobic digestion, aerobic composting, or incineration. However, anaerobic digestion has shown to be the most favorable for biodegradable materials in terms of carbon and energy footprints.[352,353] Anaerobic digestion to bio-methane consists of three main steps: pretreatment of bio-waste by mechanical sorting, wet anaerobic digestion, and raw biogas upgrading to bio-methane.[260] Biogas upgrading includes membrane separation to separate off-gases from the bio-methane. Since the off-gas consists of 99 % CO_2, we consider it an additional CO_2 source for CCU in the combined pathway in Section C.7 and C.8. The life cycle inventory for anaerobic digestion of bio-waste is taken from Ardolino et al.[247,260] However, Ardolino et al. assume landfill as the treatment for solid residues from pretreatment and solid digestate from anaerobic digestion, whereas we assume incineration to avoid potential carbon sinks.

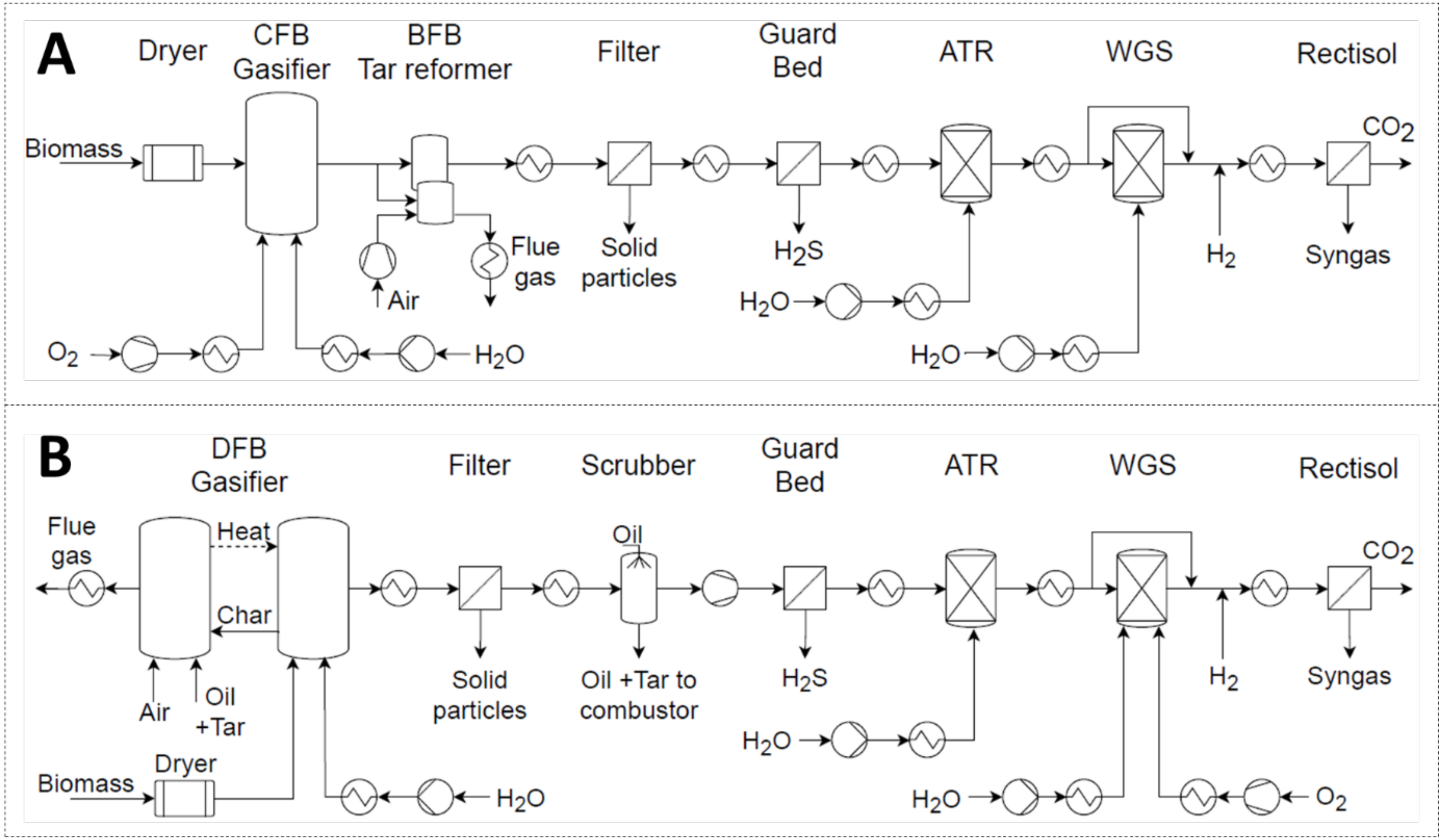

Figure C.1: Process flowsheet of the biomass gasification process based on A – a circulating fluidized bed (CFB) gasifier or B – a dual fluidized bed (DFB) gasifier. The hydrogen-to-carbon monoxide ratio (H_2/CO ratio) of 2:1 can be adjusted by the water-gas shift (WGS) reaction or hydrogen import (H_2-import).

Table C.2: Life cycle inventory for the circulating fluidized bed (CFB) and the dual fluidized bed (DFB) gasifier. Wood chips and miscanthus are used as biomass feedstock. The ash content of dry wood chips and miscanthus is 2.2 wt-% and 2.9 wt-%, respectively.[224,348] The hydrogen-to-carbon monoxide ratio of 2:1 can be adjusted by the water-gas shift (WGS) reaction or hydrogen import (H_2-import). The rapeseed oil methyl ester (RME) for the DFB gasifier is required for tar removal via scrubbing.

Gasifier			CFB	CFB	CFB	CFB	DFB	DFB	DFB	DFB
Feedstock			Wood chips	Wood chips	Miscanthus	Miscanthus	Wood chips	Wood chips	Miscanthus	Miscanthus
Syngas adjustment by			WGS	H_2-import	WGS	H_2-import	WGS	H_2-import	WGS	H_2-import
	Flow	Unit								
Product	Syngas	kg	1	1	1	1	1	1	1	1
By-product	Captured CO_2	kg	1.41	0.51	1.29	0.45	0.28	0.07	0.21	0.07
	Excess heat, low-temp.	MJ	2.27	1.49	5.03	3.27	4.08	3.44	6.90	6.08
Feedstock	Wood chips, wet	kg	3.37	2.15	-	-	3.38	2.82	-	-
	Miscanthus, wet	kg	-	-	1.95	1.25	-	-	1.99	1.75
Other inputs	Hydrogen	kg	-	0.06	-	0.06	-	0.03	-	0.03
	Oxygen	kg	0.87	0.56	0.84	0.54	0.20	0.17	0.20	0.18
	RME	kg	-	-	-	-	0.02	0.02	0.02	0.02
	Process water	kg	1.22	0.34	1.23	0.33	1.04	0.63	1.12	0.80
	Electricity	MJ	0.76	0.49	0.74	0.48	2.44	2.03	2.03	1.78
Waste	Ash	kg	0.04	0.02	0.05	0.03	0.04	0.03	0.05	0.04
Emissions	CO_2	kg	0.32	0.09	0.31	0.08	1.52	1.21	1.52	1.29

C.5 CCU-based syngas - life cycle inventory

Table C.3: Life cycle inventory data of CCU processes. Data for the reverse water-gas shift (WGS) and the dry reforming of methane were taken from Sternberg et al.[250] Data for the Sabatier process is taken from Perner et al.[267], and data for Co-electrolysis and CO_2-electrolysis from Schreiber et al.[245] and Nabil et al.[266], respectively.

	Flow	Unit	Reverse WGS	Dry reforming	Sabatier process	Co-electrolysis	CO_2-electrolysis
Product	Carbon monoxide	kg	1	1	-	-	1
	Methane	kg	-	-	1	-	-
	Syngas	kg	-	-	-	1	-
By-product	Hydrogen	kg	-	0.05	-	-	0.01
	Steam	kg	-	0.20	-	-	-
	Excess heat, high-temperature	MJ	-	1.21	-	-	-
	Oxygen	kg	-	-	-	1.50	0.57
Feedstock	CO_2	kg	1.58	0.91	2.78	1.38	1.57
	Hydrogen	kg	0.07	-	0.58	-	-
	Methane	kg	-	0.26	-	-	-
Other inputs	Electricity	MJ	4.82	7.13	3.48	31.75	17.28
	Heat	MJ	2.20	-	-	-	-
	Process water	kg	-	-	-	1.13	0.07
Emissions	CO_2	kg	0.01	0.05	0.04	-	-

C.6 Millgas-based syngas - details

COG separation

We model a simplified pressure-swing adsorption (PSA) process to separate H_2 from COG. The PSA model accounts for the electricity demand for COG compression using the compressor model from Section C.2. The minimum adsorption pressure P_{PSA}^{high} can be calculated as[354]

$$P_{PSA}^{high} = P_{PSA}^{low} \cdot \left(y_{H_2}^{COG} \cdot \frac{1 - R_{PSA}}{1 - \beta_{PSA}} \right)^{-1} \tag{C.1}$$

where P_{PSA}^{low} is the lower pressure of the pressure swing cycle, $y_{H_2}^{COG}$ is the mole fraction of H_2 in COG, R_{PSA} is the H_2 recovery rate, and β_{PSA} is the adsorbent selectivity. We assume the lower pressure as atmospheric, an H_2 recovery rate of 90 % common for modern multi-bed PSA processes, and an adsorbent selectivity of 0.02.[15,355] The resulting minimum adsorbent pressure is 20.2 bar. However, we assumed compression to 30 bar to meet the syngas requirements without additional compression after separation. The achieved H_2 purity is higher than 99 %.[15]

The simplified PSA model does not consider any adsorbent since adsorbent selection highly depends on potential gas impurities such as hydrogen sulfide. Hydrogen sulfide, in particular, may increase adsorbent consumption due to irreversible capture by the adsorbent material.[356] However, a recent study on a PSA process for biogas upgrading indicates that adsorbent consumption might not be a critical factor since environmental impacts and investment and reinvestment costs of adsorbents are low compared to electricity.[356]

BOFG separation

For CO separation from BOFG, little information is available in the open literature, and separation is most likely performed by absorption or adsorption.[15] According to Ramírez-Santos et al., the COPURESM (formerly COSORB) process is currently the only commercially available absorption process that selectively separates CO from BOFG. Ghanbari et al. considered the COPURESM process along with thermal swing adsorption in their superstructure optimization of mill gas separation.[355] However, Ghanbari et al. did not publish any process data for the COPURESM process due to confidentiality agreements. Lim et al. calculated the costs of the COPURESM process and compared it to a pressure-swing adsorption (PSA) process.[357] Unfortunately, Lim et al. published in Korean, so the authors cannot access the study results. Therefore, we only consider a simplified PSA process based on data from Kasuya et al.[269]

Blast furnace gas (BFG), containing 50-55 mol-% nitrogen, 20-28 mol-% CO, and 17-25 mol-% CO_2, could also be used as a CO source. The concentration of CO in BFG is lower than in BOFG (see Table C.4), but the higher availability of about 900 Nm^3 BFG per ton of steel compared to about 50 Nm^3 BOFG marks BFG as the larger CO source.[15] However, a selective CO separation from BFG is more challenging due to the higher concentration of nitrogen and CO_2. Furthermore, CO separation from BOFG yields about 30.5 kg (1.1 kmol) CO per ton of steel, while H_2 separation from COG only yields about 2.5 kg (1.2 kmol) H_2. Mixing the maximum available CO from BOFG and H_2 from COG would result in an H_2:CO ratio of 1.1, which is lower than the required ratio of 2:1. Therefore, CO separation from BOFG is sufficient to utilize all H_2 from COG for syngas.

Table C.4: Composition[14], volumetric flow rate[15], and lower heating values of coke oven gas and basic oxygen furnace gas.

	Coke oven gas	**Basic oxygen furnace gas**
Compounds	**Molar fraction in %**	
Nitrogen	5.8	18.1
Carbon monoxide	4.1	54.0
Carbon dioxide	1.2	20.0
Hydrogen	60.7	3.2
Methane	22.0	-
C_xH_y (assumed as ethane)	2.0	-
Water	4.0	4.0
Oxygen	0.2	0.7
Volume in m^3/t steel	50	50
Lower heating value before separation in MJ/kg	38.5	5.4
Lower heating value after separation in MJ/kg	30.6	1.5
Electricity for separation in MJ/kg product	14.6	0.7

C.7 The GWI of syngas - extended analysis of the conservative scenario

Details on fossil-based production. In the conservative scenario, the fossil production based on steam reforming or partial oxidation of natural gas leads to 5.4-6.3 kg CO_2-eq per functional unit (see Figure C.2). For electricity impacts higher than the global average in 2050, the exothermic partial oxidation results in lower GHG emissions than endothermic steam reforming due to the lower demand for external energy. However, in 2050, steam reforming with H_2 skimming performs best since it requires less natural gas per syngas than partial oxidation and steam reforming with CO_2 import. The additional heat for H_2 skimming is supplied by the H_2-recycle and resistance heaters. The remaining emissions of fossil-based production result mainly from mill gas treatment, direct emissions from steam reforming and partial oxidation, natural gas supply, and syngas disposal at the end of life (see Figure C.3).

Details on mill gas-based production. Since electricity requirements for PSA are uncertain, we varied the electricity demand for the mill gas separation in a sensitivity analysis from zero to 100 % additional electricity compared to the default modeling. The default modeling estimated the energy requirements for PSA based on the multi-stage compression described in Section C.2. The sensitivity analysis shows that even for the 100 % additional electricity, mill gas-based production performs best in GHG emissions for a wide range of electricity impacts. However, please note that adsorbent consumption is not considered in the assessment, which may increase GHG emissions from PSA.

Another rather varying than uncertain parameter is the energy efficiency of the steel mill power plant, which is set to 30 % electric efficiency and 15 % thermal efficiency in Chapter 5. A sensitivity analysis of the efficiency would be desirable but the results would not be comparable since changing the power plant efficiency also changes the functional unit. Changing the power plant efficiency affects the conventional, fossil-based production, the mill gas-based production, and all other alternative pathways. The conventional and the other alternative pathways are affected since mill gas is burned in the power plant, and the mill gas-based production is affected by the treatment of the remaining gases after separation.

Accordingly, we only make the qualitative statement that higher power plant efficiencies negatively affect mill gas-based syngas production: A higher power plant efficiency results in a higher heat and electricity output, which must be compensated by using more natural gas and grid electricity in mill gas-based production. In addition, the direct reduction of iron ore by H_2 or electricity is being discussed as an alternative low-emissions pathway to steel.[170,358] If steel production switches to direct reduction, mill gas composition and availability will change. Consequentially, it is uncertain whether COG and BOFG will still be available for syngas production in the future. Therefore, for the time being, mill gas-based production should be considered as an intermediate solution to mitigate the GHG emissions of syngas.

Details on bio-based production. The best-case bio-based production relies on gasification with a WGS reaction to adjust the syngas H_2/CO ratio. The alternative adjustment by H_2-import reduces biomass demand but increases GHG emissions for a wide range of electricity impacts (see Figure C.2). Only at carbon-free electricity, the adjustment via H_2-import is more environmentally beneficial than the WGS. Furthermore, the direct CFB gasifiers emit less GHG than the indirect DFB gasifiers since the CFB gasifier requires less electricity. In addition, the CFB gasifier requires less biomass to supply the heat for gasification.

Details on the CCU-based production. Producing syngas from CO_2 requires about 1.4–1.6 kg CO_2 per kg of syngas. In Chapter 5, CO_2 is captured from high-purity industrial point sources, requiring 0.4 MJ electricity and 0.01 MJ heat per kg CO_2.[75] However, high-purity industrial point sources might be fully exploited in the future, so lower-concentrated CO_2 sources have to be used. Capturing CO_2 from lower-concentrated CO_2 sources requires more energy, which we account for in a sensitivity analysis. We assess CO_2 capture from ambient air (direct air capture) as the lowest-concentrated CO_2 source with about 400 ppm. Data for direct air capture are taken from Deutz et al.[271], who conducted a detailed analysis of the Climeworks technology. We use the data from their “today” scenario as the most conservative assumption. The heat for direct air capture can be supplied via steam or heat pumps.

Changing the CO_2 supply from high-purity point sources to direct air capture further increases the GWI of CCU-based syngas (see Figure C.4). For CO_2 from direct air capture, CCU requires an electricity impact of 180 g CO_2-eq per kWh to reduce GHG emissions compared to fossil-based production, which is less than two-thirds of the global average in 2030. Therefore, higher-concentrated CO_2 sources should be preferred for CCU-based syngas.

Details on the combined pathways. Assessing all alternative technologies together (black dashed line in Figure C.2) does not reveal synergies between alternative syngas pathways as the best case corresponds to mill gas-based production.

