



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



Emma A.R. Zuiderveen^{a,*}, Davide Ansovini^b, Gert-Jan M. Gruter^{b,c}, Li Shen^d

^a Department of Environmental Science, Institute for Water and Wetland Research, Radboud University Nijmegen, PO Box 9010, 6500 GL, Nijmegen, the Netherlands

^b Avantium, Zekeringstraat 29, 1014 BV, Amsterdam, the Netherlands

^c Van't Hoff Institute of Molecular Sciences, University of Amsterdam, P.O. Box 94720, 1090 GS, Amsterdam, the Netherlands

^d Copernicus Institute of Sustainable Development, Utrecht University, Heidelberglaan 8, 3584 CS, Utrecht, the Netherlands

ARTICLE INFO

Keywords:

PEF
FDCA
MEG
Bio-based polymers
Ex-ante LCA
Early-stage assessment
Decarbonization
Bio-based chemicals
Bio-economy
Electrification of the chemical industry
Lignocellulosic biomass
Second generation feedstock
First generation feedstock

ABSTRACT

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

1. Introduction

The 21st-century is marked by growing concerns about climate change and the need to mitigate it becomes more urgent every passing day. Current climate change problems require radical new ways of living, producing and consuming. In order to achieve this, the Paris Agreement and the Sustainable Development Goals (SDGs) were set up; and at EU level, the Bio-economy Strategy was developed aiming at advancing the deployment of a sustainable European bio-economy (European Commission, 2018). A bio-economy shifts from a fossil-based economy to a bio-based economy and offers potential solutions for climate change and related problems such as limited resources, biodiversity loss and ecosystem degradation. Key to this strategy is the development of bio-based materials using sustainable and clean technologies (European

Commission, 2017). The chemical industry is one of the primary industries producing the building blocks for many materials, such as plastics. This industry, including the petrochemical sector, accounts for 30% of the total industry energy-use and is responsible for 18% of direct industrial GHG emissions globally (IEA, 2020). In order to lower the climate change impact of the chemical industry and to shift to a bio-economy, one of the grand challenges today within the chemical sector is to design green and sustainable materials and clean technologies (Aeschelmann and Carus, 2015). Within this context, the Horizon 2020 TERRA project was set up exploring two strategies to lower climate change impact of plastic production. Firstly, it uses biomass as a feedstock for the synthesis of a 100% bio-based PEF polymer, and secondly, it explores an electrochemical conversion technology producing it.

One of the strategies is to produce materials from other resources than fossil fuels. Bio-based production of 'drop-in' chemicals or new materials

* Corresponding author.

E-mail address: e.zuiderveen@science.ru.nl (E.A.R. Zuiderveen).

Abbreviations

TERRA	Tandem Electrocatalytic Reactor for energy/Resource efficiency and process
PEF	Polyethylenefuranoate
PET	Polyethylene terephthalate
2,5-FDCA	2,5-Furan dicarboxylic acid
MEG	Mono ethylene glycol
EG	Ethylene glycol
PG	1,2-Propylene glycol
(5-)HMF	(5-)Hydroxymethylfurfural
NaOH	Sodium hydroxide
HFCS-90	High-Fructose Corn Syrup (90%)
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
TRL	Technology Readiness Level
GHG emissions	Greenhouse gas emissions
NREU	Non-renewable energy use
CT	Cathode
AN	Anode
WWTP	Wastewater treatment plant

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

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

One comprehensive method to assess the environmental impact of a product is Life Cycle Assessment (LCA). The methodology is based on systems thinking, which evaluates the whole supply chain of a product and analyses possible trade-offs. LCA offers the possibility of identifying environmental hotspots - especially important in early-stage processes -

securing sustainability and avoiding lock-ins (Keijer et al., 2019). The life cycle environmental impacts of PEF are, to a large extent, still unknown due to early development phase of the material. One publicly available LCA of PEF, obtained from 2,5-FDCA sourced from first generation biomass (corn) and fossil and bio-based based MEG (70% and 100% bio-based content, respectively) conducted by Erhart et al. (2012), analysed PEF could potentially reduce non-renewable energy use (NREU) by 40–50% and greenhouse gas (GHG) emissions by 45–55% compared to fossil fuel based PET. The study analysed a chemical conversion of corn-based fructose into furanics to produce hydroxymethylfurfural (HMF) and the air oxidation of HMF to FDCA, based on proof-of-concept experimental data from Avantium Chemicals B.V. (Erhart et al., 2012). Just recently a comparative LCA for different types of bio-plastics was published by the Joint Research Center, including an early-assessment of PEF; It found an impact of 554 kg CO₂ eq. per 1000 L of beverage by means of 0.5 L single-use bottles from cradle-to-grave, based on thermodynamic routes for FDCA, from a mix of maize, wheat and potatoes, and MEG from sugarcane via bio-ethanol (Nessi et al., 2020). Unlike the separate conversions of MEG and 2,5-FDCA, as reported in current literature, the electrochemical process developed by the TERRA-project aimed to innovate a ground-breaking synthesis route using a one-step reactor to produce MEG and 2,5-FDCA simultaneously (Fig. 1).

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

2. Material and methods

2.1. Ex-ante LCA

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

Currently there is no consensus on a uniform framework for ex-ante LCA, but many have been recently proposed (Buyle et al., 2019; Moni et al., 2020; Thonemann et al., 2020), nonetheless, only a few bring it

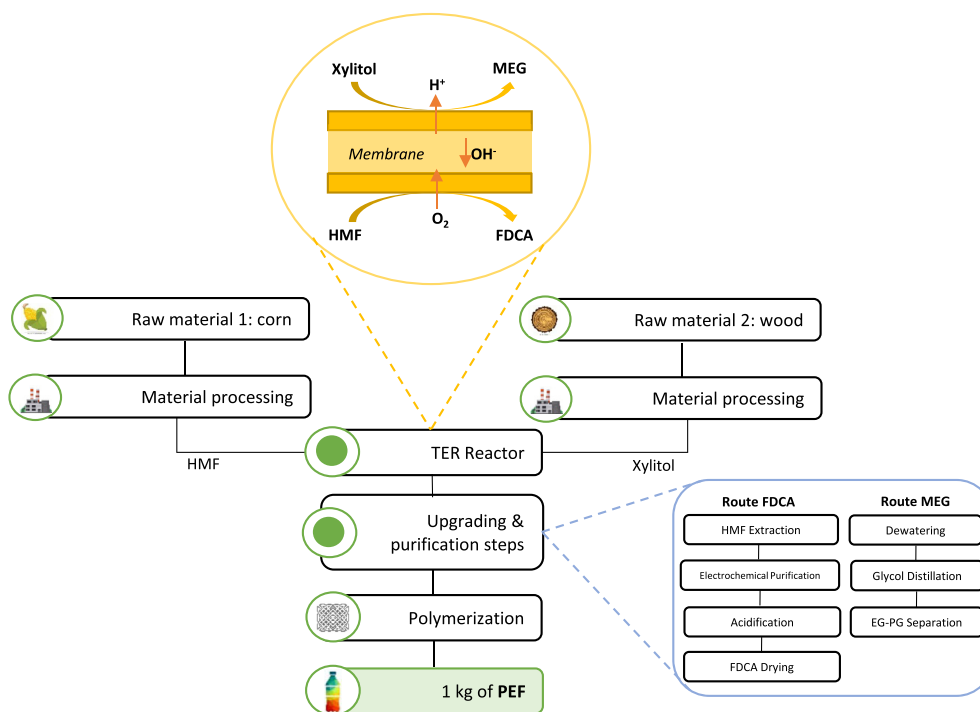


Fig. 1. Simplified scheme of PEF production based on TERRA process.

into practice (Piccinno et al., 2016; Simon et al., 2016; Tecchio et al., 2016). Previous research proposed frameworks defining ex-ante LCA by the different stages of technological development (Thomassen et al., 2019; Thonemann et al., 2020). Gavankar et al. (2015) applied TRLs to a case study on carbon nanotubes and recently van der Hulst et al. (2020) suggested a systematic approach defined by TRL ratings, applying it on a case study of CIGS solar photovoltaic laminate (Gavankar et al., 2015; van der Hulst et al., 2020). Technology Readiness Levels are based on 9 levels: TRL 1 to 3 define the lab phases, 4 to 6–7 includes process design and early pilot phase and TRL 9 means the technology is ready for commercial application (Thonemann et al., 2020). Our study is an attempt to assess a TRL2-4 technology.

