Life Cycle Assessment of steel off-gas fermentation in the context of alternative PET sourcing routes for textiles

MSc Industrial Ecology

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Executive Summary

The global production of textiles carries a significant share in global greenhouse gas emissions, with a demand projected to grow. Especially for scope 3 emissions, materials play a significant role, with polyethylene terephthalate (PET) as a dominating fibre material with unique properties. Virgin PET based on fossil oil as the conventional option is non-renewable, not aligning with a sustainable future supply route. Alternative drop-in feedstock options for PET are biobased or recycled. Biobased PET has the potential for an emission reduction, but that is not automatically the case. Also there is a trade-off with a worse performance in other impact categories because of the agricultural production. With recycled PET, there are mechanical and chemical recycling options. Mechanical recycling for fibres is feasible and established as open-loop recycling from bottles. For mechanical recycling from textiles, a blend with virgin PET becomes necessary to maintain the required quality. Chemical recycling is more promising for closed-loop recycling from textile waste, but infrastructure and design barriers are current limitations for its expansion. Because these PET sourcing routes come with different trade-offs and barriers, it is reasonable to explore other routes as well, such as basic oxygen furnace (BOF) gas fermentation and compare them with the alternatives.

In this study, Life Cycle Assessment (LCA) was conducted to determine the climate change impact of BOF gas fermentation-based PET compared to mechanically recycled and fossil-based PET. Then, the results were also compared to literature values for biobased and chemically recycled PET, embedding the results in the context of alternative sourcing routes for PET in the textile industry. In the focus technology of this study, feedstock gases rich in carbon are fermented into ethanol by microorganisms. Through several intermediates, monoethylene glycol (MEG) is made as one of the two main components of PET. Together with pure terephthalic acid (PTA), it is polymerised into PET. Several carbon-rich feedstock gases such as syngas from biomass or wastes, but also reformed natural gas have been explored in previous research and development. However, the commercially available option is to use off-gas from the steel industry from the BOF. Therefore, the examined feedstock in this LCA is BOF gas with a composition of 85% CO and 15% CO_2.

With a climate change impact of 4.95 CO_2eq / kg PET, fermentation-based PET had the highest impact within the LCA model results of this study, followed by virgin PET (2.93 kg CO_2 eq per kg PET) and then mechanically recycled PET (1.05 kg CO_2 eq per kg PET). Biobased PET literature values ranged between comparable impacts to mechanically recycled PET up to values higher than all other investigated sourcing alternatives. Chemically recycled PET had an impact between mechanically recycled PET and virgin PET. In terms of environmental contributions, for all alternatives the major share of greenhouse gas emissions was from fossil CO_2 (around 80%). Technosphere contribution hotspots were the carbon dioxide released during the fermentation and high voltage electricity production, mainly for the conditioning of the feedstock gas (compression and cooling). Also the provision of the virgin PTA component had a considerable contribution (1.11 CO_2eq / kg PET).

Under the current global electricity mix, the gas fermentation technology was concluded to not be an advisable alternative to reduce greenhouse gas emissions. A combination of a best-case renewable electricity scenario, a substitution of the missing energy from the BOF gas in the steel process with wind energy instead of natural gas and an orange-peel based PTA sourcing route could reduce the climate change impact down to be comparable to mechanically recycled PET. However, that result is only valid if the emission credit assumption for the avoided emissions in the steel process holds. Otherwise, the gas fermentation technology emits more greenhouse gas emissions than both conventional alternatives, even under the best-case scenario.

Contents

Nomenclature

Abbreviations

Abbreviation	Definition
BF	Blast furnace
BFG	Blast furnace gas
BOF	Basic oxygen furnace
CCS	Carbon capture & storage
CCU	Carbon capture & utilisation
EVA	Ethylene vinyl acetate
FU	Functional unit
GHG	Greenhouse gas
LCA	Life Cycle Assessment
MEG	Monoethylene glycol
NMVOC	Non-methane volatile organic compounds
PCY	p-cymene
PET	Polyethylene terephthalate
PTA	Pure terephthalic acid
RoW	Rest of world
TRL	Technology readiness level

1 Introduction

Globally, the clothing and shoe industry makes up to 8% of the greenhouse gas emissions, with an upwards trend towards 2050 (Sadowski et al., 2021). To stay within a 1.5 degrees pathway, emissions need to be halved until 2030 (Mc Kinsey & Company & Global Fashion Agenda, 2020). Recent predictions see this aim unlikely to be reached (Meinshausen et al., 2022). Nevertheless, it implies an urgent need for emission reduction. Especially material production is estimated to have a share of 38% in the greenhouse gas emissions of the footwear and clothing value chain (Apparel Impact Institute & Fashion for Good, 2021). Materials also play a substantial role in the scope 3 emissions, which are the hardest to quantify, but also make the largest share of the overall life cycle emissions in the fashion industry (96%). Scope 3 quantifies what is emitted indirectly through value networks upstream and downstream of a company's own direct production (scope 1) and the associated energy purchase (scope 2). Also, 25% of globally produced chemicals are associated with the textile industry, which cause significant environmental impacts (Schellenberger et al., 2019). Therefore, there is a strong need for improving the environmental performance of textile products with regard to resource use, pollution and waste generation (L'Abbate et al., 2018).

Polyethylene terephthalate (PET), a polyester, is a dominating material for fibres in the textile industry for its low price and multifaceted applicability (L'Abbate et al., 2018; Palacios-Mateo et al., 2021; Zamani et al., 2015). The synthetic fibres have unique properties such as durability, waterproofness, crease-proofness and elasticity. In 2020, 52% of total global fibres produced were made from polyester, with an increase expected (Textile Exchange, 2022).

Crude oil-derived PET is based on the esterification of two main components: virgin monoethylene glycol (MEG) and virgin purified terephthalic acid (PTA) in a respective mass ratio of 30%/70% (Vural Gursel et al., 2021). With regard to the raw material extraction, oil drilling disrupts ecosystems at the borehole location. Oil spills have tremendous local environmental and health consequences (Palacios-Mateo et al., 2021). Oil refining releases toxic substances, particles and greenhouse gases (Greene, 2014). Fossil PTA is made by oxidising *p*-xylene in air, which is based on catalytic reforming of naphta, based on crude oil (Sattler & Schweizer, 2011). Fossil MEG is made from ethylene, which gets oxidised in a direct oxidation process. Ethylene gas gets compressed to 20 bar and mixed with pure oxygen with identical pressure. After being heated to 215°C, with a silver-based catalyst, it is partially oxidised. Several recycling and scrubbing steps are taken. Then, the ethylene oxide is typically sent to the ethylene glycol process on the same site. Water and ethylene glycol at 150°C and 35 bar are brought together to react into the main product MEG. (Sattler & Schweizer, 2011; Van Uytvanck et al., 2014). Polymers are derived in a continuous process to make PET granualate (Palacios-Mateo et al., 2021; Van Uytvanck et al., 2014). The PET granulate is extruded and spun into fibres, then knitted or woven into fabrics. Associated with that are high energy demands and resulting climate change impacts (Garcia-Gutierrez et al., 2023).

Global plastic production is expected to become 4 times as high from 2016 to 2050 (Murcia Valderrama et al., 2019). At the same time, in the Paris Agreement, a >90% CO_2 reduction target has been set

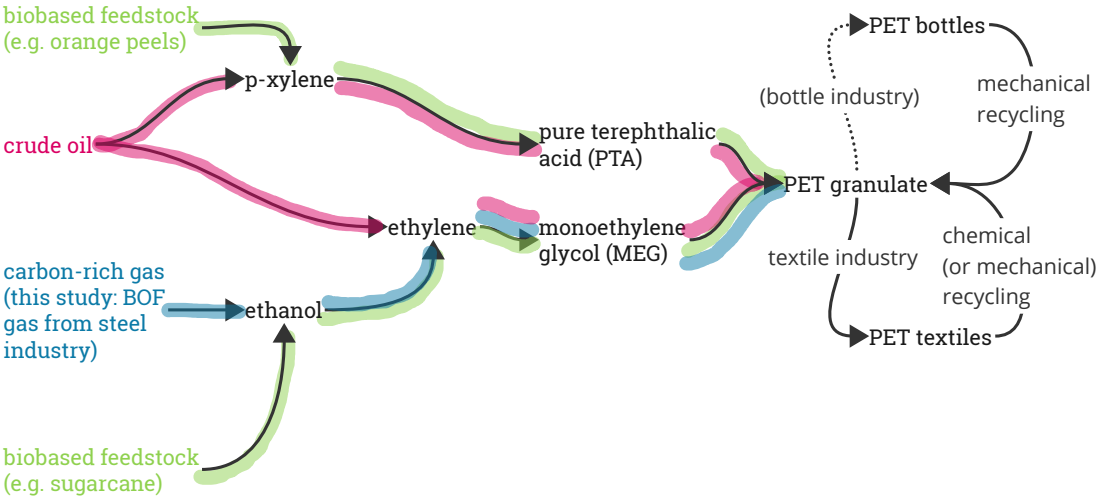

Figure 1.1: Overview about PET sourcing routes in the textile industry (simplified). Several combinations of components are possible and the routes partially overlap. Finally, the resulting PET granulate has the same chemical structure. Detailed explanations can be found in this chapter. (García-Velásquez & van der Meer, 2022; Martinol, 2023; Palacios-Mateo et al., 2021; Park & Kim, 2014; Sadeghi et al., 2021; Sattler & Schweizer, 2011; Van Uytvanck et al., 2014; Vural Gursel et al., 2021)

for the European Chemical Industry sector (1991-2050) (Murcia Valderrama et al., 2019). For the textile industry, PET poses a sustainability challenge, with the largest issues being the fossil-fuel use and the end-of-life fate (Geyer et al., 2017; Jahandideh et al., 2021). Plastics accumulate in natural systems because of their slow degradation (Rybaczewska-Blazejowska & Mena-Nieto, 2020). The replacement of fossil feedstocks with more sustainable alternatives is strongly recommended (Murcia Valderrama et al., 2019; Palacios-Mateo et al., 2021). Alternative feedstocks can be biobased, recycled or based on carbon-rich gases, with different, but partially overlapping sourcing routes (Figure 1.1). Since the resulting PET has the same chemical structure, these alternatives are considered "drop-ins" ((Vural Gursel et al., 2021)). An exception is for mechanical recycling, since that process reduces the polymerisation grade of the PET. This will be further explained in section 1.2. The "drop-ins" all have various environmental advantages and limitations and only pose a reasonable alternative if their environmental performance from a systems perspective is better than virgin PET based on crude oil.

In the following, an overview about the existing "drop-in" alternatives to virgin PET with their potentials and limitations will be given. First, bio-based PET and recycled PET (mechanically, chemically) are examined based on literature. These serve as context for the comparison of alternatives. The focus technology of the LCA model in this study is the fermentation of carbon-rich gas (BOF gas from the steel industry) into ethanol, a precursor for PET, which will be described in this chapter as well.

1.1. Bio-based PET

In general, biobased materials or -polymers are often defined as materials that are partly or fully sourced from biomass feedstock, but they can be physically, biologically or chemically treated (Textile Exchange, 2022). Biosynthetic materials are defined as polymer materials, synthetically produced, but partly or fully from renewable compounds (Gregory & Marshall, 2020). An example is fermented biomass, where the products can be used to make synthetic materials such as PET. Common so-called “first generation” feedstocks for biobased plastics in the textile industry are agricultural food crops such as corn, sugar beet or sugar cane and oil crops, for instance castor (Textile Exchange, 2022). “Second generation feedstocks” include non-edible crops such as *Miscanthus*, agricultural or industrial waste feedstocks such as wheat straw or orange peels, or lignocellulosic biomass such as timber. Here the processing is often more complicated (Textile Exchange, 2022). “Third generation feedstocks” refer to microalgae (Pishvaee et al., 2021).

For the MEG component of PET, biobased ethanol is dehydrated to ethylene and further processed

just as in the virgin route (García-Velásquez & van der Meer, 2022). In practice, the main production is in India from ethanol based on sugarcane molasses from India and imported bioethanol from Brazil. Processing of the biobased MEG to PET takes place in Thailand (García-Velásquez & van der Meer, 2022). For the PTA component of PET, demonstration-scale projects based on biobased para-xylene are carried out with various route, for example by Gevo (bioplastics Magazine, 2014; Collias et al., 2014). There is commercially available biobased PTA by Virent (Virent Inc., 2019). The overall production of PET from these precursors is also still at demonstration scale ((The Coca Cola Company, 2021)). Anellotech has proven prototype-scale biobased PTA and the production of 100% biobased PET as well and is in the transition to commercialisation (Anellotech Inc, 2021). Since biobased PET has the same chemical structure like virgin PET, it can be processed in the same recycling stream (Vural Gursel et al., 2021).

According to Garcia-Velsaquez et al. (2022), quantitative direct comparison of LCA studies on biobased PET is hardly possible as the assumptions, system boundaries and functional units vary largely. Economies of scale effects of biobased products are not included in LCA. Further, different methods to account for land use change and biodiversity impacts can substantially change the LCA results. Most of the LCA studies focus on greenhouse gas emissions, but apply different impact assessment models. Therefore, other impact categories are also difficult to compare. (García-Velásquez & van der Meer, 2022)

Also the technology level changes the overall impact (Tsiropoulos et al., 2015). However, certain trends are observable. LCA studies of biobased PET often indicate lower greenhouse gas emissions than for fossil-oil based PET (Benavides et al., 2018; García-Velásquez & van der Meer, 2022; Tsiropoulos et al., 2015). However, an LCA study by Vural et al. (2021) also concluded an overall worse environmental performance of biobased PET including higher greenhouse gas emissions. The baseline scenario was sugar cane from Brazil, as in 2020, the only company providing large-scale biobased MEG was India Glycols, who mainly use this feedstock (de Jong et al., 2020). Only in the category fossil fuel depletion, the biobased alternative performed 11% better than the virgin alternative (Vural Gursel et al., 2021). Biobased PET from wheat straw was comparable with virgin PET in terms of climate change impacts. A typical European crop mix resulted in 18% higher greenhouse gas emissions than the virgin source due to emissions associated with land use change (Vural Gursel et al., 2021). Also the high energy demands of biomass processing contributed to the higher emissions (Chen et al., 2016; Vural Gursel et al., 2021). Another LCA study by Tsiropoulos et al. (2014) concluded that bio-based polyester from first generation feedstock performs environmentally worse than virgin polyester in the impact categories acidification, ecotoxicity, eutrophication, water and land use. The main contributors were the agricultural production and transport in the value network (Tsiropoulos et al., 2015). These worse impacts in other impact categories are often associated with the biomass production, where more land, water, fertilizers and pesticides are used (García-Velásquez & van der Meer, 2022). Another large problem with bio-based plastics is the land use competition with other biomass production such as food and energy (Mülhaupt, 2013; Zamani et al., 2015). According to Textile Exchange (2022), the generation category of biomass does not necessarily align with the sustainability performance, as the specific cases with their situation of responsible management and location vary substantially. They also argue that non-food crops can decrease the available land for food crops and oftentimes even have a higher land use. This would worsen food security issues (Textile Exchange, 2022). On the other hand, crops like *Miscanthus* are able to grow on land with low fertility, where food crops could not grow anymore (García-Velásquez & van der Meer, 2022).

