Supplementary Information

Chapter 2 – 5

Environmental footprints of bio-based products for the chemical industry

Emma Anna Roosje Zuiderveen

Promotoren:
Prof. dr. M.A.J. Huijbregts
Dr. ir. R. van Zelm

Copromotoren:
Dr. S.V. Hanssen
Dr. S. Sala (Joint Research Center, Italië)

Manuscriptcommissie:
Prof. dr. B. Wicke
Prof. dr. Y. van der Meer (Maastricht University)
Dr. ir. B.R.P. Steubing (Universiteit Leiden)

Content

Chapter 2

Supplementary Information S2

Supplementary Information

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

Emma A. R. Zuiderveen[1,2*], Koen J. J. Kuipers[1], Carla Caldeira[2], Steef V. Hanssen[1], Mitchell K. van der Hulst[1,3], Melinda M.J. de Jonge[1], Anestis Vlysidis[2,4], Rosalie van Zelm[1], Serenella Sala[2], Mark A. J. Huijbregts[1,3]

[1] Department of Environmental Science, Radboud Institute for Biological and Environmental Sciences, Radboud University Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands.
[2] European Commission, Joint Research Centre, Via Enrico Fermi 2749, 21027, Ispra, VA, Italy.
[3] Department of Circularity & Sustainability Impacts, TNO, Princetonlaan 6, 3584CB Utrecht, The Netherlands
[4] School of Chemical Engineering, National Technical University of Athens, Iroon Polytechneiou 9, Zografou, 15780 Athens, Greece

Contents

Abbreviations

BBP	Bio-based products
GHG	Greenhouse gas
LCA	Life Cycle Assessment
LMM	Linear mixed-effects model
LUC	Land Use Change
NREU	Non Renewable Energy Use
RR	Response Ratio
TRL	Technology Readiness level

Arithmetic average	*The ratio of the sum to the total number*
Predicted mean	*The mean calculated by running LMM*

S.1 Methods: Decision Trees

The screening and inclusion of prospective LCAs followed two criteria. For the first criteria, we followed the decision tree in Figure S.1.1 on the scope, quality and clarity of the study. For the second criteria, we followed the decision tree in Figure S.1.2.

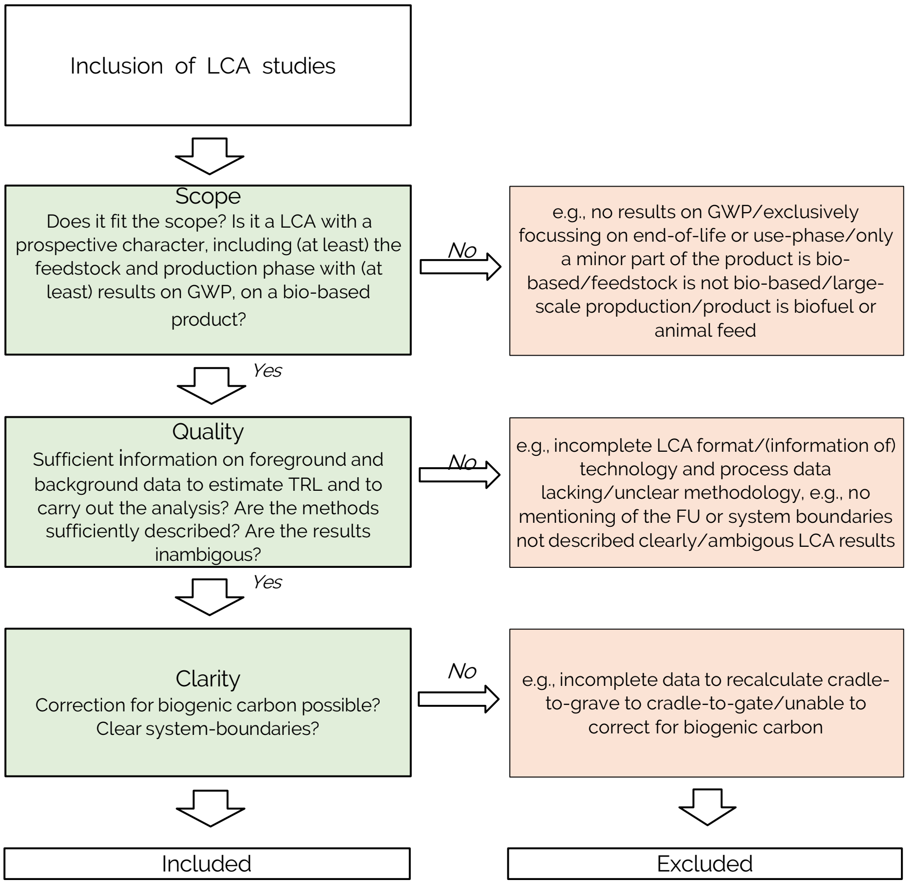

Figure S.1.1*: Decision tree study selection related to the scope of the study. Furthermore, if the quality and/or clarity was lacking the study had to be excluded as well.*

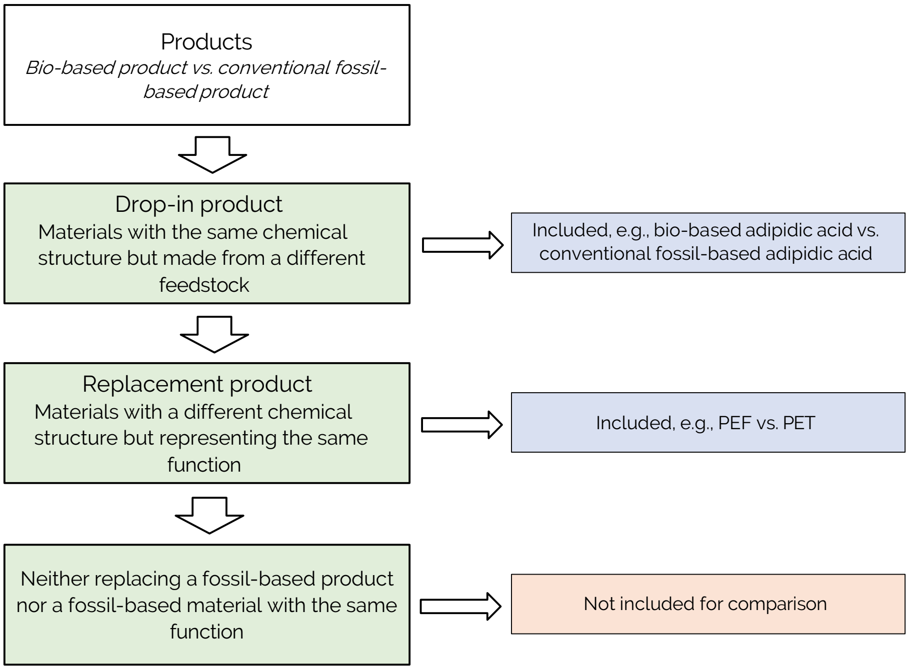

***Figure S.1.2**: Decision tree on products to include in the comparative assessment. The bio-based product is a 'drop-in' of a fossil-based product, meaning it has the same chemical structure, or it can be compared to a fossil-based product which has the same function*

S.2 Methods: Overview TRLs

Only in a few cases the TRL was addressed by the study itself. The TRL evaluation was therefore based on the TRL specification from Moni et al. (2020)[1] and afterwards regrouped into broader category classes (TRL 1-3, TRL 4-5, TRL 6-9). Studies directly based on lab- or experimental data were assigned 'TRL 1-3'; studies based on simulations of the process, including downstream steps, were assigned 'TRL 4-5'; and studies in pilot phase or operating under expected conditions were assigned 'TRL 6-9'.

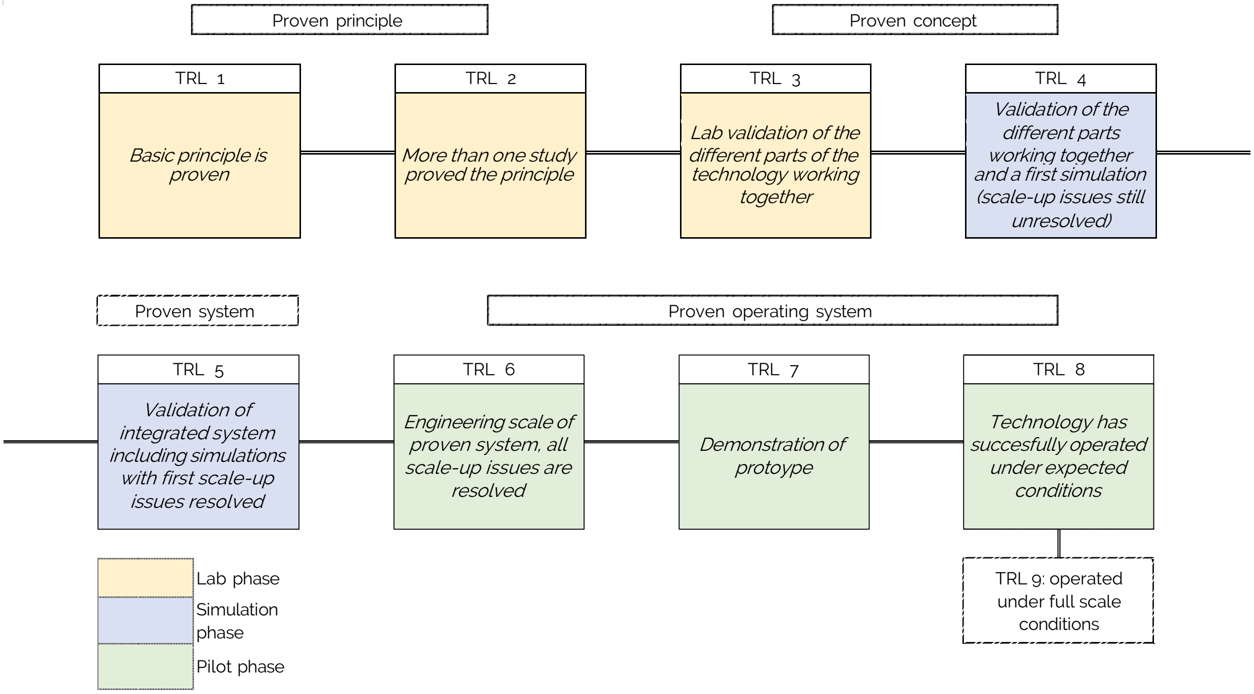

Figure S.2: *Description of TRLs (Technology Readiness Level) as applied in this study*

S.3 Arithmetic average RRs per bio-based product with corresponding 95% CI: ordered from largest reduction to highest increase.