By going from TRL 2–3 to TRL 4 in an ex-ante LCA, the design has to deal with upscaling and process changes based on a proven concept. Process design and simulation can support the LCA framework at an early developmental level (Righi et al., 2018). A conceptual pilot design, based on the functional principles of the TERRA process, including all recovery and upgrading steps is modelled (see 2.3.1 TERRA process). In order to go from TRL 4 to TRL 5 a miniplant should be evaluated and TRL 6 would cover the start of a pilot phase (Buchner et al., 2019). To go to a TRL 9 rating, apart from process changes to full-scale and technological validation, process synergies and external developments should be taken into account. Learning curves from previous similar technologies could be used at an industrial stage (Buyle et al., 2019). Our research contributes to the ex-ante LCA community and specifically to the TRL-based frameworks by defining the process by Technology Readiness Levels (TRLs). Our contribution is performing a case-study and exploring how to deal with a TRL 2–3 technology “upscaled” to TRL4. To scale up from a 50 kt pilot plant to a 200 kt plant was far beyond the scope of this research due to very high uncertainties and data unavailability.

2.2. Goal and scope definitions

The goal of this study is to assess the environmental impact of a PEF polymer based on a novel electrochemical process at an early developmental stage and to identify potential environmental hotspots. The LCA is conducted using the ISO standards (ISO 14040: 2006 and ISO 14044:

2006). The focus of this study is an electrochemical process for the simultaneous production of bio-based monoethylene glycol (MEG) and bio-based 2,5-furan dicarboxylic acid (2,5-FDCA), the building blocks for PEF. Based on the decision context, the ex-ante LCA conducted is an attributional LCA.

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

Foreground data for the Life Cycle Inventory (LCI) were collected from internal data from Avantium B.V. and personal communications with experts. Process design and simulation were modelled in ASPEN®Plus and Excel. Background data were collected from Ecoinvent databases (version 3.3) (Wernet et al., 2016), Agri-Footprint (version 1.0) (Durlinger et al., 2017) and literature data. Details on the data sources are reported in Section 2.3.

The characterization methods used were ReCiPe Midpoint (H), GWP 100a and Cumulative Energy Demand (CED). Five environmental impact categories were selected: climate change (GWP, kg CO₂ eq./FU), non-renewable energy use (NREU, MJ/FU), acidification (kg SO₂ eq./FU), eutrophication (kg PO₄³⁻ eq./FU) and land use (kg C deficit) (Huijbregts et al., 2017). Greenhouse gas emissions and energy depletion (NREU) are the two most common environmental indicators in an ex-ante LCA and can provide an accurate prediction for the impacts of unscaled production of bio-based innovation (Fernandez-Dacosta et al., 2019). However, bio-based products have been shown to present environmental trade-offs. Acidification, eutrophication and land use are often neglected in an early stage assessment but are important impact categories for especially bio-based material (Broeren et al., 2017). We have not included direct or indirect land use changes (LUC or iLUC), although they can contribute notably to climate change (De Rosa et al., 2016). However, land use

change emissions are spatially-explicit and because neither the final specific feedstock is known nor its geography, including LUC or iLUC introduces very high uncertainty when proving meaningful assessment for a technology at a very low TRL level. With the selection of environmental indicators, we aim to capture both expected benefits and potential downsides of TERRA PEF. Table 1 presents all five impact categories, their corresponding impact assessment methods and their definitions.

2.3. Life Cycle Inventory

Fig. 2a and b provide a schematic representation of the cradle-to-factory gate production process of PEF. The LCA is scoped to account for:

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

The TERRA technology is based on an experimental and conceptual design. Process modelling and simulation were carried out in ASPEN[®]-Plus and Excel. Table 2 provides a summary of the main data sources including the synthesis routes and the background infrastructure (electricity, heat and steam). This section explains feedstock production (Section 2.3.1 for both 5-HMF and xylitol), the conceptual design of the TERRA process (Section 2.3.2) and the polymerization step (Section 2.3.3). Multifunctionality and biogenic carbon removal are described in Sections 2.3.4 and 2.3.5, respectively.

2.3.1. Feedstock supply

Raw material acquisition includes biomass production, transportation and the processing steps to obtain 5-HMF and xylitol - the two raw ingredients fed into the TERRA reactor. Production of 5-HMF is based on

Table 1

The impact categories analysed and their units, the methods used for each impact category and their definitions.

Impact Categories	Unit	Impact assessment method	Definition
Non-renewable energy use (NREU)	MJ	Cumulative Energy Demand (Frischknecht et al., 2007)	Primary energy demand including fossil energy, nuclear energy and non-renewable biomass energy (Frischknecht et al., 2007).
Climate change (GHG emission)	kg CO ₂ eq.	GWP 100a (IPCC, 2013)	Greenhouse gas emissions
Freshwater eutrophication	g PO ₄ ³⁻ eq.	ReCiPe Midpoint (H) (Huijbregts et al., 2017)	Overflow of nutrient in freshwater ecosystems caused by e.g. phosphates and nitrates, measured in PO ₄ ³⁻ equivalents (Helmes et al., 2012).
Terrestrial acidification	g SO ₂ eq.	ReCiPe Midpoint (H) (Huijbregts et al., 2017)	Acidified soil due to pollution measured in SO ₂ Equivalents (Roy et al., 2014).
Land use	kg C deficit	ILCD Midpoint + (Milà i Canals et al., 2007)	Land to produce biomass either in terms of occupied land in m ² of crop or land that is to be transformed, expressed in kg carbon deficiency (Milà i Canals et al., 2007).

corn, xylitol is based on lignocellulosic biomass. First and second generation biomass feedstock rise to different challenges (see Discussion section 4.3.1). Assessment of xylitol involved high uncertainties regarding xylose production and xylitol conversion. Details on feedstock(s) can be found in section 2.3.1.1-2, and Supplementary S1.

2.3.1.1. 5-HMF (hydroxymethylfurfural). 5-HMF production steps included corn cultivation, glucose processing and fructose dehydration. Corn cultivation is assumed to take place in Europe. The LCA included corn harvesting, transportation to the Netherlands (assuming a transportation distance of 850 km by truck) and wet-milling. Corn starch is further converted into sugars (dextrose or glucose) via enzymatic hydrolysis (Tsiropoulos et al., 2013). In order to obtain fructose (90% High Fructose Corn Syrup, HFCS-90), the glucose stream goes through isomerization, refining and evaporation stages (Vink and Davies, 2015). Because of limited data availability, the corn sweetener refining is solely based on its most energy intensive step: evaporation of water after isomerization and separation (Eerhart et al., 2012). 5-HMF can be obtained by selective dehydration of fructose/HFCS-90 (HFCS 90% fructose). 5-HMF is not a bulk chemical and therefore LCA data in literature is scarce. Hence, dehydration of 5-HMF is based on a process described by Roquette and Dumesic (Chheda et al., 2007), excluding phase separation and production purification because of limited data availability. Table 3 gives a summary of 5-HMF process data.

2.3.1.2. Xylitol. Xylitol can be processed via hydrogenation of xylose, isolated from xylan-rich biomass. There is little known about the industrial xylose production in the public domain. Xylose can be synthesized by sulphuric acid hydrolysis (TSAH) from lignocellulosic material. However, because this process demands high acid and water input and is regarded as energy intensive, it is not conceived viable for our model (Zhang et al., 2014). Alternatively, xylose can be produced as a by-product of viscose production (Shen et al., 2010). In viscose production, xylose is recovered from the C5 fraction of the wood pulping process using a patented technology (see the “Danisco process” in Fig. 2). To our knowledge, this is so far the largest commercial scale xylose production.

Four viscose LCI/LCAs reported in literature were compared: viscose from Ecoinvent (version 3.3, based on generic technology), Viscose Asia, Viscose Austria and Modal Austria. The latter three are based on the specific production from Lenzing AG, one of the largest viscose producers in the world (Shen et al., 2010). Supplementary S1 covers the details of the environmental impact of these four viscose LCA datasets. The environmental impact of xylose as a by-product of viscose is determined by economic allocation. Allocation based on the physical relationship of energy/exergy does not apply because both products (viscose and xylose) are not energy products. System expansion is also not applicable because xylose is always made from processing wood (Shen et al., 2010). Based on the prices over the last ten years (2008–2018), on average the economic allocation factor for xylose is found to be 4%. The sensitivity of the allocation factors for xylose is examined in the Discussion section. Table 4 presents the environmental impact of 1 kg of xylose from viscose production.