Previous research specific on textiles concluded an overall reduction of greenhouse gas emissions for bio-based materials, but a potentially higher land use, eutrophication, or stratospheric ozone depletion (Jahandideh et al., 2021; Vinod et al., 2020). However, the acidification and photochemical ozone formation did not show a clear direction among different studies. This shows how a production specific detailed analysis of a wide range of environmental impacts becomes necessary to conclude which alternative has the better environmental performance (Rognoli et al., 2022; Textile Exchange, 2022). For bio-based plastics, the resource competition for biomass such as food and energy or a possible contribution to deforestation suggest that biological waste products should be the preferred renewable feedstock (Palm et al., 2016). However, that is not projected to be enough to fulfil the future demands and usage competition is still seen as probable (Palm et al., 2016). From a European production perspective, Garcia et al. (2022) recommended the use of local feedstock such as sugar beet and *Miscanthus* over

sugarcane (Brazil) and molasses (India). Wheat was not recommended because of the threat to food security (García-Velásquez & van der Meer, 2022).

Overall, biobased PET can often lead to a reduction in greenhouse gas emissions, but it is not necessarily the case. Either way, there is a trade-off with a worse performance in other impact categories related to the agricultural production. In addition, the environmental performance depends on the feedstock in use. Land competition with food crops and the regional options to reduce transport emissions should be considered. The background information summarised in this section gives literature-based context to the comparison of PET sourcing alternatives. For this study, a literature range for LCA results of biobased PET was utilised to serve as comparison with the focus technology gas fermentation (Garcia-Garcia et al., 2017).

1.2. Recycled PET

In 2018, 359 MT of plastics were produced globally, of that 18% was PET and the produced amount is expected to triple in the next 30 years (Sadeghi et al., 2021). Merely 9% of the produced plastics are recycled, with the majority ending up in landfills (79%) or incineration (12%) and accumulating in ecosystems (National Geographic, 2018). This reflects a non-renewable production system with an unresolved end-of-life stage. According to a review by Sadeghi et al. (2021), current recycling methods are divided into primary (closed-loop), secondary (open-loop), tertiary (pyrolysis, gasification into fuels) and quarternary recycling (incineration with heat recovery). Closed-loop recycling means that the recycled material stays within its own production system, while open-loop recycling indicates that material from another production system gets used (Sadeghi et al., 2021). For example, if a PET-based clothing item is recycled end-of-life into a new clothing item, it is closed-loop (primary) recycling. On the other hand, if it is produced from waste PET bottles, it is open-loop (secondary) recycling.

In mechanical recycling technology, the polymers are maintained. The plastics are collected and sorted, then washed and shredded. (Sadeghi et al., 2021)

PET bottles are the main source for mechanically recycled PET for textiles (open-loop recycling). Bottle-grade PET has a higher quality grade than textile fibres, so using it for textile fibres is down-cycling to a lower material quality than if it remained within a closed-loop recycling system of bottles. Because of the higher quality grade of bottle PET, the production of 100% mechanically recycled PET for fibres is feasible without quality reduction compared to virgin PET. Therefore, no blending with virgin PET is necessary. (Martinol, 2023)

Overall, PET bottle production is expected to double in the next 20 years, implying a growing supply of PET bottles, while merely 30% of PET bottles are currently recycled (Sadeghi et al., 2021). In practice, the complex supply network makes verification and transparency of the ultimate sources difficult, especially beyond 3-4 upstream layers (Martinol, 2023).

Using textile fibres for mechanical recycling in a closed loop often leads to a lower grade PET with possible contaminations, so that blending it with a certain share of virgin PET becomes necessary (Park & Kim, 2014; Sadeghi et al., 2021).

Another recycling option is chemical, where the polymers are taken apart into their monomers and repolymerised (Sadeghi et al., 2021). Chemical recycling technology is still limited and makes up 16% of recycled plastics (Sadeghi et al., 2021). It is more expensive than virgin PET, but may become competitive with upscaling (Park & Kim, 2014). And it leads to a high quality material, which can also be made from textile waste (closed-loop recycling) (Martinol, 2023). This requires establishing a fibre recycling system and special design considerations, so that the parts can be disassembled to avoid contamination (Park & Kim, 2014). Closed-loop recycling is preferable over using PET bottles from another production system, as otherwise, the textiles end up in landfill or incineration end-of-life (Martinol, 2023; Rybaczewska-Blazejowska & Mena-Nieto, 2020). Also upstream, PET bottles are conventionally made from fossil fuels, feeding off a non-renewable production system (Park & Kim, 2014). A recent LCA study by Stefanel, 2023 examined chemical recycling pathways for PET by glycolysis, methanolysis and enzymatic hydrolysis. The global warming potential was 2.00 kg CO_2 / kg PET and 1.9 kg CO_2 / kg PET for glycolysis and methanolysis, respectively. It is important to add that there were trade-offs with a worse performance in eutrophication and abiotic depletion compared to virgin PET. The enzymatic hydrolysis route performed worse with 4.91 kg CO_2 / kg PET and also had a worse

environmental profile in other impact categories. However, the latter was expected to have a decreasing climate change impact with upscaling, as the technology readiness level (TRL) rises (Stefanel, 2023).

An LCA study for Sweden emphasized that textile waste recycling leads to energy and greenhouse gas emission savings when replacing virgin fibres (Zamani et al., 2015). Sadeghi et al. (2021) state that recycled PET requires 14-17% of the energy for virgin PET. The results of an LCA study on comparing recycled, virgin and bio-based PET showed the lowest impacts for recycled PET for all ReCiPe impact categories (0.01-10.16% of impacts), while bio-based PET performed worst (Rybaczewska-Blazejowska & Mena-Nieto, 2020). Also here, the lower energy demand for recycling as for virgin production of PET was stated as the main reason for the better performance.

All in all, recycled PET has a promising environmental profile, with well-established open-loop mechanical recycling options from PET bottles. Closed-loop chemical recycling from textile fibres is limited by infrastructure and design barriers, but has a lower global warming impact than virgin PET. The Textile Exchange platform (2022) envisions a complementary use of different feedstocks for fibres to have a full replacement of fossil-based fibres. Availability of feedstock materials and technological limitations of recycling are barriers to exclusively use recycled fibres (Textile Exchange, 2022). In light of the expected future demand for PET, the limitations of recycling technology and the range of impacts from biobased feedstock, other possibilities for renewable PET sourcing are explored, such as a fermentation technology from carbon-rich gases. In this study, mechanically recycled PET from bottles (based on a process in the Ecoinvent database (Wernet et al., 2016)) and chemically recycled PET by methanolysis (based on an LCA by Stefanel, 2023) served as literature-based alternatives for comparison to the gas fermentation-based route, which is described in the next section.

1.3. Fermentation of carbon-rich gas into ethanol, a PET precursor

Carbon emissions, predominantly CO_2, are considered the main driver for global warming (Field et al., 2014; Metz et al., 2005). Anthropogenic sources strongly originate from fossil fuel combustion, biomass utilisation for energy and carbonate decomposition (Sanz-Pérez et al., 2016). Carbon capturing emerges as a technology aiming to mitigate those impacts (Metz et al., 2005). Carbon can be captured from the air or point sources such as industrial fumes (Baena-Moreno et al., 2018). Carbon capture and sequestration (CCS) stores the captured carbon in exhausted gas fields or saline aquifers (Muthuraj & Mekonnen, 2018). However, the technology is significantly limited by high energy consumption and costs as well as limited capacity and long-term security of storage sites. Carbon capture and utilisation (CCU) is the usage of the captured carbon as a replacement of fossil oil for fuels, chemicals and materials (Bruhn et al., 2016). That is to say, carbon emissions from industrial fumes are captured and used to synthesise building blocks for the chemical industry (Bruhn et al., 2016). There is a variety of chemical technologies and processes to capture the carbon (Murcia Valderrama et al., 2019). Ethanol can be produced with chemical catalysts based on rhodium (Lopez et al., 2015). Alkane production is possible with the Fischer-Tropsch process as a basis for diesel or fuel production, or to derive ethylene, then ethanol (Ail & Dasappa, 2016).

The gas fermentation technology in the focus of this research is a biological technology, where microorganisms ferment carbon-rich gases into ethanol, a precursor for PET. Biological fermentation offers benefits to chemical technologies such as mild conditions in terms of pressure and temperature, a higher resistance to contaminants and a higher product specificity (Klasson et al., 1992; Munasinghe & Khanal, 2010). In CCS and CCU, the captured carbon is often referred to as CO_2 emissions. The utilised carbon-rich gases for this study's fermentation technology are not necessarily direct CO_2 emissions, but a technosphere feedstock, which can be composed of CO_2, but can also be mainly composed of CO and can also contain H_2. Since the feedstock has economic value, it is a good by definition, and its original utilisation for energy generation leads to the release of CO_2 emissions (Müller et al., 2020). Therefore, it does not completely resemble the above definition of CCU, as the carbon-rich off gases are not exclusively composed of CO_2, but also CO or H_2. However, it is often associated with CCU technologies because of the similarity to use carbon-rich gases form industrial fumes for a chemical building block, in this case ethanol. The technology delays carbon to be released as greenhouse gases, but binds it temporarily in an ethanol-based product. The process has gained increased attention, because of its application as

alternative transportation fuel (Liew et al., 2016). The overall process until the ethanol is divided into four steps: Provision or generation of carbon-rich gas and gas pre-treatment, gas fermentation, product separation (Liew et al., 2016). Ethanol can also be converted into MEG over several intermediates. Like in the route for biobased MEG, the fermentation based ethanol gets dehydrated into ethylene with an alumina catalyst (Liptow & Tillman, 2009). The subsequent steps until the polymerisation into PET are identical to the fossil route, including the other main component crude-oil based PTA.

1.3.1. Basic oxygen furnace (BOF) gas from the steel industry for fermentation into ethanol

The currently predominant and commercially available route to ferment carbon-rich off-gases is based on off-gases from the BF-BOF (blast furnace/basic oxygen furnace) process in steel mills (Bazzanella et al., 2017; Simpson, 2011). This process makes up 71% of the current steel production (Bazzanella et al., 2017). Fossil carbon from coal, oil or natural gas is used for iron ore reduction into iron metal in the blast furnace (BF). The resulting liquid iron (pig iron) still has a relatively high carbon content. The emitted off-gas is typically composed into 55 % N_2, 21 % CO, 21% CO_2 and 3 % H_2 (Hou et al., 2011). This gas makes up by far the largest volume of process gases from the steel process (Bazzanella et al., 2017). It commonly serves for electricity and steam generation, in the furnace mill or in gas engines, often complementing the use of natural gas (Bazzanella et al., 2017; Bojic & Mourdoukoutas, 2000). Often, the steel plants have a power plant integrated, but they are often less efficient (30-40% compared to modern gas-power plants with a 60% efficiency) (Bazzanella et al., 2017).

Then, in the basic oxygen furnace (BOF), oxygen gets flushed over the hot metal which reacts with the carbon in the iron. This BOF-gas typically has a high CO-content (50-60%), the rest is CO_2 (10-20%) and N_2 (20-30%) (Handler et al., 2016). According to Handler et al., 2016, the shares of gas recovery for energy provision vary globally. In the US, the BOF-gas is reported not to be utilised at all. In Europe, one quarter of these gases is described to be combusted for heat generation (Handler et al., 2016). However, Bazzanella et al., 2017 argue that in European steel mills, BOF-gas is normally utilised, and not simply flared. Both the BF and the BOF gas, as well as coke oven gas can be utilised for fermentation, with different conversion rates depending on the gas composition (Bazzanella et al., 2017). The established commercial option is the CO-rich BOF gas, which was also the assumed feedstock in this study (Almeida Benalcázar et al., 2022; Handler et al., 2016).