Table S.3*: overview of the bio-based products, the number of data points (n), the arithmetic average RR and 95% CI; if n = 1, there is no 95% CI, which is indicated with 0; *indicates the bio-based product with their average and 95% CI below zero.*

Bio-based product	n	Arithmetic average (RR)	Lower end 95% CI	Higher end 95% CI
WOOD FIBRE/PLA/TPS BIOCOMPOSITE	1	-2.75	0.00	0.00
WOOD FIBRE/PLA BIOCOMPOSITE	1	-2.64	0.00	0.00
SPIRO-BISPHENOL	1	-1.87	0.00	0.00
BOPLA	3	-1.69	-2.06	-1.32
1,3-PROPANEDIOL	4	-1.68	-2.34	-1.02
3-HYDROXY PROPIONIC ACID	1	-1.55	0.00	0.00
BIOLUBRICANT	1	-1.54	0.00	0.00
POLYLIMONENE CARBONATE	1	-1.52	0.00	0.00
HEXANOIC ACID	4	-1.48	-1.66	-1.31
BIOPOLYETHYLENE/BAGASSE FIBERS BIOCOMPOSITE	2	-1.35	-1.36	-1.33
DIOL V	1	-1.30	0.00	0.00
POLYLACTIDE	1	-1.28	0.00	0.00
BIOPOLYMER	1	-1.23	0.00	0.00
WAX ESTERS	1	-1.19	0.00	0.00
ADIPIC ACID	5	-1.17	-1.76	-0.58
NANOCELLULOSE (MICROFIBRILLATED CELLULOSE (MFC))	6	-1.13	-1.93	-0.32
POLYOLS	3	-1.09	-1.33	-0.85
POLYESTER BINDERS	2	-1.09	-1.36	-0.81
WHEAT-GLUTEN-BASED PACKAGING FILM	1	-1.01	0.00	0.00
CELLULOSE NANOWHISKERS	2	-1.01	-3.15	1.13
LACTIC ACID	18	-0.97	-1.64	-0.29
AROMATICS	5	-0.96	-2.61	0.69
FLAX MAT/PLA BIOCOMPOSITE LAMINATES	1	-0.93	0.00	0.00
PEF	3	-0.92	-1.99	0.14
LINSEED OIL/FLAX FIBRE/MMP BIOCOMPOSITE	1	-0.92	0.00	0.00
3-PROPANEDIOL	1	-0.91	0.00	0.00
POLYITACONIC ACID	2	-0.90	-1.40	-0.41
SPIROCYCLIC DIOL	1	-0.89	0.00	0.00
1,3-BUTADIENE	6	-0.85	-1.24	-0.46
LEVOGLUCOSAN	1	-0.84	0.00	0.00
EPOXY RESIN SUPERSAP	3	-0.83	-0.90	-0.76
PP	3	-0.80	-2.01	0.40
ISOBUTANOL	2	-0.80	-1.17	-0.44
ETHYLENE	13	-0.79	-1.28	-0.30
BIOETHANOL-BASED PVC	1	-0.79	0.00	0.00
FORMIC ACID	3	-0.77	-1.25	-0.29
CURAUÁ/PP COMPOSITE	1	-0.76	0.00	0.00
PROPYLENE GLYCOL	3	-0.75	-1.71	0.21
2,3-BUTANEDIOL	4	-0.70	-0.81	-0.60
PE	1	-0.70	0.00	0.00
MULCH FILM	3	-0.68	-0.79	-0.57
1,4-BUTANEDIOL	2	-0.66	-0.82	-0.50
ALKYL POLYGLYCOSIDES	1	-0.64	0.00	0.00
STARCH-FILLED POLYPROPYLENE	2	-0.64	-0.65	-0.63
LIGNIN POWDER	1	-0.64	0.00	0.00
PLA	5	-0.60	-1.08	-0.12

CURED WOOD FLOORING COATING	1	-0.60	0.00	0.00
PROPIONIC ACID	6	-0.59	-0.78	-0.40
TEREPHTHALIC ACID	3	-0.57	-1.34	0.21
LACTIDE	8	-0.53	-0.56	-0.50
ACETONITRILE	1	-0.52	0.00	0.00
OLEFINS	1	-0.52	0.00	0.00
SODIUM POLYACRYLATE (NA-PA)	2	-0.50	-0.52	-0.48
SUCCINIC ACID	21	-0.47	-0.97	0.02
PSA BIOADHESIVE	1	-0.47	0.00	0.00
ETHYL LACTATE	2	-0.46	-0.83	-0.09
PHA	11	-0.45	-0.77	-0.13
POLYETHYLENE	1	-0.44	0.00	0.00
N-VINYL-2-PYRROLIDONE	4	-0.41	-0.50	-0.32
POLYURETHANE FOAM (PUF)	4	-0.41	-0.54	-0.28
PU FOAMS	1	-0.37	0.00	0.00
PHB	8	-0.34	-0.85	0.16
FDCA	1	-0.32	0.00	0.00
PHB/KENAF COMPOSITE	1	-0.30	0.00	0.00
CAPROIC ACID	3	-0.28	-0.60	0.03
ALGINATE-BASED PLASTIC	1	-0.27	0.00	0.00
PHENOLIC	1	-0.27	0.00	0.00
P-XYLENE	2	-0.27	-1.84	1.30
HDPE	6	-0.23	-0.48	0.01
PAG BIOADHESIVE	1	-0.22	0.00	0.00
MODAL ANTI BACTERIAL FABRIC	2	-0.22	-0.32	-0.12
BIOFILM	1	-0.19	0.00	0.00
BUTYLCATECHOL	1	-0.19	0.00	0.00
LLDPE	2	-0.18	-0.95	0.58
EPOXIDIZED SUCROSE SOYATE COMPOSITES	1	-0.17	0.00	0.00
LDPE	2	-0.17	-0.90	0.56
1,3-DIHYDROXYACETONE	3	-0.12	-0.46	0.22
SOY BIOADHESIVE	1	-0.04	0.00	0.00
HEXAMETHYLENEDIAMINE	12	-0.03	-0.10	0.05
ISOBUTENE	3	-0.02	-0.36	0.31
TANNIN BIOADHESIVE	1	0.03	0.00	0.00
KETONE WAX	1	0.04	0.00	0.00
PET	9	0.05	-0.06	0.16
METHANOL	2	0.10	-1.69	1.90
PBS	7	0.11	-0.22	0.43
PHLA	1	0.16	0.00	0.00
ACETONE	2	0.19	-0.14	0.52
2-METHYL TETRAHYDROFURAN	3	0.22	-0.19	0.63
MANGO KERNEL STARCH FILM	1	0.24	0.00	0.00
POLY(LACTIC ACID)/CELLULOSE NANOCRYSTAL/LIMONENE	1	0.34	0.00	0.00
NANOFIBRILLATED CELLULOSE (NFC)-REINFORCED EPOXY	1	0.49	0.00	0.00
NANOCELLULOSE YARN	1	0.55	0.00	0.00
MYCOBAMBOO	1	0.74	0.00	0.00
BACTERIAL CELLULOSE (BC)-REINFORCED EPOXY COMPOSITES	1	0.81	0.00	0.00
SCG/PBS COMPOSITE	1	0.89	0.00	0.00
METAL WORKING FLUIDS (MWF)	2	1.02	-1.90	3.93
CNC FOAM	1	1.05	0.00	0.00
LIGNIN BIOADHESIVE	2	1.37	0.76	1.98

S.4 Additional calculations in ‘Greenhouse gas Footprints’

Table S.4: *additional GHG emission calculations in the section ‘Greenhouse gas Footprints’.*

	GHG emissions (Gt CO2 eq./yearly)	**Percentage of global emissions yearly**	*Source*
Total GHG emissions globally	52	100%	Ritchie, H. and M. Roser. CO_2 and Greenhouse Gas Emissions. *Our World in Data* (2020)[2]
Total GHG emissions Plastics (fossil-based)	1.8	3.4%	Zheng, J. & Suh, S. Strategies to reduce the global carbon footprint of plastics (2019)[3]
Total GHG emissions Primary Industry (based on the six main platform chemicals)	0.91	2%	Galán-Martín, Á. *et al.* Sustainability footprints of a renewable carbon transition for the petrochemical sector within planetary boundaries (2021)[4]
	Ethylene	**Butadiene**	**Plastics**
Total amount produced yearly (kg)	2.01E11	1.2E10	-
GHG emissions fossil-based cradle-to-gate (kg CO2 eq. /kg chemical)	1.45	1.2	-
Bio-based potential reduction	57% (95% CI: 32, 73%)	57% (95% CI: 37, 71%)	38% (95% CI: -23, 50%)
% of GHG emissions primary industry / global	**18.3% / 0.3%**	**0.9% / 0.02%**	**- / 1.32%**
Calculation	$\frac{(RP_{BBP} \cdot GHG_{fossil}) \cdot T_{product}}{GHG_{total}} \cdot 100$ $with\ RP_{BBP}\ as\ biobased\ product\ reduction\ potential;\ GHG_{fossil}\ as\ GHG\ emissions\ fossilbased\ product;$ $T_{product}\ as\ total\ amount\ produced\ (kg/year);\ GHG_{total}\ as\ total\ GHG\ emissions\ (Primary\ Industry/Global)$		
Sources	Reduction potentials taken from S.1 and Figure 2a; Levi, P.G. and J.M. Cullen. 2018. Mapping Global Flows of Chemicals: From Fossil Fuel Feedstocks to Chemical Products[5]; Ecoinvent Centre. Ecoinvent database (Version 3.7)[6].		

S.5 Predicted mean reduction (RR) and 95% CI for GHG emissions per product category, feedstock category and TRL based on single linear mixed-effect models

Table S.5*: Change in GHG footprint response ratios (RR) of bio-based products in comparison to fossil-based counterfactual in relation to key parameters: product category, feedstock category and TRL category (corresponding to Fig. 2 in the main text). Here, predictions with corresponding 95% confidence intervals are in percentages.*

	n	Prediction [95% CI]
Product category		
Bioadhesive	13	-19% [-52% to 35%]
Biochemical	135	-46% [-56% to -35%]
Biocomposite	17	-50% [-68% to -22%]
Biofiber	11	-53% [-75% to -12%]
Biopolymer	91	-38% [-50% to -24%]
Biorefinery	19	-73% [-84% to -55%]
Feedstock category		
3rd generation feedstock	4	7% [-56% to 161%]
Agricultural & forestry residues	89	-51% [-59% to -38%]
Waste streams	61	-33% [-48% to -14%]
Pure feedstock (1st generation)	96	-49% [-58% to -38%]
Pure feedstock (2nd generation)	36	-50% [-62% to -34%]
TRL		
TRL 1-3	71	-38% [-51% to -21%]
TRL 4-5	142	-41% [-51% to -29%]
TRL 6-9	46	-58% [-69% to -44%]

S.6 Predicted mean RR and 95% CI for the GHG emissions and if it in- or excluded Land Use Changes (LUC) related GHG emissions based on single linear mixed-effect models.

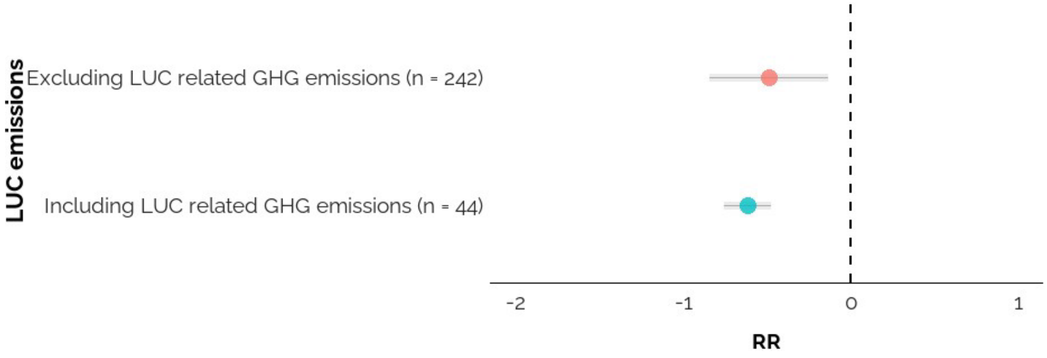

Figure S.6*: LMM on relationship RR GHG emissions and studies either in- or excluding LUC. Average estimate including LUC is -46% (95% CI: 38, 53%) and excluding LUC is -39% (95% CI: 13, 57%). Omnibus F:0.44, p-value: 0.51.*

S.7 Predicted mean RR and 95% CI per feedstock category based on single linear mixed-effect models for eutrophication, acidification, non-renewable energy-use, ozone depletion and photochemical ozone formation impacts.