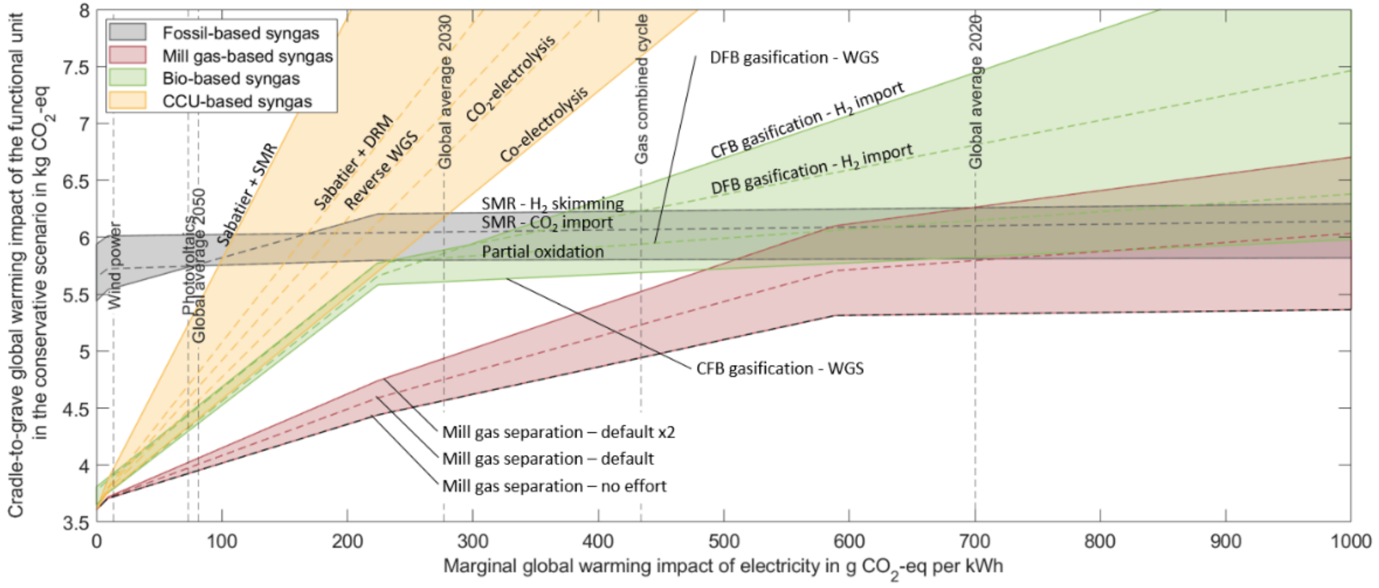

Figure C.2: Cradle-to-grave global warming impact of the functional unit (Table 5.1 in Chapter 5) for the conservative scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO_2. The black dashed line represents the lowest global warming impact of combined production. The vertical dashed lines show the global warming impact of electricity from wind power, photovoltaics, and a gas combined cycle power plant, as well as the global average for 2020, 2030, and 2050.[202,271] The global average for 2020 is calculated based on the Energy Technology Perspectives 2017 from the International Energy Agency.[359]

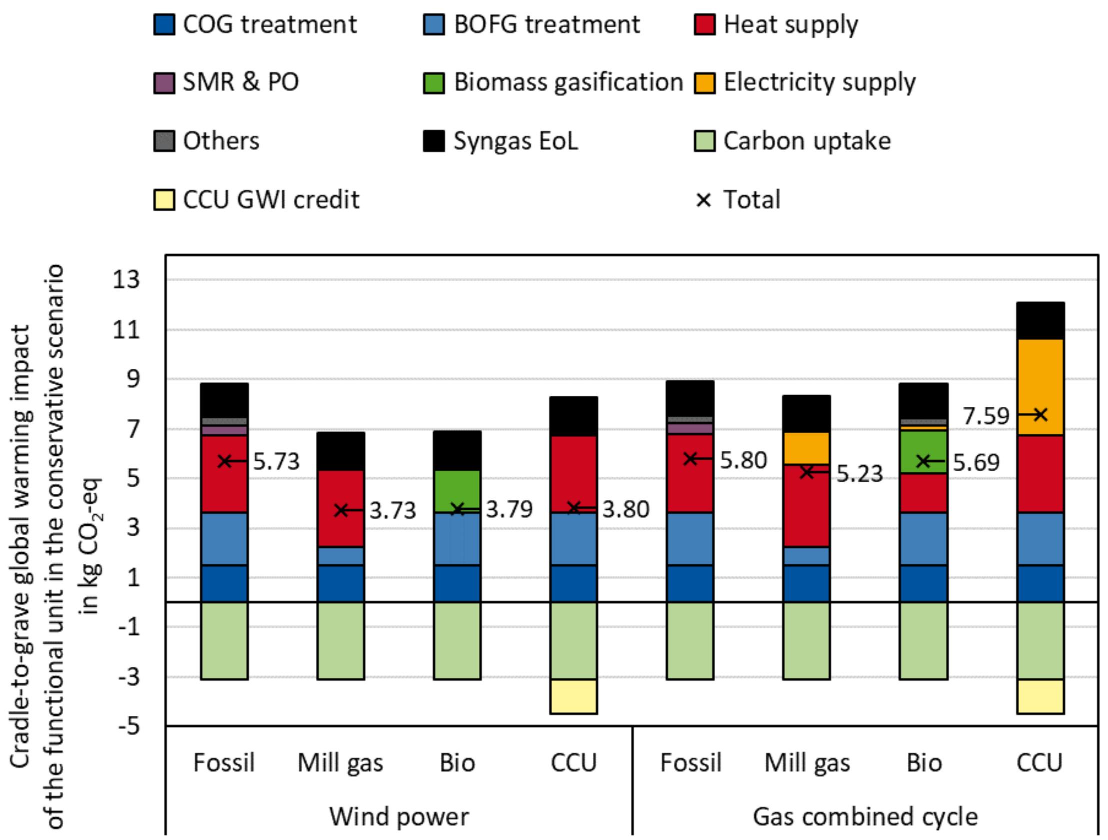

Figure C.3: Contribution analysis of the cradle-to-grave global warming impact for the conservative scenario. For simplicity, only the best fossil-based (fossil), bio-based (bio), and CCU-based (CCU) production and the default for mill gas-based (mill gas) production are shown. The four left bars show the GWI for wind power and the right bars for a gas combined cycle power plant as the marginal electricity supplier. The carbon uptake results from biomass utilization for either syngas production or heat supply. Abbreviations: BOFG = basic oxygen furnace gas, CCU = carbon capture and utilization, COG = coke oven gas, EoL = end-of-life emissions, GWI = global warming impact, PO = partial oxidation, SMR = steam methane reforming.

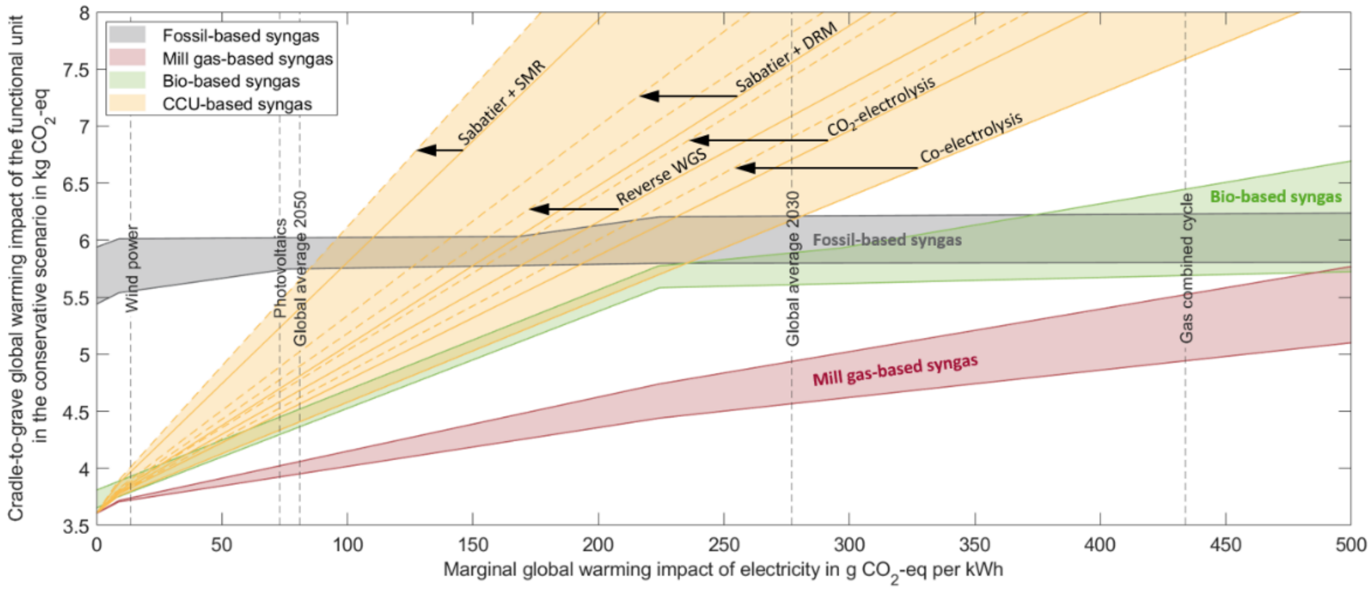

Figure C.4: Cradle-to-grave global warming impact of the functional unit (Table 5.1 in Chapter 5) for the conservative scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO_2. The black arrows show the increase in global warming impact if CO_2 is supplied by direct air capture instead of capturing from high-purity industrial point sources. The vertical dashed lines show the global warming impact of electricity from wind power, photovoltaics, and a gas combined cycle power plant, as well as the global average for 2030 and 2050.[202,271]

C.8 The GWI of syngas - extended analysis of the optimistic scenario

In this section, we conduct an extended sensitivity analysis of the electricity GWI from zero to 1000 g CO_2-eq per kWh. The extended analysis does not show major changes in the GWI performance of the alternative syngas pathways for higher electricity impacts (Figure C.5). Furthermore, assessing all alternative technologies together (black dashed line) does not reveal synergies between alternative syngas pathways, as the best case corresponds to bio-based production. For completeness, we show the contribution analysis of the alternative syngas pathways for the optimistic scenario in Figure C.6.

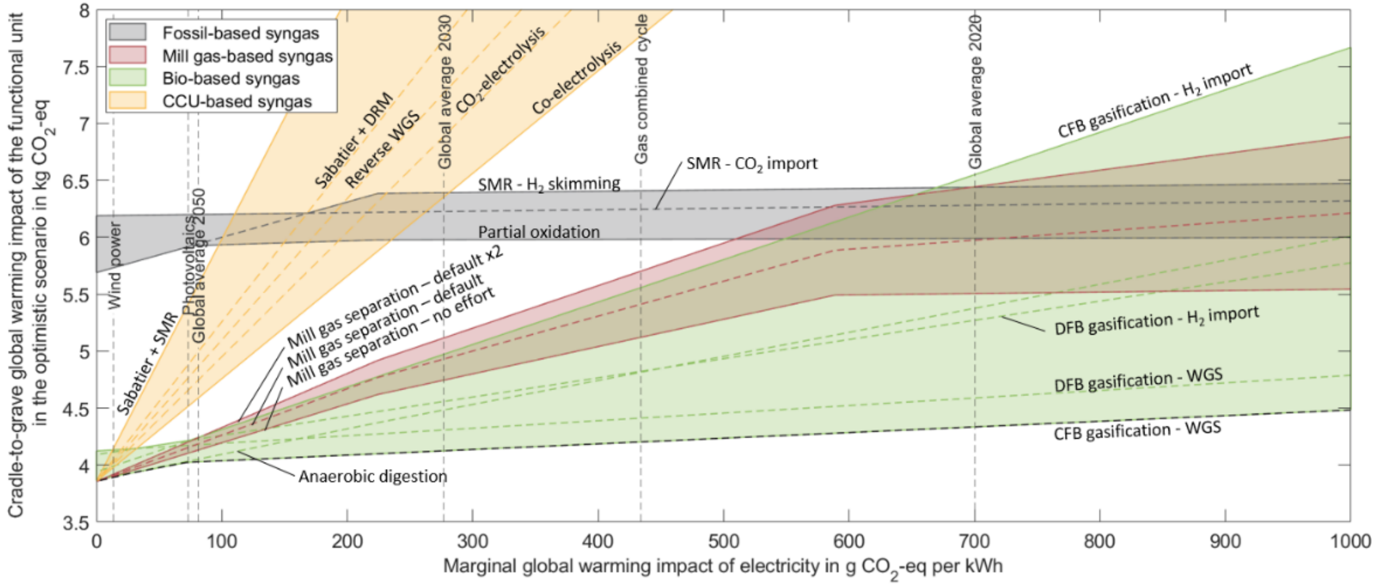

Figure C.5: Cradle-to-grave global warming impact of the functional unit (Table 5.1 in Chapter 5) for the optimistic scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO$_2$. The black dashed line represents the lowest global warming impact of combined production. The vertical lines show the global warming impact of electricity from wind power, photovoltaics, or gas combined cycle power plant, as well as the global average for 2020, 2030 and 2050.[202,271] The global average for 2020 is calculated based on the Energy Technology Perspectives 2017 from the International Energy Agency.[359]

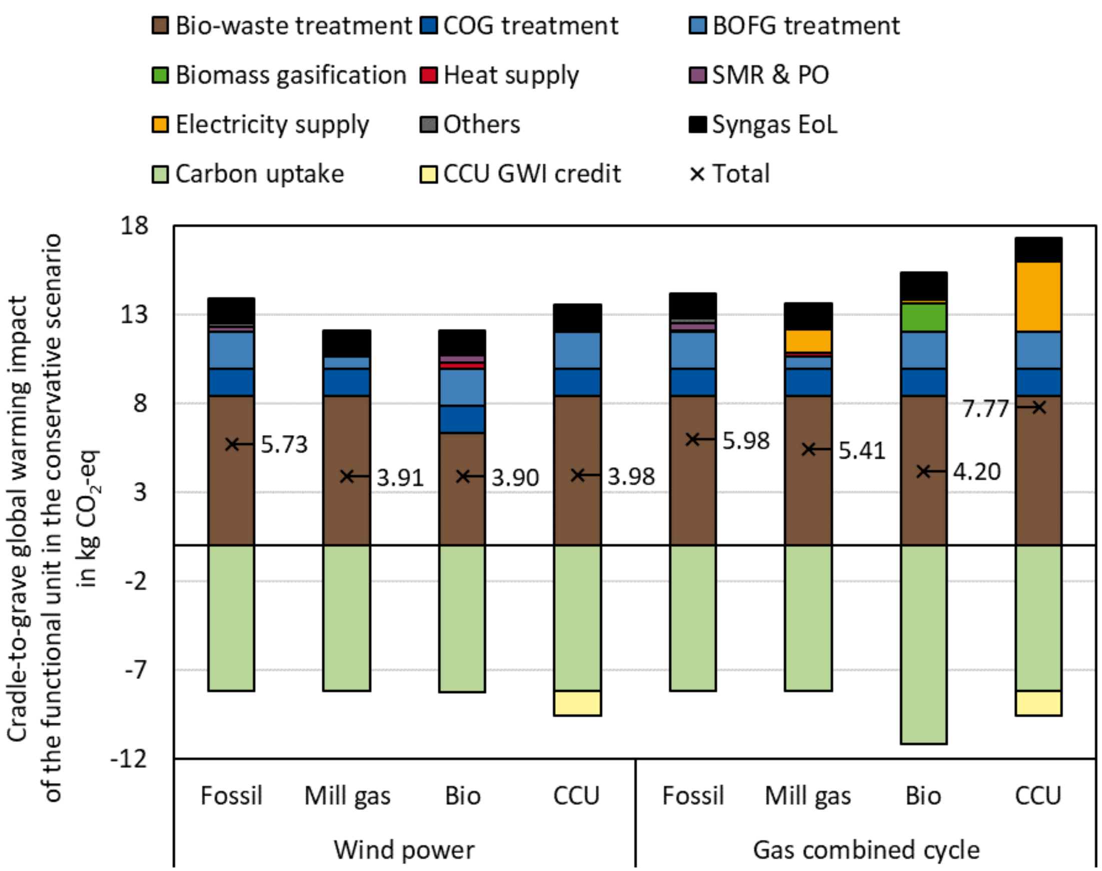

Figure C.6: Contribution analysis of the cradle-to-grave global warming impact for the optimistic scenario. For simplicity, only the best fossil-based (fossil), bio-based (bio), and CCU-based (CCU) production and the default for mill gas-based (mill gas) production are shown. The four left bars show the GWI for wind power and the right bars for a gas combined cycle power plant as the marginal electricity supplier. The carbon uptake results from bio-waste treatment. Abbreviations: BOFG = basic oxygen furnace gas, CCU = carbon capture and utilization, COG = coke oven gas, EoL = end-of-life emissions, GWI = global warming impact, PO = partial oxidation, SMR = steam methane reforming.