Besides that, also synthesis gas (syngas) can be fermented into ethanol. Syngas is a gas composition of CO, CO_2 and H_2 (Liew et al., 2016). The gas composition can vary depending on the feedstock. Feedstocks such as biomass, fossil coal or oil, other carbonaceous materials such as municipal wastes or lignocellulosic biomass are converted into syngas via gasification (Couto et al., 2015; Liew et al., 2016). Natural gas is converted into syngas by gas reforming (Handler et al., 2016). Syngas is also a by-product in oil refining and chemical production (Handler et al., 2016). For biomass-based syngas fermentation, several barriers have been present such as a low biomass use efficiency and the need for intensive pre-treatment to remove contaminants (Puiman, 2020). Gas fermenters have a relatively high tolerance for impurities. However, some impurities often need to be removed (if present) prior fermentation such as tars, particulates, aromatics, sulphur compounds, nitrogen gases. Further, the syngas often needs to be lowered in temperature and compressed. (Liew et al., 2016)

1.3.2. Fermentation process

The fermentation is carried out by autotrophic acetogenic (acid-producing) bacteria such as *Clostridium autoethanogenum* (Bazzanella et al., 2017; Daniell et al., 2012). Autotrophy means the fixation of inorganic gaseous carbon. There are several metabolic routes existent in various life forms (Thauer et al., 1977). The Wood-Ljungdahl pathway (WLP) is the most efficient pathway for microorganisms to fix carbon without photosynthesis (Fast & Papoutsakis, 2012). CO is energy and carbon source for the microorganisms. The external provision of H_2 is not necessary for the reaction, as the biological water gas shift reaction is inherent to the microorganism, leading to the following reaction equation (Simpson et al., 2007):

$$6\,CO + 3\,H_2O \longrightarrow CH_3CH_2OH + 4\,CO_2 \tag{1.1}$$

However, then only a 1/3 conversion rate of the CO into ethanol can be achieved, with the remaining

carbon leading to CO_2 emissions (Simpson et al., 2007). If there is extra H_2 available, its functions as a catalyst, and it can be another energy source. Therefore, H_2 and CO_2 can be metabolised in combination (Almeida Benalcázar et al., 2020; Simpson et al., 2007). The CO_2 can either be present in the feedstock gas or from the metabolic product of the microbial process. That allows for a 2/3 conversion rate of the CO with the following reaction equation (Simpson et al., 2007):

$$6\,H_2 + 6\,CO \longrightarrow CH_3CH_2OH + 2\,CO_2 \tag{1.2}$$

Through the intermediates acetyl-CoA and acetaldehyde, ethanol is synthesized (Latif et al., 2014; Liew et al., 2016). Other possible fermentation products are acetate, lactate, acetone and 2,3-butanediol. Acetogens naturally produce the desired products. There are more than 100 species (Latif et al., 2014). In the reactor, a fermentation medium provides micro- and macronutrients. LanzaTech, the main producer of the fermentation-based ethanol works with a continuous reactor design where there is a consistent in- and outflow of inputs and product into and out of the reactor (Handler et al., 2016). The anaerobic conditions reduce fire risks in the reactor. Also, there is less contamination with other micro-organisms since there is no sugar nor oxygen provided (Imkamp & Müller, 2007). To separate the ethanol from the fermentation broth, it is distilled. That process is energy-intensive. There are other technologies available such as gas stripping or adsorption, which each have their own trade-offs. (Liew et al., 2016)

Challenging is the limited solubility of CO_2 and H_2 in the fermentation broth. Therefore, diverse set-ups have been tried out such as different temperatures, batch or continuous reactor designs or higher pressure (Almeida Benalcázar et al., 2022; Liew et al., 2016). Yields can be enhanced with genetic engineering of acetogens. Also decisive for the yield is a low pH, the nutrient composition and the foam intensity (Liew et al., 2016).

1.3.3. State of technology

Beginning as a start-up in New Zealand, LanzaTech started their demonstration plant in Auckland in 2008 (Kempkens, 2013). In China, a LanzaTech fermentation plant was co-located with the steel producers BaoSteel (Shanghai) and Shougang Steel (Caofeidan) in 2012 (Liew et al., 2016). Shougang Steel was the first commercial plant for this technology, currently there are three commercial plants operating (LanzaTech, 2023; Solibieda, 2018). In Belgium (Ghent), LanzaTech cooperated with Arcelor Mittal, a steel producer to ferment steel mill off-gas into ethanol under the brand name Carbalyst. The corresponding project called Steelanol was subsidised by the EU Horizon 2020 program (Moreno Fernández Villamil, 2017). The plant was launched in December 2022 (Carbon Capture Technology Expo North America, 2022). In California, Aemetis Inc. uses waste from agriculture, forestry, dairy, construction and demolition for ethanol fermentation (Liew et al., 2016). Currently, there are several other plants in planning or under construction with partners such as Sekisui (Japan) or IndianOil (oil refinery offgases). There are cooperations with textile retailers such as Zara or lululemon, with packaging for Danone, and with aviation companies such as Boeing or virgin atlantic (LanzaTech, 2023). Competing companies such as IneosBio or Coskata, attempting to use biomass as feedstock, have gone bankrupt, mainly because of the higher impurities associated with the feedstock which lead to a less efficient process with extensive pre-treatments (Almeida Benalcázar, 2023).

For an application for another plastic type than PET, namely ethylene vinyl acetate (EVA) foam, which is used in running shoe mid soles, gas fermentation technology provides a promising alternative. That is because current mechanical recycling has a too low efficiency for too high costs to be commercially feasible (Guo et al., 2020). Further, the share of ethylene based on the fermented ethanol is higher than in PET, ranging from 60-90% by weight (Paiva Junior et al., 2021). LanzaTech ethanol gets dehydrated into ethylene by Technip Energies, then polymerised into EVA by Borealis. A concept shoe with this EVA (CleanCloud^{TM}) was presented on a lab scale, but is not commercially available yet. (LanzaTech, 2022; On, 2022)

For PET, it is unclear, whether gas fermentation provides an environmentally preferable sourcing route as recycled and biobased PET are also established routes and the weight share of MEG, which can be based on the fermentation ethanol, is lower (30%) (Vural Gursel et al., 2021).

1.3.4. Climate change impact of gas fermentation: research gap

The Textile Exchange platform (2022) envisions a complementary use of different feedstocks for fibres to have a full replacement of fossil-based fibres. Availability of feedstock materials and technological limitations of recycling are barriers to exclusively use recycled or biobased fibres (Textile Exchange, 2022). Because of the potential high energy demand and the connected indirect CO_2 emissions, the environmental preferability of CCU technologies cannot be guaranteed, so assessing the environmental sustainability with a metric such as LCA is advisable (Von Der Assen et al., 2014). A study by Palacios-Mateo et al. (2021) emphasized that whether alternative (and often renewable) materials are environmentally preferable to virgin polyester is highly case-dependent. It depends on the energy provision, the production process and the feedstocks under comparison. Therefore, they state the necessity to "verify the environmental sustainability of [..] CO_2-based solutions using quantitative evaluations, such as life cycle assessment (LCA)" (Palacios-Mateo et al., 2021). The overall environmental performance of carbon gas-derived polymers is not automatically better than virgin polyester. Therefore, a need for and lack of "robust LCAs" about carbon gas-based feedstocks was stated in a review (Murcia Valderrama et al., 2019).

Ethanol production through gas fermentation has been examined in a process and stochastic simulation by Almeida Benalcázar et al., 2022 to optimise production costs and greenhouse gas emissions. Steel industry off-gases, syngas from lignocellulosic biomass and an H_2-CO_2 mixture were included as feedstocks. To derive the global warming potential, the CO_2 equivalents for the process steps, steam and electricity provision from the local grid, flaring of off-gases from the bioreactor, wastewater treatment and the end-of-life combustion of ethanol as fuel were calculated. The BOF feedstock had the best economic performance, while the H_2-CO_2 mixture had the lowest global warming potential (distributed around median <10g CO_2eq/MJ ethanol). For the BOF (distributed around median <50 g CO_2 eq/MJ ethanol), the final impact was highly dependent on the assumption on how the energy gap through the missing BOF gas in the steel process was filled. (Almeida Benalcázar et al., 2022)

A process simulation by de Medeiros et al., 2021 optimised the process in terms of ethanol price, energy efficiency and carbon footprint for gasified biomass as feedstock (wood residues 3g CO_2 eq/MJ ethanol, sugarcane bagasse 10g CO_2 eq/MJ ethanol). However, it did not include the production of the gas feedstock and the possible heat integration assessed in Almeida Benalcázar et al., 2022. (de Medeiros et al., 2021)

Another simulation and multiobjective optimalisation design by Michailos et al., 2019 with gasified biomass as a feedstock concluded 11.5g CO_2 emissions per MJ fuel. They described the low CO conversion as the main weakness of the technology (Michailos et al., 2019). Roy et al., 2015 compared the impacts of different biomass gasification from *Miscanthus* and treatment routes on the CO_2 emissions of the ethanol from fermentation. Untreated syngas had a lower impact (1.27 instead of 1.32 kg CO_2eq/L ethanol), and the syngas generation with chemical looping gasification lowered the impact (1.19-1.24 kg CO_2eq/L ethanol) (Roy et al., 2015).

A recent study about carbon-rich gas fermentation technology with methodological focus on LCA was conducted by Handler et al., 2016. They analysed the process based on internal LanzaTech primary data. Various biomass feedstocks converted into syngas via gasification were claimed to lead to a carbon emission reduction of around 90% compared to fossil ethanol (1.5-11.7 g CO_2eq/MJ ethanol). Further, steel mill BOF-gas was examined as an alternative, with a claimed 60% reduction in carbon emissions (31.4 g CO_2eq/MJ ethanol). End-of-life was included in that study, but the final product was ethanol, not PET. The emissions of the ultimate combustion of ethanol as fuel were included in the assessment. Utilities such as electricity and steam had a large share in GHG emissions, while the fermentation broth ingredients were less decisive (Handler et al., 2016). Also, the assumption was made that the feedstock BOF gas would normally be entirely flared into CO_2 emissions, without energy recovery, therefore the utilisation was fully counted as an emission credit (Handler et al., 2016). This assumption was criticised by Bazzanella et al., 2017 and Almeida Benalcázar et al., 2022. In Europe, the major share of the BOF-gas is recycled for on-site heat and electricity generation and only a minimal share is flared into CO_2 emissions without energy recovery (Keys et al., 2019). Therefore, a carbon credit of 1.19 t CO_2/ton BOF gas applied by Handler et al., 2016 was not seen as representative, resulting in misleading final CO_2 emissions (Bazzanella et al., 2017). The alternative use of the BOF gas as a feedstock requires replacement of the missing energy provision, so Almeida Benalcázar et al., 2022 suggested a system expansion to account for alternative energy supply. According to steel process

engineer Dr. Axel Boeke, already from a pure economic perspective, it is reasonable to minimise the losses through flaring. Flaring can occur with contaminated gas, when there is technical maintenance or when there is an excess of off-gas (Boeke, 2023).

Further, the energy from the gas cooling is used for steam generation for the distillation. Handler et al., 2016 counted the CO_2 equivalents of providing any excess heat beyond the heat needed for the distillation as a carbon credit. However, it can not be ensured that the excess energy is utilised elsewhere and actually replaces heat provision with fossil fuels. Bazzanella et al., 2017 stated the "need for LCAs with appropriate methodology and boundary conditions including existing valorisation of streams considered as alternative feedstock" (Bazzanella et al., 2017). A more transparent LCA is needed that follows the recommendations given by Bazzanella et al., 2017 and Almeida Benalcázar et al., 2020 in order to assess the environmental impact of the gas fermentation technology into ethanol. Based on that, the overall impact for PET produced from ethanol based on this technology can be examined and compared to alternative routes. This leads to the following research question:

What is the climate change impact of BOF-gas-fermentation based PET compared to alternative PET routes (mechanically recycled, virgin, biobased, chemically recycled) and what are the main contributors?

2 Methodology

Life cycle assessment (LCA) offers a standardised method to quantify the environmental impacts associated with a product's life cycle (Finnveden et al., 2009). Therefore, it is an effective method to compare material alternatives for the same product. In Figure 2.1, a framework for the methodology is given with an overview of the data sources. These are further described in section 2.2. The BOF-gas fermentation based PET sourcing route was modeled as a foreground system with the LCA method. A comparison with virgin PET and mechanically recycled PET was drawn within the LCA model, based on processes from the Ecoinvent database. For a comparison with biobased and chemically recycled PET, literature values were included (Garcia-Garcia et al., 2017; Stefanel, 2023). For this study, the python-based Brightway2 LCA package was operated through its interface, the Activity Browser (Mutel, 2017; Steubing et al., 2020). For the background system and for parts of the foreground processes, the Ecoinvent 3.8 database was used with the system model "Allocation, cut-off by classification" (Wernet et al., 2016). As characterisation factors, the Environmental Footprint 3.0 impact assessment model was applied to align with the the upcoming EU regulation on reporting of environmental claims (European Commission, 2023).

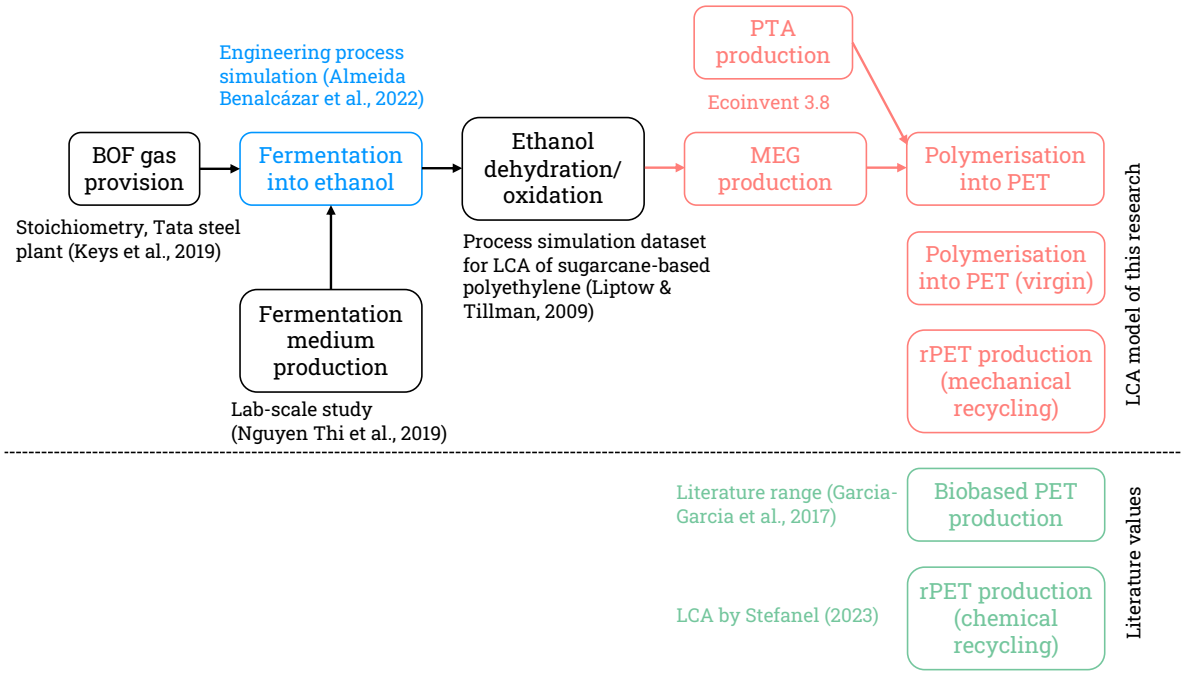

Figure 2.1: Overview of inventory data sources and methodological framework. The colours correspond with the respective data source label.