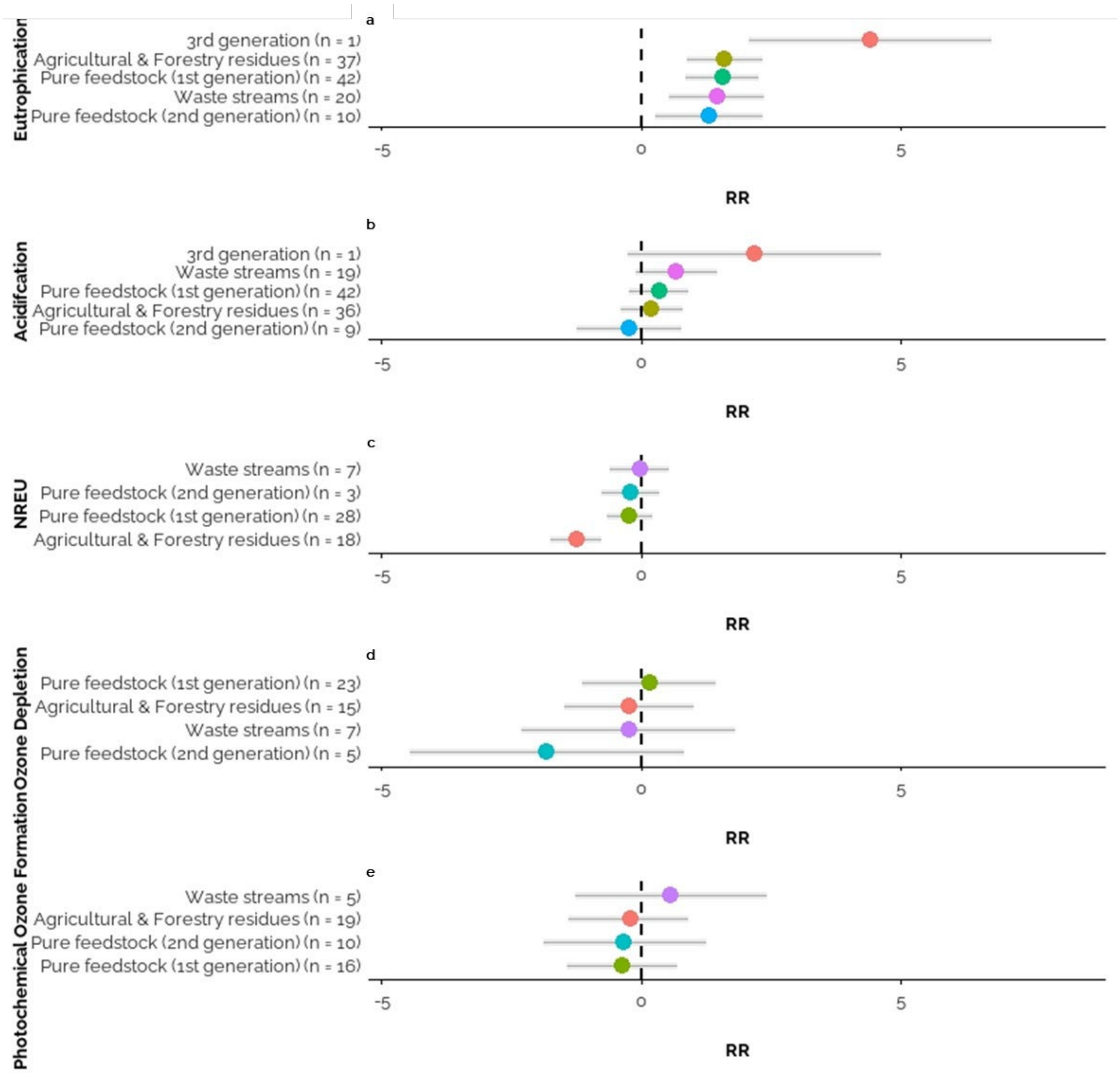

Figure S.7*: LMM on relationship RR environmental footprints and feedstock category: (a) Eutrophication: omnibus F: 1.58, p-value: 0.19; (b) Acidification: omnibus F: 1.08, p-value: 0.37; (c) NREU: omnibus F: 7.32, p-value: 0.0006*; (d) Ozone Depletion: omnibus F: 0.65, p-value: 0.59; (e) Photochemical Ozone Formation: omnibus F: 0.25, p-value: 0.85. *For NREU, the feedstock category as single effect proved significant, but due to the low number of data points for each category we consider this result highly uncertain.*

S.8 Predicted mean RR and 95% CI per product category based on single linear mixed-effect models for eutrophication, acidification, non-renewable energy-use, ozone depletion and photochemical ozone formation impacts.

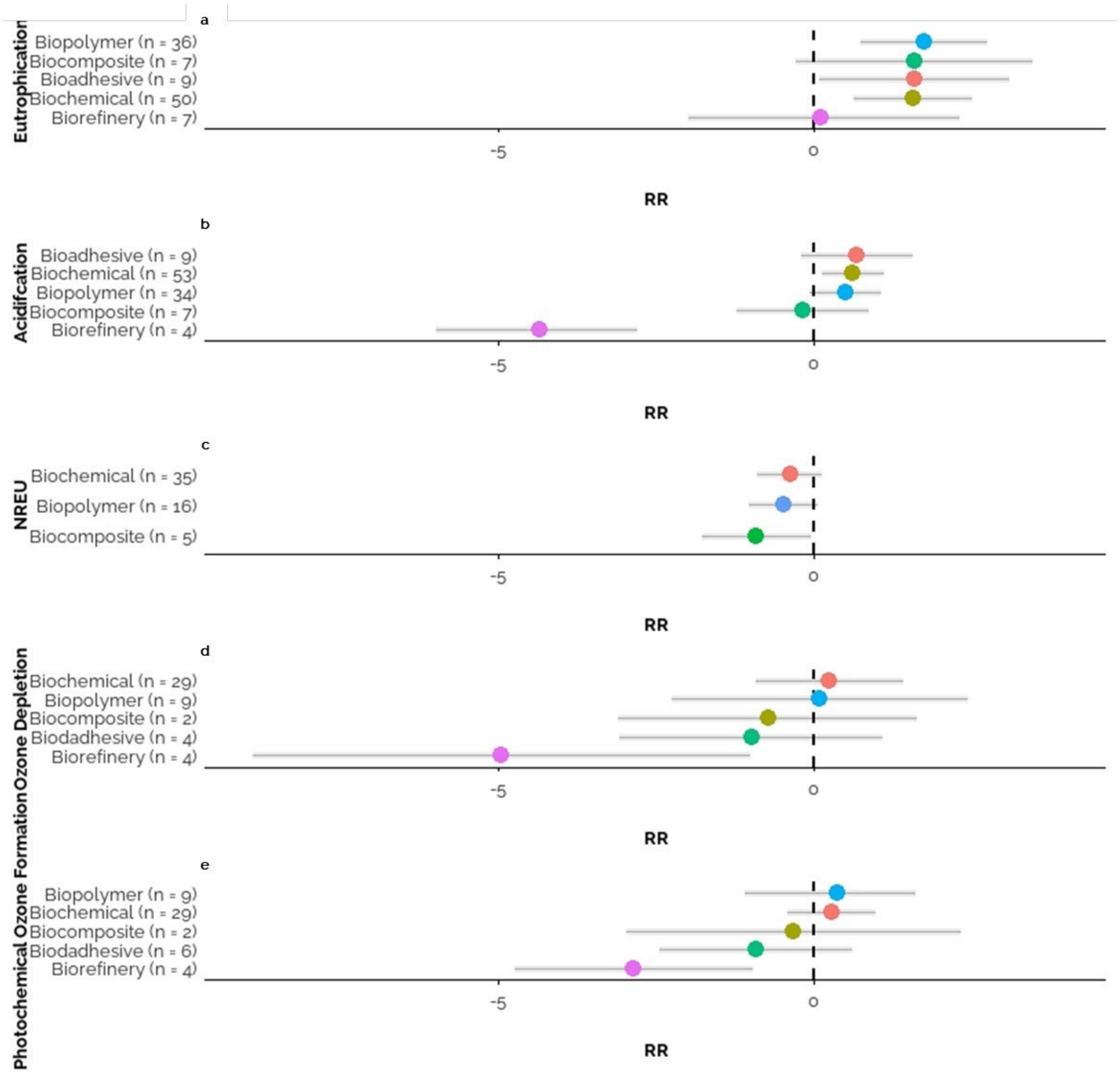

Figure S.8: *LMM on relationship RR environmental footprints and product category: (a) Eutrophication: omnibus F: 0.46, p-value: 0.76; (b) Acidification: omnibus F: 9.08, p-value: 2.20E-05*; (c) NREU: omnibus F: 0.50, p-value: 0.61; (d) Ozone Depletion: omnibus F: 1.44, p-value: 0.26; (e) Photochemical Ozone Formation: omnibus F: 2.62, p-value: 0.047*.*

S.9 Overview of arithmetic average RRs and corresponding 95% CI for greenhouse gas emissions, eutrophication, acidification, non-renewable energy-use, ozone depletion and photochemical ozone formation impacts

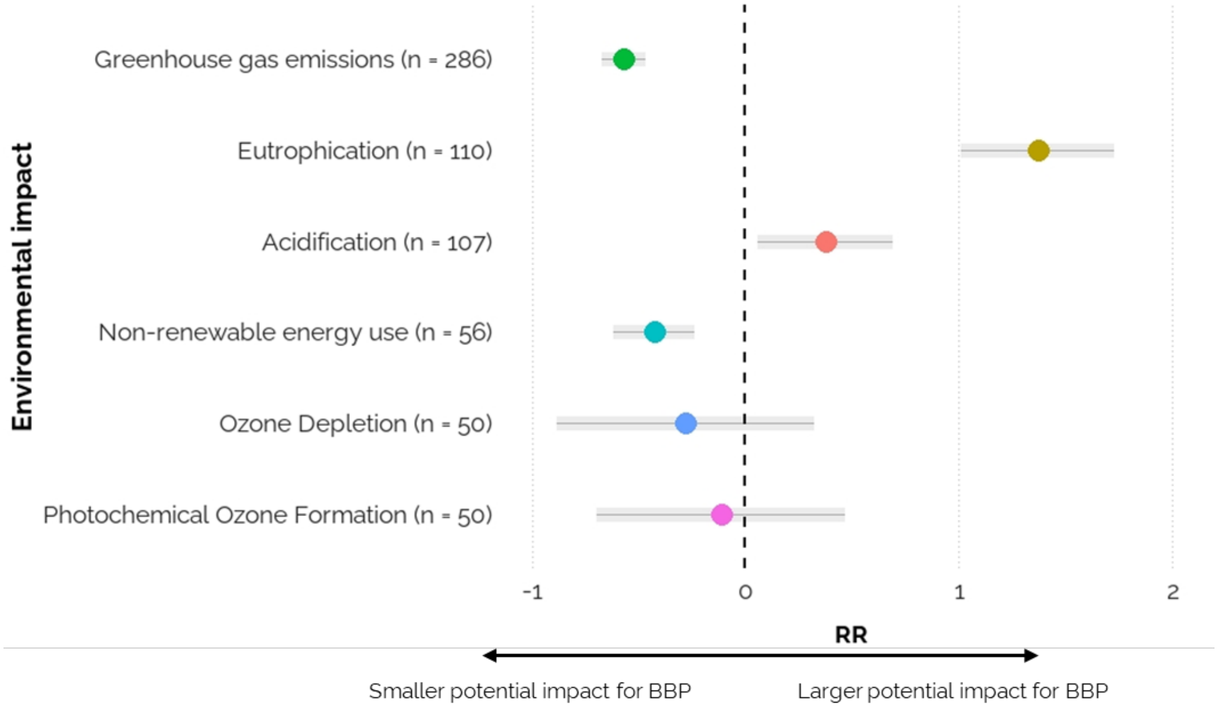

Figure S.9: *Plot showing overall* ***arithmetic averages*** *and 95% CI of GHG, Eutrophication, Acidification, NREU, Ozone Depletion and Photochemical Ozone Formation impacts. Both arithmetic averages and predicted mean RRs from LMM (Figure 3 in the main text) show the same trends. In percentages, on average the GHG footprint is reduced with 43% (95% CI: 37, 49%), eutrophication is increased with 293% (95% CI: 175, 464%), acidification is increased with 45% (95% CI: 6, 99%), NREU is reduced with 35% (95% CI: 21, 46%), ozone depletion is reduced with 24% (95% CI: -59, 38%) and photochemical ozone formation is reduced with 11% (95% CI: -50, 60%).*

S.10 Overview of the predicted mean and 95% CI of the RRs across all product types and studies for all environmental impacts with n ≤ 30. Separate random-effects models were ran for each impact category.