C.9 Syngas from plastic waste gasification

An additional pathway for syngas offers plastic recycling via gasification, which we assess in the following. Alternative processes for the treatment of plastic waste include mechanical and chemical monomer recycling, and incineration. Davidson finds that mechanical recycling of plastic waste performs best from an environmental perspective, followed by chemical monomer recycling and incineration.[148] However, mechanical recycling is only applicable for pure plastic mono-streams without major contaminants or additives, and chemical monomer recycling is currently still at a low technology readiness level.[11,286] Therefore, plastic waste is currently often treated by waste incineration with energy recovery, which we assume as the conventional treatment in the following analysis.

We consider a mixed plastic waste composition according to Biron[360], resulting in a lower heating value of 39.6 MJ/kg plastic waste (see Table C.5). For the energy recovery from waste incineration, we assume an electric efficiency of 10.6 % and a thermal efficiency of 30.4 %, according to Eriksson et al.[361]

For plastic gasification to syngas, data availability is scarce. Accordingly, we assess a simplified plastic gasification process following Schwarz et al.[21] The gasification process is based on stochiometry and requires 5 MJ of heat per kg of mixed plastic waste. The heat is supplied internally by char combustion, and the char is subtracted from the syngas output. The syngas hydrogen-to-carbon-monoxide ratio is adjusted to 2:1 by a water-gas shift reaction, and oxygen and process water demands are calculated based on stochiometry. Overall, plastic gasification requires 0.84 kg mixed plastic waste per kg syngas, which adds 3.5 MJ electricity and 10.1 MJ heat to the functional unit of the optimistic scenario (see Table 5.1 in Chapter 5).

Syngas from mixed plastic waste gasification emits more GHG than biomass gasification and similar amounts as mill gas separation (see Figure C.7). In contrast, plastic-based syngas emits less GHG than fossil- and CCU-based production. Therefore, plastic-based syngas is a viable option if marginal biomass and bio-waste are unavailable and mixed plastic is otherwise treated by waste incineration.

Table C.5: Mixed plastic waste composition and lower heating value.[360]

Compontent	**Amount in wt-%**	**Lower heating value in MJ/kg**
Polyethylene, low density	23	44.6
Polyethylene, high density	19	44.6
Polypropylene	14	42.7
Polyvinyl chloride	6	21.2
Polystyrene	9	42.0
Polyethylene terephthalate	10	23.2
Others (not considered)	19	-

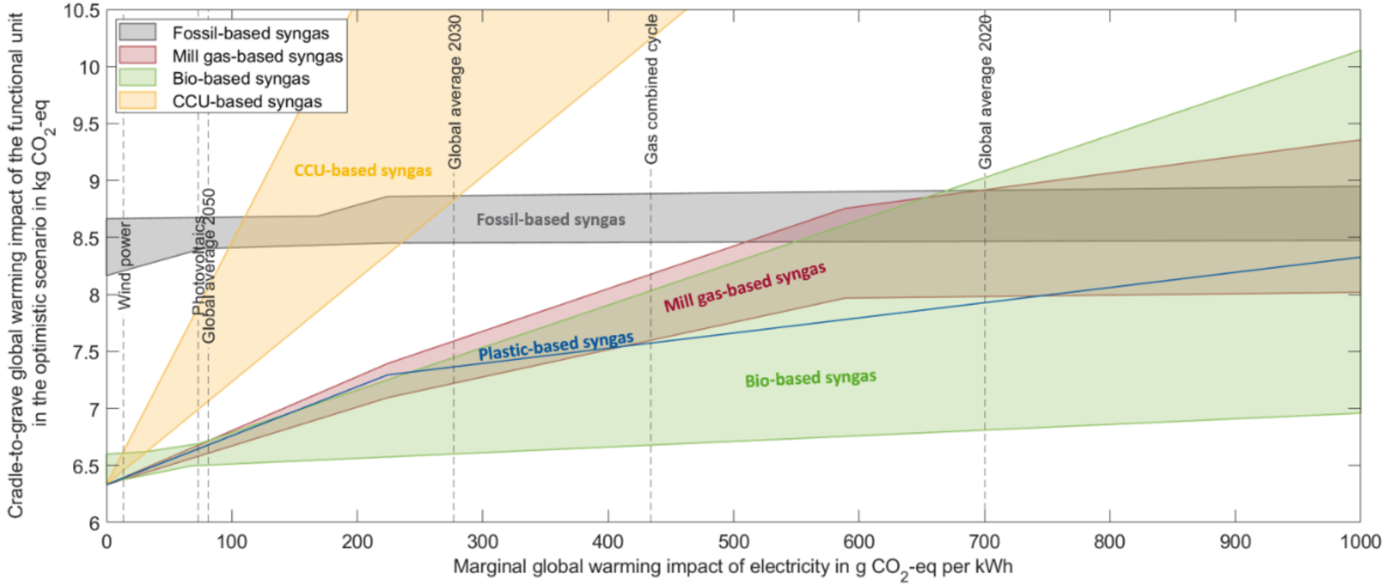

Figure C.7: Cradle-to-grave global warming impact of the functional unit (Table 5.1 in Chapter 5) for the plastic scenario as a function of the marginal global warming impact of electricity. The colored areas represent the range of the global warming impact of the considered feedstock: grey = natural gas, green = biomass, red = mill gas, and yellow = CO_2. The blue line represents the global warming impact of plastic gasification. The vertical lines show the global warming impact of electricity from wind power, photovoltaics, or gas combined cycle power plant, as well as the global average for 2020, 2030, and 2050.[202,271] The global average for 2020 is calculated based on the Energy Technology Perspectives 2017 from the International Energy Agency.[359]

C.10 Environmental impacts beyond climate change - all impact categories

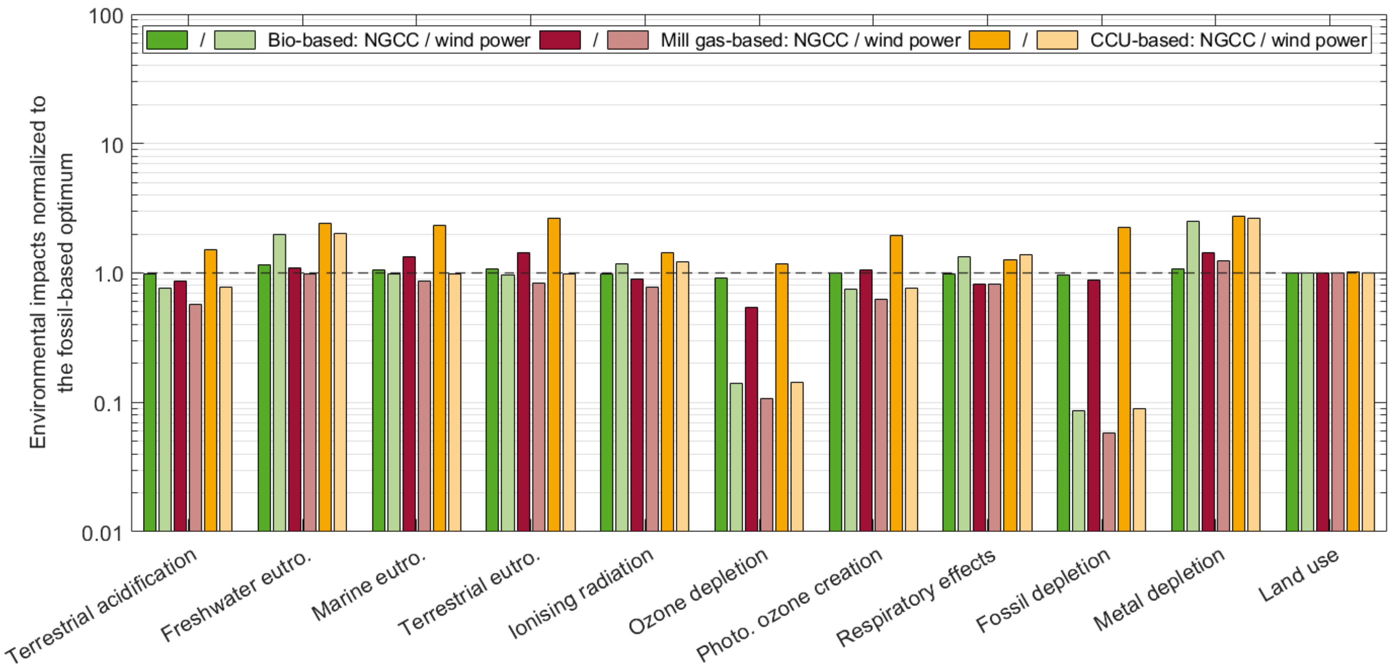

Figure C.8: Environmental impacts of the optimal bio- (green), CCU- (orange), and mill gas-based production (red) normalized to the environmental impacts of the optimal fossil-based production (horizontal, dashed line) for the conservative scenario. Dark colors represent the results calculated with electricity from a natural gas combined cycle (NGCC) power plant and bright colors with wind power. For mill gas-based production, the results are shown for the default electricity demand (see Section C.6 for details). Further abbreviations: eutro = eutrophication, photo = photochemical.

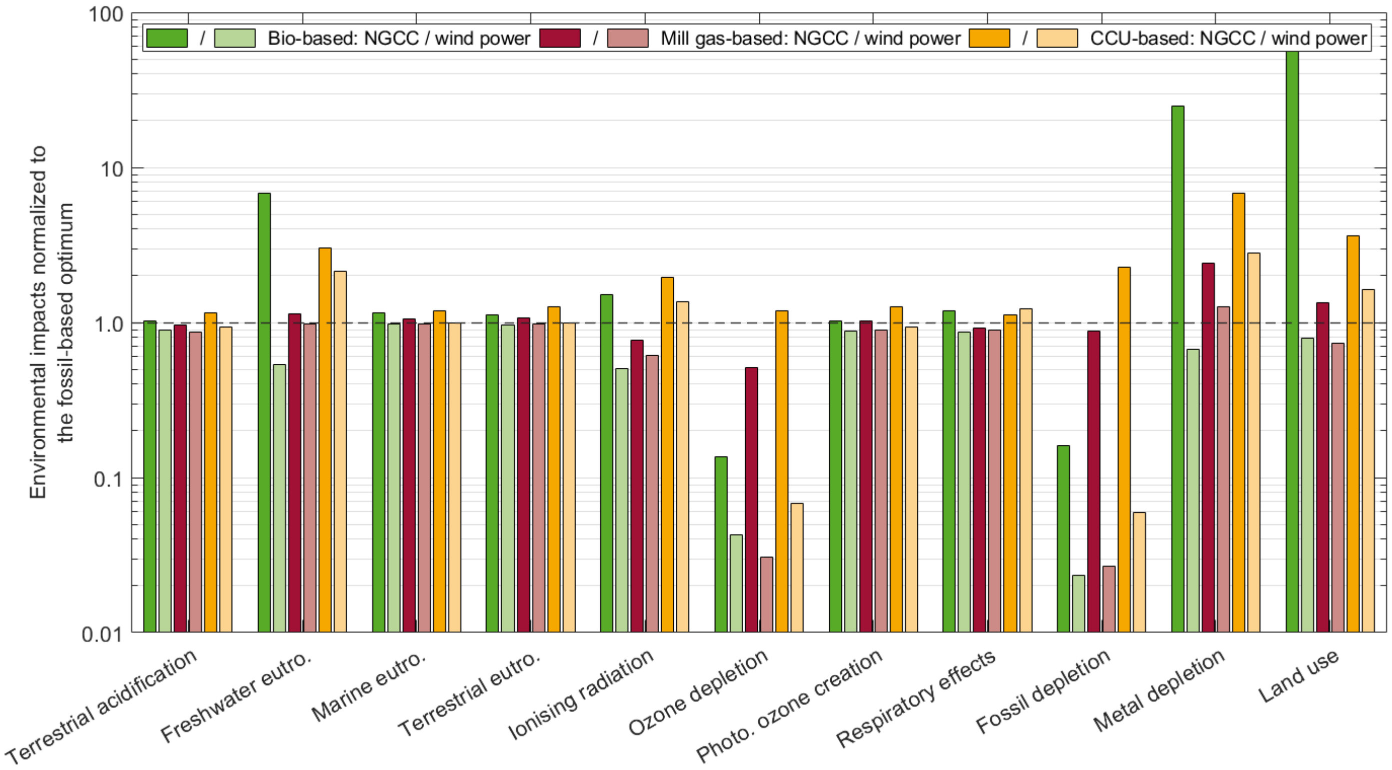

Figure C.9: Environmental impacts of the optimal bio- (green), CCU- (orange), and mill gas-based production (red) normalized to the environmental impacts of the optimal fossil-based production (horizontal, dashed line) for the conservative scenario. Dark colors represent the results calculated with electricity from a natural gas combined cycle (NGCC) power plant and bright colors with wind power. For mill gas-based production, the results are shown for the default electricity demand (see Section C.6 for details). Further abbreviations: eutro = eutrophication, photo = photochemical.

APPENDIX D

Supplementary information on the planetary boundaries of plastics

D.1 Scope definition and data sources

This study is based on a bottom-up model from Meys et al., representing the life cycle of >90 % of global plastics.[5] In the first section, we introduce the intermediate flows considered in the bottom-up model and all datasets of the corresponding processes. The datasets are based on detailed life cycle inventories that comprise full energy and mass balances. Over 400, mostly industrially validated, technology datasets are used in the model. For all further details on process data, we refer to Meys et al.[5], while for details on incorporating the planetary boundary framework into the model, we refer to Section D.2.1.

D.1.1 Included intermediate flows

The bottom-up model covers chemicals, plastics, and plastic wastes. Chemicals required as intermediates for plastics production are included in the model. In summary, the model includes the following flows:

Chemicals: Acetic acid, acetone, acetonitrile, acrylic acid, acrylonitrile, adipic acid, allyl chloride, ammonia, aniline, benzene, butadiene, C4 fraction, calcium chloride, calcium oxide, caprolactam, carbon dioxide, carbon monoxide, caustic soda (50 %), chlorine, cumene, cyclohexane, dichloropropylene, diethylene glycol, dimethyl terephthalate, dinitrotoluene, dipropylene glycol, epichlorohydrin, ethanol, ethylbenzene, ethylene, ethylene glycol, ethylene oxide, formaldehyde, glycerin, hexamethylenediamine, hydrogen, hydrogen cyanide, methanol, methyl acrylate, methylene diphenyl diisocyanate, monoethanolamine, naphtha, natural gas, nitric acid (60 %), nitrobenzene, nitrogen, oleum (33 %), oxygen, o-xylene, phenol, polybutadiene, polyol (polyester-based), polyol (polyether-based), propionitrile, propylene, propylene glycol, propylene oxide, p-xylene, pyrolysis gasoline, silicon carbide, sodium carbonate, sodium chloride, styrene, sulfur trioxide, sulfuric acid, synthesis gas (2:1), terephthalic acid, toluene, toluene diisocyanate, vinyl chloride, xylenes (mixed).

Plastics: Polyamide 6, polyamide 66, PET pellets (fiber-grade), PET pellets (bottle-grade), polyacrylonitrile fiber, polyethylene HD, polyethylene LD, polyethylene LLD, polypropylene, polystyrene GP, polystyrene HI, polyurethane flexible, polyurethane rigid, polyvinylchloride.

Plastic packaging wastes: Polyethylene, HD, polyethylene, LD, polyethylene, LLD, polypropylene, polystyrene, GP, polystyrene, HI, PET pellets (bottle-grade).

Non-packaging plastic wastes: Polyamide 6, polyamide 66, PET pellets (fiber-grade), polyacrylonitrile fiber, polyethylene, HD, polyethylene, LD, polyethylene, LLD, polypropylene, polystyrene, GP, polystyrene, HI, polyurethane, flexible, polyurethane, rigid, polyvinylchloride.

D.1.2 Datasets and mitigation pathways

The following table (Table D.1) shows all flows, production technologies and literature sources of the original bottom-up model.[5] Compared to the original model, we include additional datasets for the sensitivity analysis on biomass feedstocks (Table D.2) and electricity generation (Table D.3). The grid mix of the International Energy Agency's Net-zero 2050 scenario is calculated according to Table D.4. For the background system, we used aggregated datasets from ecoinvent if available. If available, we used datasets at the global level (GLO). Otherwise, we used Rest-of-the-World (RoW), Europe (RER), and German (DE) data.

Table D.1: Summary of flows, production technologies, and data sources of the plastic industry's bottom-up model adapted from Meys et al.[5] Comments address the availability of technologies for each GHG mitigation pathway. The numbers in the comments represent the mitigation pathways in which the technology is available: 1: fossil-based plastics, 2: bio-based plastics, 3 CCU-based plastics, 4: A combination of all technologies, except for chemical recycling to monomers, and 5: An optimistic outlook including chemical recycling to monomers.