2.1. Goal and scope definition

The goal of this LCA was to compare the environmental impacts of BOF gas fermentation-based PET with recycled and virgin PET, as well as biobased PET for an application in the textile industry. Overall, the intended aim was to support decision-making on low-carbon polyester sourcing routes in the textile industry. The sports shoe and clothing producer ON Running was the commissioner, but the results are applicable to the textile industry in general, also providing comparisons of the material options to the public.

The impact category focus was on climate change impacts, as there was only foreground data available for greenhouse gas emissions. The impacts in other impact categories could only be derived from the background system. A BOF gas-to-gate scope was taken, because differences between the alternatives only apply in the cradle-to-gate part. The environmental impact in use and end-of-life can be assumed to be the same for all alternatives since the produced PET has an identical chemical structure (Müller et al., 2020). In line with the goal of comparison of the CCU process with the current process, the scope is sufficient. However, end-of-life-fate of the PET is especially relevant for a net carbon balance. Decisive is the fate of the carbon captured in the material. Since it is ultimately re-released into the atmosphere, the captured carbon cannot be counted as negative emissions (Tanzer & Ramírez, 2019).

The functional unit (FU) was defined as:

1 kg of PET granulate at the factory gate

For a comprehensive comparison with the same scope until the factory gate, the following alternatives to produce PET pellets for fibres were compared directly in an LCA model:

- BOF gas fermentation-based PET, LCA foreground model
- Virgin PET (fossil-based), Ecoinvent
- Mechanically recycled PET (from bottles, 100%), Ecoinvent

For further comparison of relevant alternatives, the following values were added from literature, also with a cradle-to-gate scope to ensure comparability:

- Biobased PET, 30% and 100%, literature range (Garcia-Garcia et al., 2017)
- Chemically recycled PET, methanolysis, literature value (Stefanel, 2023)

The focus was on the material provision and not the final textile product, so that the results are more universally applicable for several products made from polyester granulate. According to the decision tree by Müller et al. (2020), mass was the selected unit since this is the most widespread approach for chemicals and materials and the final product has the same chemical structure for all alternatives (Müller et al., 2020).

Technologically, an optimised reactor for both minimal greenhouse gas (GHG) emissions and operating costs was assumed following a process simulation from Almeida Benalcázar et al. (2022). The geographical scope was set to a universal global setting, with a sensitivity analysis towards several best-case scenarios in Belgium, where the main producer of the technology, LanzaTech has a cooperation with a steel plant (Moreno Fernández Villamil, 2017). The time frame for the base case reflects the current situation, with the current technology level and background system. Transport was excluded from all alternatives to focus the results on the technology. Means of transport and transport distances can vary depending on the supply chain setting and production location of all alternatives and are not directly inherent to the technologies of comparison. Transport was expected to make a low contribution to the overall emissions, which was also described in Handler et al. (2016) and should only be included in the examination of specific production locations. Factory plant production was included for all alternatives and foreground processes.

Table 2.1: Original input data from simulation of gas fermentation (per hour) (Almeida Benalcázar et al., 2022)

Flow	Original data	Unit	Composition
NH_3 input	109.08	kg	
Gas feedstock input	601382.109	mol	85 mol% CO, 15 mol% CO_2
Off-gas	500498.42	mol	33.4 mol% CO, 66.6 mol% CO_2
Ethanol throughput	2061.87	kg	
Liquid outflow	66.25	m^3	31.1g/L ethanol concentration
Energy from cooling of gas feed	5548.7	kWh	
Electric energy for compression of gas feed	1789.5	kWh	
Heat for distillation of ethanol	5155.3	kWh	
Liquid in fermentor	506	m^3	

2.2. Inventory data collection

For the LCA modeling of the BOF gas-fermentation, simulation data from Almeida Benalcázar et al. (2022) for the foreground processes was connected with Ecoinvent 3.8 background processes for utilities and materials (Almeida Benalcázar et al., 2020; Wernet et al., 2016). A detailed overview about the data sources and methodological framework can be found in Figure 2.1. The original simulation data for the gas fermentation was based on 2061.87 kg ethanol throughput per hour (Table 2.1, conversions in SI1, C1).

Based on the molar composition of the off-gas, the carbon emissions could be derived, assuming all CO to be flared into CO_2. Water needed for the reaction could be derived from stoichiometry as 3 mol of water were needed for 1 mol of ethanol. The fermentation and distillation part of the inventory was based on expert consultation of Eduardo Almeida Benalcázar with the following assumptions:

- For the BOF gas feedstock, a composition of 85 mol % CO and 15 mol % CO_2 was assumed.
- BOF gas conditioning included cooling and compression.
- From the BOF gas conditioning, heat integration for the distillation was assumed, so that no extra energy input was needed for the distillation. 2.69 kWh was available from the cooling and 2.5 kWh could be integrated for the distillation with an efficiency of 85 % (per kg of ethanol produced). The excess heat could not be utilised elsewhere as a turbine is not economic, so it was not considered. (Almeida Benalcázar et al., 2022)
- A cleaning step of the BOF gas was neglected, as main contaminants are nitrogen, water and hydrogen (West, 2020). The microorganisms can consume nitrogen and hydrogen, water does not cause problems as the bioreactor also contains water. Other gases such as CH_4 can be present in the gas feed, but they make up 1-2 %, so they were neglected
- The liquid outflow from the reactor included waste biomass and the medium, as well as the ethanol product with an assumed concentration of 31.1 g/L. 5% of the ethanol leaves the bioreactor as volatile off-gases but was neglected here (the original concentration was 29.4 g/L).
- A liquid production volume of 506 m^3 was assumed for the bioreactor.
- A large share of the carbon in the BOF gas is not consumed by the microorganisms, because of the CO_2 generation inherent to the microbial process (subsection 1.3.2) (Simpson et al., 2007). Leftover CO gets combusted into CO_2, and recycling of this gas stream is not feasible, as impurities such as N_2 and CH4 would accumulate (Ciferno & Marano, 2002).
- Ethanol drying of the 95% aceotrope after distillation was neglected because of its minor contribution to energy consumption.
- For the distillation cooling, water at ambient temperature is used, which was neglected as it was a minor energy expense

(Almeida Benalcázar et al., 2022)

Further, possible co-products such as acetic acid or butanol were neglected as the ethanol reaction was assumed to be optimised for ethanol production, without co-product recovery and minimum

production of co-products, following the assumption made in Handler et al. (2016). Also, except for acetic acid, the productivity for butanol, butyrate or caproate is not high enough to be economically feasible (Diender et al., 2016). From the conditioning step of the BOF gas, heat integration was assumed following the simulation data from Almeida Benalcázar et al. (2022). The steam that can be generated from the cooling of the BOF gas was seen as sufficient to cover the heat needed for the subsequent distillation of the ethanol product (Almeida Benalcázar et al., 2022). Therefore, a multifunctionality situation from an LCA modeling perspective was avoided, as no other heat input for the distillation was added to account for the heat integration. Leftover heat beyond that could not be utilised anymore (Almeida Benalcázar et al., 2022). For the concurrent steps into PET, byproducts were excluded already in the dataset, as the Ecoinvent data for "cut-off by classification" of co-products was used.

The composition of the fermentation medium was based on a lab-scale experiment (Thi et al., 2020). Ethanol dehydration was obtained from another process simulation dataset on sugar-cane based polyethylene in Brazil (Liptow & Tillman, 2009). The subsequent conversion steps from ethylene into PET as well as the alternative processes were derived from Ecoinvent 3.8 background processes, with adjusted in- and outputs. Here, no differences in the steps from ethylene to PET were made between the virgin and the fermentation-based route to ensure better comparability (Wernet et al., 2016). For the BOF gas impacts, thermodynamic and stochiometric calculations gave conservative estimations of the emissions and energy needed. Then, efficiencies were integrated based on data from Keys et al. (2019) (detailed calculations in SI1, C6; full inventory in SI_inventory).

Factory plants were scaled following the scaling in the Ecoinvent processes (Hischier & Kunst, 2020). For the ethanol fermentation plant, 90 000 t of yearly ethanol production capacity was assumed, with a 20 year operating time. Scaling was also performed according to the respective Ecoinvent documentation (Ecoinvent, 2021).

For the LCA modeling of the alternative process of mechanically recycled PET, the Ecoinvent 3.8 process *polyethylene terephthalate production, granulate, bottle grade, recycled* for the geography *RoW* (rest of world) was used as it includes all regions except for Switzerland, therefore representing a realistic comparison. This dataset excluded transport and represents a more comparable scope (cradle to factory gate), compared to the corresponding market dataset for a global scenario (cradle-to-grave). It reflects mechanical recycling from bales of sorted waste PET bottles into granulate PET at the factory gate (Kägi et al., 2021). For the virgin PET alternative, the Ecoinvent 3.8 process *polyethylene terephthalate production, bottle grade* was used for the geography *RoW*, excluding Europe and Quebec (Canada), as its cradle-to-gate scope was also seen as most suitable for comparison. It reflects a production mix of commercially available technologies through the esterification of MEG and PTA (Fröhlich et al., 2021).

2.3. Multi-functionality and allocation

Providing the BOF gas is a technosphere flow and not an environmental flow such as an emission as it is taken directly from the steel mill and therefore stays part of the technosphere the entire time (Müller et al., 2020). Its provision is the only part of the steel process that is different compared to the conventional situation, therefore only this part of the steel production system is considered. BOF gas provision is a multifunctional process in the steel production as it functions as two goods. For the fermentation, it is a material feedstock. As already argued in subsection 1.3.4, for the steel production it originally functions as energy feedstock for heat and electricity generation and the major share is usually not directly flared (Keys et al., 2019). Both these functions have economic value and therefore are no waste flows. According to ISO 14044, there is a hierarchy how to computationally solve the multifunctionality (Müller et al., 2020):

1. **Subdivision into smaller processes** was not possible as the corresponding processes of BOF gas formation, utilisation for energy generation and material feedstock provision are connected and no separate data was available to describe them independently.
2. **System expansion** would change the functional unit to also incorporate the energy generation. This would conflict with the goal of comparison with the other PET sourcing routes.
3. **Substitution** was the applied strategy. Within the system of the fermentation-based PET, a credit was given for the emissions that could be avoided by not using the BOF gas for energy provision.

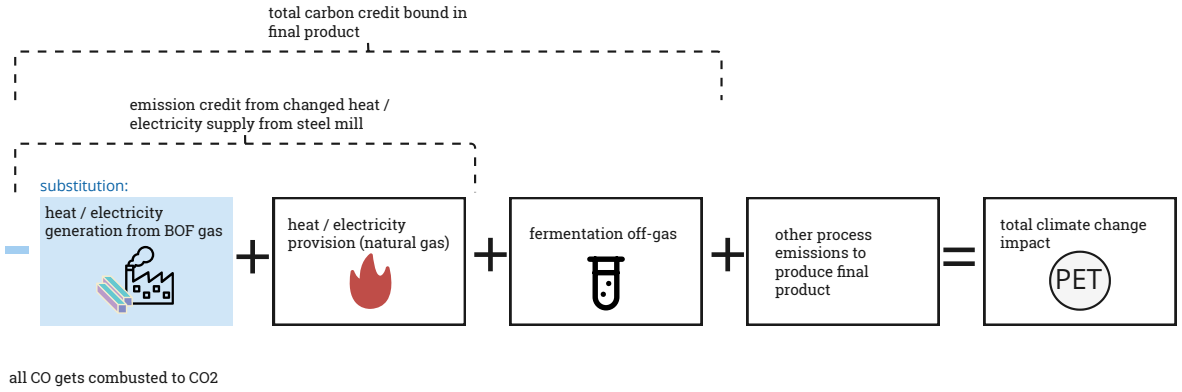

Figure 2.2: Carbon balance visualisation: Substitution, derivation of the total carbon credit bound in the product and the final climate change impact.

At the same time, the missing heat or electricity had to be substituted with another heat or electricity source, which also became part of the PET-production system with the corresponding emissions.

4. **Allocation** was not applicable as a higher hierarchy solution was found.

The difference between avoided emissions from the energy generation from BOF gas and the impacts associated with the alternative energy provision provided the emission credit from the changed energy supply in the steel mill (Figure 2.2) (calculations in SI1, C5). This credit was fully allocated to the PET system, as well as the substitution energy supply for the steel mill, so that formally, there is no change in the emissions of the steel system. The difference between the emission credit and the emissions during the fermentation give the total carbon credit bound in the final product. For the total climate change impact of providing the functional unit, other process emissions were also included to derive the final product. This allocation method provided a solution to include the environmental burdens and benefits of using the BOF gas as feedstock, while not changing the functional unit or the impacts of the steel system. Most importantly, this methodological choice narrows the analysis down to the purpose of comparison of the alternatives within the scope. It shows the change compared to the reference case and does not imply a possible infinite or physical removal of emissions along the full life cycle.

The energy content under thermodynamically optimal conditions was 2.4 MJ per kg BOF gas (with 85 mol% CO content) (Jenkins & Mullinger, 2023). Various utilisation shares for the BOF gas in the steel process have been reported, depending on the site. The assumption used in this study was calculated from data from Keys et al. (2019) for the large-scale Tata steel plant in Ijmuiden (NL). So it was assumed that 85.9% of the energy contained in the BOF gas are used on-site for electricity generation (conversion efficiency of 38%) and 14.1% for heat generation (conversion efficiency 86.8%)(Keys et al., 2019). A common replacement gas input was natural gas (Keys et al., 2019). Depending on the power plant, BOF gas made up between 13.7-35.8% of the total energy input from all work arising gases (Keys et al., 2019) (Detailed calculations in SI1, C6).

2.4. Life cycle inventory

An overview about the structure of the life cycle inventory of the fermentation-based PET alternative is given in the flowchart (Figure 2.3). As described in the previous section, the BOF gas that would be used for energy generation in the steel process gets substituted with replacement heat and electricity. This substitution becomes part of the system boundaries. In detail, the BOF gas feedstock comes with the credit of avoiding the emissions from the energy generation from BOF gas, but with the ecological burden of substituting this energy with heat from natural gas and electricity from the global electricity mix. In the subsequent processes, the BOF gas gets conditioned (cooled and pressurised) and fermented into ethanol. After distillation, the ethanol gets processed into MEG through several intermediates. Together with PTA, it gets polymerised into the final product PET. This is reflected by the output of 1 kg PET granulate, the functional unit in this LCA.