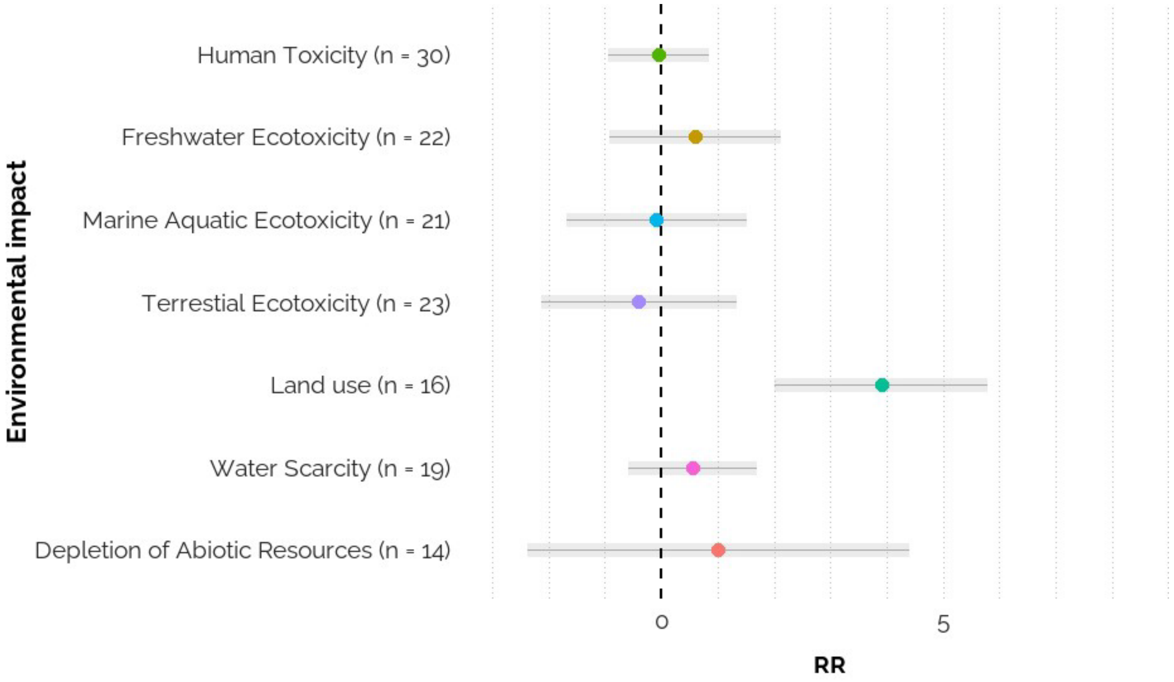

Figure S.10*: plot showing predicted mean and 95% CI of the other environmental impacts' RRs (with n ≤ 30) collected from the 130 studies (Human Ecotoxicity, Freshwater Ecotoxicity, Marine Aquatic Ecotoxicity, Land Use, Water Scarcity, Depletion of Abiotic Resources).*

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Chapter 3

Supplementary Information S3

Supplementary Information

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

Emma A. R. Zuiderveen[1,2*], Davide Ansovini[3], Gert-Jan M. Gruter[3,4], Li Shen[5]

[1] Department of Environmental Science, Radboud Institute for Biological and Environmental Sciences, Radboud University Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands.
[2] European Commission, Joint Research Centre, Via Enrico Fermi 2749, 21027, Ispra, VA, Italy.
[3] Avantium, Zekeringstraat 29, 1014 BV, Amsterdam, the Netherlands
[4] Van't Hoff Institute of Molecular Sciences, University of Amsterdam, P.O. Box 94720, 1090 GS, Amsterdam, the Netherlands
[5] Copernicus Institute of Sustainable Development, Utrecht University, Heidelberglaan 8, 3584 CS, Utrecht, the Netherlands

Contents

S1 Life cycle inventory

S1.1 5-HMF (hydroxymethylfurfural) from corn fructose

From corn to glucose

As shown in **Figure 2**, 5-HMF is made via dehydration of fructose which is obtained from corn glucose. The harvested corn is processed in a wet-milling plant to extract starch. The decision for wet-milling to process starch instead of dry-milling is based on the fact that the latter produces a lower purity starch compared to the former. Higher purity is more suitable to produce a high purity glucose. Corn starch is further converted into sugars (dextrose or glucose) by enzymatic hydrolysis (Tsiropoulos et al., 2013).

LCA results reported by Tsiropoulos, Cok, & Patel (Tsiropoulos et al., 2013) of glucose production from European corn were used in the baseline model for NREU and GHG emissions including corn cultivation, wet-milling and glucose production (**Table 3**). Their study was based on Ecoinvent 2.2 data aiming to evaluate NREU and GHG emissions for corn production in Europe. Results on acidification, eutrophication and land use were not reported. Therefore, literature data(Chheda et al., 2007; Hobbs, 2009; Vink and Davies, 2015) and ecoinvent data were used for the assessment of the three missing impact categories for processes of corn cultivation, wet milling and dextrose/glucose production. All data is represented in **Table 3**.

From glucose to fructose

In order to obtain fructose (90% High Fructose Corn Syrup, HFCS-90), the glucose stream goes through isomerization (to an equilibrium fructose: glucose 42:58 mixture), refining and evaporation stages. Chromatographic separation is used to separate the fructose from most of the glucose (Hobbs, 2009). The steps to purify the sugar stream are rather difficult to assess because of lack of literature data. A similar approach as described in earlier LCA research (Eerhart et al., 2012) on PEF production was therefore adopted. Only the most energy intensive step during the corn sweetener refining step is assessed: evaporation of water after isomerization and separation. Previous research suggests a NREU of 3.9 MJ per kg fructose (Eerhart et al., 2012); input modelling was based on natural gas (30.3 MJ/kg).

Dehydration of fructose to 5-HMF

5-HMF is not a bulk chemical and the LCA data in literature is scarce. 5-HMF can be obtained by selective dehydration of fructose/HFCS-90 (HFCS 90% fructose). For this study, the dehydration of 5-HMF is based on a process described by Roquette and Dumesic (Chheda et al., 2007). Based on the published data, dehydration of fructose to 5-HMF requires 1.65 MJth/kg 5-HMF final energy (heat duty and reboiler duty). It should be noted that this energy requirement does not include phase separation nor production purification due to unavailable information. This thermal energy is assumed to be supplied by a natural gas boiler. In the dehydration step, a conversion efficiency of 95% and a selectivity of 89% lead to 1.83 kg of fructose to produce 1 kg of HMF. The solvents used during the process are methyl isobutyl ketone (MIBK)/2-butanol/DMSO but are assumed without losses. Working with a biphasic system modified with DMSO to dehydrate fructose to HMF has not been proven economically feasible (Chheda et al., 2007). The feasibility of the choice of the solvents is further discussed in section 4.2. For this study it has only served as a simplified model.

S1.2 Production of xylitol from xylose

All four fibres are produced from wood pulp using classical or modified viscose production (i.e. Modal) with xylose as one of the by-products from the pulping process. Viscose Austria and Modal Austria, produce viscose via an integrated plant including both pulp and fibre production. It is highly optimized in terms of energy and material (re-)use. For Viscose Asia, the process heat and power supply were largely based on coal and no pulp mill integration with the fibre production is present (Shen et al., 2010). Xylose as a by-product of the Lenzing Viscose Austria process, has the lowest impacts and is therefore used as baseline for the NREU and GHG emissions in our study. However, data on eutrophication, acidification and land use impact are largely missing. These impact categories will be approximated by using Ecoinvent data (3.3) and by applying economic allocation (4% for xylose). **Figure S1** provides the overview of xylose data used in the baseline analysis.

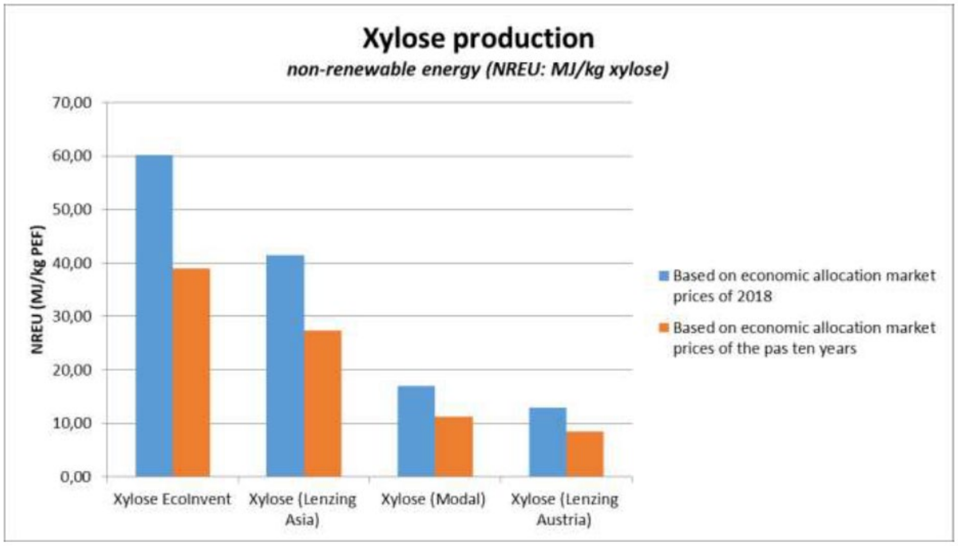

Figure S1: impacts of the four viscose LCA datasets, comparing Xylose Ecoinvent data, xylose Lenzing Asia, Xylose Modal and Xylose Lenzing Austria.

S2 Sensitivity Analyses

S2.1 Share of renewable electricity, different scenarios

Table S1: Share of renewable electricity, different scenarios.

Grid electricity mix	**2018 Baseline**	**2030 low ren: 23.5%**	**2030 high ren: 43.5%**	**2050 ren: 86%**	**2050 ren: 100%**
Coal	42.5%	38%	18%	0%	0%
Natural gas	35.2%	35%	35%	3%	0%
Nuclear	8.7%	3.5%	3.5%	11%	0%
Offshore wind	0.5%	8%	18%	35%	35%
Onshore wind	7.1%	8%	11%	19%	20%
Solar	0%	2%	6%	13%	35%
Hydropower	4.6%	1.5%	1.5%	9%	10%
Other renewables	4.6%	5%	7%	10%	0%

S2.2 Waste water treatment modelling – extra note

A pilot project at DuPont (plastic and fiber plant) in 2001 to recycle wastewater, aiming at closing the water cycle, has been successful in reducing wastewater by 90%. A three-step treatment system was applied: the purified water could then be re-used in the factory. They used an (1) alternating aerobic anoxic sludge process (N and P elimination), (2) ultra-filtration membrane system (suspended solid elimination) and (3) hyper filtration (nitrate, chloride and sulfate reduction)(Dohmann et al., 2001). However, an in-depth study to set up and calculate wastewater recycling of TERRA wastewater is well beyond the scope of this project. Nonetheless, it shows there are definitely options to reduce the impact of eutrophication and acidification when wastewater is treated and re-used.

S2.3 Separation of HMF from DMSO – extra note

Separating HMF from DMSO by distillation will lead to the intensification of the carbon emission of HMF. However, studying again Dumesic's research on 5- HMF production and the use of dimethyl sulfoxide (DMSO) and MIBK/2-butanol as solvents, they suggest low-temperature separation processes such as vacuum evaporation or vacuum distillation for HMF purification in this biphasic system (Chheda et al., 2007).

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Chapter 4

Supplementary Information S4

Supplementary Information

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

Emma A. R. Zuiderveen[1,2], C. Caldeira[2], T. Vries[3], N.J. Schenk[3], M.A.J. Huijbregts[1,4], S. Sala[2], S.V. Hanssen[1], R. van Zelm[1]

[1] Department of Environmental Science, Radboud Institute for Biological & Environmental Sciences, Radboud University, Nijmegen, the Netherlands
[2] European Commission, Joint Research Centre, Via Enrico Fermi 2749, 21027, Ispra, VA, Italy
[3] BioBTX, Zernikelaan 17, 9747 AA, Groningen, The Netherlands
[4] Department of Circularity & Sustainability Impacts, TNO, Princetonlaan 6, 3584CB Utrecht, The Netherlands
E-mail contact: emma.zuiderveen@ru.nl

1. **Materials & methods**

1.1 BioBTX

The BTX production pathways (Figure 1 in the main text) from both mixed plastic waste and biomass is based on the Integrated Cascading Catalytic Pyrolysis process developed by BioBTX, a pilot-company located in the Netherlands. Firstly, the feedstock is the thermally cracked; secondly, the pyrolysis vapours are catalytically converted to BTX; thirdly, the BTX is separated and collected. BioBTX' primary data is based on a capacity of 48 kt feedstock/year and includes the core technology and downstream steps (BioBTX, 2022).