Name of flow	**Production technology**	**Source**	**Pathway**
acetic acid	carbonylation of methanol	IHS PEP Yearbook[257]	[1,2,3,4,5]
acetone	oxidation of cumene	IHS PEP Yearbook[257]	[1,2,3,4,5]
acetonitrile	market for acetonitrile	IHS PEP Yearbook[257]	[1,2,3,4,5]
acrylic acid, ester grade	from propylene by ammoxidation	IHS PEP Yearbook[257]	[1,2,3,4,5]
acrylonitrile	propylene ammoxidation	IHS PEP Yearbook[257]	[1,2,3,4,5]
acrylonitrile	monomer recovery from polyacrylonitrile wastes	Meys et al. (2020)[362]	[5]
adipic acid	benzene oxidation via cyclohexanol	IHS PEP Yearbook[257]	[1,2,3,4,5]
adipic acid	monomer recovery from polyamide 66 wastes	Meys et al. (2020)[362]	[5]
allyl chloride	propylene chlorination	IHS PEP Yearbook[257]	[1,2,3,4,5]
ammonia	Haber-Bosch process	Matzen et al. (2015)[363]	[1,2,3,4,5]
ammonium sulfate	market for ammonium sulfate	ecoinvent V3.5[202]	[1,2,3,4,5]
aniline	reduction of nitrobenzene	IHS PEP Yearbook[257]	[1,2,3,4,5]
benzene	solvent extraction from pyrolysis gasoline	IHS PEP Yearbook[257]	[1,2,3,4,5]
benzene	solvent extraction from pyrolysis gasoline	IHS PEP Yearbook[257]	[1,2,3,4,5]
benzene	separation of xylenes by adsorption	IHS PEP Yearbook[257]	[1,2,3,4,5]
benzene	separation of xylenes by crystallization	IHS PEP Yearbook[257]	[1,2,3,4,5]
benzene	methanol to aromatics	IHS PEP Yearbook[257]	[1,2,3,4,5]
butadiene	market for butadiene	ecoinvent V3.5[202]	[1,2,3,4,5]
butene-1	market for butene, mixed	ecoinvent V3.5[202]	[1,2,3,4,5]
calcium chloride	market for calcium chloride	ecoinvent V3.5[202]	[1,2,3,4,5]
calcium oxide	market for lime	ecoinvent V3.5[202]	[1,2,3,4,5]
caprolactam	production from toluene	IHS PEP Yearbook[257]	[1,2,3,4,5]
caprolactam	monomer recovery from polyamide 6 wastes	Meys et al. (2020)[362]	[5]

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Name of flow	**Production technology**	**Source**	**Pathway**
carbon dioxide	several industrial point sources, (ammonia/ and hydrogen via Rectisol, biomass gasification via Rectisol, ethylene oxide via potassium carbonate, waste incineration via monoethanolamine, fermentation of biomass)	IHS PEP Yearbook[257], von der Assen et al. (2016)[75]	[3,4,5]
carbon dioxide	direct air capture	Deutz et al. (2021)[271]	[3,4,5]
carbon monoxide	partial condensation of synthesis gas	IHS PEP Yearbook[257]	[1,2,3,4,5]
chlorine	electrolysis of hydrochloric acid	IHS PEP Yearbook[257]	[1,2,3,4,5]
chlorine	electrolysis via oxygen-depolarized cathodes	IHS PEP Yearbook[257]	[1,2,3,4,5]
chlorine / caustic soda (50 %)	electrolysis of NaCl in membrane cell	IHS PEP Yearbook[257]	[1,2,3,4,5]
chlorine / caustic soda (50 %)	electrolysis of NaCl in diaphragm cell	IHS PEP Yearbook[257]	[1,2,3,4,5]
chlorine / caustic soda (50 %)	electrolysis of NaCl in mercury cell	IHS PEP Yearbook[257]	[1,2,3,4,5]
cooling water	market for water, decarbonised, at user	IEA[359]	[1,2,3,4,5]
cumene	alkylation of benzene with propylene	IHS PEP Yearbook[257]	[1,2,3,4,5]
cyclohexane	hydrogenation of benzene	IHS PEP Yearbook[257]	[1,2,3,4,5]
deionized water	market for water, decarbonised, at user	ecoinvent V3.5[202]	[1,2,3,4,5]
dimethyl terephthalate	esterification of terephthalic acid with methanol	IHS PEP Yearbook[257]	[1,2,3,4,5]
dimethyl terephthalate	monomer recovery from PET wastes	Meys et al. (2020)[362]	[5]
dinitrotoluene	nitration of toluene	IHS PEP Yearbook[257]	[1,2,3,4,5]
epichlorohydrin	chlorohydrination of allyl chloride	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethanol	hydrolysis and fermentation	Humbird et al. (2011)[338]	[2,4,5]
ethylbenzene	alkylation of benzene with ethylene (zeolite catalyst)	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	UOP/HYDRO methanol to olefins	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	catalytic dehydration of ethylene (adiabatic fixed-bed)	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	catalytic dehydration of ethylene (fluidized-bed)	IHS PEP Yearbook[257]	[1,2,3,4,5]

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Name of flow	**Production technology**	**Source**	**Pathway**
ethylene	DMTO methanol to olefins (C2/C3 = 1.5)	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	Steam cracking of naphtha	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	DMTO methanol to olefins (C2/C3 = 2.5)	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene	monomer recovery from polyethylene wastes	Meys et al. (2020)[362]	[5]
ethylene glycol, diethylene glycol	thermal hydration of ethylene oxide	IHS PEP Yearbook[257]	[1,2,3,4,5]
ethylene glycol, diethylene glycol	monomer recovery from PET wastes	Meys et al. (2020)[362]	[5]
ethylene oxide	ethylene oxidation	IHS PEP Yearbook[257]	[1,2,3,4,5]
formaldehyde	oxidation of methanol (ferric-molybdate cat.)	IHS PEP Yearbook[257]	[1,2,3,4,5]
formaldehyde	oxidation of methanol (silver cat.)	IHS PEP Yearbook[257]	[1,2,3,4,5]
gasoline	market for petrol, unleaded	ecoinvent V3.5[202]	[1,2,3,4,5]
glycerin	oxidation of allyl chloride via epichlorohydrin	IHS PEP Yearbook[257]	[1,2,3,4,5]
hexamethylene-diamine	from acrylonitrile via diponitrile	IHS PEP Yearbook[257]	[1,2,3,4,5]
hexamethylene-diamine	from acrylonitrile via diponitrile (electrohydrodimerization)	IHS PEP Yearbook[257]	[1,2,3,4,5]
hexamethylene-diamine	monomer recovery from polyamide 66 wastes	Meys et al. (2020)[362]	[5]
hydrochloric acid	market for hydrochloric acid, without water	ecoinvent V3.5[202]	[1,2,3,4,5]
hydrogen	steam methane reforming and water-gas-shift	IHS PEP Yearbook[257]	[1,2,3,4,5]
hydrogen	Water-gas shift and amine separation of CO_2	IHS PEP Yearbook[257]	[1,2,3,4,5]
hydrogen	low-temperature electrolysis	Agora Verkehrswende[282]	[1,2,3,4,5]
hydrogen cyanide	market for hydrogen cyanide	ecoinvent V3.5[202]	[1,2,3,4,5]
methane	from CO_2	Müller et al. (2011)[333], de Saint Jean (2014)[364]	[3,4,5]
methanol	from synthesis gas	IHS PEP Yearbook[257]	[1,2,3,4,5]
methanol	from CO_2	Pérez-Fortes et al. (2016)[365]	[3,4,5]
methanol	monomer recovery from PET wastes	Meys et al. (2020)[362]	[5]
methyl acrylate	esterification of acrylic acid	IHS PEP Yearbook[257]	[1,2,3,4,5]

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Name of flow	**Production technology**	**Source**	**Pathway**
methylene diphenyl diisocyanate	phosgenation of benzene	IHS PEP Yearbook [257]	[1,2,3,4,5]
methylene diphenyl diisocyanate	monomer recovery from polyurethane, rigid wastes	Meys et al. (2020) [362]	[5]
miscanthus	market for miscanthus, chopped	ecoinvent V3.5 [202]	[2,4,5]
monoethanolamine	market for monoethanolamine	ecoinvent V3.5 [202]	[1,2,3,4,5]
naphtha	pyrolysis of all plastic waste fraction. The carbon efficiency of pyrolysis was assumed to be 63 % by Meys et al, while the process was modeled based on industrially verified data. [5,257] Thus, the yield of pyrolysis depends on the chemical composition of the plastics and ranges from about 29 % for polyvinylchloride over about 47 % for polyethylene therephthale, polyamide, polyacrolynitrile, and polyurethane to about 64 % for polyethylene and polypropylene. Polystyrol achieves the highest yield with about 69 %.	Meys et al. (2021), IHS PEP Yearbook [5,257]	[1,2,3,4,5]
naphtha	market for naphtha	ecoinvent V3.5 [202]	[1,2,3,4,5]
natural gas (raw material)	market for natural gas, high pressure	ecoinvent V3.5 [202]	[1,2,3,4,5]
nitric acid (60 %)	from ammonia (dual pressure)	IHS PEP Yearbook [257]	[1,2,3,4,5]
nitric acid (60 %)	from ammonia (mono pressure)	IHS PEP Yearbook [257]	[1,2,3,4,5]
nitrobenzene	nitration of benzene (adiabatic)	IHS PEP Yearbook [257]	[1,2,3,4,5]
nitrobenzene	nitration of benzene (conventional)	IHS PEP Yearbook [257]	[1,2,3,4,5]
nitrogen	air separation by pressure-swing adsorption	IHS PEP Yearbook [257]	[1,2,3,4,5]
n-pentane	market for pentane	ecoinvent V3.5 [202]	[1,2,3,4,5]
oleum (33.3 %)	33.3 % oleum from sulfur trioxide and sulfuric acid	Meys et al. (2021) [5]	[1,2,3,4,5]
oxygen	cryogenic air separation	IHS PEP Yearbook [257]	[1,2,3,4,5]
o-xylene	Separation of xylenes by adsorption	IHS PEP Yearbook [257]	[1,2,3,4,5]
o-xylene	Separation of xylenes by crystallization	IHS PEP Yearbook [257]	[1,2,3,4,5]
PET pellets (bottle-grade)	upgrading of PET fiber-grade to bottle-grade	IHS PEP Yearbook [257]	[1,2,3,4,5]

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Name of flow	**Production technology**	**Source**	**Pathway**
PET pellets (fiber-grade)	polycondensation from dimethyl terephthalate and ethylene glycol	IHS PEP Yearbook[257]	[1,2,3,4,5]
PET pellets (fiber-grade)	polycondensation from dimethyl terephthalate and ethylene glycol	IHS PEP Yearbook[257]	[1,2,3,4,5]
PET pellets (fiber-grade)	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
phenol	oxidation of cumene	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyacrylonitrile fiber	melt extrusion	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyamide 6	continous PA 6 production	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyamide 66	continous PA 66 production	IHS PEP Yearbook[257]	[1,2,3,4,5]
polybutadiene	solution polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyethylene, HD	gas-phase polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyethylene, HD	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polyethylene, LD	autoclave polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyethylene, LD	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polyethylene, LLD	solution polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyethylene, LLD	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polypropylene	gas-phase polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polypropylene	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polystyrene, GP	bulk polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
polystyrene, GP	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polystyrene, HI	bulk polymerization (incl. Polybutadiene)	IHS PEP Yearbook[257]	[1,2,3,4,5]
polystyrene, HI	mechanical recycling from plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]
polyol for PUR, rigid	from adipic acid and diethylene glycol	IHS PEP Yearbook[257]	[1,2,3,4,5]
polyol for PUR, rigid	monomer recovery from polyurethane, rigid wastes	Meys et al. (2020)[362]	[5]
polyurethane, flexible	Continous production of flexible polyurethane	von der Assen et al. (2015)[335]	[1,2,3,4,5]
polyol for PUR, flexible	from propylene/ethylene oxide and glycerol	IHS PEP Yearbook[257]	[1,2,3,4,5]

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Name of flow	Production technology	Source	Pathway
polyol for PUR, flexible	monomer recovery from polyurethane, flexible wastes	Meys et al. (2020)[362]	[5]
polyurethane, rigid	Continous production of flexible polyurethane foam	von der Assen et al. (2015)[335]	[1,2,3,4,5]
polyvinyl chloride	suspension polymerization	IHS PEP Yearbook[257]	[1,2,3,4,5]
process water	market for water, decarbonised, at user	ecoinvent V3.5[202]	[1,2,3,4,5]
propylene	Lurgi methanol to propylene	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	dimerization of ethylene	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	ethylene disproportionation	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	Steam cracking of naphtha	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	UOP/HYDRO methanol to olefins	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	DMTO methanol to olefins (C2/C3 = 1.5)	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	DMTO methanol to olefins (C2/C3 = 2.5)	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene	monomer recovery from polypropylene wastes	Meys et al. (2020)[362]	[5]
propylene glycol, dipropylene glycol	propylene oxide oxidation	IHS PEP Yearbook[257]	[1,2,3,4,5]
propylene oxide	chlorohydrine process	IHS PEP Yearbook[257]	[1,2,3,4,5]
p-xylene	Separation of xylenes by adsorption	IHS PEP Yearbook[257]	[1,2,3,4,5]
p-xylene	Separation of xylenes by crystallization	IHS PEP Yearbook[257]	[1,2,3,4,5]
p-xylene	methanol to aromatics	IHS PEP Yearbook[257]	[1,2,3,4,5]
pyrolysis gasoline	Steam cracking of naphtha	IHS PEP Yearbook[257]	[1,2,3,4,5]
silicon carbide	market for silicon carbide	ecoinvent V3.5[202]	[1,2,3,4,5]
sodium carbonate	market for sodium bicarbonate	ecoinvent V3.5[202]	[1,2,3,4,5]
sodium chloride	sodium chloride production, powder	ecoinvent V3.5[202]	[1,2,3,4,5]
steam	natural gas boiler	IHS PEP Yearbook[257]	[1,2,3,4,5]
steam	electric boiler	IHS PEP Yearbook[257]	[3,4,5]
steam	from biomass	Pérez-Uresti et al. (2019)[366]	[2,4,5]
styrene	alkylation of benzene with ethylene (liquid-phase)	IHS PEP Yearbook[257]	[1,2,3,4,5]
styrene	alkylation of benzene with ethylene (gas-phase)	IHS PEP Yearbook[257]	[1,2,3,4,5]
styrene	monomer recovery from polystyrene wastes	Meys et al. (2020)[362]	[5]

Continued on next page

Name of flow	**Production technology**	**Source**	**Pathway**
sulfur trioxide	market for sulfur trioxide	ecoinvent V3.5[202]	[1,2,3,4,5]
sulfuric acid	market for sulfuric acid	ecoinvent V3.5[202]	[1,2,3,4,5]
synthesis gas (2:1)	natural gas steam reforming	IHS PEP Yearbook[257]	[1,2,3,4,5]
synthesis gas (2:1)	mixing of hydrogen and CO (2:1)	Meys et al. (2021)[5]	[1,2,3,4,5]
synthesis gas (2:1)	gasification of biomass	see Appendix C	[2,4,5]
thermal energy	various hydrocarbons	Meys et al. (2021)[5]	[1,2,3,4,5]
thermal energy	resistance heater	Meys et al. (2021)[5]	[3,4,5]
terephthalic acid	oxidation of p-xylene	IHS PEP Yearbook[257]	[1,2,3,4,5]
terephthalic acid	monomer recovery from PET wastes	Meys et al. (2020)[362]	[5]
toluene	solvent extraction from reformate	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene	solvent extraction from pyrolysis gasoline	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene	separation of xylenes by adsorption	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene	separation of xylenes by crystallization	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene	methanol to aromatics	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene diisocyanate	phosgenation of toluene	IHS PEP Yearbook[257]	[1,2,3,4,5]
toluene diisocyanate	monomer recovery from polyurethane, flexible wastes	Meys et al. (2020)[362]	[5]
vegetable oil	market for vegetable oil methyl ester	ecoinvent V3.5[202]	[1,2,3,4,5]
vinyl chloride	ethylene chlorination and ethylene dichloride pyrolysis	IHS PEP Yearbook[257]	[1,2,3,4,5]
vinyl chloride	monomer recovery from polyvinylchloride wastes	Meys et al. (2020)[362]	[5]
xylenes, mixed	solvent extraction from reformate	IHS PEP Yearbook[257]	[1,2,3,4,5]
xylenes, mixed	solvent extraction from pyrolysis gasoline	IHS PEP Yearbook[257]	[1,2,3,4,5]
xylenes, mixed	methanol to aromatics	IHS PEP Yearbook[257]	[1,2,3,4,5]
all plastic wastes	energy recovery	Doka[206,207]	[1,2,3,4,5]
all plastic wastes	landfilling	ecoinvent V3.5[202]	[1,2,3,4,5]
all plastic packaging waste	sorting of plastic packaging waste	Meys et al. (2020)[362]	[1,2,3,4,5]

End of table

Table D.2: Biomass feedstocks for the sensitivity analysis.