A simplified inventory table of the modeled technosphere and biosphere flows (Table 2.2) shows the quantities of the flows with regard to their respective foreground process. A full list of technosphere and biosphere inventory flows for all alternatives can be found in SI2-SI4 and the detailed inventory with detailed sources and calculations in SI_inventory. There were 13554 technosphere flows, 1455 biosphere flows with characterisation factor and 506 flows without characterisation factor. Out of the latter, two flows may be of concern for the climate change impact ('carbon dioxide, non-fossil', 'air' and 'air' 'non-urban air from high stacks'). However, the values are not higher than 0.017 kg CO_2 / kg PET, so they can be neglected, as they would not change the overall results substantially.

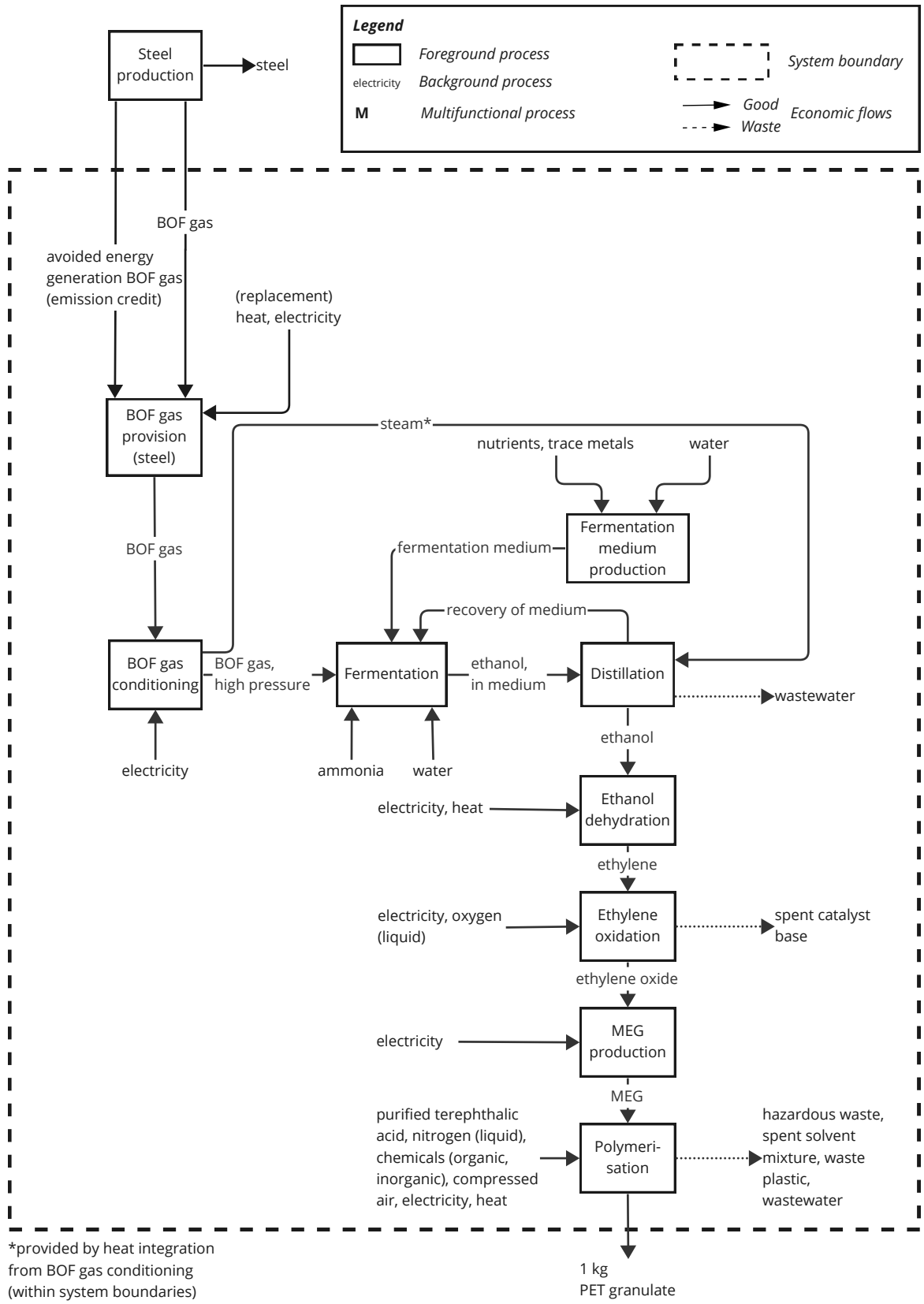

Figure 2.3: Flowchart including all major flows relevant to the modeled system of fermentation based PET production. Factory plants were excluded in this visual representation for better overview.

Table 2.2: Simplified life cycle inventory of the modeled system of fermentation based PET production, technosphere inputs and biosphere outflows (*italic*). **bold** = foreground technosphere outputs. Full inventory with detailed calculations and sources in SI_inventory. Full technosphere flow inventory in SI4. Full biosphere flow inventory in SI2, SI3.

Process / subprocess	amount, unit
energy generation BOF gas (steel)	**1 kg**
carbon dioxide, fossil	*1.447 kg*
BOF gas provision (steel)	**1 kg**
market group for heat, district or industrial, natural gas	0.295 MJ
electricity production, natural gas, conventional power plant	0.219 kWh
energy generation BOF gas (steel), credit	-1 kg
BOF gas conditioning	**1 kg**
market group for electricity, high voltage	0.868 kWh
market for chemical factory, organics	4.00E-10 unit
BOF gas provision (steel)	1 kg
fermentation medium production	**1 m^3**
tap water production, conventional treatment	1000 kg
market for sodium chloride, powder	2.11 kg
market for calcium chloride	0.101 kg
market for ammonium chloride	1 kg
market for sodium bicarbonate	1 kg
potassium chloride production	0.33 kg
market for fodder yeast	0.5 kg
market for sodium hydrosulfide	0.5 kg
market for sodium phosphate	1.64 kg
market for acetoacetic acid	0.015 kg
market for magnesium sulfate	0.03 kg
market for manganese sulfate	0.005 kg
market for copper sulfate	0.0018 kg
market for zinc monosulfate	0.0018 kg
market for iron sulfate	0.001 kg
market for copper sulfate	0.0001 kg
market for boric acid, anhydrous, powder	0.0001 kg
market for molybdenite	0.0001 kg
nickel sulfate production	0.0001 kg
fermentation	**1 kg**
market for ammonia, anhydrous, liquid	0.053 kg
tap water production, conventional treatment	0.001 kg
market for ethanol fermentation plant	5.56E-10 unit
fermentation medium production	0.032 m^3
BOF gas conditioning	8.867 kg
carbon dioxide, fossil	*10.68 kg*
ethanol distillation	**1 kg**
market for wastewater from anaerobic digestion of whey	-0.032 m^3
market for chemical factory, organics	4.00E-10 unit
fermentation	1 kg
ethanol dehydration	**1 kg**
market group for electricity, medium voltage	0.5 kWh
market group for heat, district or industrial, natural gas	5.6 MJ
market for chemical factory, organics	4.00e-10 unit

Table 2.2 continued from previous page

Process / subprocess	amount, unit
ethanol distillation	1.7 kg
methane	*0.0015 kg*
carbon monoxide, fossil	*0.0002 kg*
carbon dioxide, fossil	*0.327 kg*
nitrogen dioxide	*0.000012 kg*
NMVOC, unspecified origin	*0.000011 kg*
nitrogen oxides	*0.0015 kg*
sulfur dioxide	*0.0001 kg*
ethylene oxidation	**1 kg**
market for chemical factory, organics	4.00e-10 unit
market group for electricity, medium voltage	0.33 kWh
market for oxygen, liquid	0.463 kg
market for spent catalyst base from ethyleneoxide production	-0.0005 kg
ethanol dehydration	0.825 kg
biosphere flows unchanged, as in original ecoinvent data	
monoethylene glycol production, from ethylene oxide	**1 kg**
market group for electricity, medium voltage	0.107 kWh
market for chemical factory, organics	4.15e-10 unit
ethylene oxidation	0.710 kg
biosphere flows unchanged, as in original ecoinvent data	
polymerisation into PET	**1 kg**
market for antimony	2.86e-04 kg
market for chemical factory, organics	4.00e-10 unit
market for chemical, organic	2.11e-05 kg
market for chemicals, inorganic	9.31e-06 kg
market for compressed air, 600 kPa gauge	7.51e-02 m^3
market for diethylene glycol	4.12e-03 kg
market group for electricity, medium voltage	7.95e-02 kWh
market for hazardous waste, for incineration	-6.75e-05 kg
market for heat, from steam, in chemical industry	3.88e-01 MJ
market group for natural gas, high pressure	2.78e-01 m^3
market for nitrogen, liquid	2.20e-02 kg
market for phosphoric acid, industrial grade, without water, in 85% solution state	2.74e-05 kg
market for purified terephthalic acid	8.63e-01 kg
market for spent solvent mixture	-1.14e-03 kg
market for waste plastic, mixture	-6.51e-04
market for wastewater, average	-4.20e-04
market for wastewater, unpolluted	-6.75e-05
monoethylene glycol production, from ethylene oxide	3.35e-01 kg
biosphere flows unchanged, as in original ecoinvent data	

Table 2.3: Overview about the scenarios applied as sensitivity analysis in relation to the global base scenario for the modeled system of fermentation based PET production. Detailed flow properties can be found in SI_inventory

Scenario	Region	Electricity supply	Heat supply	BOF gas energy replacement in steel process	Materials supply	PTA/xylene source
base	GLO	EI global mix	EI global mix	Heat / electricity natural gas	GLO / RoW	fossil
1	BE	100 % renewable, wind	EI Europe mix	Heat / electricity natural gas	BE / Europe where available	fossil
2	BE	100 % renewable, wind	EI Europe mix	Electricity 100 % renewable, wind	BE / Europe where available	fossil
3	BE	100 % renewable, wind	EI Europe mix	Electricity 100 % renewable, wind	BE / Europe where available	bio-based (orange peels), 2% of fossil impact

2.5. Sensitivity analysis: Scenario description

To assess the environmental performance of the fermentation process under a best-case scenario (1), all electricity sources were set to 100% renewable energy from wind (Ecoinvent process *electricity production, wind, 1-3MW turbine, offshore BE*) (Table 2.3). Heat sources were kept the same as in the base scenario. Also, the scenario was adjusted to regional material inflows for Belgium, the location of the Steelanol plant Ghent, where available (Moreno Fernández Villamil, 2017). For scenario 1, the BOF gas replacement energy was kept from the base scenario (natural gas for heat and electricity). For scenario 2, the generated energy from BOF gas in the steel process (as described above) was assumed to be substituted by 100% electricity from wind energy. Therefore, the heat provision was assumed to be electrified, so that the entire energy could come from wind. In scenario 3, the same assumptions as in scenario 2 were complemented with an assumed reduction of the xylene/PTA impact down to 2% of the original contribution. This assumption was based on an LCA by Volanti et al. (2019) about orange peels as a precursor for xylene. That feedstock was reported to reduce global warming impact of fossil PTA down to 2% of the emissions from the fossil case, but with a trade-off of higher water consumption. Other impact categories such as particulate matter formation, terrestrial acidification and land use would stay comparable to the fossil case. The route involves extracted limonene from orange peels and the formation of p-cymene (PCY) as an intermediate (Volanti et al., 2019).

3

Results

3.1. Impact assessment

The impact assessment included the characterisation results for the full set of impact categories for the modeled alternatives (Figure 3.2). The full table of characterisation results is attached in SI5. Since the available foreground data for the fermentation part did not include environmental flows for other impact categories but global warming, the focus of this LCA was set on this category. For the global base scenario, fermentation-based PET had an almost 5-fold impact on climate change (4.95 kg CO_2 eq / kg PET) compared to mechanically recycled PET (rPET) (1.05 kg CO_2 eq / kg PET) (Figure 3.1). The impact of virgin PET was also 2.03 kg CO_2 eq lower than fermentation PET (2.93 kg CO_2 eq per kg PET). In comparison to the literature range for LCA results for biobased PET from Garcia-Garcia et al., 2017, the biobased PET can have climate change impacts close the the impact of rPET, but can also reach the highest values among all alternatives. This depends on differing assumptions, system boundaries and feedstocks in the underlying LCA studies. With 100% biobased PET, the minimum value can be lower than for 30% biobased PET, but it can also reach a higher maximum value. (Garcia-Garcia et al., 2017) In a recent LCA study by Stefanel, 2023, the best performing route for chemically recycled PET was methanolysis (1.90 kg CO_2 eq / kg PET). This was less than half the impact of the fermentation PET, but higher than the impact of mechanically recycled PET. The glycolysis route had a comparable global warming impact (2.00 kg CO_2 eq / kg PET). For that study, the IPCC GWP 100 impact assessment model was used, which could have an influence on the comparability of the results. (Stefanel, 2023).

For the other impact categories, most impact differences between the alternatives followed a similar hierarchy like for climate change, with rPET giving the lowest and the fermentation PET giving the highest impacts (Figure 3.2). For freshwater ecotoxicity, rPET had a higher impact than virgin PET, but the impact was still much lower than for fermentation PET. Similarly, for land use, the rPET impact was slightly higher than for virgin PET, but both alternatives performed better than the fermentation PET. Overall, mechanically recycled PET performed best, followed by virgin PET, while fermentation PET had the worst environmental performance.