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

2.3.2. The TERRA process

The TERRA process is subdivided into three sections (see Fig. 2b): (1) electrochemical reactor, (2) MEG separation and purification and (3) 2,5-FDCA separation and purification. A detailed description of separation and purification steps is given in Textbox 1. The TERRA reactor is further

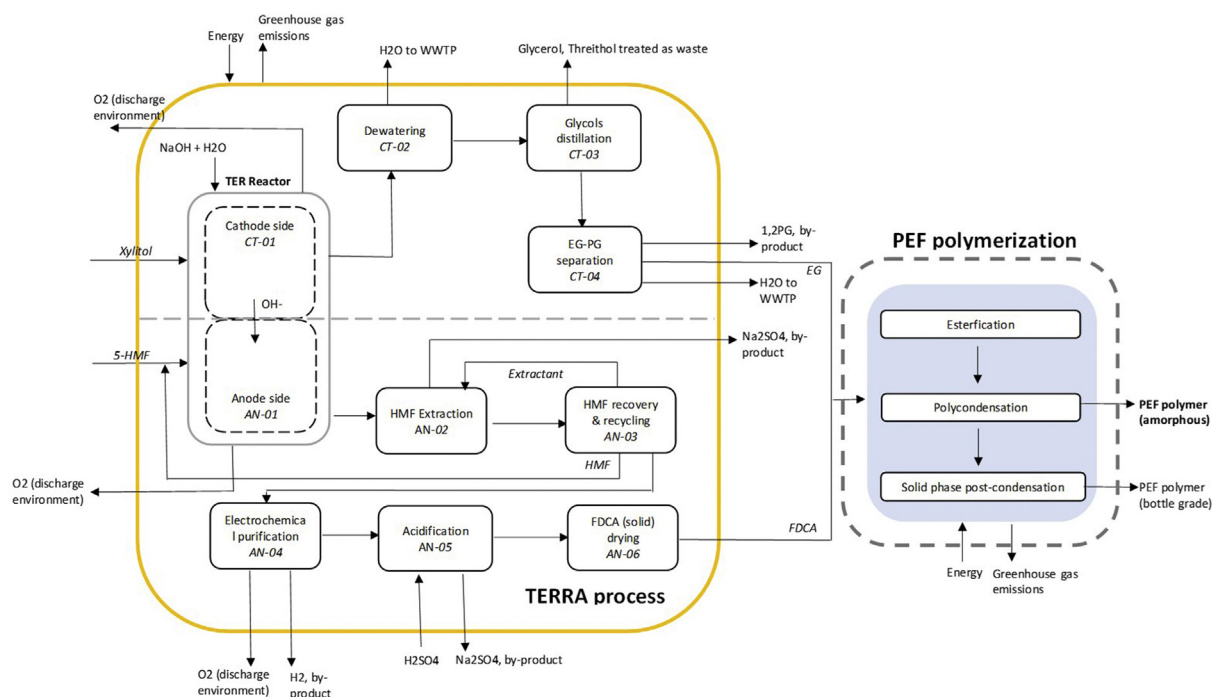


Fig. 2a. schematic representation of raw material acquisition for 5-HMF and xylitol. Boxes in blue indicate multiple processes which were treated as one-unit process in the LCA model. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

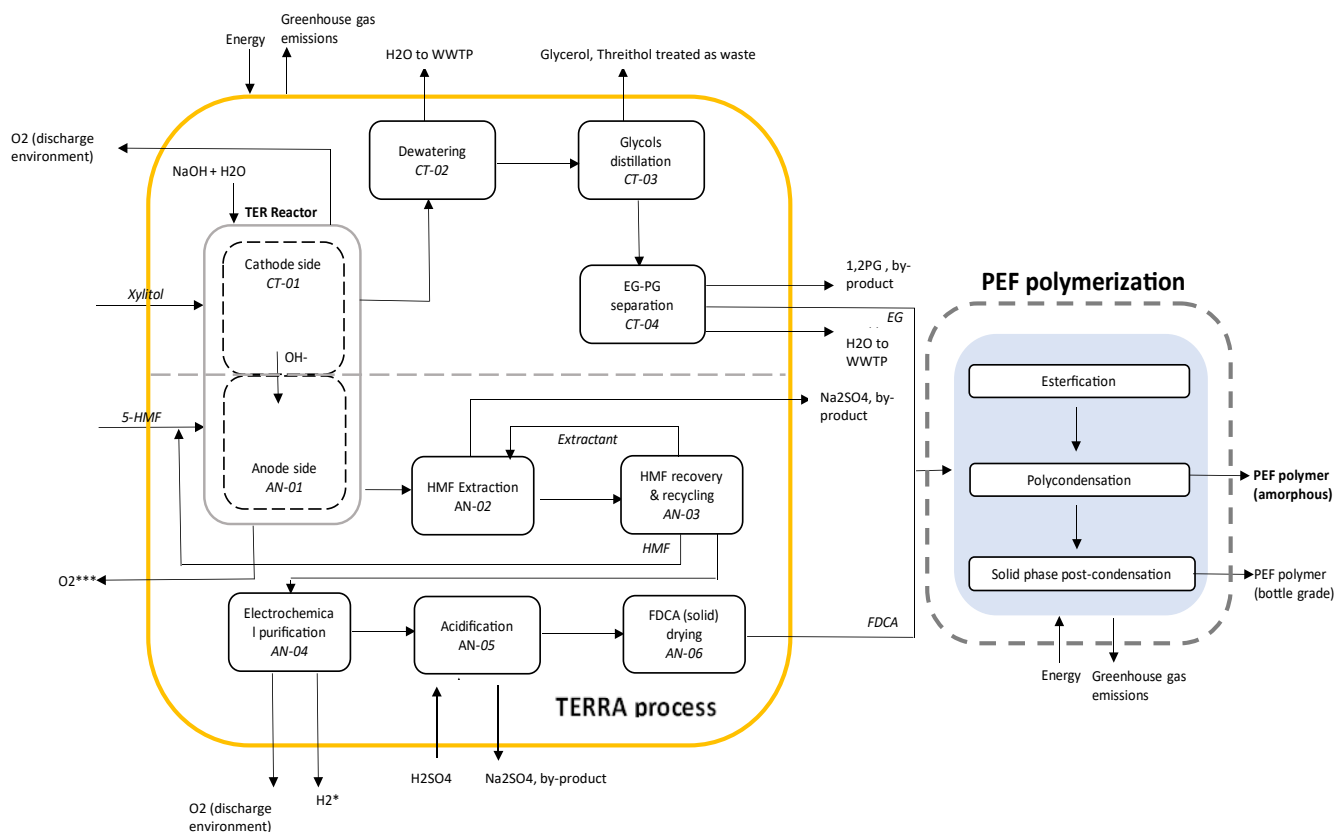


Fig. 2b. schematic representation of TERRA process and polymerization steps. Boxes in blue indicate multiple processes which were treated as one-unit process in the LCA model. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

discussed in 2.3.2.1 and a short process overview is given in section 2.3.2.2. The process design is based on experimental and theoretical data for a continuous production.

2.3.2.1. TERRA reactor. The electrochemical TERRA reactor supports the simultaneous conversion of xylitol into MEG and HMF into FDCA, separated by a porous membrane. The electrochemical reactor follows

Table 2

Summary of data used in the baseline analysis in this study. See detailed description in subsections.

	Data source	Notes
<i>Feedstock</i>		
Glucose production	Literature, complemented with ecoinvent 3.3	From European Corn based on Tsiropoulos et al. (Tsiropoulos et al., 2013) For corn cultivation, energy and GHG emissions are taken from Tsiropoulos et al. (Tsiropoulos et al., 2013) For the other impact categories, the Ecoinvent French average corn production is assumed. See Table 3 in Section 2.3.1.
Fructose/HFCS-90	Own Model	Modified based on calculations Eerhart, Faaij & Patel (Eerhart et al., 2012)
5-HMF (dehydration)	Own Model	Based on industry: Dumesic and Roquette processes. (Chhedha et al., 2007)
Xylose production	Modified Ecoinvent 3.3/Literature	From European wood pulp from via viscose production in Europe. Modified literature data from Shen et al. (2010) based on a European production.
Xylitol (hydrogenation)	Own Model	Based on standard industrial process described in literature.
TERRA process TERRA Reactor	Own Model	Primary data collected from Avantium, see Section 2.3.2.
Recovery and upgrading of MEG and FDCA	Own Model	Based on process simulation, see Section 2.3.2.
Wastewater treatment	Ecoinvent 3.3	Average Europe without Switzerland.
Electricity	Ecoinvent 3.3	Dutch electricity production, from grid.
Steam	Ecoinvent 3.3	Steam production, as energy carrier, in chemical industry [RER]
<i>Polymerization</i>		
PEF polymerization	Ecoinvent 3.3	Europe. Modified Based on PET polymerization.