1.2 Carbon accounting

The system boundary was set to cradle-to-grave with an incineration end-of-life scenario based on the chemical structure of BTX. The fossil carbon content can therefore lead to an additional 3.36 kg CO_2 eq./kg BTX (Table S.1). In the case of bio-BTX, the additional CO_2 emissions were considered neutral. This was justified following the biogenic global warming potential (GWP_{bio}) approach by Cherubini et al. (2011) and allocating temporary carbon storage in bio-products based on Guest et al., (2013), where biogenic carbon can be considered neutral, because both the crop rotation period and the storage period in the technosphere are short. This method accounts for the fate of the carbon embedded in the end products.

Table S.1: data on carbon content BTX and related emissions

	Chemical formula	Molar weight (g/mol)	CO_2 emissions related to carbon content
Benzene	C_6H_6	78.11	3.38 kg CO_2
Toluene	C_7H_8	92.14	3.35 kg CO_2
Xylene	C_8H_{10}	106.16	3.32 kg CO_2

1.3 Allocation

Figure S.1 indicates the points of allocation in the MPW- and bio-BTX pathways. Table S.2 is an overview of the different allocation factors including calculations.

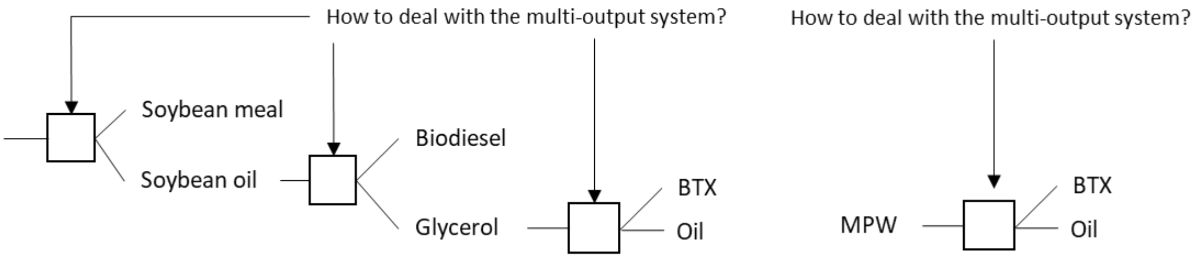

Figure S. 1: overview of points of allocation in both MPW- and bio-BTX pathways.

Table S. 2: allocation factors for mass, economic and energy allocation. Fossil-BTX production is based on economic allocation only, due to the aggregated dataset in Ecoinvent, see 1.1.6 for more information. MPW = Mixed Plastic Waste; LHV = Lower Heating Value; BTX = benzene-toluene-xylene.

	Products	Calculation	Allocation factor
Mass allocation	MPW BTX	m_p / m_t	BTX: 0.69 Oil: 0.31
	Bio BTX	m_p / m_t	Meal: 0.19 Oil: 0.81 Biodiesel: 0.90 Glycerol: 0.10 BTX: 0.48 Oil: 0.52
Energy allocation	MPW BTX	m_{px} LHV / ($m_{p1,2,3}$ $LHV_{p1,2,3}$) LHV BTX: 40.5 LHV natural gas: 47.1 LHV light fuel oil: 43	BTX: 0.67 Oil: 0.33
	Bio BTX	m_p LHV / ($m_{p1,2}$ $LHV_{p1,2}$) LHV BTX: 40.5 LHV biodiesel: 43.5 MJ/kg LHV glycerol: 18 MJ/kg LHV Soybean meal: 15.4 MJ/kg LHV Soybean oil: 37 MJ/kg	Meal: 0.64 Oil: 0.36 Biodiesel: 0.96 glycerol: 0.04 BTX: 0.46 Oil: 0.54
Economic allocation	MPW BTX	m_p $Price_p$ / ($m_{p1,2,3}$ $Price_{p1,2,3}$), prices taken from 2011-2022 with the exception of bio-oil, data was available for 2011, 2018, 2019, 2020. 1. Bio-oil price 2. Bio-oil as light fuel oil price	1. BTX: 0.33 Oil: 0.67 2. BTX: 0.79 Oil: 0.21
	Bio BTX	m_p $Price_p$ / ($m_{p1,2,3}$ $Price_{p1,2,3}$), prices taken from 2011-2022 with the exception of bio-oil, data was available for 2011, 2018, 2019, 2020. 1. Bio-oil price 2. Bio-oil as light fuel oil price m_p $Price_p$ / ($m_{p1,2}$ $Price_{p1,2}$) for glycerol and biodiesel (2011-2021)	Soybean oil: 0.34 Soybean meal: 0.66 Biodiesel: 0.93 Glycerol: 0.07 1. BTX: 0.16 Oil: 0.84 2. BTX: 0.59 Oil: 0.41

1.4 Distillation

An additional distillation step is applied to the crude BTX output, based on a simplified distillation step. Calculations are based on Piccinno et al., (2016), sum over each of the three chemicals is taken:

$$Q_{distillation} = \frac{C_p * m_{mix} * (T_{boil} - T_0) + \Delta H_{vap} * m_{dist} * (1.2 * R_{min} + 1)}{\eta_{heat} - 0.1} \qquad (1)$$

where C_p is the specific heat capacity, m_{mix} and m_{dist} the mass of the mixture and distillate, T_{boil} the boiling point and T_0 the room temperature, ΔH_{vap} the enthalpy of evaporation, R_{min} the minimum reflux ratio (set to 1, due to lack of information), and η_{heat} the heating efficiency is, heating losses are assumed to be 31% (Piccinno et al., 2016).

1.5 Evaluating emerging technologies

Here, we follow the framework of van der Hulst et al., (2020) based on three successive steps to evaluate technology maturing up to industrial scale. The upscaling involves both technical aspects as well as adjustments to background processes. The steps are shown in Table S.3.

Table S. 3: stepwise approach for technology maturing. TRL = Technology Readiness level; MPW = Mixed Plastic Waste; ICCP = Integrated Cascading Catalytic Pyrolysis; SSP = Shared Socioeconomic pathway.

Steps	**Modelled changes**	**Current scale (2022)**	**Commercial scale (base scenario; 2022)**	**Industrial scale (2050)**	**Fossil-based production (2022, 2050)**
Phase I: definition TRL stage	Technical Development	TRL 7	TRL 9	TRL 9	TRL 9
	Feedstock	Biomass, MPW	Biomass, MPW	Biomass, MPW	Oil, naphtha
	Technology	ICCP	ICCP	ICCP	Catalytic reformate & steam cracking
Phase II: process changes, size scaling and process synergies	Process changes	-	Including downstream steps, increased yield and energy input	Increased energy efficiency based on a generic energy reduction rate of 1% per year (Bazzanella and Ausfelder, 2017; Blok, 2004; IEA et al., 2013)	-
	Product scaling	0.8 kton/year	48 kton/year	Since the FU is formulated as "1 kg of BTX production" and assuming linear size scaling, interventions remain the same.	-
	Process synergies: *Heat recovery &*	-	An on-site gas system is	An on-site gas system is	-

	Reduction of waste streams		proposed producing electricity with waste gasses: • A boiler with Elec_{eff} of 28% is applied (U.S. Department of Energy, 2016)	proposed producing electricity with co-produced gasses: • A boiler with Elec_{eff} of 28% is applied (U.S. Department of Energy, 2016)	
Phase III: industrial learning and external developments	Changes to background processes	-	Electricity market of 2020 (Ecoinvent, 2020)	Electricity market of 2050 (Mendoza Beltran et al., 2020), based on narrative: • SSP2 RCP2.6 (baseline) • SSP2 RCP4.5 • SSP2 RCP1.9	Same as industrial scale BTX production
		-	End of life processing. • C-loss: burned or waste to energy: 100%	Plastic flows, SSP2 RCP 2.6 baseline scenario for 2050 (Stegmann et al., 2022) • C-loss: Burned or waste to energy: 13% • C-stock: Landfill, chemical and mechanical recycling: 87%	Same as industrial scale BTX production

1.6 Electricity use in fossil-BTX pathway

The Ecoinvent 3.8 datasets on naphtha-based BTX is formatted as a unit process, therefore "electricity" as input from the technosphere is not indicated as such. For this reason, the electricity use could not be automatically adapted to the future electricity market dataset. Table S.4 includes the total electricity for fossil-BTX which was separately assessed.

Table S. 4: total electricity use in fossil-BTX process, to adapt to a electricity market of 2050. Data on primary energy and share of electricity is taken from the original PlasticsEurope data documentation (PlasticsEurope, 2013).

	Primary energy (MJ)	Share electricity of total energy demand (%)	Share mass (%)	Total electricity in MJ per kg BTX
Benzene	80.3	0.5	48	0.19
Toluene	65.7	0.3	33	0.07
Xylenes	67.6	1	19	0.13

1.7 Impact assessment PB-LCIA

In the following section the PB-LCIA impact assessment is discussed step by step, with a summary in Table S.5. The LCI elementary flows are converted into impacts on the Safe Operating Spaces (SOS) of the Planetary Boundaries (PB) by multiplying the flows with characterization factors (1) taken from Ryberg et al. (2018). For the missing CFs on biosphere integrity, the approach of Galán-Martín et al. (2021) was adopted.

The transgression level is defined as the impact of the product in relation to the safe operating space of the PB (2). This involves downscaling, i.e. allocating, the safe operating space to the level of BTX production (3). This is done based on the sharing principle 'equal per capita', assuming it is fair to share equally among the population. To then translate one's personal share of SOS to the chemical BTX, allocation was based on economic value. This based on the assumption that a higher economic value promotes well-being and therefore should result in a larger share of the SOS. For more explanation on the transgression level definitions, read Tulus et al. (2021).

Furthermore, the life cycle impact assessment requires a continuous input, because PBs are expressed in annual threshold levels (Steffen et al., 2015). Therefore, the functional unit should include a time dimension (kg/year; Ryberg et al., 2018). In our case this is defined as total annual BTX production (in weight). However, this cancels out in the formula 3 and 4.

(1) $\mathrm{IMP}_{b,\,BTX} = \sum LCI_{e,BTX}\; CF_{eb}$

(2) $\mathrm{TL}_{b,\,BTX} = \frac{IMP_{b,BTX}}{sos_{b,BTX}}$

(3) Based on equal per capita approach and gross value added: $\mathrm{sos}_{b,\,BTX} = \frac{SOS_b}{pop^{TOT}}\, pop_{btx}\, \frac{GVA_{BTX}}{GVA^{TOT}}$

Combining (2) and (3) gives:

(4) $\mathrm{TL}_{b,\,BTX} = \frac{IMP_{b,BTX}\; GVA^{TOT}}{SOS_b\; price_c}$

$LCI_{e,BTX}$ is a LCI elementary flow e in BTX production, CF_{eb} is the characterization factor for the LCI elementary flow *e* linked to PB *b* (for an overview of the PBs, see Table S.3). The characterization factors are taken from Ryberg et al. (2021, 2018), see Supplementary-file S.2. The pop^{tot} represents the total population and pop_{btx} the population that benefits from BTX production, which was assumed equal in this case. The GVA_{BTX} is the gross value added associated with BTX, GVA^{TOT} is the total gross value added of the world.

Table S. 5: AESA methods and definitions, summary of Planetary Boundary concepts and the PB-LCIA method.