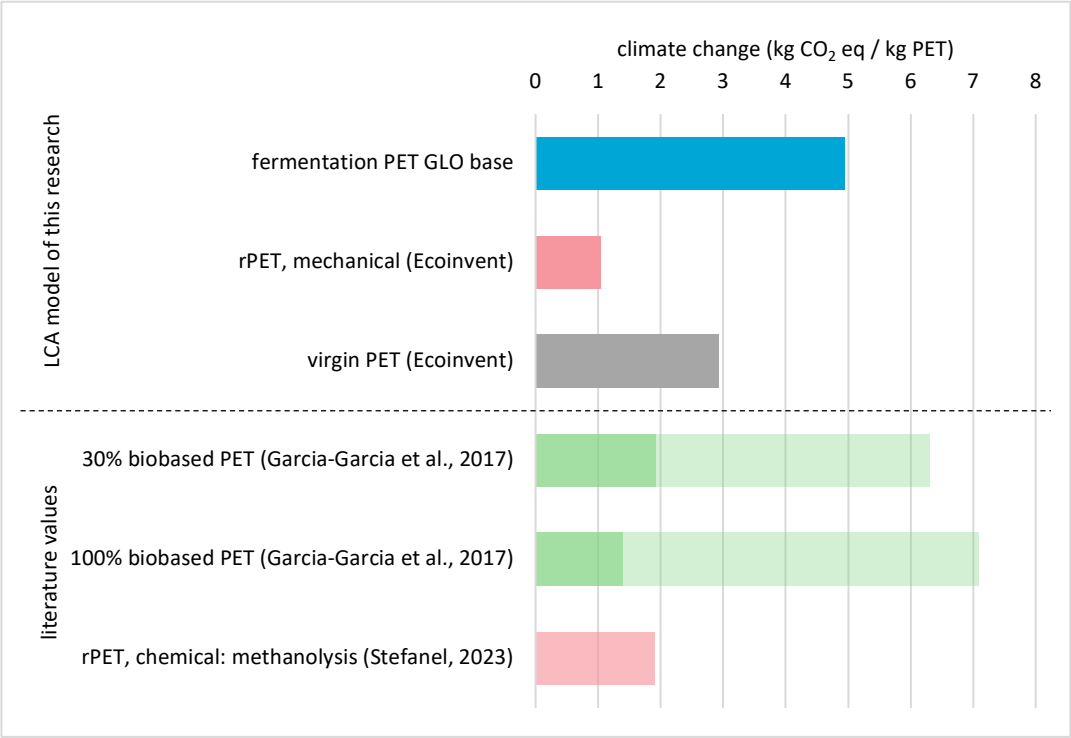

Figure 3.1: Climate change impact of fermentation-based PET (GLO) compared to virgin and recycled (r) PET (RoW), per 1 kg PET granulate to the factory gate (FU). Further, the comparison with the literature range LCA results for biobased PET and chemically recycled PET by methanolysis was drawn (Garcia-Garcia et al., 2017; Stefanel, 2023). 30% biobased PET incorporates only the MEG component to be biobased, while for 100% PET, also the PTA is biobased (Garcia-Garcia et al., 2017). In this LCA model, the Environmental Footprint impact assessment method was applied (European Commission, 2023), while for chemically recycled PET, the IPCC method was used (Stefanel, 2023).

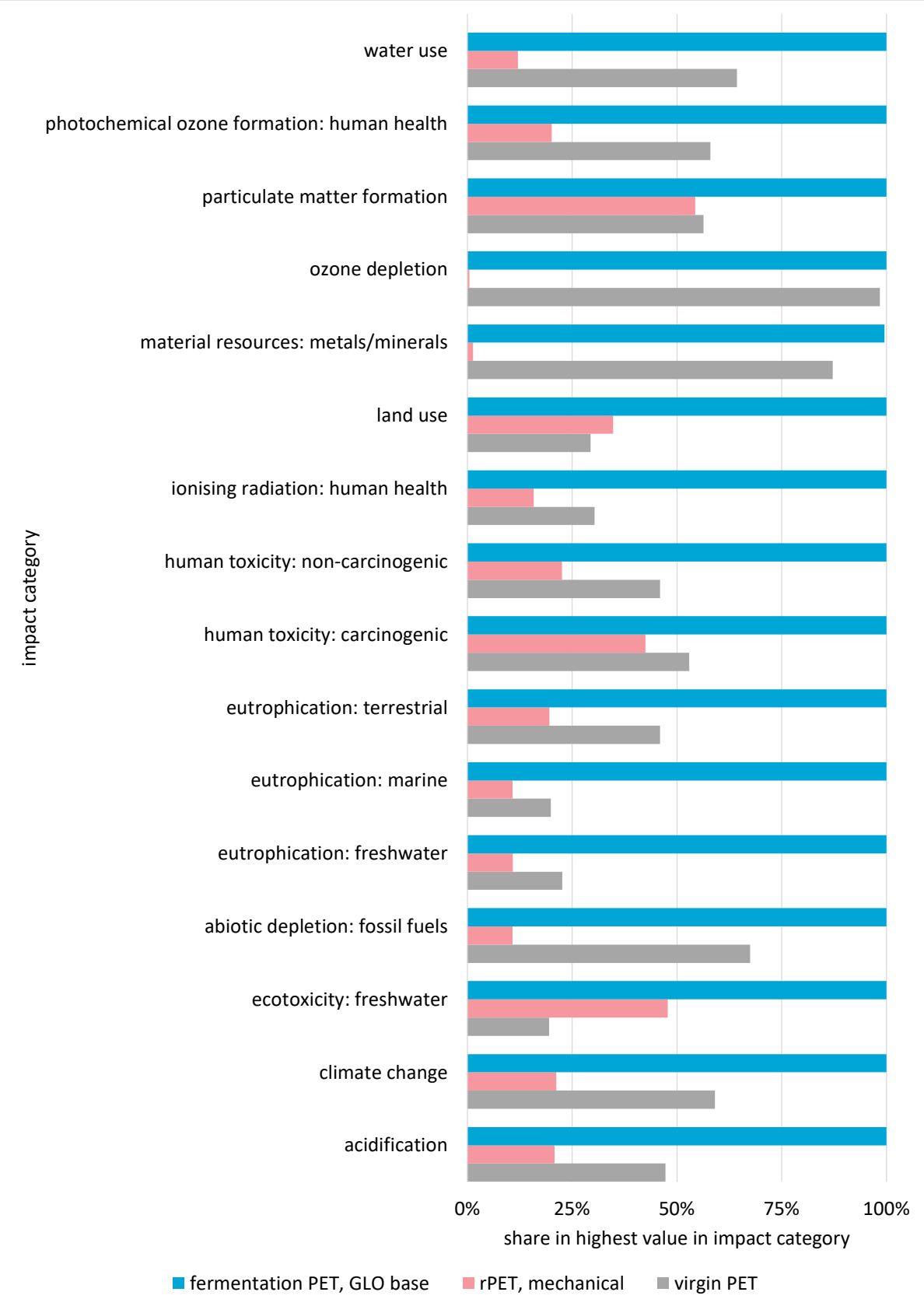

Figure 3.2: Impact assessment of fermentation-based PET (GLO) compared to virgin and mechanically recycled (r) PET (RoW), per 1 kg PET granulate to the factory gate (FU). Result from the LCA model of this study. The fermentation part included foreground data for the climate change impact, but the other impact categories were based on background data

3.2. Contributions

For environmental flows, around 80% of the climate change emissions were contributed by fossil carbon dioxide emissions for all three alternatives (Figure 3.3). A minor share was caused by fossil or non-fossil methane emissions (cut-off threshold at 1.2 %, SI6).

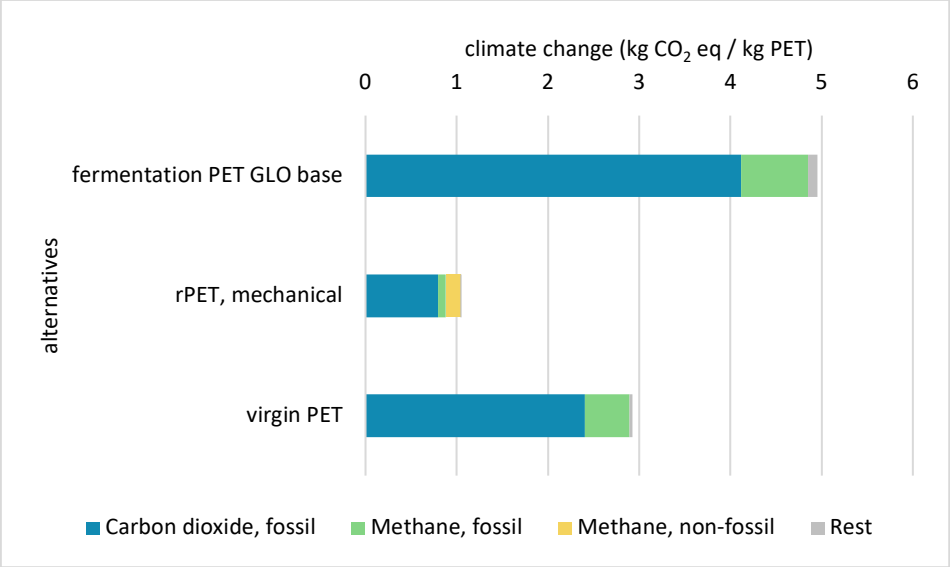

Figure 3.3: Environmental flow contributions to climate change of fermentation-based PET (GLO) compared to virgin and mechanically recycled (r) PET (RoW), per 1 kg PET granulate to the factory gate (FU). Cut-off threshold at 1.2 %, SI6

A major share of the climate change contributions to fermentation-based PET consisted of carbon dioxide released during the fermentation process (3.56 kg CO_2eq / kg PET, 39%) (Figure 3.4). This stems from the microbial process itself, where only a 1/3 conversion rate of CO into ethanol can be achieved, as the feedstock composition includes mainly CO and no H_2 (Simpson et al., 2007) (subsection 1.3.2). Further, there was a high contribution from high voltage electricity (2.77 kg CO_2eq / kg PET, 30%), because a global energy mix was assumed, with a high share of fossil energy. Especially the gas conditioning showed a large high voltage electricity consumption (0.87 kWh / kg BOF gas or 2.6 kWh / kg PET granulate) for the gas compression. Merely the electricity for the gas conditioning made up 19.7% of the overall climate change impact (1.82 kg CO_2eq / kg PET). The higher pressure is needed to increase the solubility of the feedstock gas in the medium to maximise the yield (Liew et al., 2016). Production of xylene, a precursor of PTA and the production of PTA contributed 1.11 kg CO_2eq for 1 kg of PET, making up 12% of the total emissions for fermentation-based PET. Further, the credit from the substitution made up a considerable reduction in the overall emissions (-4.28 kg CO_2eq / kg PET, 46%). Without this credit, the total emission result would be substantially higher (9.23 CO_2eq / kg PET). Smaller contributions were heat, hard coal, wastewater treatment for the fermentation and the polymerisation into PET.

For virgin PET, xylene and PTA contributed with 38% to the overall impact. Also high voltage electricity made up a large share of the contributions (24%). Recycled PET had some larger contributions from electricity and heat, but the overall impact was substantially smaller than for the alternatives.

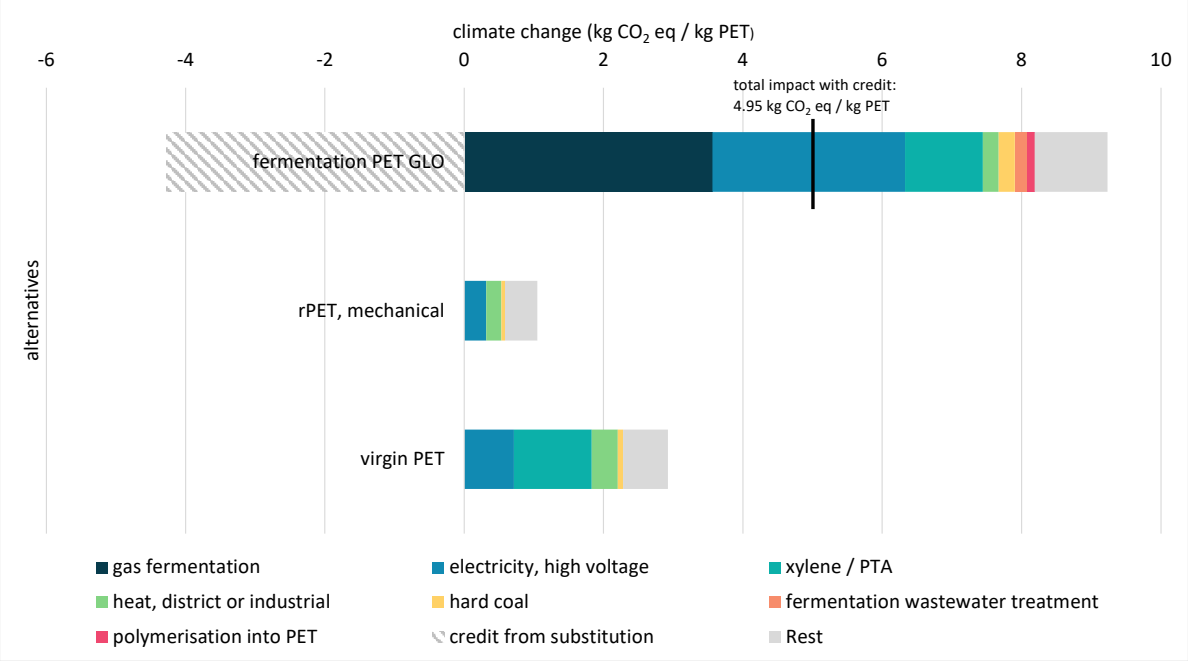

Figure 3.4: Climate change contributions of fermentation-based PET (GLO) compared to virgin and mechanically recycled (r) PET (RoW), per 1 kg PET granulate to the factory gate (FU), cut-off level at 0.7% for fermentation-based PET, contributions for alternatives were aggregated (details in SI7)

Following the carbon balance outlined in chapter 2, the contributions to the total climate change impact result of the fermentation PET could also be divided into the carbon credit that comes with the changes in the steel process and the total carbon that is formally bound in the final product (Figure 3.5, calculations in SI1, C5). It could be shown how the BOF gas was provided with an emission credit of -3.77 kg CO_2eq / kg PET when it enters the system, so the full changes associated with the utilisation of the BOF gas were accredited to the PET system. However, the carbon balance also shows that the total carbon credit that was formally bound in the final product was largely diminished by the 3.56 kg CO_2eq / kg PET that are released during the fermentation, inherent to the microbial process itself (Simpson et al., 2007). Other process emissions were caused by electricity consumption, especially for gas compression before fermentation, but also for further processing of the ethanol into PET, including the PTA production and other background processes.