Biomass feedstock	**Dataset**	**Source**
bagasse, from sweet sorghum	market for bagasse, from sweet sorghum	ecoinvent V3.5 [202]
bagasse, from sugarcane	market for bagasse, from sugarcane	ecoinvent V3.5 [202]
bark chips	market for bark chips, wet, measured as dry mass	ecoinvent V3.5 [202]
wood chips	market for wood chips, wet, measured as dry mass	ecoinvent V3.5 [202]
wood pellets	wood pellet production	ecoinvent V3.5 [202]

Table D.3: Electricity generation technologies for the sensitivity analysis. Photovoltaic with high full load hours (high FLH) is represented by photovoltaic in the Middle East approximated by the dataset for Saudi Arabia.

Generation technologies	**Dataset**	**Source**
wind power, onshore	electricity production, wind, 1-3MW turbine, onshore	ecoinvent V3.5 [202]
geothermal power	electricity production, deep geothermal	ecoinvent V3.5 [202]
hydro power	electricity production, hydro, run-of-river	ecoinvent V3.5 [202]
nuclear power	electricity production, nuclear, pressure water reactor	ecoinvent V3.5 [202]
photovoltaic	electricity production, photovoltaic, 3kWp slanted-roof installation, multi-Si panel, mounted	ecoinvent V3.5 [202]
photovoltaic, high FLH	electricity production, photovoltaic, 3kWp slanted-roof installation, multi-Si panel, mounted (SA)	ecoinvent V3.5 [202]

Table D.4: Technology shares of the 2030's electricity grid mix according to the International Energy Agency's Net-zero 2050 scenario.[63] The carbon capture and storage (CCS) technologies were modeled according to Galán-Martín et al.[115] For the grid mix, we omit marine power, and hydrogen and ammonia based power due to lack of data. The neglected technologies account for 2.5 % of the grid mix. Consequentially, we scaled the sum of share of the considered technologies to 100 %.

Generation technologies	**Dataset**	**Share in %**	**Source**
coal without CCS	electricity production, hard coal	8.1	ecoinvent V3.5[202]
coal with CCS	electricity production, hard coal	0.8	ecoinvent V3.5[202], Galán-Martín et al.[115]
natural gas without CCS	electricity production, natural gas, combined cycle power plant	17.1	ecoinvent V3.5[202]
natural gas with CCS	electricity production, natural gas, combined cycle power plant	0.5	ecoinvent V3.5[202], Galán-Martín et al.[115]
oil	electricity production, oil	0.5	ecoinvent V3.5[202]
nuclear	electricity production, nuclear, pressure water reactor	10.4	ecoinvent V3.5[202]
hydro power	electricity production, hydro, reservoir, non-alpine region	16.1	ecoinvent V3.5[202]
bioenergy	heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014	3.9	ecoinvent V3.5[202]
wind	electricity production, wind, >3MW turbine, onshore	22.0	ecoinvent V3.5[202]
solar photovoltaic	electricity production, photovoltaic, 570kWp open ground installation, multi-Si	19.2	ecoinvent V3.5[202]
geothermal	electricity production, deep geothermal	0.9	ecoinvent V3.5[202]
concentrated solar power	electricity production, solar thermal parabolic trough, 50 MW	0.6	ecoinvent V3.5[202]

D.2 Methods

D.2.1 Adapting the planetary boundary framework

The elementary flows of the bottom-up model are defined according to ecoinvent v3.5, which includes 2080 elementary flows to the compartments air, water, soil, and from natural resources. We consider all 2080 elementary flows and determine their characterization factors for each Earth-system process by using the characterization models from Galán-Martín et al.[115] for change in biosphere integrity, from D'Angelo et al.[116] for the N-cycle and from Ryberg et al.[114] for all further Earth-system processes. In the following, we describe the elementary flows that we additionally characterized based on the original characterization models, modifications to the already existing characterization factors, and further changes.

Climate change

We include all characterization factors for GHG emission from Ryberg et al.[114] For CO_2, they define the characterization factor by dividing the change of atmospheric CO_2 concentration between the pre-industrial value (from the year 1765) and the value estimated by an RCP2.6 scenario in 2300 by the total anthropogenic CO_2 emissions from the year 2000 to 2300 (based on an RCP2.6 scenario).[114,367] However, the compared time horizons do not match. Therefore, we set the time horizons consistently from 1765 to 2300. The characterization factor for a change in atmospheric CO_2 concentration due to a continuous CO_2 emission is $1.79 \cdot 10^{-11}$ ppm/(yr kg) and, thereby, 33 % smaller compared to Ryberg et al.[114] To convert the change in atmospheric CO_2 concentration to radiative forcing, we adopt the characterization model from Ryberg et al. Additionally, we include all elementary flows emitted to air that follow the EU definition for NMVOC, i.e., organic compounds with a boiling point lower than or equal to 250 °C.[368] We conservatively consider these flows as potential CO_2 precursors and calculate their characterization factors based on their carbon content.

Furthermore, we include elementary flows that represent unspecified groups of compounds from ecoinvent that do not have a specific carbon content:

- VOC, volatile organic compounds, unspecified origin
- Aldehydes, unspecified
- Hydrocarbons, aliphatic, alkanes, cyclic
- Hydrocarbons, aliphatic, alkanes, unspecified
- Hydrocarbons, aliphatic, unsaturated
- Hydrocarbons, aromatic

- Hydrocarbons, chlorinated
- Hydrocarbons, unspecified
- NMVOC, non-methane volatile organic compounds, unspecified origin

For these elementary flows, we use the characterization factor of NMVOC given by Ryberg et al.[297] Moreover, we do not characterize non-fossil emissions, including CO_2, CH_4, and CO, which was not explicitly stated in previous literature but is in accordance with the ILCD recommendations.[97]

Ocean acidification

For ocean acidification, we adopt the same changes as for climate change: We match the time horizons for characterizing CO_2, include CO_2 precursors, approximate groups of CO_2 precursors by NMVOC, and exclude non-fossil emissions. Ocean acidification is measured as the global mean saturation state of aragonite in surface seawater (Ω_{arag}).

Change in biosphere integrity

We calculate the characterization factors for change in biosphere integrity following Galán-Martín et al.[115] The first stressor of change in biosphere integrity is climate change. The calculation of climate change as a stressor is tailored to the change in biosphere integrity and thereby differs from the calculation of the planetary footprint of climate change from Ryberg et al.[114] However, we consider the same elementary flows as mentioned above. For further details, the reader is referred to Galán-Martín et al.[115]

The second stressor is land use, represented by land occupation in ecoinvent. We adopt the method from Galán-Martín et al. to quantify the impact of land occupation based on mean species abundance loss following Hanafiah et al.[369] However, Hanafiah et al. do not provide data for all land types in the ecoinvent database.[202] Hence, we match the types of land occupation from Hanafiah et al. and ecoinvent v3.5 according to Table D.5. We use the maximum values of each type of land occupation as a conservative approximation.

Nitrogen cycle (N-cycle)

To quantify the N-cycle footprint, we use the characterization model from D'Angelo et al.[116]

Phosphorus cycle (P-cycle)

Ryberg et al. provide a characterization factor for phosphorus emitted to the ocean via freshwater systems.[114] However, we conservatively add all phosphorus-containing substances emitted to other compartments to the assessment. To account for these compounds, we multiply the characterization factor for pure phosphorus emitted to the

Table D.5: Matching of land types between Hanafiah et al.[369] and ecoinvent v3.5[202].

Classification in ecoinvent v3.5	**Classification in Hanafiah et al.**	**Loss in mean species abundance**
Occupation, annual crop, extensive	Permanent crop, extensive	0.70
Occupation, annual crop, intensive	Permanent crop, intenstive	0.90
Occupation, arable land, unspecified use	Arable	0.90
Occupation, arable	Arable	0.90
Occupation, bare area (non-use)	Primary vegetation	0
Occupation, cropland fallow (non-use)	Arable, non-irrigated, fallow	0.70
Occupation, dump site	Dump site	0.95
Occupation, field margin/hedgerow	Primary vegetation	0
Occupation, forest, intensive	Forest, intensive, short-cycle	0.80
Occupation, forest, primary (non-use)	Forest, extensive	0.30
Occupation, forest, secondary (non-use)	Forest	0.50
Occupation, forest, unspecified	Forest	0.50
Occupation, grassland, natural (non-use)	Primary vegetation	0
Occupation, grassland, natural, for livestock grazing	Pasture and meadow, extensive	0.30
Occupation, inland waterbody, unspecified	Water bodies, artificial	1
Occupation, lake, natural (non-use)	Sea and ocean	0
Occupation, pasture, man made	Pasture and meadow	0.90
Occupation, pasture, man made, extensive	Pasture and meadow, extensive	0.30
Occupation, pasture, man made, intensive	Pasture and meadow, intensive	0.90
Occupation, permanent crop, extensive	Permanent crop, extensive	0.70
Occupation, permanent crop, intensive	Permanent crop, intensive	0.90
Occupation, seabed	Benthos	0
Occupation, unspecified	Permanent crop, intenstive	0.90
Occupation, unspecified (non-use)	Primary vegetation	0
Occupation, wetland	Primary vegetation	0
Occupation, river, artificial	Water courses, artificial	1
Occupation, river, natural (non-use)	Sea and ocean	0
Occupation, seabed, natural (non-use)	Sea and ocean	0
Occupation, snow and ice (non-use)	Pasture and meadow, extensive	0.30

ocean with the mass fraction of phosphorus in the phosphorus-containing elementary flows. Furthermore, we include the transport of the phosphorus-containing compound from the compartment it was initially emitted to the ocean.

$$CF_{P-containing\ compound} = 10^{-9} \cdot fr_p \cdot k_{transport,i} \tag{D.1}$$

For phosphorus-containing compounds emitted to the air, we conservatively assume that 100 % of the phosphorus-containing compound ultimately end up in the ocean. Thus $k_{air-to-ocean}$ equals 1. For the compartment of water, we further distinguish between the sub-compartments ocean and all further water bodies. The k-factor for emissions of phosphorus-containing compounds to the sub-compartment ocean is 1 by definition. In contrast, emissions to all other water bodies have a k-factor of 0.86, accounting for sedimentation based on Ryberg et al.[114] Phosphorus-containing compounds emitted to soil are assumed to partially end up in freshwater due to run-off from rainfall. Thus, we multiply the characterization factors for phosphorus-containing compounds to the compartment soil with a k-factor of 0.42, which is the most conservative estimate for the run-off factors from Hart et al.[370] For subsequent transport from freshwater to the ocean, we again use the k-factor of 0.86, giving a total k-factor of 0.3612.

Aerosol loading

For aerosol loading, we use all characterization factors for the elementary flows considered by Ryberg et al.[114] We additionally characterize the following elementary flows to the compartment air that have not yet been characterized using the characterization factor for generic carbon from Ryberg et al. as a proxy:

- Carbon-14
- Elemental carbon
- Organic carbon

Furthermore, we include all elementary flows defined as NMVOC and the same elementary flows representing unspecified groups of compounds as for climate change (see above). Ryberg et al. define an average characterization factor for NMVOC emitted to an urban environment and one for NMVOC emitted to a rural environment. Accordingly, we use the characterization factor of NMVOC, urban, for all elementary flows emitted to the sub-compartment urban air, close to ground. In contrast, we use the characterization factor of NMVOC, rural for all other sub-compartments, i.e., lower stratosphere + upper troposphere; non-urban air or from high stacks; unspecified; and low population density, long-term.

Freshwater use

For freshwater use, we consider all elementary flows from ecoinvent v3.5, which are associated with bluewater according to the definition of Falkenmark et al.[371]

- Water; water; ground-
- Water; water; unspecified
- Water, cooling, unspecified natural origin; natural resource; in water
- Water, lake; natural resource; in water
- Water, river; natural resource; in water
- Water, turbine use, unspecified natural origin; natural resource; in water
- Water, unspecified natural origin; natural resource; in water
- Water, unspecified natural origin; natural resource; in ground
- Water, well, in ground; natural resource; in water

In accordance with the ecoinvent nomenclature, elementary flows sourced from the compartment of natural resources keep a positive algebraic sign, thereby indicating water consumption. In contrast, elementary flows to the compartment water get a negative algebraic sign, indicating bluewater recovery. We conservatively assess freshwater use for evaporated water, as we assume that all evaporated water is lost and does not return to freshwater reservoirs. However, Gerten et al. highlight the need to reassess the boundary value for freshwater use and human freshwater consumption.[372] Furthermore, human freshwater use may not reflect all types of human interference with the global water cycle, which should be incorporated in a future reassessment.[309] Thus, the results for freshwater use shown in this study should be interpreted with caution.

Stratospheric ozone depletion

We extended the model from Ryberg et al. with the following elementary flows of ozone-depleting substances emitted to the compartment air following the Montreal Protocol[373]:

- HCFC-124
- HCFC-21
- R10

We additionally include N_2O as proposed by Algunaibet et al.[127] For the compound HCFC-21, we could not find a value for the fraction release ratio and assumed it to be 100 % as a conservative assumption.

Land-system change

We considered all elementary flows from ecoinvent v3.5 for the compartment of natural resources that describe a transformation from or to forest:

- Transformation, from/to forest, extensive
- Transformation, from/to forest, intensive
- Transformation, from forest, primary (non-use)
- Transformation, from/to forest, secondary (non-use)
- Transformation, from/to forest, unspecified

In accordance with the ecoinvent nomenclature, transformation processes from forest keep a positive algebraic sign, indicating forest depletion. In contrast, transformation processes to forest get a negative algebraic sign, indicating forest recovery.

Novel entities

The process of novel entities considers the release of substances and modified life forms with unwanted geophysical or biological effects on the environment. As mentioned in Section 6.3 and 6.5, neither control variables nor a SOS have yet been defined. To enable the quantification, Persson et al. evaluate options to define control variables at several steps in the impact pathways of novel entities, from production-based to release and effect-focused variables.[113] However, none of the proposed control variables comply with all defined criteria to assess novel entities, i.e., feasibility, relevance, and comprehensiveness. Furthermore, Kosnik et al. proposed a frame-work for determining levels of chemical pollution and the corresponding SOS for novel entities. Determining such levels, however, remains challenging due to limited data availability.[301]

Increasing plastic recycling, as suggested in the Section 6.3, would reduce the amount of plastics that enter the environment. Thus, plastic recycling reduces plastic pollution and the pressure on novel entities. In contrast to recycling, the pressure on novel entities due to plastic pollution is not reduced when switching from fossil to renewable feedstocks while producing the same plastics with the same use phase and end-of-life treatment. However, producing plastics that provide the same function but possess other end-of-life characteristics, such as biodegradable plastics, may be a viable option.

Planetary Boundaries

In Chapter 6, we apply the planetary boundaries proposed by Röckström et al., which define a safe operating space for all activities on Earth.[287] From this safe operating space, we subtract the natural background level, i.e., the natural state of the Earth-system processes. Thereby, we yield a safe operating space for human activities (SOS), according to Table D.6. In Chapter 6, the SOS will exclusively refer to the safe operating space for human activities. The SOS can be allocated to the plastics industry based on downscaling principles.[124] This corresponding share of the SOS will define the thresholds for absolute environmental sustainability of the plastics industry.

In contrast to the planetary boundary for the N-cycle defined by Steffen et al.[111], we only assess the chemical fixation of nitrogen. Accordingly, the original value of 62 Tg is reduced to 39.7 Tg representing the share of chemical fixation according to Algunaibet et al.[127]

Table D.6: Planetary Boundaries define a safe operating space for all activities on Earth. Subtracting the natural background level yields the safe operating space for human activities, to only which is referred to as SOS in this study. If the natural background level is higher than the planetary boundary, subtracting the planetary boundary from the natural background level yields the SOS for humanity.

Earth-system process	**Unit**	**Planetary boundary**	**Natural back-ground level**	**Safe operating space for humanity**
Climate change – energy imbalance	W/m^2	1	0	1
Ocean acidification	Ω_{arag}	2.752	3.44	0.688
Change in biosphere integrity	%	90	100	10
Nitrogen cycle	Tg	39.7	0	39.7
Phosphorus cycle	Tg	11	1	10
Atmospheric aerosol loading	Aerosol optical depth	0.25	˜0.15	0.11
Freshwater use	km^3	4000	0	4000
Stratospheric ozone depletion	Dobson units	275.5	290	14.5
Land-system change	%	75	100	25

D.2.2 Inventory modeling

For the life cycle inventory, we adapted the model from Meys et al., which was originally designed to assess GHG emissions only, to consistently assess planetary footprints.[5] To assess the impacts of plastics production on the N-cycle footprint, we follow the procedure from D'Angelo et al. and calculate the total amount of fixed nitrogen by fertilizer production and application in the supply chain of the plastics industry.[116] The method allows for a direct calculation of the N-cycle footprint compared to the originally proposed characterization factors from Ryberg et al., which are considered to have higher uncertainty.[114,116]

The planetary boundary for freshwater use is based on the global consumption of blue water.[110] In our model, blue water consumption consists of process water and cooling water consumption in the foreground system and other additional consumptions such as irrigation in the background system. We conservatively assume that process water consumption corresponds to a one-to-one use of blue water. To estimate the blue water consumption from cooling water applications, we use the average values for cooling water evaporation from BASF, a large manufacturer of chemicals and plastics.[374] We assumed all evaporation as blue water loss as a conservative assumption for freshwater use.