Table 3

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

Baseline	NREU (MJ) ^a	GHG emissions ^a (kg CO ₂ eq.)	Eutrophication ^b (g PO ₄ ³⁻ eq.)	Acidification ^b (g SO ₂ eq.)	Land use ^b (kg C deficit)
Total glucose production (including corn cultivation, wet milling and starch to glucose conversion)	8.5	0.88	0.157 [2]	7.08 [2]	1.09 [2]
From glucose to fructose [1]	5.65	0.23	<0.001	<0.1	<0.001
Dehydration of fructose to 5-HMF [2]	1.52	0.04	<0.001	<0.1	<0.001
Cradle to factory gate 5-HMF production	13.69	1.14	0.16	7.1	1.1

[1] results from own model using Vink and Davies (2015), and Ecoinvent 3.3 as the background data, see the text.

[2] Own model based on Chhedha et al. (2007), see the text.

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

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

Table 4

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

	NREU (MJ/kg xylose)	GHG emissions (kg CO ₂ eq./kg xylose)	Eutrophication (g PO ₄ ³⁻ eq.)	Acidification (g SO ₂ eq.)	Land use (kg C deficit)
Impact of Xylose from viscose production	8.5 ^a (up to 40) ^b	-0.11 ^a (up to 1.7) ^b	0.191 ^c	27 ^c	1.22 ^c

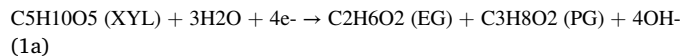
^a Data source Shen et al. (2010), lower value: Lenzing Austria Viscose is used by the baseline.

^b The upper value represents the allocated impact using Lenzing Viscose Asia (Shen et al., 2010).

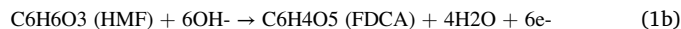
^c Based on Ecoinvent (v3.3) process "Viscose fibre {GLO} viscose production".

Eq. (1a) and Eq (1b) in the cathodic and anodic compartment respectively, with electrons flowing to the cathode, and a global cell reaction of Eq. (1c):

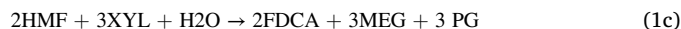
The cathodic half reaction being:



And the anodic half reaction:



Giving a global cell reaction of:



The TERRA reactor simulation model is based on a 50 kilo metric tonne (kt) (theoretical) plant. A detailed mass balance flow-sheet is given in Fig. 3. The pilot design is based on cells of 2.5 m² with a total of 5151 cells requiring an area of at least 12,878 m². The 50 kton/year pilot plant based on 8000 operating hours. Each cell has a cell voltage of 3 V and a current density of 1000 A/m². FDCA and MEG production are each based on a faradaic yield of 50%.

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

In the effluents from the anode, the excess 5-HMF is removed from the stream containing Na-FDCA through liquid-liquid extraction via MIBK (methyl isobutyl ketone) solvent. The by-products at the anode are oxygen and the sodium salt of formyl furancarboxylic acid (Na-FFCA). In the next step, the HMF-free stream is sent to an electrochemical purification reactor, where the aldehyde impurity is selectively oxidized into

Textbox 1

Separation and purification steps TERRA process

Cathode-side: recovery of MEG.

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

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

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

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

Anode side: recovery of FDCA.

There are four major steps to purify 2,5-FDCA from the anode side (see Fig. 3):

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

Electrochemical purification. The remaining HMF and Na-FDCA impurities are selectively converted into Na-FDCA by electrochemical purification. H₂ evolution during this step is treated by system expansion by substitution by avoiding industrial H₂ produced from steam reforming of natural gas. The outflow of this process contains mainly Na-FDCA (in water) and traces of HMF and NaOH.

Acidification. This step recovers FDCA from Na₂-FDCA by adding H₂SO₄ (0.84 kg H₂SO₄/kg PEF) which also leads to 1.22 kg H₂SO₄/kg PEF as a by-product which is modelled in LCA by system expansion by substitution. During this step, FDCA precipitates and is removed by filtration. The water goes through a wastewater treatment plant. The acidification step leads to large quantities of waste water: 3.57 kg waste water/kg PEF. A large amount of heat is generated upon acidification which is directly re-used during the next step of drying, assuming a heat transfer efficiency of 70%.

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

the sodium salt of FDCA. After the electrochemical treatment, Na-FDCA is acidified with H₂SO₄, converting the salt into 2,5-FDCA and generating Na₂SO₄ as by-product. Upon acidification, 2,5-FDCA precipitates out and can be removed from the aqueous stream through filtration. The purified 2,5-FDCA solid is washed with water in washing drums to remove remaining impurities and finally it is sent to a dryer for complete removal of water.

2.3.3. PEF polymerization

Polymerization of PEF occurs via $n\text{FDCA} + n\text{EG} \rightarrow \text{PEF} + (2n-1)\text{H}_2\text{O}$. The current stage of development makes it difficult to estimate the required energy for polymerization. Research suggests a lower temperature and a faster operation time compared to conventional PET polymerization (Ma et al., 2012). However, because of insufficient data a more conservative method was chosen: PEF polymerization is estimated by assuming similar energy requirements as for the petrochemical polymerization of PET. Ecoinvent data (v3.3) on PET polymerization was modified to use in the baseline (see Table 2). Amorphous PET polymerization can be divided into two unit-processes: (1) esterification and (2) poly-condensation (PlasticsEurope, 2017). For polymerization, a molar ratio of 1:1 FDCA:MEG is applied.

2.3.4. Multifunctionality

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

From the TERRA reactor, we applied system expansion by

substitution for the output flows of H₂, Na₂SO₄, PG and the surplus of MEG; these by-products were modelled as avoided burdens. Specifically, the avoided processes are, based on Ecoinvent 3.3 data and PlasticsEurope data:

- H₂ based on hydrogen by steam reforming (Hydrogen (reformer) E, industrial data 2.0),
- Na₂SO₄ based on global production by three production routes: from natural occurring Na₂SO₄, as by-product of other processes and from industrial production (Mannheim process, sodium sulphate | market for | APOS, U),
- PG based on oxidation of propylene oxide (global market, Propylene glycol, liquid | market for propylene glycol | APOS, U).
- The surplus of EG is based on oxidation of ethylene oxide (global market, ethylene glycol | market for | APOS, U).

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

2.3.5. Biogenic carbon removal

In this study, biogenic carbon removed from the atmosphere during biomass cultivation is accounted for. The embedded biogenic carbon is calculated based on the molecular formulation of the polymer, which leads to 1.96 kg CO₂ eq./kg PEF. This approach maintains carbon balances by keeping track of the physical carbon flow in each substance flow within the cradle-to-gate boundaries. The approach is in line with e.g. the European Commission's Product Environmental Footprint, which states that bio-based carbon contained in products shall be deducted when calculating GHG emissions (European Commission, 2009), and with PAS