Planetary Boundary (PB)	**Control Variable (CV)**	**Safe Operating Space (SOS)**
Climate change	Atmospheric CO2 concentration (ppm) Energy imbalance at top-of-atmosphere (W m^{-2})	72 1
Stratospheric ozone depletion	Stratospheric O3 concentration (DU)	15

Ocean acidification	Carbonate ion concentration (Ωarag)	0.69
Biogeochemical flows	Global: P flow from freshwater to ocean (Tg P yr^{-1}) Global: biological fixation of N (Tg N yr^{-1})	6.6 62
Land-system change	Global: area (%) of original forest cover	25
Freshwater use	Global: maximum consumptive blue water use (km^{3}yr^{-1})	4000
Biosphere integrity	Biodiversity intactness (% BII loss)	10

PB-LCIA

Method	Characterization-based: CFs linking LCIA to PBs (Ryberg et al., 2021, 2018). Additionally, for biosphere integrity, CF is based on the approach of Galán-Martín et al. (2021), build on work from Hanafiah et al. (2012) and updated using Wilting et al. (2017) and GLOBIO 3.5 MSA values (Schipper et al., 2016).
Sharing Principle	Equal per capita (EPC) and gross value added (GVA)
Equation PB-LCIA	$IMP_{pb,BTX} = \sum_{e \in E} LCI_{eBTX} CF_{epb} \quad , \qquad \forall pb \in PB,$ *where* $IMP_{pb,BTX}$ *is the impact of the production of BTX (per FU) related to the planetary boundary (pb), where PB is the total of all the planetary boundaries,* LCI_{eBTX} *is the life cycle inventory elementary flow e (expressed over time) associated with BTX production,* CF_{epb} *is the characterization factor (CF) that maps the elementary flow e onto the control variable.*
Equation transgression level	$TL_{pb,\, BTX} = \frac{IMP_{pb,BTX}\; GVA^{TOT}}{SOS_{pb}\; price_c}$ *where* $IMP_{pb,BTX}$ *is the LCI impact mapped onto the control variable (CV) of planetary boundary pb. The* GVA^{TOT} *is the total gross value added of the world - the global GVA is retrieved from The World Bank database. To be consistent, the basic prices (*$price_c$*) are taken from Tulus et al. (2021): 2.55 (xylene), 0.73 (toluene) and 0.88 (benzene) in USD2018. The* SOS_{pb} *is the total SOS for* CV_{pb}*. For the steps to arrive at this equation, see Supplementary S.10 and the work of Tulus et al., 2021.*

1.8 Resource use perspective

Mixed plastic waste

Currently, MPW is most commonly incinerated with energy recovery (Jeswani et al., 2021). To model the energy recovery from incinerating mixed plastic waste, the PEF guidelines (EC, 2021) are followed (5). An average Dutch incineration efficiency is assumed: 33.3%, with 28% for electricity and 9.3% thermal efficiency, and 4% of electricity for self-consumption (Corsten et al., 2013). Only electricity is considered in our model. Nevertheless, the heat generated could be further used leading to additional benefits. To account for the avoided product, i.e. bio-oil, light fuel oil is used. The lower heating value from different sources are shown in Table S.6. Based on the Product Environmental Footprint (PEF) the following energy recovery formula is used:

$$E_{recovery} = E_{ER} - LHV \times E_{se,heat} \times X_{ER,heat} - LHV \times E_{se,elec} \times X_{ER,elec} \qquad (5)$$

Where $E_{recovery}$ is the energy recovery with credits for avoided primary energy (which is the overall GHG benefit/disadvantage); E_{ER} the emissions and resources consumed for energy recovery (modelled with Ecoinvent 3.8: Waste plastic, mixture {CH}| treatment of, municipal incineration); $E_{se,heat}$ and $E_{se,elec}$ are the emissions and resources consumed that would have arisen from specific substituted energy source (as Ecoinvent 3.8: Electricity, medium voltage {NL}| market for Heat, district or industrial, natural gas {RER}| market group for); $X_{ER,heat}$ and $X_{ER,elec}$ is the efficiency of energy recovery (28% for electricity and 9.3% thermal efficiency); LHV is the lower heating value of the material used for energy recovery (Table S.6).

Table S. 6: different data on LHV of plastics and mixed plastic waste.

Material*	Lower Heating Value (MJ/kg)	Source
MPW: DKR-350	32.9 *PET: 22.7; PE: 43; PP: 33; PVC: 19*	Calculated based on composition
MPW	44	Jeswani et al. (2021)
Plastics	23 – 42	Bergsma et al. (2011)

* Mixed-plastic waste contains impurities (0.1 kg/kg MPW).

Crude glycerol

Crude glycerol can be refined to provide the pharmaceutical, food and cosmetic industry with pure glycerol, which is valuable but only economically feasible for large producers (Kaur et al., 2020). Direct combustion of glycerol is challenging due to its high viscosity and low energy density, therefore, recent developments are made to convert glycerol into fuel, hydrogen, biogas and/or co-generate heat and power(Monteiro et al., 2018; Tan et al., 2013). The main alternative uses of glycerol are therefore modelled as (Table S.7): purification of glycerol (Cespi et al., 2014) and combustion of biogas, fermented from glycerol (Stucki et al., 2011) to generate electricity and heat (Ecoinvent, 2020). The counterfactual of pure glycerol, i.e. synthetic glycerol, is based on synthetization of propylene via epichlorohydrin and is taken from Ecoinvent (3.8).

Table S. 7: overview data on alternative uses for crude glycerol.

Heat and power via biogas (fermentation)

Biogas yield	1004.30	m^3/t DM	(Stucki et al., 2011)
per kg crude glycerol	0.80	m^3/kg DM	
CH4 content	50%		(IEA, 2020)
Electricity efficiency	35%		(IEA, 2020)
Thermal efficiency	50%		(IEA, 2020)
MJ per m3 biogas	18	MJ/m^3 for 50% CH4 content	(IEA, 2020)

	Modelled	Amount	unit
Input	Electricity*	0.57	MJ
Input	Heat*	3.47	MJ
Input	Crude glycerol	1	kg
Output	Biogas	0.8034	m3

<table>
<tr><td></td><td>
<table>
<tr><td>Input</td><td>Biogas</td><td>0.8034</td><td>m3</td></tr>
<tr><td>Input</td><td>Processing (based on: heat and power co-generation, biogas, gas engine)</td><td>1</td><td>kWh</td></tr>
<tr><td>Input</td><td>Processing (based on: heat and power co-generation, biogas, gas engine)</td><td>1</td><td>MJ</td></tr>
<tr><td>Output</td><td>Electricity</td><td>5.12</td><td>MJ</td></tr>
<tr><td>Output</td><td>Heat</td><td>7.23</td><td>MJ</td></tr>
</table>
* Energy consumption per m^3 of biogas: 0.158 kWh of electricity and 3.470 MJ heat per m^3 biogas (Stucki et al., 2011).
</td></tr>
<tr><td>Purification of glycerol</td><td>Glycerol refining: 1.2 kg CO_2 eq./kg crude glycerol (Cespi et al., 2014).</td></tr>
<tr><td>Synthetic glycerol</td><td>Ecoinvent 3.8: Glycerine {RER}| production, from epichlorohydrin.</td></tr>
<tr><td>Heat and power (direct combustion)</td><td>LHV glycerol: ~16 MJ/kg. Glycerol has a very high activation energy resulting in an auto-ignition temperature of 370 °C. Conclusion: Direct combustion of glycerol is challenging due to its high viscosity and low energy density.</td></tr>
<tr><td>Syngas production (steam reforming)</td><td>Steam reforming producing syngas (white et al., 2018). Conclusion: still in development, not considered as "common use".</td></tr>
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2. Results

2.1 Endpoint results

Table S.8: ReCiPe 2016 endpoint results for commercial scale (2022) and future scenario (2050) BTX-pathways. BTX = benzene, toluene and xylene.

Product	Endpoint	Unit / kg BTX	Commercial	Future
MPW-BTX	Resources	USD (2013)	2.49E-02	1.46E-02
Bio-BTX			1.94E-01	1.79E-01
Fossil-BTX			5.66E-01	5.65E-01
MPW-BTX	Human Health	DALY	4.60E-06	1.39E-06
Bio-BTX			5.78E-06	1.82E-06
Fossil-BTX			6.15E-06	3.35E-06
MPW-BTX	Ecosystems	Species·yr	1.35E-08	4.19E-09
Bio-BTX			1.36E-07	1.26E-07
Fossil-BTX			1.67E-08	8.40E-09

2.2 Midpoint results

Table S.9: ReCiPe 2016 midpoint results for commercial scale (2022) and future (2050) BTX-pathways. BTX = benzene, toluene and xylene.

Product	Midpoint impact category	Unit / kg BTX	Current	Future
MPW-BTX	Freshwater ecotoxicity	1,4-DBC eq.	1.5E-04	1.1E-04
Bio-BTX			1.9E-03	1.8E-03
Fossil-BTX			1.1E-04	1.0E-04
MPW-BTX	Marine ecotoxicity	1,4-DBC eq.	2.6E-04	2.0E-04
Bio-BTX			4.0E-03	4.0E-03
Fossil-BTX			2.4E-04	2.5E-04
MPW-BTX	Terrestial ecotoxicity	1,4-DBC eq.	6.7E-03	4.0E-03
Bio-BTX			6.9E-01	6.9E-01
Fossil-BTX			2.8E-03	3.4E-03
MPW-BTX	Fossil resource scarcity	kg oil-eq	1.2E-01	4.6E-02
Bio-BTX			6.0E-01	4.9E-01
Fossil-BTX			1.4E+00	1.4E+00
MPW-BTX	Mineral resource scarcity	Kg Cu eq.	9.2E-04	6.2E-04
Bio-BTX			8.7E-03	8.6E-03
Fossil-BTX			3.2E-04	3.4E-04
MPW-BTX	Freshwater eutrophication	kg P eq.	3.5E-05	5.3E-06
Bio-BTX			1.8E-04	1.4E-04
Fossil-BTX			2.5E-05	2.2E-05
MPW-BTX	Marine eutrophication	kg N eq.	5.3E-06	3.7E-06
Bio-BTX			2.5E-04	2.5E-04

Fossil-BTX			3.0E-06	3.0E-06
MPW-BTX	Terrestial acidification	kg SO_2 eq.	1.3E-03	4.5E-04
Bio-BTX			1.1E-02	9.1E-03
Fossil-BTX			4.7E-03	4.6E-03
MPW-BTX	Global warming potential	kg CO_2 eq.	4.6E+00	1.3E+00
Bio-BTX			3.2E+00	-3.7E-01
Fossil-BTX			5.2E+00	2.3E+00
MPW-BTX	Water consumption	m^3	8.0E-03	1.5E-02
Bio-BTX			4.2E-02	6.1E-02
Fossil-BTX			3.2E-02	3.5E-02
MPW-BTX	Ionizing radiation	kBq Co-60 eq.	2.0E-01	3.9E-02
Bio-BTX			1.6E-01	5.5E-02
Fossil-BTX			2.1E-02	1.1E-02
MPW-BTX	Land occupation	m^2·annual crop eq.	8.9E-03	5.7E-03
Bio-BTX			1.4E+01	1.4E+01
Fossil-BTX			6.5E-03	7.6E-03
MPW-BTX	Land transformation	m^2 annual crop eq	2.3E-05	1.5E-05
Bio-BTX			2.2E-04	2.3E-04
Fossil-BTX			6.3E-06	7.4E-06
MPW-BTX	Ozone depletion	kg CFC11 eq.	5.3E-07	4.5E-07
Bio-BTX			3.0E-05	3.0E-05
Fossil-BTX			7.2E-08	6.2E-08
MPW-BTX	Particulate matter formation	kg PM2.5 eq.	4.7E-04	1.6E-04
Bio-BTX			4.4E-03	3.1E-03
Fossil-BTX			1.9E-03	1.8E-03
MPW-BTX	Toxicity, carcinogenic	1,4-DBC eq.	6.2E-03	4.6E-03
Bio-BTX			2.1E-02	1.9E-02
Fossil-BTX			5.8E-03	5.7E-03
MPW-BTX	Toxicity, non-carcinogenic	1,4-DBC eq.	1.6E-02	9.7E-03
Bio-BTX			1.6E-01	1.6E-01
Fossil-BTX			3.5E-03	3.7E-03

Table 10: Table S.9: Environmental Footprint midpoint results commercial scale (2022) BTX-pathways. BTX = benzene, toluene and xylene

Midpoint impact category	**Unit**	**Biobased BTX**	**MPW-BTX**	**Fossil-BTX**
Climate change	kg CO2 eq	2.9E+00	4.8E+00	5.2E+00
Ozone depletion	kg CFC11 eq	3.0E-07	3.5E-08	6.1E-10
Ionising radiation	kBq U-235 eq	8.4E-02	1.7E-02	1.2E-04
Photochemical ozone formation	kg NMVOC eq	1.4E-02	1.3E-03	5.1E-03
Particulate matter	disease inc.	8.5E-08	5.5E-09	6.7E-08
Human toxicity, non-cancer	CTUh	8.7E-08	5.9E-09	3.1E-09
Human toxicity, cancer	CTUh	1.3E-09	1.5E-10	4.4E-10
Acidification	mol H+ eq	1.8E-02	1.6E-03	6.2E-03
Eutrophication, freshwater	kg P eq	7.2E-04	3.6E-05	4.7E-07

Eutrophication, marine	kg N eq	1.7E-02	4.5E-04	9.7E-04
Eutrophication, terrestrial	mol N eq	5.6E-02	5.0E-03	1.1E-02
Ecotoxicity, freshwater	CTUe	3.8E+02	8.4E+00	9.7E-01
Land use	Pt	6.9E+02	8.8E-01	4.1E-03
Water use	m3 depriv.	1.5E+00	1.8E-01	1.4E+00
Resource use, fossils	MJ	2.8E+01	8.6E+00	6.1E+01
Resource use, minerals and metals	kg Sb eq	5.3E-06	1.7E-07	2.0E-08

2.3 Absolute assessments results

Table S.11: PB-LCIA results for commercial (2022) and future (2050) scale BTX-pathways. SoSOS = Share of Safe Operating Space.