D.2.3 Regionally-adapted downscaling

We are not aware of a scientific consensus or a purely objective way to downscale the planetary SOS to a sector or a region. In this study, we employed a downscaling approach via consumption expenditure, which is explained in Section 6.3. This downscaling approach weighs regional differences by purchasing power. However, high-income countries have a higher purchasing power than low-income countries, even though these low-income countries represent a larger share of the world population. Thus, the chosen approach underrepresents this larger share of the world's population. Accordingly, we quantify a regionally-adapted share of SOS that gives greater consideration to the population distribution in the following:

First, we calculate a regional share of SOS of the plastics industry for all regions in EXIOBASE. For this purpose, we use the Leontief equation to calculate the gross output matrix X_i, which represents the production of goods induced by the final consumption expenditure Y_i of the region i:

$$X_i = (I - A)^{-1} \cdot Y_i \tag{D.2}$$

where A is the technology matrix of the product-by-product input-output table. The total plastics production $x_{plastics,i}$ induced by the final consumption expenditure Y_i corresponds to the plastics-row in the gross output matrix X_i.

In the following, the regionally-adapted approach differs from the approach in Section 6.3. In Section 6.3, we determine the share of SOS of the plastics industry by dividing the total plastics production by the gross world product. At a global level, the gross world product is equivalent to the total global consumption expenditure $\sum Y$. However, in regionalized assessments, the total consumption expenditure $\sum Y_i$ is not the same as the gross domestic product of region i due to imports and exports. Thus, we determine the regional share of SOS $SoSOS_{plastics,i}$ by dividing the total plastics production induced by the consumption of country i $x_{plastics,i}$ by the total final consumption expenditure of this country Y_i.

$$SoSOS_{plastics,i} = \frac{x_{plastics,i}}{\sum Y_i} \tag{D.3}$$

This regional share of SOS differs widely, e.g., 0.5 % for India, 1.1 % for China, and 1.8 - 3.5 % for the most populated European countries. To determine the regionally-adapted share of SOS of the global plastics industry $SoSOS_{plastics}$, we weigh the regional shares by the regions' population p_i.

$$SoSOS_{plastics} = \frac{\sum SoSOS_{plastics,i} \cdot p_i}{\sum p_i} \tag{D.4}$$

This approach results in a regionally-adapted share of SOS of 1.0 %. In our opinion, the regionally-adapted share of SOS is even more egalitarian than the global average, as it accounts for the distribution of the world's population. However, it is associated with greater uncertainties. Thus, we decided to use the global average share of SOS in Chapter 6.

It is important to note that this approach, in general, can cause double counting and overestimation of the SOS for a particular sector, as the sum of X is larger than the sum of Y. Still, we employed this approach, because most plastics are not consumed directly by final consumers, and therefore the Y element corresponding to plastics is close to zero. Moreover, plastics production lies at the very early stage of the supply chain or ”degree of fabrication”, and therefore the double-counted part, mainly incorporated in the value-added from the extraction and transportation of crude petroleum and natural gas, is likely to be minimal. Alternatively, one can use the direct value-added by the plastics sector for its production induced by each country's final consumption, which does not lead to double counting.

D.3 Results

D.3.1 Details on technology pathways

In Chapter 6, the **fossil-based pathway** (see Figures 6.3 and 6.4 in Chapter 6) serves as a reference using only best-available fossil technologies. Steam crackers and solvent extraction processes convert naphtha into ethylene, propylene, benzene, toluene, and xylene. These base chemicals are used in incumbent, industrialized processes to produce plastics. Furthermore, natural gas is combusted for heat generation.

In contrast, the **bio-based pathway** (see Figures 6.4 in Chapter 6) comprises biomass gasification to syngas and fermentation to ethanol. Ethanol is a precursor for ethylene production. The syngas, a mixture of hydrogen and carbon monoxide, is a precursor for methanol synthesis. Subsequently, the methanol is converted to ethylene, propylene, benzene, toluene, and xylene, which again build the basis for incumbent plastics production. The corresponding technologies for the conversion of methanol to olefins and aromatics are already market ready. In contrast to the fossil-based pathway, heat supply includes no fossil fuels but excess heat from biomass gasification and fermentation, and heat from the incineration of recycling residues.

Also the **CCU-based pathway** (see Figures 6.4 in Chapter 6) converts methanol to olefins and aromatics for subsequent plastics production. However, in this pathway, methanol synthesis is based on hydrogen from water electrolysis and CO_2. CO_2 sources include direct air capture, the incineration of recycling residues, and point source within the plastics industry. Heat supply comprises electrical steam boilers, resistance heaters, and heat from the incineration of recycling residues.

All three pathways comprise two versions, one with current (23 %) and one with maximum (94 %) recycling rates. For current recycling rates, only mechanical recycling is deployed. Mechanical recycling converts packaging waste to recycled plastics, which can substitute virgin plastics production. In addition to mechanical, chemical recycling via pyrolysis is deployed for maximum recycling rates. Chemical recycling converts non-packaging waste into refinery feedstock. The remaining plastic waste can go to waste incineration with energy recovery or landfills. At **maximum recycling rates**, 94 % of plastic waste is recycled, and 6 % is landfilled, while no waste goes directly to incineration. Only residues from recycling are combusted for energy recovery.

The **climate-optimal pathway** (see Figures 6.3 in Chapter 6) is equal to the bio-based pathway with maximum recycling rates (Figures 6.4 in Chapter 6).

The **balanced pathway** (see Figures 6.3 in Chapter 6) combines bio- and CCU-based production with maximum recycling rates. Compared to the climate-optimal pathway, 72 % of methanol production switches from biomass utilization to CCU using hydrogen from water electrolysis and CO_2. CO_2 sources comprise the incineration of recycling residues and the remaining biomass gasification. Unlike in the CCU pathway, no direct air capture is needed due to CO_2 emission from the remaining biomass gasification and the smaller share of CCU-based production. Furthermore, reducing bio-based methanol production results in less excess heat from biomass gasification, which is replaced by electrical steam boilers.

D.3.2 Contribution analysis

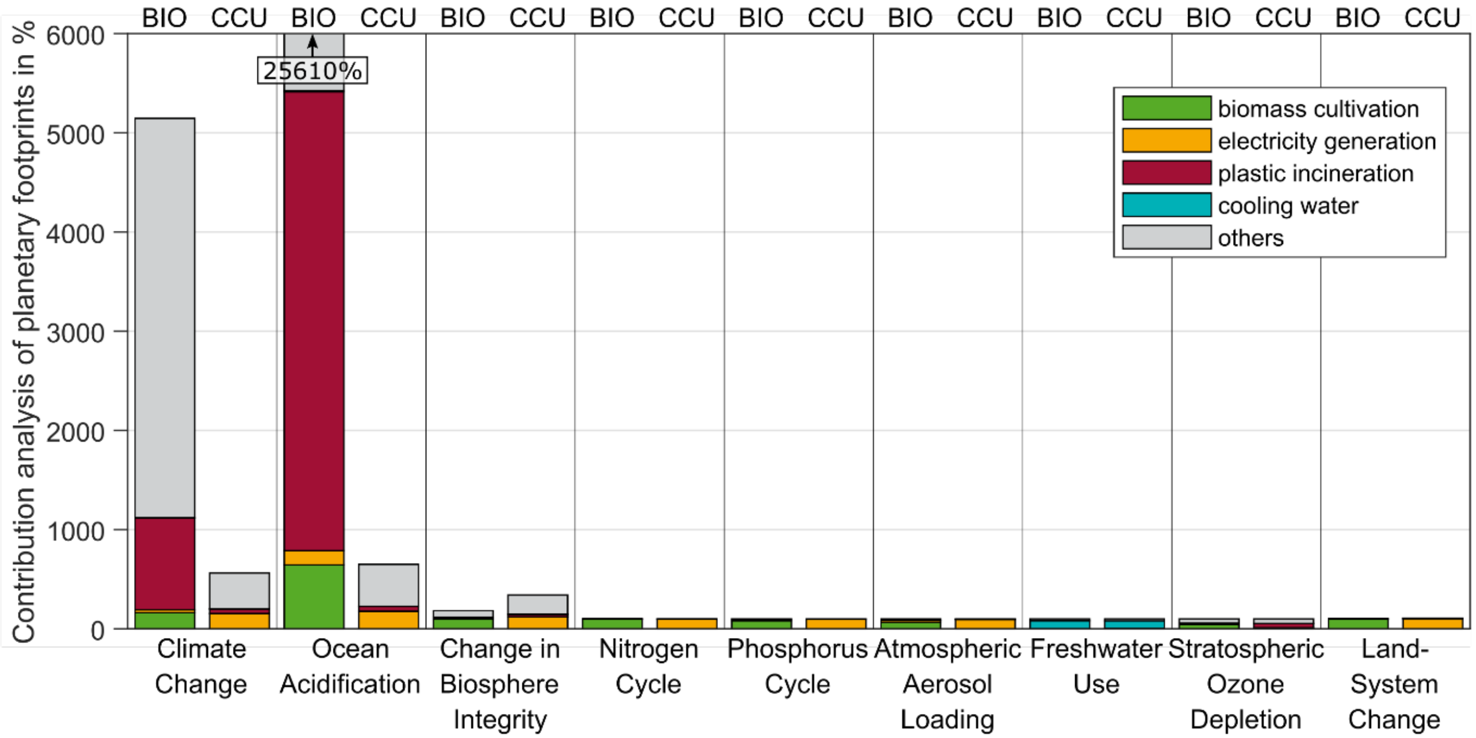

Figure D.1: **Extended contribution analysis of the planetary footprints of the plastics industry.** The figure shows the process contribution to the planetary footprints for all Earth-system processes. The left of each pair shows the pathways based on biomass (BIO) and the right shows the pathway based on CCU, both employing maximum recycling rates. For simplicity, the carbon uptake from the biomass growth phase is not shown. The net footprints correspond to the lower value of the green and light blue bars in Figure 6.3 in Chapter 6.

D.3.3 Sensitivity analysis for recycling technologies

Since we identify recycling as a key enabler towards absolute environmentally sustainable plastics, we conduct a sensitivity analysis on recycling technologies. In all cases, recycling is limited to maximum recycling rates of 94 %, which is in line with the literature.[37] In this study, recycling rates are defined as the ratio between all waste plastics sorted for mechanical recycling or recycled chemically divided by the total amount of plastic waste. In contrast, effective recycling rates additionally account for losses during the sorting and recycling processes. Accordingly, effective recycling rates of 70 %, which Meys et al. found to be required for net-zero GHG emission plastics, correspond to recycling rates of 94 %.[5]

The reference case from Chapter 6 is mechanical recycling of packaging waste and pyrolysis to refinery feedstock of non-packaging wastes (MR+PY). Mechanical recycling and pyrolysis improve the sustainability of plastics with increasing recycling rates, thereby confirming the LCA results from recent literature for mechanical recycling.[20] For chemical recycling via pyrolysis, however, the LCA literature indicates burden shifting from climate change to photochemical ozone formation due to NO_x, SO_x, and other direct emissions.[20,142] These emissions also directly impact aerosol loading. In contrast, our results show higher direct emissions from plastic incineration than from pyrolysis, such that both mechanical and chemical recycling reduce impacts on aerosol loading. Future studies should therefore investigate the impact on aerosol loading for pyrolysis to avoid potential burden shifts.

Chemical recycling to monomers could boost circularity compared to current practice, albeit being not market-ready. Therefore, we apply an optimistic scenario to assess the potential of chemical recycling, which converts plastic waste into monomers with a 95 % yield.

Already at current recycling rates, chemical monomer recycling (MR+CR) would replace pyrolysis and reduce all planetary footprints compared to the reference case (MR+PY, see upper values in Figure D.2). Chemical monomer recycling reduces virgin resource consumption, i.e., naphtha, biomass, and electricity, which are the main contributor to the planetary footprints (Figure 6.4 and D.1 from Chapter 6). The consumption is reduced due to the higher yield of chemical monomer recycling compared to pyrolysis. For pyrolysis, the overall yield from waste polymer to naphtha is already less efficient than the assumed yield of chemical monomer recycling (95 %). Moreover, pyrolysis requires reproducing monomers from naphtha, leading to additional losses. In contrast, chemical recycling directly yields monomers, which additionally enhances the efficiency of chemical monomer recycling. Thereby, increasing recycling efficiencies is most beneficial at maximum recycling rates, where planetary footprints decrease between 21 and 97 % compared to the reference case with pyrolysis (MR+PY).

In summary, chemical monomer recycling could enable absolute environmental sustainability for CCU-based plastics at maximum recycling rates and significantly improve the sustainability of bio-based plastics. Therefore, getting chemical monomer recycling market-ready is the key towards absolute environmentally sustainable plastics. In the meantime, increasing recycling rates and pyrolysis yield improve plastics' sustainability.

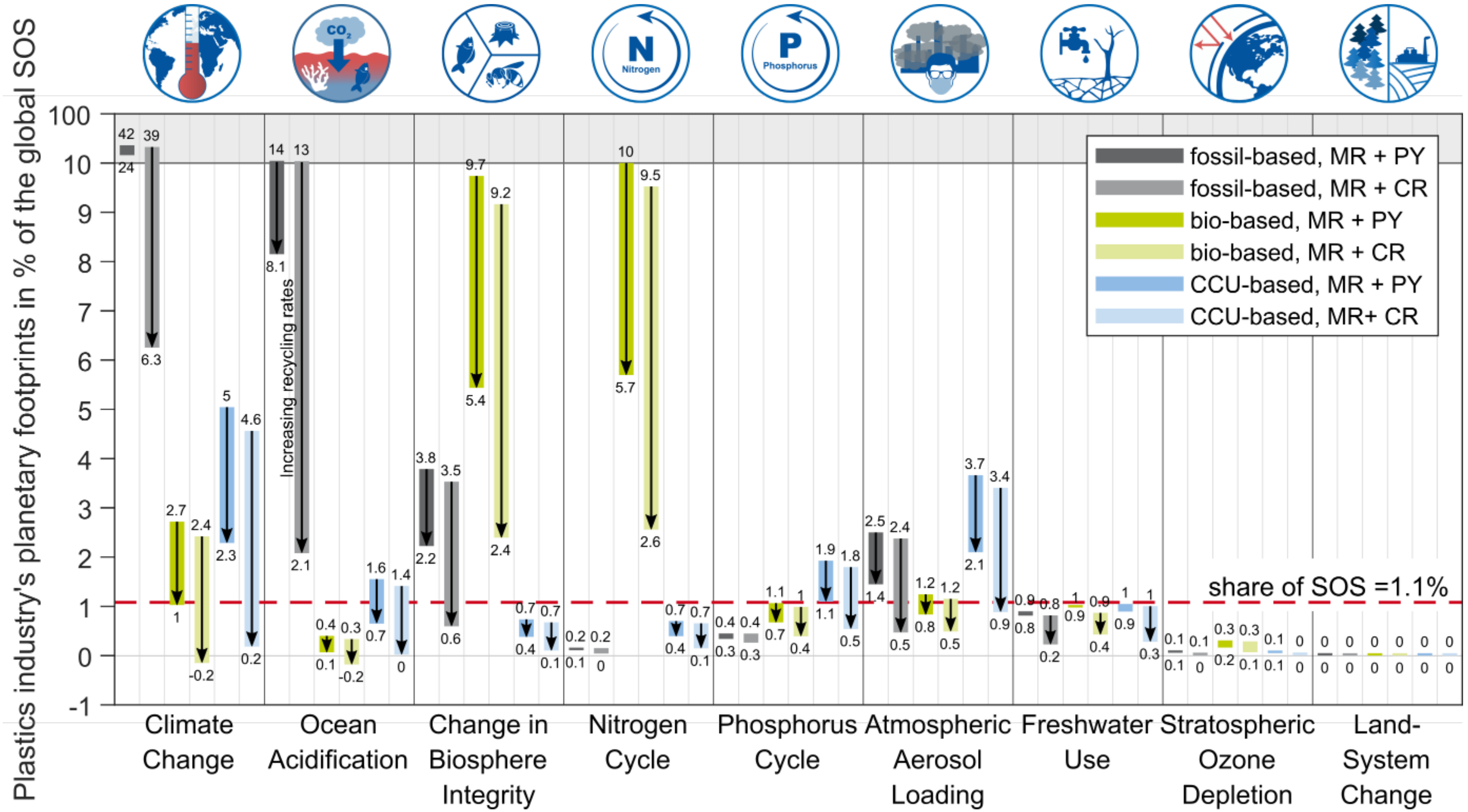

Figure D.2: **Sensitivity analysis of the planetary footprint of the plastic industry for recycling technologies.** The planetary footprints are calculated by minimizing the environmental impact of climate change. The pathways include fossil-based (grey), bio-based (green), and CCU-based (blue) plastics with the current (upper value) and the maximum (lower value) recycling rates. Arrows indicate increasing recycling rates. Freshwater use for the pathway "bio-based, MR + PY" is the only exception, where the lower value represents the current recycling rate. For each of the three pathways, there are two scenarios, one with mechanical recycling and chemical recycling via pyrolysis (MR+PY) and one with mechanical recycling and chemical recycling to monomers (MR+CR).