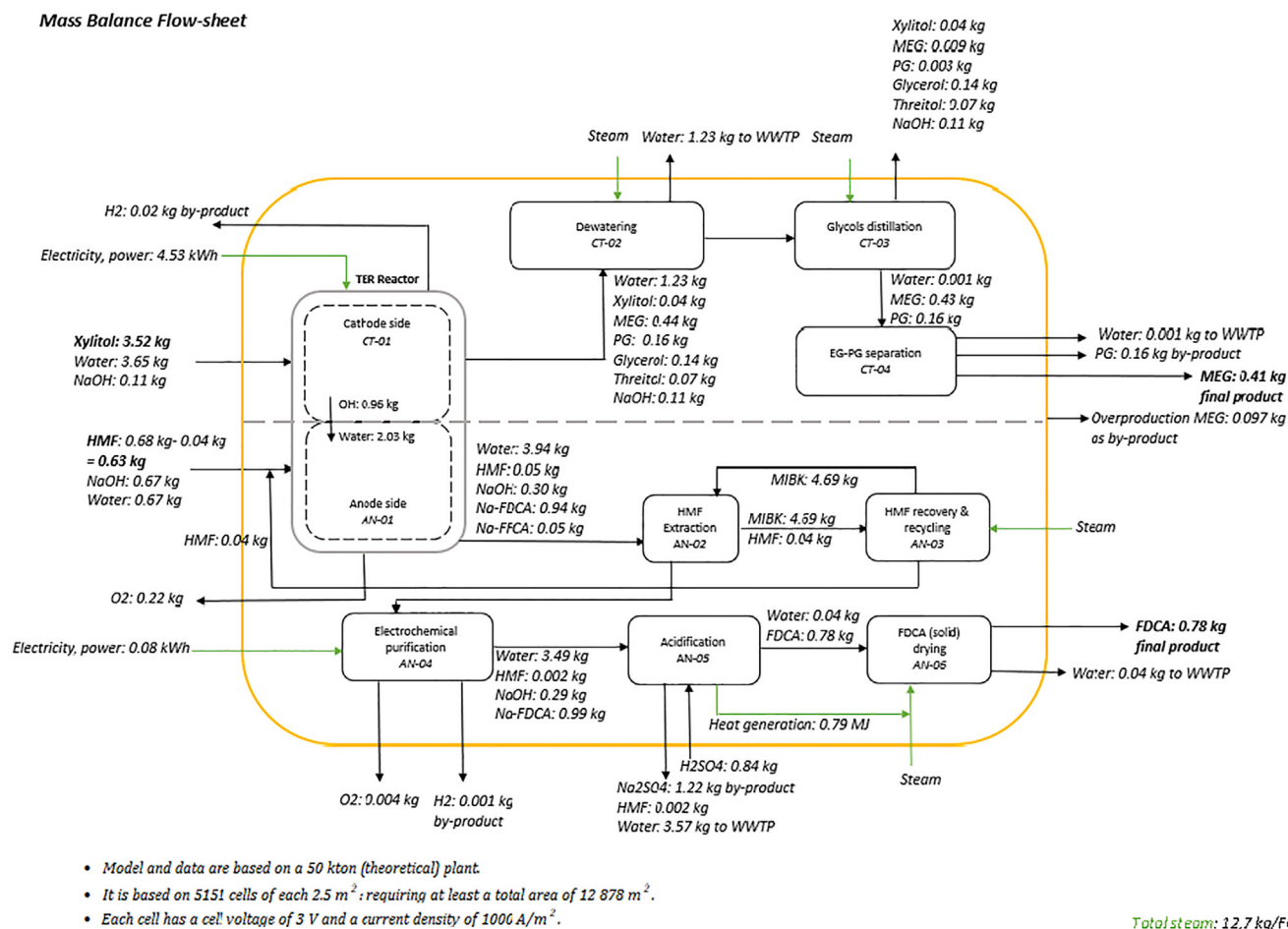


Fig. 3. Mass balance flow sheet of the TERRA process, all inputs and outputs are normalised to 1 kg of PEF. Green arrows represent energy-related streams (with a total of 12.7 kg/FU). See abbreviations explained in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2050 on carbon footprints, which states that carbon storage in products should be calculated based on the amount of carbon contained in the product (BSI, 2011). It has also been applied in other LCAs of bio-based materials (Broeren et al., 2017; Cok et al., 2014; Kim and Dale, 2008; Tsiropoulos et al., 2015; Vink and Davies, 2015). Note that carbon removed from the atmosphere can be emitted again if it is fully oxidized (as CO₂) during the product's end-of-life which is outside the scope of this paper. In addition, emissions caused by (indirect) land use change are not included. The results of GHG emissions (i.e. Climate change impact) in Section 3 are reported for both with biogenic carbon removals (the default) and also without (expressed as 'Gross GHG emissions').

3. Results

The cradle-to-gate environmental impacts of TERRA PEF for the five selected environmental impact categories are presented in Table 5. Fig. 4 shows the breakdown in life cycle stages and key processes. The TERRA process itself (both 2,5-FDCA and MEG production) is the most important contributor for all categories (63–88% of the impacts) except for land use, which is dominated by the agriculture phase attributed to the feedstock production (xylitol and 5-HMF). Land uses of corn production and wood production account for 65% and 30% of the total land use impact, respectively. In the other four impact categories, the feedstock production accounts for 10–35% of the total impacts. The production of 5-HMF contributes 17% and xylitol 13% to the total NREU impact. For acidification, the impact contributed by feedstock production is 34%: 5-HMF production accounts for 18% and xylitol production for 16%. The

Table 5
Cradle-to-factory gate environmental impact of 1 kg of TERRA PEF.

Impact category	Unit	Impact
Climate change	kg CO ₂ eq	4.2
of which:		-1.9
- Biogenic carbon removals		
- Gross GHG emissions w/o biogenic carbon removals		6.1
Non-renewable energy use	MJ	98
Freshwater eutrophication	g PO ₄ ³⁻ eq.	7.5
Terrestrial acidification	g SO ₂ eq.	39.8
Land use	kg Carbon deficit	15.5

environmental impacts of the polymerization step are insignificant (<5% of the total impacts). Since the TERRA process alone takes the lion's share of the impacts in the four categories, below in sections 3.1 and 3.2 the detailed interpretations of the NREU, the GHG emissions, the acidification and the eutrophication are presented.

3.1. NREU and GHG emission of the TERRA process

The results on 2,5-FDCA and MEG processing can be separately evaluated. The total electricity requirement of the TERRA reactor is partitioned between the cathodic and anodic side, based on the total output mass of the main products. Overall, a large part of the impacts is caused by the electrochemical reactor's electricity demand. However, 2,5-FDCA production contributes to more than half of the impacts (see Fig. 4). Downstream purification of 2,5-FDCA involves sophisticated

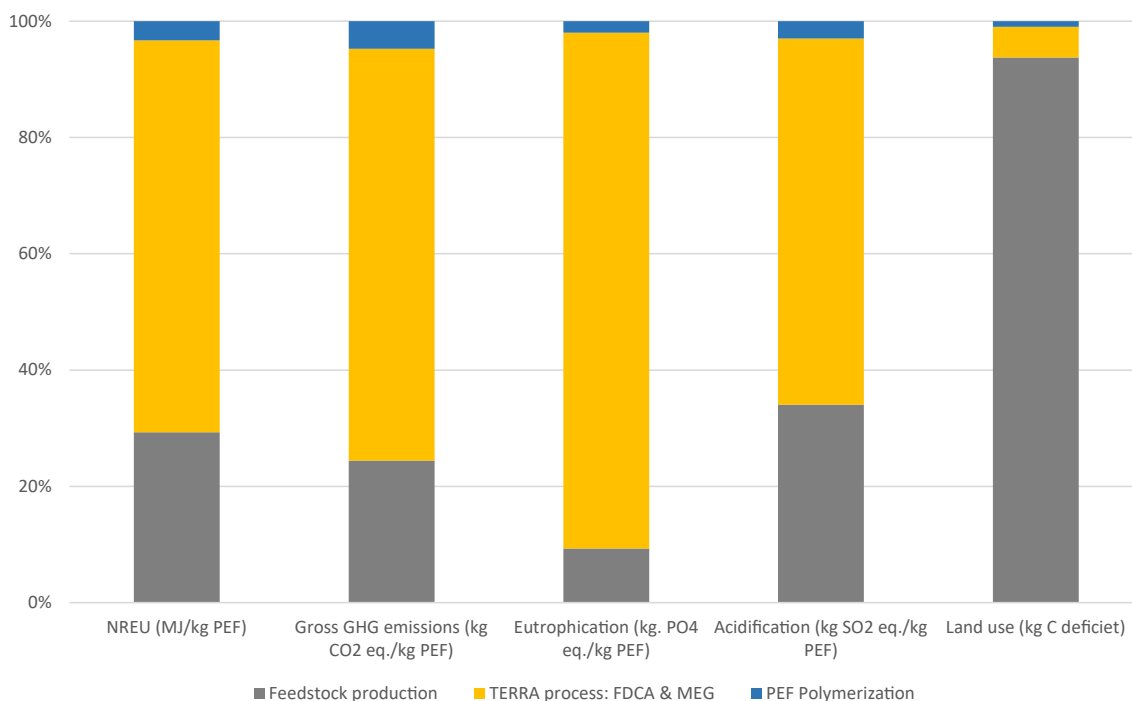


Fig. 4. Breakdown of Cradle-to-factory gate environmental impacts of 1 kg TERRA PEF polymer by production phases. “Gross GHG emissions” do not take into account biogenic carbon removal. “Net GHG emissions”, in which the biogenic carbon removals are accounted for, can be found in Table 5.

design and requires multiple steps, nonetheless, electricity use at the anode side dominates the impact: it accounts for nearly 70% of the NREU or 60% of the GHG emissions of 2,5-FDCA production. This is largely caused by a larger allocation factor, 66% is assigned to 2,5-FDCA, based on mass allocation. Allocation based on the physical relationship of energy/exergy does not apply here because both products are not energy products. The second biggest impact for 2,5-FDCA processing originates from the acidification step, it contributes 7% to NREU and 13% to GHG emissions impact. This impact is mainly caused by wastewater treatment (66% for NREU and 58% for GHG emissions).