Product	**Planetary Boundary**	**SoSOS current**	**SoSOS future**
MPW-BTX	Climate_Change (CO2 concentration)	109	32
Bio-BTX	Climate_Change (CO2 concentration)	47	0
Fossil-BTX	Climate_Change (CO2 concentration)	115	45
MPW-BTX	Climate_Change (Energy imbalance)	103	0.4
Bio-BTX	Climate_Change (Energy imbalance)	53	0
Fossil-BTX	Climate_Change (Energy imbalance)	109	0.6
MPW-BTX	Stratospheric Ozone Depletion	0	0
Bio-BTX	Stratospheric Ozone Depletion	0	0
Fossil-BTX	Stratospheric Ozone Depletion	0	0
MPW-BTX	Ocean Acidification	35	0.1
Bio-BTX	Ocean Acidification	15	0
Fossil-BTX	Ocean Acidification	37	0.1
MPW-BTX	Biochemical flow P	3	0
Bio-BTX	Biochemical flow P	5	2
Fossil-BTX	Biochemical flow P	2	1
MPW-BTX	Biochemical flow N	0	0
Bio-BTX	Biochemical flow N	21	21
Fossil-BTX	Biochemical flow N	0	0
MPW-BTX	Land-system change	0	0
Bio-BTX	Land-system change	0	0
Fossil-BTX	Land-system change	0	0
MPW-BTX	Freshwater use	67	31
Bio-BTX	Freshwater use	75	59
Fossil-BTX	Freshwater use	9	10
MPW-BTX	Biosphere integrity	10	3
Bio-BTX	Biosphere integrity	68	61
Fossil-BTX	Biosphere integrity	11	5

Table 12: Carrying-capacity based normalization for LCA (Bjørn and Hauschild, 2015; Sala et al., 2020)*. Total production of BTX per year was taken as 1.22E11 kg (ref).*

Impact category	**Unit**	**Normalisation factor**	**Biobased BTX**	**MPW-BTX**	**Fossil BTX**
Ecotoxicity, freshwater	CTUe	1.3E+14	3.5E-01	7.7E-03	9.0E-04
Climate change	kg CO2 eq	6.8E+12	5.2E-02	8.5E-02	9.3E-02
Eutrophication, freshwater	kg P eq	5.8E+09	1.5E-02	7.5E-04	9.9E-06
Resource use, fossils	MJ	2.2E+14	1.5E-02	4.7E-03	3.3E-02
Particulate matter	disease inc.	5.2E+05	1.3E+00	1.3E-03	1.6E-02
Eutrophication, marine	kg N eq	2.0E+11	1.0E-02	2.8E-04	5.9E-04
Land use	Pt	1.3E+13	6.7E+00	8.4E-03	3.9E-05
Photochemical ozone formation	kg NMVOC eq	4.1E+11	4.2E-03	3.9E-04	1.5E-03
Resource use, minerals and metals	kg Sb eq	2.2E+08	3.0E-03	9.4E-05	1.1E-05
Human toxicity, non-cancer	CTUh	4.1E+06	2.6E-03	1.7E-04	9.2E-05
Acidification	mol H+ eq	1.0E+12	2.2E-03	1.9E-04	7.5E-04
Eutrophication, terrestrial	mol N eq	6.1E+12	1.1E-03	9.0E-06	1.9E-05
Water use	m3 depriv.	1.8E+14	1.0E-03	1.2E-04	9.2E-04
Human toxicity, cancer	CTUh	9.6E+05	1.6E-04	1.9E-05	5.6E-05
Ozone depletion	kg CFC11 eq	5.4E+08	6.7E-05	7.8E-06	1.4E-07
Ionising radiation	kBq U-235 eq	5.3E+14	1.9E-05	4.0E-06	2.9E-08

2.4 Sensitivity Analysis: electricity market scenarios for 2050

Alongside the baseline scenario for the SSP2 narrative on the electricity market of 2050, two more scenarios were tested: a representative concentration pathway of 1.9 W/m^2 (RCP1.9) as well as 4.5 W/m^2 (RCP4.5) in 2100 (Stehfest et al., 2014). 1.0416

Table S.13: ReCiPe 2016 global warming potential results for future (2050) BTX-pathways. The baseline scenario for the SSP2 narrative on the electricity market of 2050: RCP 2.6; a more optimistic scenario of 1.9 W/m2 (RCP1.9); and a more conservative scenario of 4.5 W/m2 (RCP4.5) in 2100. BTX = benzene, toluene and xylene.

Product	**Midpoint impact category**	**Unit / kg BTX**	**RCP 1.9**	**RCP 2.6**	**RCP 4.5**
MPW-BTX	Global warming potential	kg CO_2 eq.	1.25E+00	1.32E+00	1.51E+00
Bio-BTX			-0.46E+00	-0.40E+00	-0.073E+00
Fossil-BTX			2.3E+00	2.3E+00	2.4E+00

2.5 Sensitivity Analysis: plastic recycling scenarios for 2050

Alongside the 2°C-Circulair Economy, we tested less optimistic scenarios of SSP2 baseline and SSP2-RCP 2.6. The SSP2 baseline scenario included 14% chemical or mechanical recycling, 17% landfill stock and 69% littered or incineration with energy recovery. The SSP2-RCP2.6 scenario included 29% recycling, 58% landfill stock and 13% littered or incineration with energy recovery (Stegmann et al., 2022).

Table S.14: Global warming potential results for future (2050) BTX-pathways applying different recycling scenarios.

Product	Midpoint impact category	Unit / kg BTX	2°C-CE	RCP baseline	RCP 2.6
MPW-BTX	Global warming potential	kg CO_2 eq.	1.3	3.2	1.3
Bio-BTX			-0.4	1.6	-0.4
Fossil-BTX			2.3	4.1	2.3

2.6 Sensitivity Analysis: Glycerol production from other feedstock

Glycerol production has a big impact on the production of bio-BTX. Figure S.2 shows the environmental impact of different glycerol production routes. These are: glycerol from palm oil (Ecoinvent 3.8: Glycerine {MY} | esterification of palm oil), glycerol from rapeseed oil (Ecoinvent 3.8: Glycerine {Europe without Switzerland} | esterification of rape oil) and glycerol from soybean oil from Brazil (Ecoinvent 3.8: Glycerine {Br} | esterification of soybean oil).

The default of glycerol as a co-product of US soybean bio-diesel has the lowest impact in terms of GHG, acidification, land use and water consumption. Glycerol from rapeseed oil and soybean oil from Brazil have higher GHG emissions, resulting from large impacts from clear-cutting of primary forest to arable land. Likewise, palm oil is known for its large GHG impact from direct land-use changes (Achten and Verchot, 2011), but also cultivation of the palm fruit bunches themselves is very GHG intensive. For the USA produced glycerol, no LUC emissions were included in line with PAS2050 guidelines (PAS2050, 2011).

If cultivation requires land use conversion from (tropical) forest to agricultural land, the resulting GHG emissions are high and in regard to the impact of biodiesel and glycerol, it often exceeds fossil-based emission levels (Uusitalo et al., 2014). In this regard, and based on the other agricultural relevant impact categories (Figure S.2), glycerol from soybean biodiesel production in the USA has the lowest impact out of the four options. However, the use of other feedstock, e.g. lignin (Fan et al., 2020), could further decrease bio-BTX's impact, this is discussed in the discussion section.

Moreover, the total GHG emissions of bio-BTX increases from 3 kg CO_2-eq./kg BTX to 4.3 (rape oil), 8.8 (from palm oil) and 11.8 (Brazil) kg CO_2-eq./kg BTX.

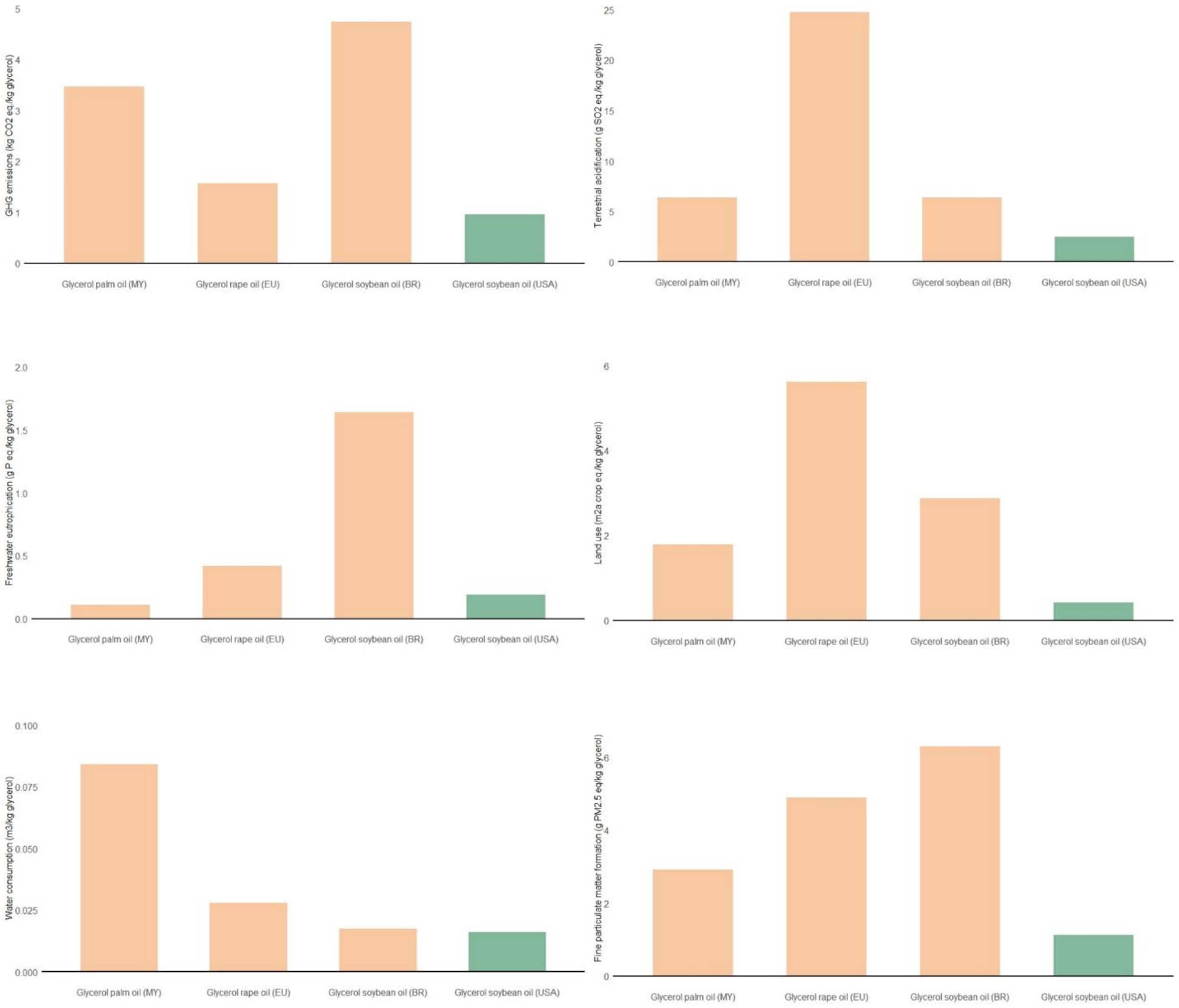

Figure S. 2: results on the production of 1 kg of glycerol made from (1) palm oil (left bar); (2) rapeseed oil (one to the right); (3) soybean oil from Brazil (one from the right bar); (4) soybean oil USA (right bar). Top left: GHG emissions, middle top: Terrestrial acidification, top right: Freshwater eutrophication, bottom left: Land use, middle left: Water consumption, bottom right: Fine particulate matter formation. Green bar represents the base case glycerol from soybeans (USA).