D.3.4 Sensitivity analysis of biomass sources

Energy crops are the default biomass used in Chapter 6. Using energy crops transgresses the plastic industry's share of SOS in biosphere integrity and the N-cycle footprint by about four times even at maximum recycling rates (see Figure D.3). Therefore, we analyze the planetary footprints of energy crops in the following. Furthermore, biomass cultivation, which is the main contributor to the planetary footprints of bio-based plastics, differs by biomass type. Thus, we conduct a sensitivity analysis for lignocellulosic biomass, including woody biomasses and two types of bagasse as industrial by-products. Bagasse is a by-product of sugar production from sugarcane and ethanol production from sweet sorghum. We exclude edible biomass from the sensitivity analysis to avoid competition with the food industry and compare the types of biomasses based on a dry mass basis. The following analysis focuses on bio-based plastics at maximum recycling rates (see Figure D.3).

In this study, energy crops are represented by miscanthus. We found that miscanthus has a higher N-cycle foot-print than other lignocellulosic biomasses resulting from higher nitrogen-containing fertilizer use (see Figure D.3). In contrast, previous literature predicts lower nutrient requirements for energy crops when compared to other crops and little to no need for additional fertilizer when cultivated on arable land.[220,375] Thus, the fertilizer demand for cultivating energy crops assumed in ecoinvent might be too conservative. The lower nutrient requirements of energy crops from literature align with the assumptions for sweet sorghum and sugarcane production from ecoinvent, where more nitrogen-containing fertilizer is used compared to miscanthus production. However, ecoinvent applies economic allocation between ethanol, bagasse, and other co-products for ethanol production from sweet sorghum and between sugar, sugarcane, and other co-products for sugar production from sugarcane. Since bagasse has a significantly lower price than the main products, the environmental impacts are mainly allocated to the main product. Thus, the N-cycle footprint of bagasse is lower than for miscanthus. However, using bagasse as a feedstock for plastics may increase the price of bagasse, resulting in higher environmental impacts. Furthermore, production volumes are limited by the demand for the bagasse's main products. In contrast, woody biomass significantly reduces the N-cycle footprint compared to miscanthus since forestry demands less fertilizer than cultivating energy crops.[202] By using woody biomass, the plastic industry could operate within the share of SOS for the N-cycle footprint.

In ecoinvent, miscanthus is assumed to grow mainly on arable land. However, Roncucci et al. found similar yields for energy crops on low-fertility land if about the same amount of nitrogen fertilizer (50 kg per hectare per year) is used as assumed in ecoinvent.[375] Accordingly, the high impacts in biosphere integrity resulting from the occupation of arable land can be reduced if energy crops are cultivated on marginal land with lower fertility. In addition, using marginal land for biomass cultivation may increase its availability.

Considering the other biomass types, bagasse has the lowest impact on biosphere integrity due to the high yields of their corresponding crops (see Figure D.3). Again, economic allocation favors the low environmental impact of bagasse. In contrast, except for bark chips, woody biomass worsens biosphere integrity compared to energy crops due to the lower yield of woody biomass per hectare resulting in higher land occupation.[202] In addition, even plastics produced from bark chips transgress their share of SOS.

Despite the land occupation, footprints in land-system change are low for all investigated biomass types. Since the biomass types are assumed to be cultivated on cropland or are by-products almost no transformation of forested land is required. However, the control variable of the land-system change planetary boundary currently only considers the transformation of forested land, while the literature suggests to assess land-system changes beyond forested land in the future. Holding land-system change of any kind at minimum will require further sustainable intensification of agriculture to cope with increasing demand for biomass. Without sustainable intensification, large-scale cultivation of energy crops on cropland may pressure crop markets and induce indirect land-use change, potentially leading to deforestation and a higher burden on the Earth system process of land-system change. On the one hand, the macro trend from the historical data reported by the Intergovernmental Panel on Climate Change shows a declining deforestation rate over the last century, primarily due to yield improvements.[152,153] On the other hand, the literature disagrees on future trajectories of yield improvement and land use change.[376] Thus, future research should assess potential impacts of bio-based plastics on land-system change in more detail.

For GHG-related planetary footprints, bagasse and woody biomasses perform similar to energy crops, except for wood pellets. Wood pellets have higher impacts on climate change and ocean acidification due to additional efforts for pelletizing and drying. The additional efforts also cause higher impacts in aerosol loading compared to other biomass feedstocks. For the other biomass feedstocks, the largest share of aerosol loadings results from biomass cultivation, which originates from the construction of agricultural machinery. The machinery construction requires steel, which is currently predominantly produced by blast furnace processes using coal as a reduction agent. Thus, a switch to steel production based on alternative reducing agents may improve aerosol loading of coal-related processes.

In summary, energy crops may offer the highest additional availability and thus be the primary prospect for the large-scale production of bio-based plastics. The planetary footprint of energy crops can be reduced by deploying alternative biomass feedstocks. However, each feedstock comes with a trade-off, either by high biosphere integrity loss or limited availability. A balanced mix of feedstocks may exploit the advantages of each feedstock while keeping the trade-offs at a minimum. Thereby, building on various biomass feedstocks may enable sufficient availability and absolute environmental sustainability for the plastic industry if bio-based production is combined with high recycling rates.

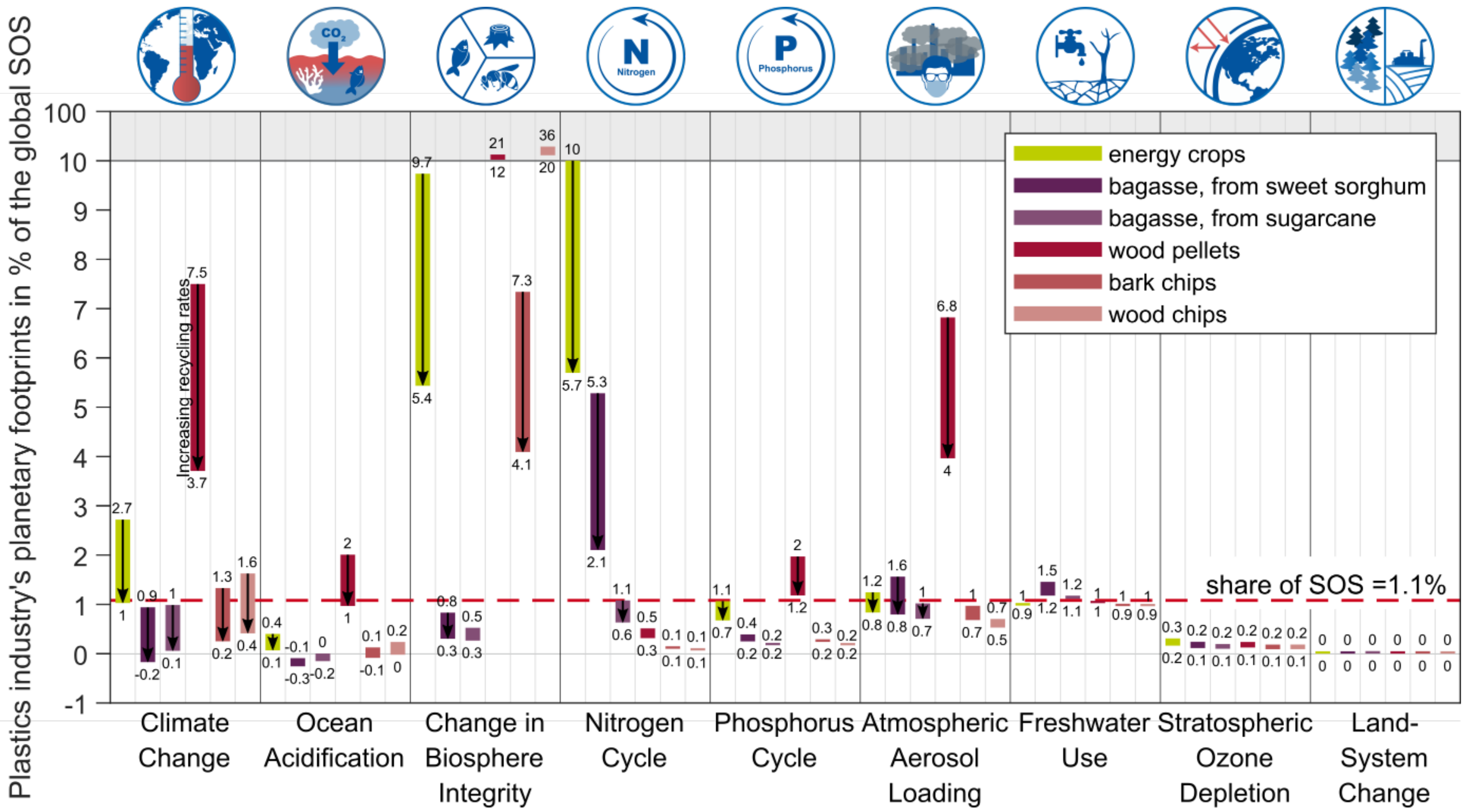

Figure D.3: **Sensitivity analysis of the planetary footprint of the plastic industry for biomass feedstocks.** Energy crops are used for bio-based plastics in Chapter 6. The bio-based supply chain is calculated by minimizing the environmental impact of climate change when using energy crops. For the sensitivity analysis, we use the same supply chain and replace energy crops with other biomass feedstocks on a dry mass basis. All pathways show bio-based plastics with the current (upper value) and the maximum (lower value) recycling rates. Arrows indicate increasing recycling rates. Exception, where the lower value represents the current recycling rate, are the P-cycle footprint for bagasse from sugarcane and wood chips, and the freshwater use for all feedstocks except for both types of bagasse.

D.3.5 Sensitivity analysis of renewable energy

CCU-based plastics strongly rely on renewable electricity generation. Even the most ambitious forecasts for the 2030's grid mix[63] would compromise the environmental sustainability of CCU-based plastics. Therefore, we further assess which electricity generation technologies could be promising for producing sustainable CCU-based plastics. For this purpose, we assess the planetary footprints of CCU-based plastics when entirely relying upon either geothermal, nuclear, water, solar, or wind power. The planetary footprints most sensitive to electricity generation are the P-cycle footprint, aerosol loading, and all GHG-related planetary footprints, namely climate change, ocean acidification, and biosphere integrity. In this analysis, we focus on CCU-based plastics at maximum recycling rates (Figure D.4).

Currently, CCU-based plastics based on electricity from photovoltaic (PV) and geothermal power do not achieve absolute environmental sustainability due to the remaining GHG emissions from plant construction. Furthermore, PV and geothermal power exceed the planetary boundary for the P-cycle footprint and aerosol loading. However, the P-cycle footprint is reduced to 4.0 % of the SOS for PV with high full load hours and 3.0 % of the SOS for geothermal energy compared to 5.8 % of the SOS for the 2030's grid mix (see Figure 6.3 in Chapter 6). Aerosol loading increases to 6.0 % by PV and 7.8 % by geothermal power compared to 5.9 % of the SOS for the 2030's grid mix. The P-cycle footprint results from construction, which for geothermal power plants and photovoltaic panels is linked to coal-based energy. Additionally, the construction of geothermal power plants is linked to coal-based steel production, while photovoltaic panels require copper for wiring. Along with direct emissions from steel production, the mining of copper and coal causes the P-cycle footprint. Aerosol loading is mostly linked to coal-based energy for the construction of the geothermal power plant and photovoltaic panels.

Reducing footprints from construction could make both technologies viable options for sustainable plastics production. For instance, decarbonizing the electricity supply used for construction decreases the construction's climate change impact of PV and geothermal energy by 40 and 65 %, respectively.[377] Increasing full load hours would further reduce the specific impact of the construction phase. In particular, for PV full load hours could double in regions with high solar intensity, such as the Middle East, when compared to regions with lower solar intensity like Germany. With higher full load hours (photovoltaic, high FLH in Figure D.4), the electricity output per PV panel increases. The impacts from the construction phase remain unchanged and, thus, relatively decrease per energy output. However, even in solar-intense regions, current PV construction needs to be further decarbonized to comply with the planetary boundaries.

Considerably more sustainable are CCU-based plastics using either nuclear, wind, or hydropower. Hydropower even enables absolute environmental sustainability for CCU-based plastics with maximum recycling rates. However, hydropower is limited to regional topography.

In contrast, nuclear power is not limited to regional topography but exceeds the share of SOS for aerosol loading and freshwater use. Moreover, using nuclear power for CCU-based plastics increases the impact of ionizing radiation, which is strongly linked to human health impacts. Using nuclear power increases ionizing radiation by about 20-times compared to fossil-based and about 216-times compared to CCU-based plastics with wind power. Furthermore, the disposal of nuclear fuel rods is controversially discussed and could jeopardize absolute environmental sustainability.

For wind power, the construction is the main contributor to the remaining planetary footprints. In particular, for the P-cycle footprint and aerosol loading, improving steel and copper production will further reduce planetary footprints. Similar to PV, wind-intense regions enable high full load hours for wind power and, thereby, grant low planetary footprints. Full load hours would also tackle non-renewable resource depletion, which is often discussed for wind turbines and may be considered unsustainable from a general perspective. In the context of environmental sustainability, however, resource depletion does not directly threaten the stability of the Earth-system.[378] Thus, wind power may be the best choice for environmentally sustainable plastics.

In summary, wind, nuclear, and hydropower are the most promising prospects towards sustainable production of CCU-based plastics. However, including any of the assessed renewable electricity technologies in the grid mix will bring the plastics industry closer towards absolute environmental sustainability. Maximizing full load hours and decreasing footprints from construction could go alongside with increasing recycling yield to enable absolute environmental sustainability.

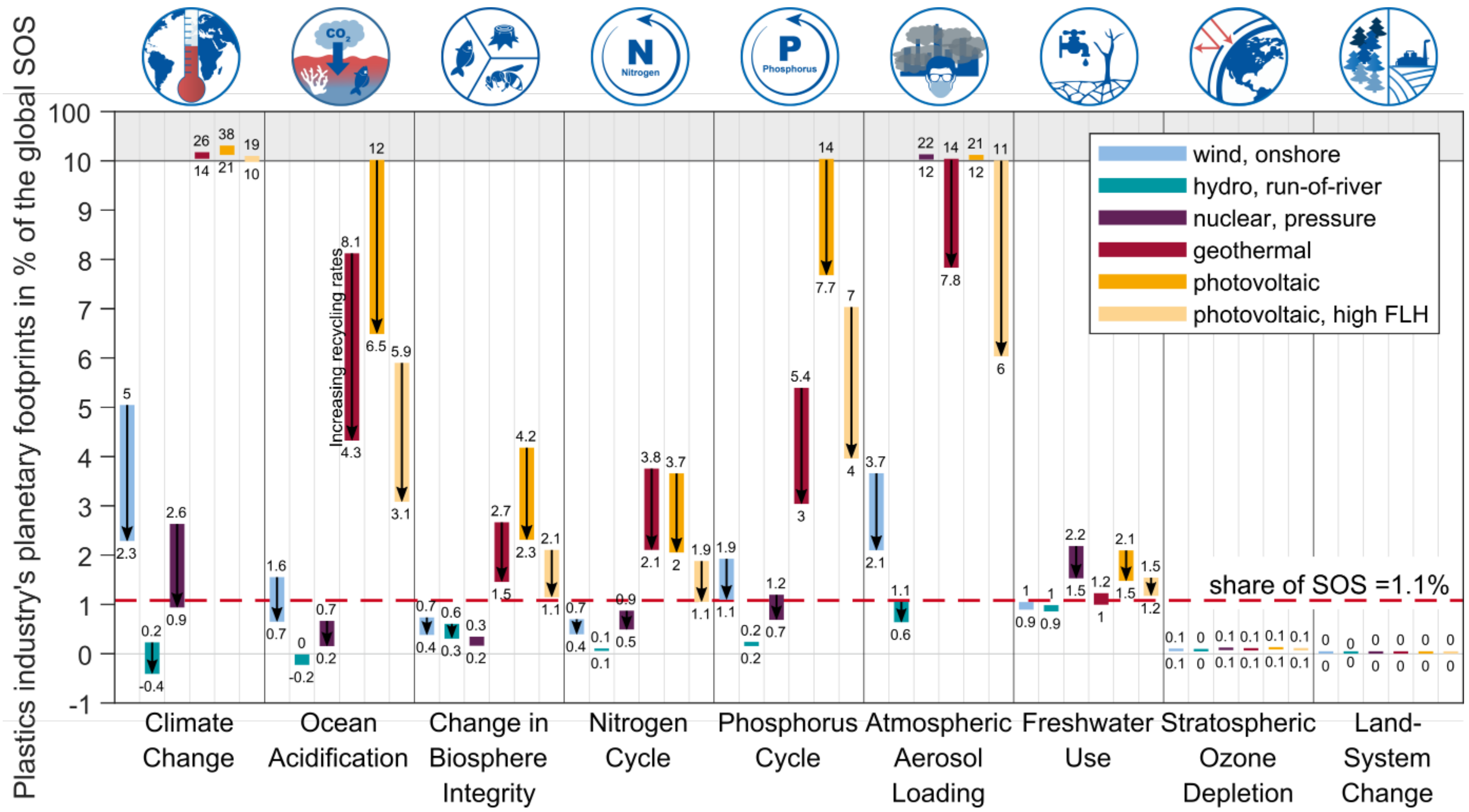

Figure D.4: **Sensitivity analysis on the planetary footprint of CCU-based plastics for electricity generation technologies.** Onshore wind power is used for CCU-based plastics in Chapter 6. The CCU-based supply chain is calculated by minimizing the environmental impact of climate change when onshore wind power. For the sensitivity analysis, we use the same supply chain and replace wind-powered electricity with other electricity generation technologies on an energy basis. All pathways show CCU-based plastics with the current (upper value) and the maximum (lower value) recycling rates. Arrows indicate increasing recycling rates. For photovoltaic, we include two datasets: One from Germany and one representing solar-intense regions with higher full hours (high FLH), which we approximate by photovoltaic from Saudi Arabia.