The impact of MEG production shows a similar pattern (see Fig. 5): 57% of the NREU is attributed to the reactor itself, dominated by its electricity use. A substantial part (65%) of the impact is attributed to the heat requirements during recovery (dewatering 33% & glycol distillation 32%). Likewise, of the total gross GHG emissions related to MEG production, 74% results from the recovery steps (glycol distillation 50% and dewatering 24%, see Fig. 5c). Nearly half of the GHG emissions from the distillation process originate from steam production, which is based on combustion of natural gas. About 43% of the GHG emissions of the distillation step are caused by waste treatments (both waste water and hazardous waste incineration, see Fig. 5c). In terms of technological improvements, a higher selectivity towards EG/PG and therefore fewer by-products, could potentially mean a lower impact from the glycol distillation step. For example, by applying another electrode or improved reaction conditions within the process. Furthermore, increasing reactant concentration and reducing the amount of water in the system could positively impact the results.

3.2. Eutrophication and acidification of the TERRA process

The TERRA process plays a key role in the eutrophication (88%) and acidification (63%) impact of PEF (see Fig. 4). For both 2,5-FDCA and MEG production, wastewater treatments (WWT) during the purification and recovery phases contribute most substantially. WWTs account for 60% of the total cradle-to-factory gate eutrophication impact and for 24% to total acidification impact. In the case of acidification, the impact mainly originates from corn cultivation (ammonia as fertiliser), heat

production from coal and sulfur dioxide production (for xylose production).

Modelling wastewater treatment was based on background data from Ecoinvent, assuming an average Europe WWT plant. However, in order to treat such a large quantity of wastewater (approx. 5 kg wastewater/kg PEF), an on-site WWT facility built at the production site can be expected. This could lead to reduced impacts since wastewater from the TERRA process contains less complexed organic compounds compared to municipal wastewater. For a TRL 2–3 technology, a detailed design of an on-site WWT plant is beyond the scope. Nevertheless, some possibilities of process optimisation are explored in the Discussion Section 4.3.

4. Discussion

4.1. Future scenarios: renewable electricity

One of the core motivations of developing electrochemical process' is its accessibility to renewable electricity in the future. Within this study, future scenarios were developed to evaluate the environmental impact of the future TERRA PEF, increasing the share of renewable electricity in our electricity mix. Four different future electricity scenarios were based on the ambition of the 2019 Dutch Climate Agreement (Rijksoverheid, 2019) (see Table S1 for detailed scenarios). Two scenarios were developed for both near-term future 2030 and medium-term future 2050 (Capros, P., De Vita, A., Höglund Isaksson, L., Winiwarter, W., Purohit, P., Bottcher, H., ... & Witzke, 2013; European Commission, 2018; 2016; Government of the Netherlands, 2016; van den Hoven and Jacob, 2013). The selection of these years were based on (1) the full development of a low level technology to commercial scale, which will take at least 10 years, and (2) the milestones set by many climate policies and laws for 2030 and 2050 (Rijksoverheid, 2019).

The future electricity scenarios were directly applied to the electricity consumption of the TERRA reactor and indirectly to the electricity consumption for the production of NaOH. NaOH is the second largest NREU contributor to the TERRA reactor (Fig. 5). The assumptions of fuel mix and the updated LCA results are shown in Table 6. By 2050, the entire electricity grid of the Netherlands would become carbon neutral. As a

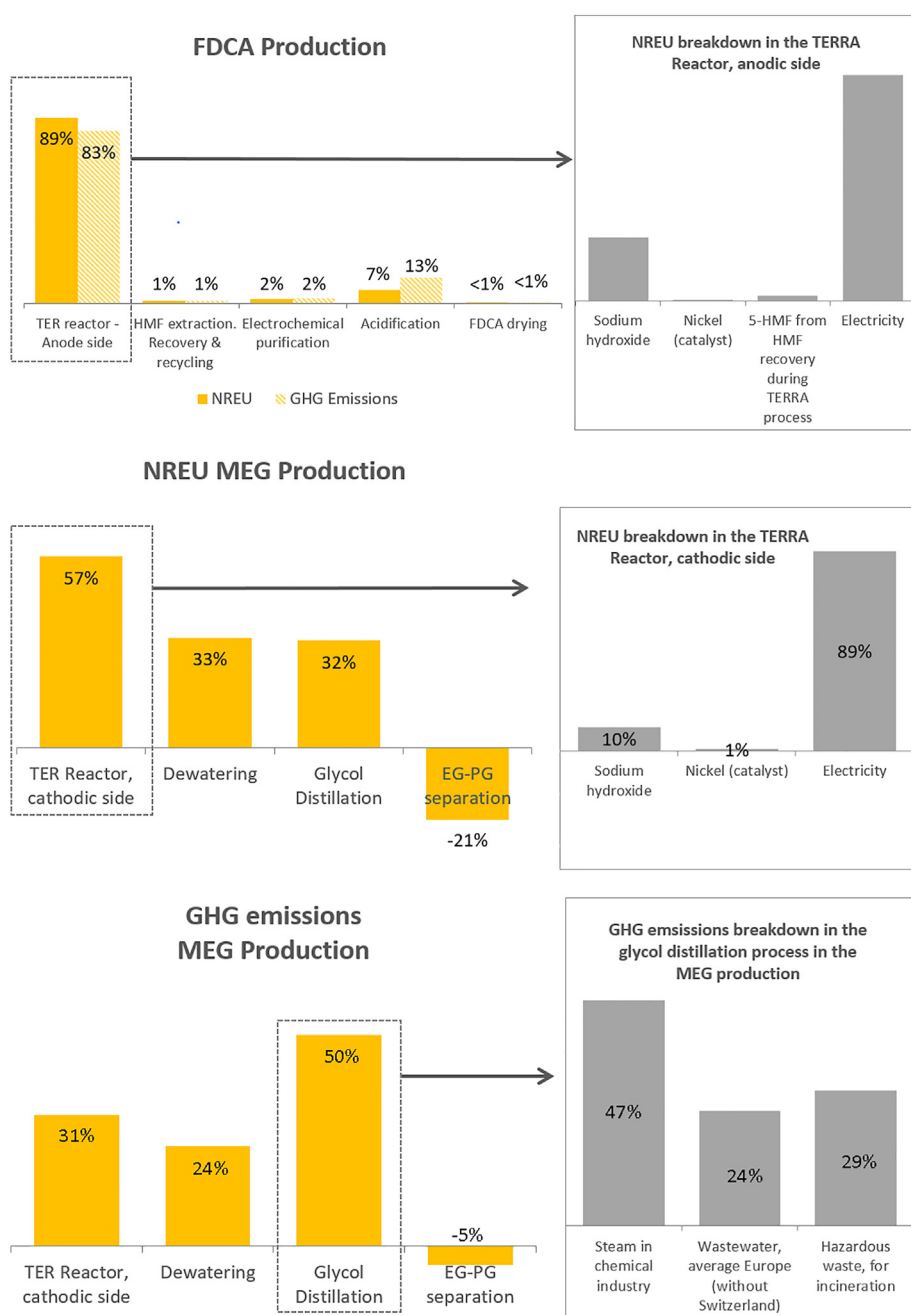


Fig. 5. Breakdown of NREU and GHG emissions of FDCA and MEG in the TERRA reactor (allocation based on the mass outputs). 5a (top): Breakdown for FDCA production in the TERRA process, on the left: contribution in percentage by the major processes; on the right: breakdown NREU of anodic side of TERRA reactor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

result, the impact of NREU of TERRA PEF would decrease to 46 MJ/kg PEF, representing a reduction of 53%. The impact of GHG emissions (including biogenic carbon removal) would decrease to 1.68 kg CO₂ eq., representing a total reduction of 60%.