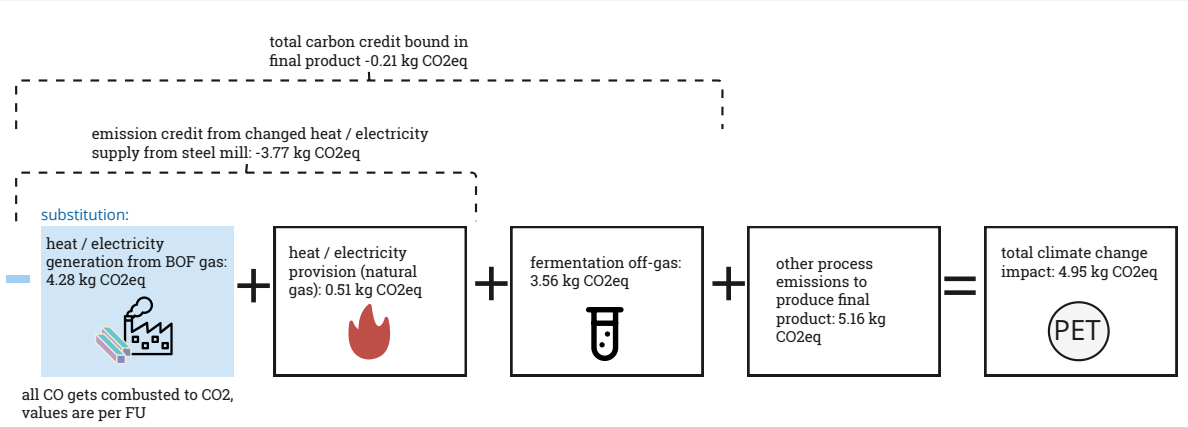

Figure 3.5: Carbon balance visualisation: Substitution, derivation of the total carbon credit bound in the product and the final climate change impact, per 1 kg of PET granulate (calculations in SI1, C5).

3.3. Sensitivity analysis: Results

In a best-case scenario (1) for Belgium as a production location and 100% renewable electricity from wind energy for all electricity inputs in the foreground processes, a large reduction of the climate change impact of the fermentation PET could be achieved (from 4.95 to 2.7 kg CO_2eq / kg PET, 46% reduction, scenario 1) (Figure 3.6). In this scenario (1), the substituted energy for the BOF gas in the steel process would still come from natural gas. If that energy was fully electrified and supplied with 100% wind energy in Belgium, the impact would be 0.5 kg CO_2eq / kg PET lower (scenario 2).

Sourcing xylene, the precursor for PTA, from biobased resources, could reduce the 1.11 kg CO_2 eq / kg PET contribution of the xylene/PTA. If under scenario 2, the xylene would be based on orange peel, with a reduction of the climate change impact down to 2% (0.02 kg CO_2 eq / kg PET), the overall impact of the PET would go down to 1.12 kg CO_2eq / kg PET (scenario 3). These final impacts include the emission credit of 4.28 kg CO_2eq / kg PET. Without assuming that credit, the overall impact results would be much higher, as also illustrated in Figure 3.6. Applying the orange peel PTA route for virgin PET could reduce its impact to 1.84 kg CO_2 eq / kg PET. All in all, rPET still had the lowest climate change impacts among all alternatives.

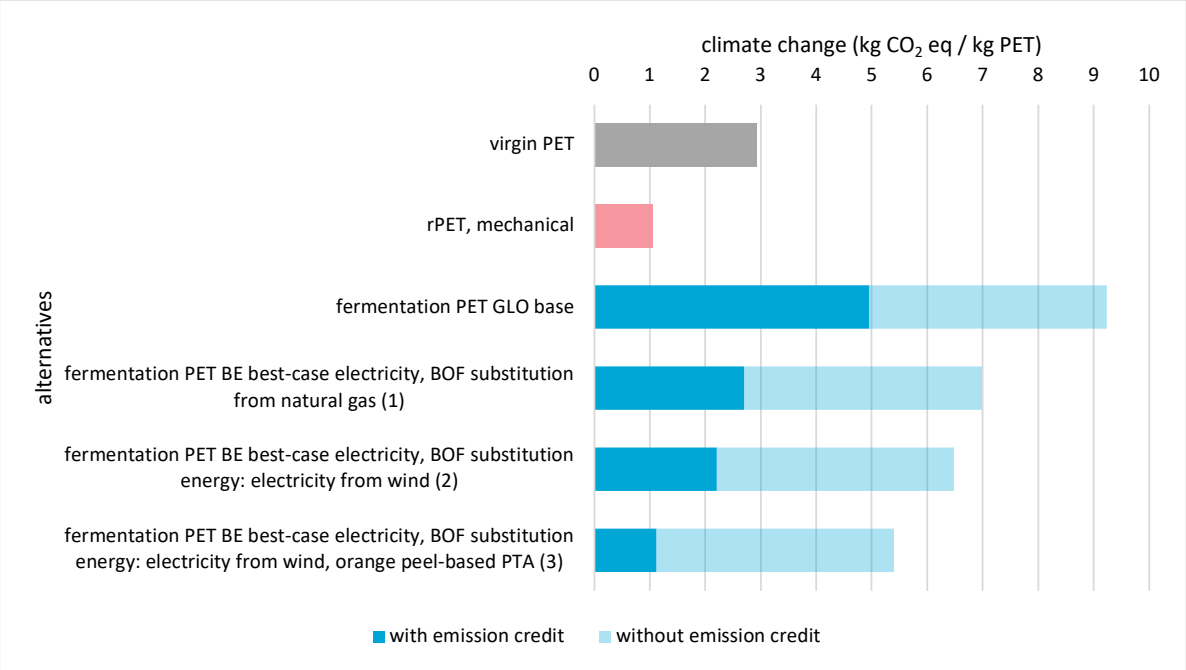

Figure 3.6: Sensitivity analysis results for improvement scenarios 1-3 for the fermentation PET compared to the base case and the reference alternatives, with and without the emission credit for avoiding the energy generation from BOF gas in the steel process. The reference alternatives (virgin PET, rPET) were not adjusted for the scenarios, so the comparison is under unequal circumstances, but give reference values.

4

Discussion

To the best knowledge of the author, this study was the first to perform an LCA of BOF-gas fermentation technology up until the final end product PET. Previous environmental studies focused on ethanol as final product (Almeida Benalcázar et al., 2022; de Medeiros et al., 2021; Handler et al., 2016; Michailos et al., 2019). A comparison with assumptions and results of previous studies is drawn in this chapter. Further, this research provided a comparison with other PET sourcing routes. Directly in the LCA model and based on Ecoinvent 3.8 processes, the climate change impacts were compared with virgin and mechanically recycled PET from bottles (Wernet et al., 2016). Further, comparisons with literature ranges and values for biobased and chemically recycled PET were drawn (Garcia-Garcia et al., 2017; Stefanel, 2023). This examined the gas fermentation technology in a new context for an application as PET in the textile industry and supports decision-making in the industry. The context was complemented by two expert consultations about the current industry situtation, one with Lucie Martinol about recycled PET in the textile industry and one with Axel Boeke about BOF gas utilisation in the steel industry. Further, this research made the hotspot contributors along the gas fermentation process transparent and showed the improvement potential of the technology under different scenarios. There are certain limitations to the LCA method and the LCA model of this study which are discussed in the following. Despite of these limitations, reliable conclusions could be drawn from the results.

4.1. Methodological limitations of LCA

For the LCA method, a certain degree of subjectivity in modeling decisions and assumptions remains, which could potentially bias the results. For the fermentation part of this model, Eduardo Almeida Benalcázar was consulted to validate the inventory, but there was no validation from an external industrial party with regard to the fermentation technology. Also, the assumptions chosen for the sensitivity analysis can have a subjectivity bias (Müller et al., 2020). However, the goal was to show the best-case scenarios, not necessarily the most realistic scenarios.

Furthermore, LCA does not directly include the social and economic perspectives such as working conditions, profitability and affordability (Curran & Curran, 2014). These aspects need to be considered as well to come to a holistic decision, but go beyond the scope of this study. Further, conventional LCA is not dynamic (Brander, 2016). That is to say, the temporary storage of carbon in the product is only assessed for a frozen moment in time and within the off-gas-to-gate boundaries of the assessment. The later re-release of the bound carbon in end-of-life and the time moment of that release are not included, so the results predominantly serve the goal of comparison between the alternatives, but do not give an absolute carbon balance for the entire life cycle, neither in time. A static quantification of the end-of-life emissions for 1 kg PET would be feasible, but lies outside the system boundaries of this study and would not add further value for the goal of comparison between the alternative sourcing routes, since the chemical structure of the product is identical for all alternatives.

The LCA results of this study and the literature-based LCA values are based on different impact assessment methods. While for this LCA, the Environmental Footprint 3.0 method was used, Stefanel, 2023 used the IPCC GWP 100a. For the biobased PET, the range reflects several LCA studies with

different assumptions and impact assessment models. However, the literature values are still helpful as a context since the main emission type contributing to global warming was CO_2, where the impact factor is 1 for both the methods, since CO_2eq were the unit to measure global warming.

4.2. Model limitations

For confidentiality reasons, no primary data from the industry was available for the model. However, in the study by Almeida Benalcázar et al. (2022), which was the underlying simulation for the fermentation parts of the inventory, the results were classified as comparable with the results by Handler et al. (2016), if the assumptions were the same in terms of heat integration (Almeida Benalcázar et al., 2022). Therefore, the inventory data based on that simulation can be taken as realistic enough to derive purposeful results. Because of the lack of primary data, only the impact category climate change was in the focus of the study, as there was no data available on emissions relevant for other impact categories for the fermentation part. Based on the background system, it is evident that fermentation technology performs worse in various impact categories compared to alternative technologies. But foreground biosphere flows for the fermentation parts of the model would complement the model to have a precise assessment and a complete picture of the environmental impacts.

To ensure broader applicability, this study was limited to a more general global case. For the analysis of a specific situation, the context can be relevant. As already seen in the contributions (Figure 3.4) and sensitivity analysis (Figure 3.6), the electricity mix has considerable impact on the overall results. Further, transport was excluded for the foreground system, but needs to be taken into account for the specific supply chain at hand. The final decision where to source the polyester also depends on the temporal and spacial availability of alternative sourcing routes. For example, it can be decisive if and what kind of secondary material (closed-loop or open-loop) is accessible and economic for recycled PET.

For the BOF gas composition, deviating compositions than the 85% CO and 15% CO_2 composition assumed in this study were described such as 57% CO, 14% CO_2, 14% N_2, 12% H_2O, 3% H_2 (West, 2020). But if the contaminants N_2 and H_2O are neglected, as they do not disturb the microbial reactions, the share of CO is around 80%, which is similar to the assumption in this study. A higher share of hydrogen could improve the carbon utilisation rate of the fermentation, leading to lower emission results during the fermentation (Simpson et al., 2007).

The fermentation medium production is based on a lab-scale experiment. Therefore, industrial production may be more efficient with upscaling. In the model, some proxies were used and components below concentrations of 1g/L of medium and other components such as vitamins were excluded. Since they may include purification steps, there may be some relevant impacts. On the other hand, Handler et al. (2016) reported the fermentation medium to be of minor contribution, so the assumptions were seen as sufficiently detailed for the purpose of this study.

In the sensitivity analysis, for an equal comparison with the alternatives rPET and virgin PET, a best case electricity scenario would also need to be applied for these alternatives. However, for the purpose of showing the reduction potential for the fermentation technology, the results are sufficient. And the rPET performs better even under the differing electricity scenarios, so the overall ranking of the results would not change. Only for the virgin PET, assuming a best-case electricity mix could change the impact in a way relevant for the comparative ranking of the impacts for all alternatives.

Table 4.1: Major differences in assumptions, scope and results between this study and the LCA by Handler et al., 2016

Aspect of LCA model	Handler et al. (2016)	this study	reference for this study
assumed BOF gas utilisation in the steel process	in Europe, 1/4 of gases; in US fully flared without further use	major share utilised for on-site heat and electricity generation, minimal share flared	Keys et al. (2019), Bazanella et al. (2017), Almeida Benalcázar (2022), Boeke (2023)
CO_2 emission credit for BOF gas utilisation	flaring without energy recovery, utilisation in fermentation was counted as full CO_2 emission credit of avoided emissions (focus on regions where BOF gas is not utilised)	BOF gas would normally be utilised for heat/electricity generation, CO_2 emission credit of avoided emissions, but also substitution of missing heat/electricity	Keys et al. (2019), Bazanella et al. (2017), Almeida Benalcázar (2022), Boeke (2023)
fermentation in- and output data	estimations in consultation of LanzaTech process engineers	engineering process simulation	Almeida Benalcázar et al. (2022) & expert consultation of Eduardo Almeida Benalcázar, Thi et al. (2020)
final product	ethanol	PET, based on ethanol as precursor	n/a
scope	gradle-to-grave	BOF-gas-to-gate	n/a
assumed energy utilisation from gas cooling	steam generation for distillation, excess heat as CO_2 emission credit	steam generation for distillation, not assured that excess heat is utilised elsewhere, actually replacing heat provision with fossil fuels, so no CO_2 emission credit was given, turbine for heat recovery not economic	Almeida Benalcázar et al. (2022)
carbon credit bound in product	2.12 kg CO_2 eq / kg ethanol	0.63 kg CO_2 eq / kg ethanol	calculations in SI8
climate change impact	0.84 kg CO_2eq / kg ethanol	6.73 kg CO_2eq / kg ethanol	calculations in SI8

4.3. Comparison with similar studies for ethanol as final product

As already discussed in subsection 1.3.4, the LCA by Handler et al. (2016) was criticised for its assumptions in terms of the carbon credit for the feedstock and of heat integration (Almeida Benalcázar et al., 2022; Bazzanella et al., 2017). The major differences in assumptions, scope and results are summarised in Table 4.1. Handler et al. (2016) assumed a carbon credit bound in the product of 2.12 kg CO_2 eq / kg ethanol (conversion assuming calorific value of 26.8 MJ/kg ethanol). In this study, 0.21 kg CO_2 eq were bound per kg PET, which equals to 0.63 kg CO_2 eq / kg ethanol. This shows the more conservative approach taken in this study, also including the substitution of the missing BOF gas for the steel process with natural gas. Converting the results from Handler et al. (2016) gives a climate change impact of 0.84 kg CO_2 / kg ethanol, while in this LCA, the net ethanol GHG emissions were 6.73 kg CO_2 / kg ethanol. This shows how the climate change impact of ethanol from BOF gas was 2.7x higher than the standard petroleum reference (2.52 kg CO_2 / kg fuel), and not 67% reduced as stated in Handler et al. (2016) (calculation steps in SI8).