D.3.6 Planetary footprints of plastics in 2050

In Chapter 6, we show that the plastics industry can achieve absolute environmental sustainability for production volumes of 2030 in an optimistic scenario. The scenario comprises chemical recycling to monomers with a 95 % yield, wind power as the source of electricity, and energy crops as biomass feedstock. From 2030 to 2050, production increases by 27-163 %, depending on the type of plastic (see Table 6.1 in Chapter 6). The increasing production compromises absolute environmental sustainability in 2050 for any technology combination, even when applying the optimistic scenario (see Figure D.5).

For bio-based plastics with maximum recycling rates, biosphere integrity and the N-cycle footprint are transgressed by 337 % and 353 % compared to the plastics industry's share of SOS, while for CCU-based plastics with maximum recycling rates, aerosol loading is transgressed by 64 %. In addition, even a linear combination of both mitigation strategies does not allow for absolute environmentally sustainable plastics when applying a share of SOS of 1.1 %.

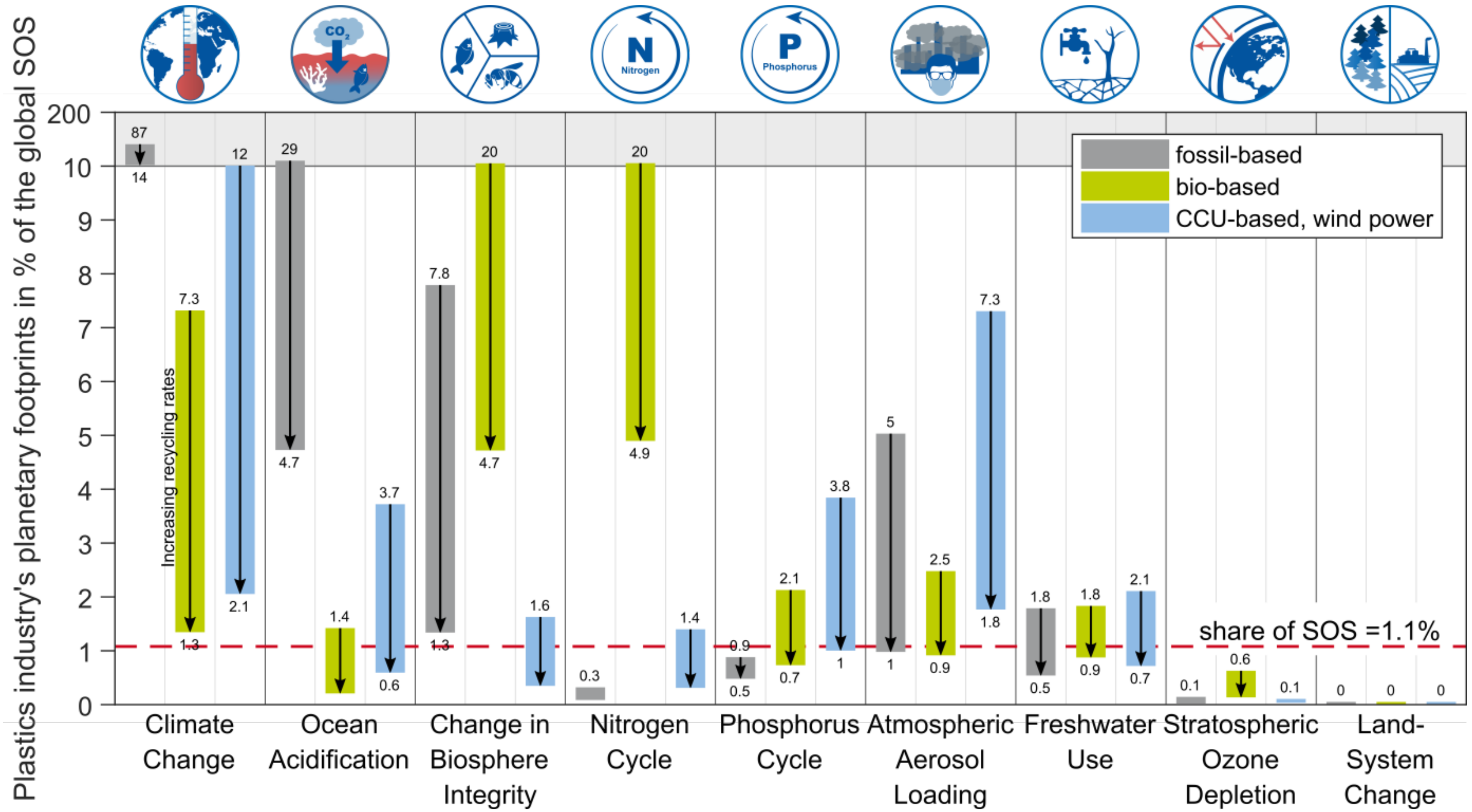

Figure D.5: **The planetary footprint of the plastic industry for three pathways in 2050.** The planetary footprints are calculated by minimizing the environmental impact of climate change. The pathways include fossil-based (grey), bio-based (green), and CCU-based (light and dark blue) plastics with the current (upper value) and the maximum (lower value) recycling rates. Arrows indicate increasing recycling rates. The only exception is freshwater use of bio-based plastics, where the lower value represents the current recycling rate.

APPENDIX E

Publications and student theses

This thesis originates from the author's research during his time as a scientific staff at the Chair of Technical Thermodynamics at RWTH Aachen University from March 2018 to October 2022. Parts of this thesis have already been published as described in Chapter 2 and in the beginning of Chapter 3, 4, 5, and 6. André Bardow provided ideas and guidance as well as edits to these publications and this dissertation.

List of publications

Journal papers

Bachmann, M., Zibunas, C., Hartmann, J., Tulus, V., Suh, S., Guillén-Gosálbez, G., Bardow, A. Towards circular plastics within planetary boundaries. *Nature Sustainability*, 1-12, 2023.

Bachmann, M., Völker, S., Kleinekorte, J., Bardow, A. Syngas from what? Comparative life cycle assessment for syngas production from biomass, CO_2, and steel mill off-gases. *ACS Sustainable Chemistry and Engineering*, 2023.

Bachmann, M., Marxen, A., Schomäcker, R., Bardow, A. High-performance, but low cost and environmental impact? Integrated techno-economic and life cycle assessment of Polyoxazolidinone as a novel high-performance polymer. *Green Chemistry*, 24(23):9143-9156, 2022.

Hense, J., Bachmann, M., Polte, L., von der Assen, N., Jupke, A. Integrated Process Design and Life Cycle Assessment of Carbon Monoxide Provision from Basic Oxygen Furnace Gas. *Chemie Ingenieur Technik*, 94(10):1524-1535, 2022.

Bachmann, M., Kätelhön, A., Winter, B., Meys, R., Müller, L.J., Bardow, A. Renewable carbon feedstock for polymers: environmental benefits from synergistic use of biomass and CO_2. *Faraday Discussions*, 230:227-246, 2021.

During his time at the Chair of Technical Thermodynamics, M.B. additionally contributed to the following publications which do not form a part of this thesis:

Meys, R., Kätelhön, A., Bachmann, M., Winter, B., Zibunas, C., Suh, S. Bardow, A. Achieving net-zero greenhouse gas emission plastics by a circular carbon economy. *Science*, 374(6563):71-76, 2021.

Armstrong, K., Bachmann, M., Bardow, A, Cao, X.E., Cassiola, F., Cummings, C., Dowson, G., Kamali, A.R., Leitner, W., Manyar, H., McCord, S., North, M., Pant, D., Park, A., Pérez-Fortes, M., Platt, E., Poon, J., Ramírez, A., Sick, V., Styring, P., Tanzer, S.E., Tanveer, W., Thomas, O., Whiston, K. Life cycle and upscaling: general discussion. *Faraday Discussions*, 230:308-330, 2021.

Kleinekorte, J., Fleitmann, L., Bachmann, M., Kätelhön, A., Barbose-Póvoa, A., von der Assen, N., Bardow, A. Life cycle assessment for the design of chemical processes, products, and supply chains. *Annual Review of Chemical and Biomolecular Engineering* , 11:203-233, 2020.

Müller, L.J., Kätelhön, A., Bachmann, M., Zimmermann, A., Sternberg, A., Bardow, A. A guideline for life cycle assessment of carbon capture and utilization. *Frontiers in Energy Research*, 8:15, 2020.

Reports and books

Furthermore, M.B. contributed to the following reports and books:

Bachmann, M., Deutz, S., von der Assen, N. Die Methode der Ökobilanz für Kunststoffe sowie deren Recycling, 2022. *In preparation.*

Langhorst, T., McCord, S., Zimmermann, A., Müller, L.J., Cremonese, L., Strunge, T., Wang, Y., Villa Zaragoza, A., Wunderlich, J., Marxen, A., Armstrong, K., Buchner, G., Kätelhön, A., Bachmann, M., Sternberg, A., Michailos, S., Naims, H., Winter, B., Roskosch, D., Faber, G., Mangin, C., Olfe-Kräutlein, B., Styring, P., Schomäcker, R., Bardow, B., Sick, V. Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO_2 Utilization (Version 2.0), 2022.

Zimmermann, A., Müller, L.J., Wang, Y., Langhorst, T., Wunderlich, J., Marxen, A., Armstrong, K., Buchner, G., Kätelhön, A., Bachmann, M., Sternberg, A., Michailos, S., McCord, S., Villa Zaragoza, A., Naims, H., Cremonese, L., Strunge, T., Faber, G., Mangin, C., Olfe-Kräutlein, B., Styring, P., Schomäcker, R., Bardow, B., Sick, V. Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO_2 Utilization (Version 1.1), 2020.

Zimmermann, A., Müller, L.J., Marxen, A., Armstrong, K., Buchner, G., Wunderlich, J., Kätelhön, A., Bachmann, M., Sternberg, A., Michailos, S., Naims, H., Styring, P., Schomäcker, R., Bardow, B. Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO_2 Utilization, 2018.

Student theses supervised during this work

While working at the Chair of Technical Thermodynamics, M.B. supervised and co-supervised the student theses listed in the following. The work of all students is gratefully acknowledged.

Genau, S. Absolute environmental sustainability assessment of mobility concepts considering planetary boundaries. Master thesis, RWTH Aachen University, 2022.[a]

Brake, J. Untersuchung des Energiebedarfs für Umwandlungsvefahren von Hüttengasen zu Synthesegas inklusive Sensitivitätsanalyse zur Ermittlung der Haupteinflussgrößen auf den Prozess (in German). Master thesis, Fraunhofer UMSICHT and RWTH Aachen University, 2022.[b]

Hartmann, J. Integrating Life Cycle Assessment and Planetary Boundaries into a multi-criteria optimization framework for the chemical industry. Master thesis, RWTH Aachen University, 2021.[c] Jan Hartmann investigated the planetary boundary framework for application to the plastics industry. In his master thesis, he implemented and enhanced the planetary boundary framework and conducted a first analysis of the planetary footprints of plastics. With his work, Jan Hartmann laid the foundation for the analysis in Chapter 6 of this thesis.

Lipp, M. Optimization-based analysis of lock-in effects on the decarbonization of the chemical industry. Master thesis, RWTH Aachen University, 2021.[c]

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[a] Co-supervised with Stefan Eichwald.

[b] Co-supervised with Christian Geitner.

[c] Co-supervised with Christian Zibunas.

Fehér, S. Consistent uncertainty assessment in life cycle optimization models towards a decarbonized chemical industry. Master thesis, RWTH Aachen University, 2020.[c]

Adams, S. The supply of Sustainable Aviation Fuels for Europe. Master thesis, ETH Zürich and RWTH Aachen University, 2020.[d]

Münnich, P. Optimizing Marginal Greenhouse Gas Abatement Costs in Energy-Intensive Process Industries. Master thesis, RWTH Aachen University, 2020.[c] Paul Münnich generated marginal abatement cost curves of the chemical, steel, and cement industry and investigated interactions and synergies between these industries. As part of his thesis, Paul Münnich reviewed and curated life cycle inventories of bio- and CCU-based syngas production that were used in the syngas production system in Chapter 5.

Dibos, S. Optimizing the climate change mitigation potential of the chemical industry based on biogenic feedstocks. Bachelor thesis, RWTH Aachen University, 2020.

Derwein, D. Integrated optimization of power-to-gas and CCS technologies for biogas production in regional energy systems. Master thesis, Chalmers University of Technology and RWTH Aachen University, 2019.[e]

Hermesmann, M. Multiobjective Optimization of Biobased Gasification Technologies for the Production of Environmentally Beneficial Platform Chemicals. Master thesis, Chalmers University of Technology and RWTH Aachen University, 2019.[e] Matthias Hermesmann investigated biomass gasification technologies for producing bio-based methanol. In particular, Matthias Hermesmann applied, adjusted and improved existing simulation models at Chalmers University and generated life cycle inventories from these simulation models. These life cycle inventories were used in Chapter 3, 4, 5, and 6 of this thesis.

Ganter, A. Assessing the Environmental Impacts of the FastOx® Gasifier as a Waste Utilization Technology. Bachelor thesis, University of California, Davis and RWTH Aachen University, 2019.[f]

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[d] Co-supervised with Maximilian Held and Kyle Seymour.

[e] Co-supervised with Johan Ahlström.

[f] Co-supervised with Alissa Kendall.

Conference contributions

In addition, M.B. attended and contributed to the following conferences:

Bachmann, M., Zibunas, C., Tulus, V., Hartmann, J., Guillén-Gosálbez, G., Bardow, A. The planetary footprint of global plastic production. *Gordon Research Conference on Industrial Ecology 2022*, Newry, USA, 2022.

Bachmann, M., Bardow, A. Towards absolute sustainable plastics - from linear to circular production. *World Plastics Summit 2022*, Monaco, 2022.

Bachmann, M., Münnich, P., Bardow, A. Syngas from what? Comparative Life Cycle Assessment of CO_2-based Syngas and alternative Renewable Pathways. *Faraday Discussions*, online, 2021.

Bachmann, M., Müller, L.J., Winter, B., Meys, R., Sternberg, A., Bardow, A. The benefits of industrial symbiosis: combining CO_2 and biomass as renewable carbon feedstocks for polymers. *10th International Society for Industrial Ecology Conference*, Beijing, China, 2019.

Bachmann, M., Müller, L.J., Winter, B., Meys, R., Bardow, A. Combined Life Cycle Assessment of CO_2 and Biomass as Renewable Carbon Feedstock for Polymers. *17th International Conference on Carbon Dioxide Utilization*, Aachen, Germany, 2019.

Bachmann, M., Müller, L.J., Kätelhön, A., Bardow, A. CO_2 abatement cost curves for the chemical industry: A systems approach. *Gordon Research Conference on Industrial Ecology 2018*, Les Diablerets, Switzerland, 2018.

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