4.2. Alternative allocation

Allocation strategies highly influence the results, especially in early-phase assessments. There are many uncertainties within the process and regarding products which are not embedded in the market yet. The baseline scenario adopted system expansion by substitution for H₂, Na₂SO₄, PG (propylene glycol) and the excess of EG (ethylene glycol) from the TERRA reactor. Approximately 28% of the total impact of the TERRA PEF (at the point of substitution) can be avoided by avoided burdens. Alternatively, if mass allocation is applied, it results in a substantial decrease of NREU impact by 39%. This decrease is mainly the

result of the relatively high co-production contribution of sodium sulphate. Per kg of PEF 1.22 kg of Na₂SO₄ is produced. Similarly, applying economic allocation results in an increase of NREU by 20%, mainly because FDCA is very valuable. Another allocation strategy can be applied to deal with side streams originally treated as waste in the baseline. Allocation by calorific values leads to a slight decrease of NREU by 6%. This strategy assumes waste within the TERRA process to be burned, including extra by-products (the polyol side stream with organic contamination, discussed in [Textbox 1](#)).

[Fig. 6](#) provides a summarized overview of the variation of the cradle-to-factory gate NREU of 1 kg TERRA PEF, resulting from future electricity scenarios, a different source of xylose with higher impact, and various allocation approaches adopted for the by-products from the TERRA process. It can be concluded that regardless of the data uncertainty and different choices of allocation approaches, the access to renewable electricity in the future is key to a successful sustainable innovation.

Table 6

Cradle to factory gate NREU and GHG emissions of TERRA PEF based on 4 future electricity scenarios in the Netherlands versus the 2018 baseline.

	2018 Baseline	2030 low ren: 23.5%	2030 high ren: 43.5%	2050 ren: 86%	2050 ren: 100%
<i>Total renewable share</i>	13.6%	23.5%	43.5%	86%	100%
<i>Emission factor (kg CO₂ eq./kWh)</i>	0.59	0.54	0.334	0.0275	0.0014
NREU of TERRA PEF (MJ/kg PEF)	98	83	70	59 MJ/kg	46 MJ/kg
(reduction compared to the baseline)		(↓15%)	(↓28%)	(↓39%)	(↓53%)
Gross GHG emissions of TERRA PEF (kg CO ₂ eq./kg PEF)		6.0	5.7	4.5	4.0
Net GHG emissions of TERRA PEF (kg CO ₂ eq./kg PEF), with biogenic carbon removal	4.2	4.0 (↓2.3%)	3.8 (↓6.2%)	2.7 (↓26%)	1.7 (↓34%)

4.3. Model uncertainties and limitations conceptual chain design

4.3.1. Biomass feedstock

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

In this study, the uncertainty of the impact of xylose is strongly influenced by the type of viscose production. Ecoinvent viscose production is modelled based on global average viscose process, whereas Viscose Austria (used in the baseline) is based on a state-of-the-art viscose

plant including an integrated pulp mill. It is highly optimized in terms of energy and material optimisation (Shen et al., 2010). Applying 4% economic allocation on viscose production using the Ecoinvent viscose dataset would result in a NREU of 27 MJ/kg xylose, a threefold higher impact compared to 8.5 MJ/kg xylose applied in the baseline. This will in turn lead to a significant increase of NREU by 21% for the TERRA PEF. Therefore, the source and production process of viscose is a sensitive assumption for the environmental impact of TERRA PEF.

Moreover, the sensitivity of the economic allocation factors was analysed. Based on the most recent available prices in 2018, a slightly higher allocation factor is obtained (6%), which leads to a slightly higher impact of xylose, namely, 12.95 MJ/kg xylose (vs. 8.5 MJ/kg xylose based on 4% allocation factor; see Fig. S1). However, the price fluctuations in xylose and viscose have insignificant effect on the total impact of TERRA PEF (e.g. less than 5% increase in NREU). It is concluded that the recent price fluctuation of xylose is not a sensitive parameter for the TERRA PEF.

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

4.3.2. TERRA technology

Potential environmental hotspots at this point of stage are (1) its electricity-use, which is one of the main contributors, (2) the complexity of purification and recovery steps, even though the TERRA cell simultaneously produces the two main products, and (3) the fossil-based heat used in the recovery and purification steps. In contrast, a powerful potential environmental advantage is the significant reduction in environmental impact when renewable electricity is used. Another potential

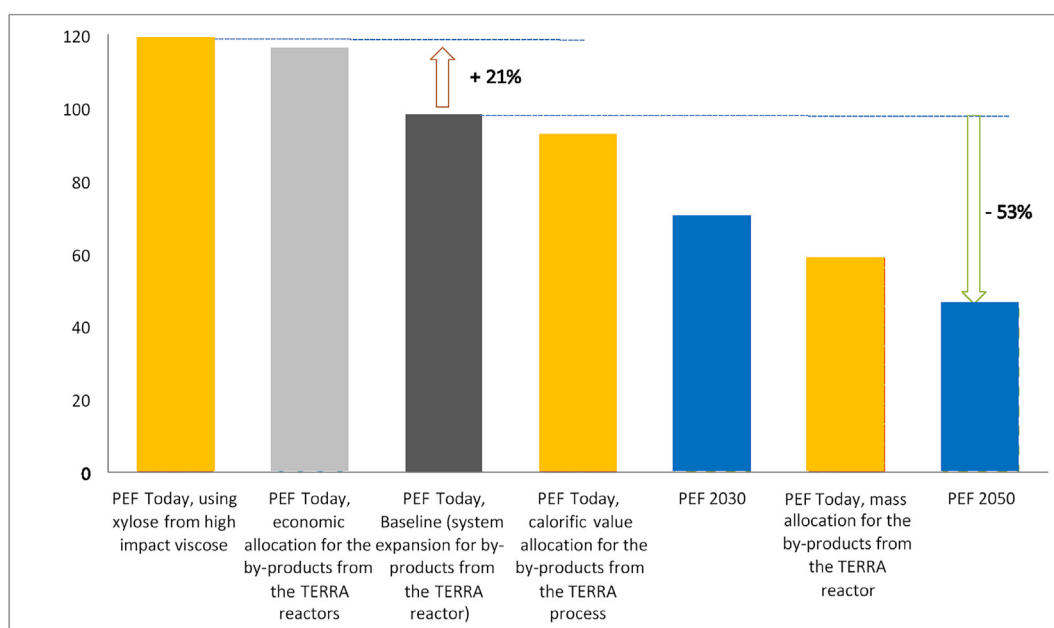


Fig. 6. Results on cradle-to-factory gate NREU (MJ/kg) of TERRA PEF based on different allocation approaches, future electricity mixes and a higher impact sourced xylose.

advantage is the use of electrochemical cells within the chemical industry, and in this case, to produce the monomers of the new polymer PEF. From the work that has been done, recommendations to decrease environmental impact would be to (1) increase selectivity of the electrochemical reactor in order to reduce the amount of by-products, (2) search for clean and affordable feedstock based on lignocellulosic biomass, and (3) reduce the amount of wastewater by reducing the total water required in the process or by recycling water in the system.

Carrying out an ex-ante LCA has given methodological insights. First of all, the use of TRLs to define an ex-ante LCA is very helpful and practical, and makes it easier to compare ex-ante LCAs in the future. The use of process design and simulation software to go from lab-scale to a theoretical pilot-scale is highly recommended in an early-stage assessment. In addition, it is recommended to apply different allocation strategies and sensitivity analyses. Modelling second generation biomass can involve many uncertainties and asks for creative solutions (4.3.1). At last, besides GHG emissions and NREU impact, this study once again stresses the need to include more impact categories. Apart from the five categories included in the study, at least assessing its water footprint would be recommended in future research.