These numbers also show that the more conservative carbon credit alone can not be the only reason for the large differences in the final global warming impact. Differences can also occur because of deviating data sources to model the fermentation process. The detail of published inventory data was not sufficient in Handler et al., 2016 to make a comparison, as no input numbers for utilities such as electricity and steam were provided. Since Handler et al., 2016 utilised estimations in direct consultation with LanzaTech process engineers, the data may potentially be more precise than the process simulation data used in this study by Almeida Benalcázar et al., 2022. However, as already discussed, the simulation for the fermentation parts of the inventory was classified as comparable with the results by Handler et al. (2016), if the assumptions were the same in terms of heat integration (Almeida Benalcázar et al., 2022). The heat integration assumption could be another cause of the differences in results. There was another emission credit given by Handler et al., 2016 for the excess heat from gas cooling, which was not included in this study. However, there was also no number provided about how much difference in final global warming impact that assumption causes. Since the scope by Handler et al., 2016 was larger with an inclusion of end-of-life combustion of the product, the final impact in comparison would be even higher in this study if end-of-life was included.

Almeida Benalcázar et al. (2022) provided results under various assumptions for the energy substitution at steel production. Without any substitution, the climate change impact was distributed around a median of (about) 50 g CO_2 / MJ ethanol, which would be converted into 1.34 kg CO_2 / kg ethanol. However, with coal or electricity as energy source for the substitution in the steel process, these values would incline up to 13.35 kg CO_2 / kg ethanol and 24.5 kg CO_2 / kg ethanol, respectively. If the

extra energy came from wind, they would be 1.42 kg CO_2 / kg ethanol. (Almeida Benalcázar et al., 2022)

This shows how there was a large sensitivity in the model by Almeida Benalcázar et al. (2022) regarding the substituted energy in the steel process (Almeida Benalcázar et al., 2022). Compared to this study, the overall climate change impact was within the range of these values, but with a lower sensitivity for the assumed energy substitution (Figure 3.6).

4.4. Discussion of gas fermentation technology

As seen in Figure 3.4, there are several hotspot contributors that can be modified to improve the gas fermentation technology in order to become environmentally competitive compared to the alternative routes. Under a best-case electricity scenario and with orange-peel based PTA, the impacts of the fermentation PET could become as low as 1.12 kg CO_2 / kg PET (Figure 3.6). However, the implementation of these best-case circumstances is unlikely to be feasible in the near future. A full electrification with wind energy for the heat replacement in the steel process can include complications to switch from a system based on gas to an electrical heat system. Further, the orange-peel based route for the PTA is still only developed on a lab-scale and currently not commercially available (Tibbetts et al., 2021). The underlying LCA study by Volanti et al., 2019 was an early stage evaluation of the impact before upscaling it to industrial scale. Therefore, the impact could still change with upscaling. But the reduction down to 2% of the fossil impact of xylene / PTA shows the projected potential of improvement for this contributor. Other xylene sourcing routes based on feedstocks from crops such as corn and sugar beet lead to a 2.6-3x higher climate change impact and also higher impacts in other categories (land use, water consumption, terrestrial acidification), thus not presenting a feasible alternative to fossil PTA (Volanti et al., 2019). The climate change impact also depends on the chemical route: in an LCA by Gian et al., 2022 for *Miscanthus*, the thermochemical route from bio-oil based on pyrolysis of the biomass feedstock had a 39% lower impact than the fossil alternative, while the biochemical route from sugars caused close to a 1.5x higher climate change impact (Gian et al., 2022).

The overall impact when using BOF gas as feedstock also depends on the assumptions about changes in the steel process. As seen in Figure 3.4, the substitution of the energy missing from the BOF gas makes a smaller, but relevant contribution to the overall impact. In addition, industrial CO_2 originally stems from fossil carbon sources predominantly, so cannot automatically be declared as a renewable source (Omaye, 2002). Also for the assumptions in this study, the BOF gas typically stems from fossil carbon sources (Boeke, 2023). Ultimately, the carbon from fossil coal that the steel industry uses for iron ore reduction and later for energy generation would just be replaced with natural gas or renewable energy, but the emissions from the fossil coal would later also be re-released in the end-of-life of the PET containing product. Therefore, it is clearly not a carbon-neutral, nor a carbon-negative route (Tanzer & Ramírez, 2019). Framing the gas fermentation as using waste carbon emissions to make a product has dangerous consequences for the user implications. A communicated use of a supposed waste product for a material can lead to a rebound effect of increased consumption and falsely diminish the incentive to decrease PET consumption (Tanzer & Ramírez, 2019). The best application for the BOF gas may remain for energy generation within the steel process and not for materials, as the energy still needs replacement in the steel process and the fermentation has considerable emissions as well. Further, if the emissions from the BOF gas that are taken as a credit in this study could be reduced or avoided in the first place as part of steel decarbonisation, the credit would not be legitimate anymore. Or the credit could be partially or fully allocated to the steel process. This could raise the climate change impact for gas fermentation PET up to 9.23 kg CO2 eq / kg PET for the base case. More generally, CCU was projected to only potentially capture about 0.5% (chemicals) and and 5.5% (fuels) of global anthropogenic emissions (Le Quéré et al., 2015). The carbon that can be captured for polymer production makes too low of a share in the global anthropogenic carbon emissions to result in a significant mitigation of global warming, even if all plastic produced globally was based on that technology. Still, it reduces direct fossil-fuel and biomass dependency to produce plastics. (Muthuraj & Mekonnen, 2018)

An alternative feedstock gas composition and source could be more promising than the BOF gas from the steel process. Also in the simulation by Michailos et al., 2019, the low conversion of the carbon in the CO was identified as a major weakness of the technology. If the feedstock gas was composed with more H_2, the fermentation process could be more carbon-efficient, so that up to a 2/3 instead of a

1/3 carbon conversion rate could be achieved (Simpson et al., 2007). That way, the 2.35 kg CO_2 eq / kg PET contribution from the gas fermentation could be reduced substantially. For example, BF or BOF gas could be enriched with H_2 to have a higher carbon conversion into ethanol and lower carbon gas emissions during the fermentation. However, hydrogen as a high-energetic reactant could also impose a large contributor to the overall impact (Müller et al., 2020). Almeida Benalcázar et al. (2022) concluded an H_2-CO_2-mixture with H_2 from water electrolysis and CO_2 from generic industrial combustion to have the lowest global warming impact of the feedstocks examined (median <10g CO_2 / MJ ethanol). Using biomass-derived syngas has the potential to achieve a low greenhouse gas emission profile (de Medeiros et al., 2021). However, the industrial application still faces barriers to remove contaminants in extensive pre-treatments (Puiman, 2020).

5

Conclusion & Outlook

5.1. Conclusion

This LCA provides a quantitative comparison of the climate change impacts associated with gas fermentation-based PET production using steel BOF gas as a feedstock, in contrast to virgin PET and mechanically recycled PET as alternatives. Literature values for biobased and chemically recycled PET routes were included for further comparison. All the results were embedded in the situational context of the alternative sourcing routes for the textile industry. The research question can be answered:

What is the climate change impact of BOF-gas-fermentation based PET compared to alternative PET routes (mechanically recycled, virgin, biobased, chemically recycled) and what are the main contributors?

The climate change impact result for this LCA of BOF-gas-fermentation based PET was 4.95 kg CO_2eq / kg PET under a global electricity scenario. This is substantially higher than the impact for the alternatives virgin PET and mechanically recycled PET. These findings are in direct contrast to those reported in the previous LCA conducted by Handler et al., 2016, where a 60% reduction in carbon emissions was concluded for BOF gas fermentation-based ethanol compared to fossil fuels. The literature values for bio-based PET ranged from a global warming impact comparable to that of mechanically recycled PET up to an impact higher than all the compared alternatives (Garcia-Garcia et al., 2017). Chemically recycled PET had an impact higher than mechanically recycled PET, but lower than virgin and fermentation-based PET (Stefanel, 2023).

The main contributors of the climate change impact of BOF-gas-fermentation based PET include the gas fermentation process, high voltage electricity, particularly for gas compression, and the sourcing of the PTA component, which relies on fossil xylene. Under optimal, but rather unrealistic conditions, the gas-fermented PET could pose a feasible alternative for PET sourcing. If the electricity is from renewable sources, the route becomes preferable to virgin PET. To have a comparable carbon emission profile like mechanically recycled PET, the PTA component would need to be sourced bio-based and reach an impact reduction down to 2%. This has been projected for orange peel as PTA feedstock (Volanti et al., 2019). In addition, foreground system electricity would need to be 100% renewable (wind energy). Under these conditions (scenario 3), the climate change impact could be 1.12 CO_2eq / kg PET, so almost as low as for mechanically recycled PET under a global electricity mix (1.05 CO_2eq / kg PET). A further reduction could be achieved with a feedstock gas that contains more hydrogen, so that a higher share of the carbon gas can be utilised by the microorganisms (Simpson, 2011). However, there is a risk that the higher emissions associated with the different feedstock compensate this improvement.

Despite the recognised limitations of the LCA method, this LCA effectively quantifies greenhouse gas emissions, an important aspect in assessing the sustainability of PET sourcing. The model's limitation due to missing primary data could be addressed by leveraging simulation data from a reliable source such as Almeida Benalcázar et al., 2022, which has been validated through comparison to the LCA study utilising primary industry data by Handler et al., 2016 (Almeida Benalcázar et al., 2022). Consequently,

this comprehensive model offers a sufficiently detailed representation of reality to ensure applicability of its results.

These results suggest a need for cautious consideration when applying gas fermentation for PET production. Under the current global electricity mix, the results of this LCA suggest that it is not advisable to choose this technology as a decarbonisation option over virgin or recycled PET. This technology can be seriously considered as an alternative only if two conditions are met: firstly, a reliable supply of 100% renewable electricity (here: wind energy in Belgium) must be ensured, and secondly, the PTA component should be sourced from a biobased source that results in a substantial reduction in emissions.

The provision of low carbon and fossil-free PET to fulfill the projected future demand for this material with unique properties remains a challenge. Currently, there is no feasible route to source the demanded PET in a climate-neutral way. Biobased PET can possibly reduce greenhouse gas emissions, but trade-offs in other impact categories occur, associated with the agricultural production of feedstocks (Jahandideh et al., 2021; Vinod et al., 2020). Here it is especially important to consider land competition with food crops (Garcia-Garcia et al., 2017). Mechanically recycled PET can be obtained from bottles; however, this process is considered downcycling and follows an open-loop system. Ultimately, the final textile products still accumulate at the end of their life cycle (Rybaczewska-Blazejowska & Mena-Nieto, 2020). Moreover, PET bottles typically originate from fossil fuel sources (Park & Kim, 2014). In chemical recycling, textile waste can also be recycled, which would be closed-loop recycling, but is is more expensive and lacks the collection infrastructure. Also, specific design requirements for disassembly become necessary (Park & Kim, 2014). However, it has a relatively low climate change impact among the alternatives (Stefanel, 2023). Overall, from a climate change perspective, mechanically recycled PET remains the option with the lowest emissions, but as discussed, there are other barriers that limit this alternative. Sustainable PET sourcing requires careful navigation through trade-offs to identify the least harmful options for the specific case, based on a quantitative assessment.

5.2. Outlook

Complementing the input data for this LCA inventory with primary measuring data from the industry would improve the accuracy of results. Additionally, that would enable a comprehensive impact assessment across various environmental impact categories. For example, eutrophication impacts may be of concern and could be assessed in more detail with primary data of the nutrient concentrations of the wastewater from the gas fermentation reactor. Further research could explore the enrichment of the BOF of other feedstock gas with hydrogen. In detail, the trade-off of supplying the high-energy feedstock H_2 and achieving a higher carbon yield in the microbial process (Simpson et al., 2007) could be explored. Also the gasification of plastic waste into syngas and subsequent gas fermentation may be a possibility for a closed-loop system. Overall, the exploration of other sources of syngas, biobased or based on municipal wastes could be interesting for further LCA studies.

Since the share of gas fermentation based material is rather low in PET as an application (Vural Gursel et al., 2021), it may be more impactful to apply it for other final products such as ethanol or ethylene. Overall, the textile industry may not be the optimal application of this technology as it does not resolve the end-of-life fate of PET based textiles. Here, chemical recycling may be the more interesting route. More suitable application industries could be packaging, fuels or cosmetics.

In the pursuit of sustainable production and consumption, it is important to acknowledge that the least environmentally impacting clothing item is the one that is not produced at all, reducing the demand for PET. While reducing emissions from material sourcing is essential and valuable to provide the basic needs for every human, it should not encourage a pattern of increased unnecessary consumption. Measures aimed at prolonging the lifetime of textile items through timeless design, high durability and second-hand markets remain substantial to preserve resources for upcoming generations.

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Supplementary Information

The following documents can be found as attachments to this thesis. The LCA inventory gives all modeled flows and their quantities, units, locations, references and comments. Correspondingly, a calculation file is provided, which includes all calculations referred to in the text and inventory. The LCA inventory Excel file was read into Brightway2 with the attached python read-in script, so that the LCA calculations could be performed with the Activity Browser. However, the Brightway2 environment and the corresponding Ecoinvent and biosphere3 databases must be precisely the same as in this project's inventory. Therefore, the entire Brightway2 installation with the project and all needed databases was also attached to this thesis as a zip folder to ensure full transparency of the model.

Table 1: Overview of SI documents

	File name	Description
LCA inventory	"SI_inventory.xlsx"	For base scenario GLO, scenario 1,2; to read into Brightway2 with Python read-in script
Inventory calculations	"SI_calculations.xlsx"	Calculations to derive values for LCA inventory, output data from LCA analysis SI1-SI7
Python read-in script	folder: "python script_inventory into Brightway2"	Python script to read LCA inventory into Brightway2, provided by ON
Brightway2 project	"Brightway_project.zip"	In the Activity Browser, under *Preferences*, the Brightway directory can be set to the folder unpacked from this zip file, then the project "project_with_ei382" gives the database for the fermentation PET ("CCU_PET") and the matching Ecoinvent 3.8.2 database ("ecoinvent_database") and biosphere3 database for the environmental flows. The database "export" was used to export the ecoinvent processes that needed to be copied and adjusted in the Excel file.