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

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

4.4. Comparing TERRA PEF with other reported LCA for PEF

Very little research is done on the environmental impact of PEF, even though PEF has gained much interest and is regarded as a very promising polymer. There are different routes to produce the FDCA and EG building-blocks (Hwang et al., 2020), the present study is the first to

report on the environmental impact of an electrochemical route. Eerhart et al. (2012) reported a cradle-to-factory gate LCA of a partly bio-based PEF obtained from 2,5-FDCA sourced from first generation biomass (corn) and fossil and bio-based based MEG. The study analysed a chemical conversion of corn-based fructose into Furanics to produce hydroxymethylfurfural (HMF) and the air oxidation of HMF to FDCA (Eerhart et al., 2012). Just recently a LCA report of the Joint Research Center (EU science hub) (Nessi et al., 2020) was published for a cradle-to-grave impact of 100% bio-based PEF. It was also an early-stage assessment. It assumed sugarcane for bio-MEG production and a mix of maize, wheat and potatoes for FDCA production. Conversion of HMF into FDCA was based on an oxidation process of p-xylene conversion in PTA production (Nessi et al., 2020). Fig. 7 shows the comparison of the LCA results from the three studies, including the present one.

The three studies differ substantially in terms of their LCA results. Both Eerhart et al. (2012) and this study reported the significant contribution from biomass production, whereas the JRC report identified the thermochemical conversion to play a dominant role (see Fig. 7). This leads to a mixed conclusion when PEF based on the thermochemical route is compared with PET. PEF could offer nearly 50% impact reduction based on Eerhart et al. (2012), or could lead to a three-fold increase in environmental impacts according to the JRC report (Nessi et al., 2020). Eerhart et al. (2012), included a CHP for onsite power and heat. The CHP for burning humins, a process residue, made the process self-sufficient in terms of energy, and thus significantly reducing PEF's primary energy requirements.

The impacts of the electrochemical PEF identified by this study land somewhere in between (see Fig. 7), with a somewhat higher impact compared to the current petrochemical PET, but substantially lower than the impacts reported by the JRC report (which is also an ex-ante LCA). Climate impact of PET and bio-PET (30% bio-based) ranges from 3,9 kg CO₂ eq./kg polymer (PET) to 1.9–2.6 kg CO₂ eq./kg polymer bio-PET (bio-based MEG made from sugarcane) (Shen et al., 2012; Tsiropoulos et al., 2015). However, on a kilogram basis PET and PEF are not comparable; it has not the same full functionalities such as barrier properties and thermal properties. Although the electrochemical conversion has the advantage of relying on electricity and the cell is highly efficient as it produces simultaneously two products, the downstream purification steps still consume a large amount of heat, similar to many thermochemical processes. Nevertheless, PEF is not a fully commercialized product; it is *not* yet able to compete with PET, whose production and supply chain have been optimized over many decades. The large differences observed from literature should not be interpreted black and white. These studies should be used to provide directions on future development to reduce the impacts and support responsible innovation.

5. Conclusions and recommendations

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

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

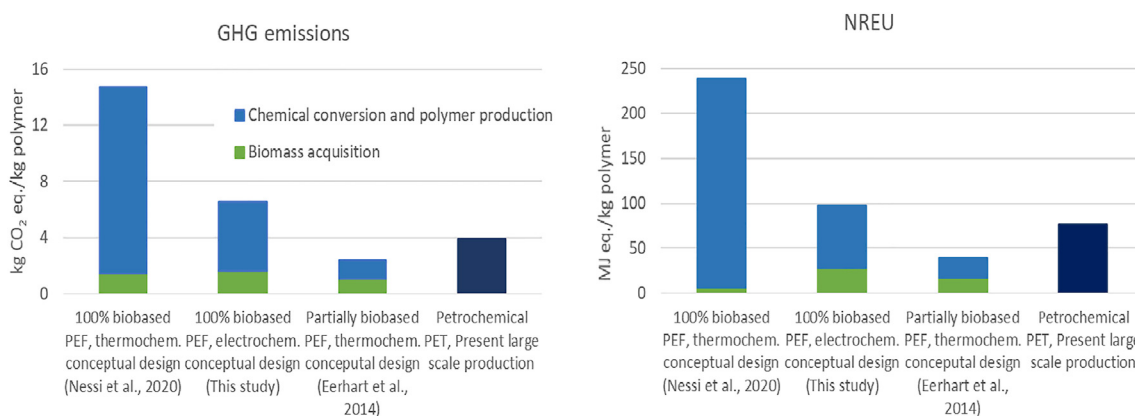


Fig. 7. Cradle-to-factory gate results on NREU and GHG emissions of 1 kg PEF reported in different LCA studies (Eerhart et al., 2012; Nessi et al., 2020), this study and compared with those of PET (PlasticsEurope, 2017; Shen et al., 2012). Impact from Nessi et al. (2020) was taken up to cradle-to-gate to harmonize results. To further harmonize the different results on PEF, the net GHG emissions are displayed, including the carbon credits from biogenic carbon storage.

electrochemical reactor could benefit greatly from a transition towards renewable electricity in the future.

Different allocation strategies, especially for the impact of xylose/xylitol, affect the LCA results significantly. However, they do not change the overall conclusions on the identified environmental hotspots (i.e. electricity use). In this study, xylitol was used as a model compound to approximate the mixed hemicellulose sugars. Shifting toward lignocellulosic biomass to produce glucose could replace corn feedstock for 2,5-FDCA production and a mixed C5/C6 sugar (side) stream from the hemicellulose fraction could be used for hydrogenation-hydrogenolysis to produce MEG. Future research should focus on clean and affordable hemicellulose sugars to replace xylitol.

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

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

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

Conflicts of interest

There are no conflicts to declare.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was in collaboration with Copernicus Institute of Sustainable Development, Van't Hoff Institute of Molecular Sciences and Avantium B.V. Special thanks to all authors. Special thanks to Li Shen for all her time and support. The project aimed at supporting the Horizon 2020 project TERRA: Tandem Electrocatalytic Reactor for energy/Resource efficiency And process intensification.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cesys.2021.100036>.

References

- Aeschelmann, F., Carus, M., 2015. Biobased building blocks and polymers in the world: capacities, production, and applications—status quo and trends towards 2020. *Ind. Biotechnol.* 11, 154–159. <https://doi.org/10.1089/ind.2015.28999.fae>.
- Broeren, M.L.M., Zijp, M.C., Waaijers-van der Loop, S.L., Heugens, E.H.W., Posthuma, L., Worrell, E., Shen, L., 2017. Environmental assessment of bio-based chemicals in early-stage development: a review of methods and indicators. *Biofuels, Bioprod. Biorefin.* 11, 701–718. <https://doi.org/10.1002/bbb.1772>.
- Buchner, G.A., Stepputat, K.J., Zimmermann, A.W., Schomäcker, R., 2019. Specifying technology readiness levels for the chemical industry. *Ind. Eng. Chem. Res.* 58, 6957–6969. <https://doi.org/10.1021/acs.iecr.8b05693>.
- Burgess, S.K., Leisen, J.E., Kraftschik, B.E., Mubarak, C.R., Kriegel, R.M., Koros, W.J., 2014. Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). *Macromolecules* 47, 1383–1391. <https://doi.org/10.1021/ma5000199>.
- Buyle, M., Audenaert, A., Billen, P., Boonen, K., Van Passel, S., 2019. The future of ex-ante LCA? Lessons learned and practical recommendations. *Sustain* 11, 5456. <https://doi.org/10.3390/su11195456>.
- Capros, P., De Vita, A., Höglund Isaksson, L., Winiwarer, W., Purohit, P., Bottcher, H., et al., 2013. EU Energy, Transport and GHG Emissions Trends to 2050-Reference Scenario 2013. European Union. <https://doi.org/10.2833/17897>.
- Chheda, J.N., Román-Leshkov, Y., Dumesic, J.A., 2007. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.* 9, 342–350. <https://doi.org/10.1039/b611568c>.
- CIRFS European man-made fibres association, 2016. World man-made fibres production. <https://www.cirfs.org/KeyStatistics/WorldManMadeFibresProduction.aspx> accessed 3.6.20.
- Cok, B., Tsiropoulos, I., Roes, A.L., Patel, M.K., 2014. Succinic acid production derived from carbohydrates: an energy and greenhouse gas assessment of a platform chemical toward a bio-based economy. *Biofuels, Bioprod. Biorefin.* 8, 16–29. <https://doi.org/10.1002/bbb.1427>.