2.7 Sensitivity Analysis: Allocation strategies

In the figure down below the results when applying mass, energy and economic allocation on the GHG emissions of the BTX pathways are shown. Other ways to handle multifunctionality were not applied. Substitution was not applicable because glycerol is a by-product and not the main product, and the co-products in the final step are not marginal - it would lead to skewed impacts. In addition, system expansion was not a solution because the goal of the study is focused on the determination of the impact of the production of 1 kg of BTX (Moretti et al., 2020).

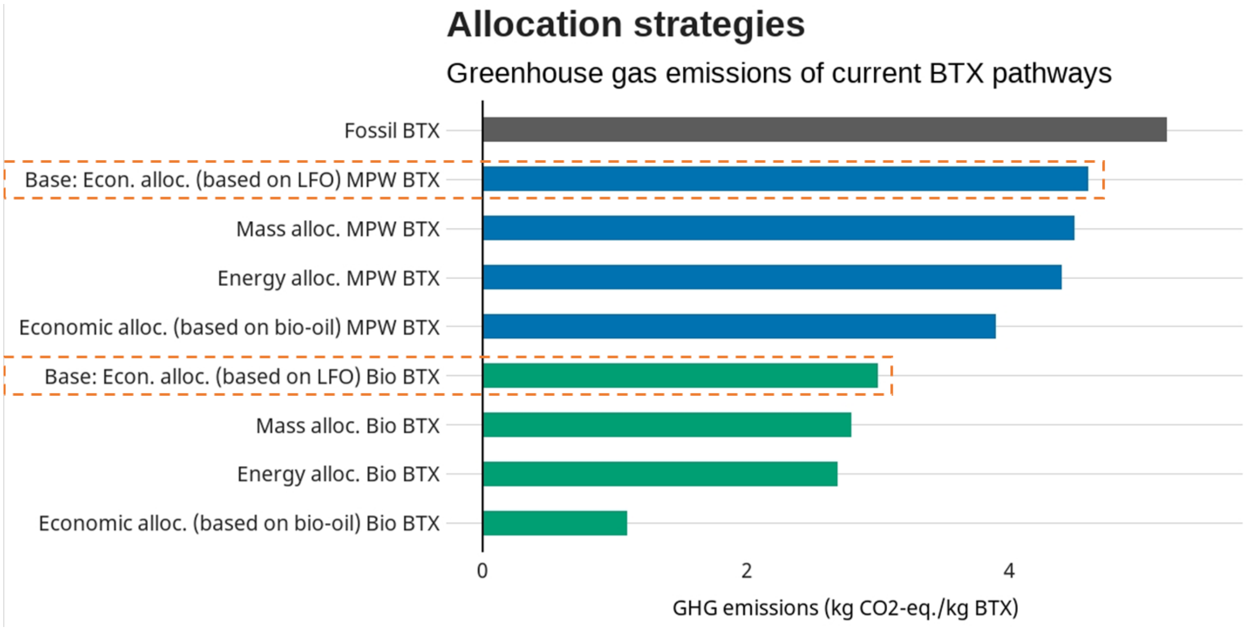

Figure 3: Climate change results of MPW and bio-BTX applying mass, energy and economic allocation. The base scenario is indicated with the orange box. BTX = benzene-toluene-xylene; MPW = Mixed Plastic Waste; LFO = Light Fuel oil.

3. Discussion

3.1 Impact other types of biomass feedstock

Table S.15: Greenhouse gas (GHG) emissions, freshwater eutrophication, acidification and land use impact of biomass cultivation per kg of BTX, based on yields from literature. The percentage are the in- or decrease in impact compared to soybean cultivation impact. N.A. = not available.

	Based on a yield of:	GHG impact (per kg BTX)	Eutrophication	Acidification	Land use	*Source*
Lignin	10%[i]	N.A	N.A	N.A	N.A	N.A
Sugarcane bagasse	12.5%[j]	0.05 **-95%**	0.0001 **-48%**	0.028 **+632%**	2.8 **-73%**	*Ecoinvent 3.8*
Pine wood	13.3%[k]	0.30 **-74%**	0.00006 **-71%**	0.00128 **-66%**	28.57 **+180%**	*Ecoinvent 3.8*
Sawdust	6.4%[l]	0.13 **-89%**	0.0001 **-72%**	0.0006 **-85%**	7.03 **-31%**	*Ecoinvent 3.8*
Willow wood	27%[l]	0.23 **-80%**	0.0002 **+15%**	0.0015 **-60%**	3.52 **-66%**	*Ecoinvent 3.8*
Soybean[n]	This study	1.17	0.000193	0.00377	10.2	*Ecoinvnt 3.8*

i (Vural Gursel et al., 2019); j (Ghorbannezhad et al., 2018); k (Mendes et al., 2016); l (Balasundram et al., 2020); m based on mass allocation of 0.25 (Carpio and Simone de Souza, 2017) of sugar from sugarcane production, Brazil. n the impact of soybean cultivation as allocated to glycerol production.

3.2 Plastic feedstock supply

Table S.16: Data and calculations on plastic waste feedstock and it availability for BTX production. BTX = benzene-toluene-xylene.

	2020	2030	2050	Source
Plastic generated annually (Mt)	512	702	1078	(Stegmann et al., 2022)
Plastic waste generated annually (Mt)	436	572	953	(Stegmann et al., 2022)
Total plastic waste generated (Mt)	6300	-	12000	(Geyer et al., 2017)
BTX production annually (Mt)	122	143	195	(IEA, 2020, 2018)
Plastic waste required to cover annual BTX production	79%	71%	58%	(yield * BTX production)/annual plastic waste
Total plastic waste required to cover BTX production from total plastic waste generated	5.5%	-	4.6% *Up to 2050: 4.84 Gt BTX produced in total => 77% of current generated 6300 Mt waste*	(yield * BTX production)/total plastic waste
Share of biogenic carbon content	-	-	If 45%, *an additional 1.5 kg CO_2-eq. per kg MPW-BTX is avoided due to biogenic carbon content (net zero emissions)*	(0.45 * 3.36 kg CO_2)

3.3 Substitution

To compare to the data of Yang et al. (2022), substitution was applied to the bio-BTX product system. This involved substitution of bio-oil, treated as ‘light fuel oil {RER}| market for’ and the on-site generated electricity as grid electricity. This resulted in credits of in total 2.25 kg CO_2 eq./kg bio-BTX. However, the impact of the process itself increased as well (due to avoidance of allocation), which was mainly affected by an increased impact of glycerol production, i.e., 4.03 kg CO_2 eq./kg bio-BTX.

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Chapter 5

Supplementary Information S5

Supplementary Information

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

Emma A. R. Zuiderveen[1,2,*], M.A.J. Huijbregts[1,4], C. Caldeira[2,3], S. Sala[2], R. van Zelm[1], S.V. Hanssen[1 *]

[1] Department of Environmental Science, Radboud Institute for Biological & Environmental Sciences, Radboud University,
Nijmegen, the Netherlands

[2] European Commission, Joint Research Centre, Via Enrico Fermi 2749, 21027, Ispra, VA, Italy

[3] Syensqo Lyon Research and Innovation Center, 85 Avenue des Freres Perret 69190 Saint-Fons, France

[4] Department of Circularity & Sustainability Impacts, TNO, Princetonlaan 6, 3584CB Utrecht, The Netherlands

[*] Corresponding author: emma.zuiderveen@ru.nl / steef.hanssen@ru.nl

Contents

1. Methods

1.1 Inventory table

Table 17: Inventory table containing inventory and supply chain data, and other relevant values.

Parameter	Specification	Value	Unit	Source
		Biomass		
Fertilizer GHG emissions	Woody biomass	0.055	kg CO_2-eq/kg dbm	Based on multiple sources, from Hanssen et al. (2020)
	Woody biomass (willow)	0.07	kg CO_2-eq/kg dbm	Therasme et al. (2021)
	Woody biomass (RoW, willow)	0.02	kg CO_2-eq/kg dbm	Ecoinvent
	Woody biomass (DE, willow)	0.018	kg CO_2-eq/kg dbm	Ecoinvent
	Woody biomass (RoW, poplar)	0.020	kg CO_2-eq/kg dbm	Ecoinvent
	Grasses	0.03	kg CO_2-eq/kg dbm	Tadele et al. (2019)
	Grasses (Miscanthus)	0.054	kg CO_2-eq/kg dbm	Hamelich & Hoogwijk, 2007
	Grasses (CH, organic)	0.009	kg CO_2-eq/kg dbm	Ecoinvent
	Grasses (RoW, permant grassland)	0.009	kg CO_2-eq/kg dbm	Ecoinvent
	Grasses (RoW, organic)	0.083	kg CO_2-eq/kg dbm	Ecoinvent
	Sugarcane (South America)	0.073	kg CO_2-eq/kg dbm	Based on multiple sources, from Hanssen et al., (2020)
	Sugarcane (RoW)	0.151	kg CO_2-eq/kg dbm	Based on multiple sources, from Hanssen et al., (2020)
	Sugarcane	0.11	kg CO_2-eq/kg dbm	Edwards et al. (2010)
	Sugarcane	0.04	kg CO_2-eq/kg dbm	Kikuchi et al. (2013)
	Sugarcane (BR)	0.047	kg CO_2-eq/kg dbm	Ecoinvent
	Sugarcane (RoW)	0.041	kg CO_2-eq/kg dbm	Ecoinvent
Harvesting GHG emissions	Harvesting, combine	0.015	kg CO_2-eq/kg wbm	Ecoinvent
	Harvesting, sugarcane	0.0025	kg CO_2-eq/kg wbm	Ecoinvent
	Harvesting, ground crops	0.0009	kg CO_2-eq/kg wbm	Ecoinvent
	Mowing (for grasses)	0.004	kg CO_2-eq/kg wbm	Ecoinvent
	Tillage, ploughing	2.4E-6	kg CO_2-eq/kg wbm	Ecoinvent
	Tillage, harrowing	2.2E-6	kg CO_2-eq/kg wbm	Ecoinvent
	Tractor, agriculture (0.05 tkm)	1.56	kg CO_2-eq/tkm	Ecoinvent
Total cultivation GHG emissions	Woody biomass	0.07	kg CO_2-eq/kg dbm	Therasme et al. (2021)
	Woody biomass	0.1	kg CO_2-eq/kg dbm	Njakou Djomo et al. (2010)
	Woody biomass	0.11	kg CO_2-eq/kg dbm	Caputo et al. (2014)
	Woody biomass	0.09	kg CO_2-eq/kg dbm	IEA, 2013
	Wood chips	0.05	kg CO_2-eq/kg dbm	Ecoinvent
	Grasses	0.04	kg CO_2-eq/kg dbm	Zucaro et al., 2014
	Sugarcane	0.12	kg CO_2-eq/kg cane	Powar et al., 2021
	Sugarcane	0.08	kg CO_2-eq/kg cane	Renouf et al., 2010
	Sugarcane	0.04	kg CO_2-eq/kg cane	Renouf et al (2016)
	Agricultural residues	0.03	kg CO_2-eq/kg dbm	GREET
	Agricultural residues	0.03	kg CO_2-eq/kg dbm	Allocated share corn (Ecoinvent, 2020), 0.1 (market value-based)

Moisture content	Woody biomass	50%	percentage	Bachmann et al. (2023), PBL
	Grasses (Miscanthus)	30%	percentage	Benalcázar et al. (2017)
	Agricultural residues (corn stover)	30%	percentage	Benalcázar et al. (2017)
	Agricultural residues (other)	50%	percentage	Benalcázar et al. (2017)
	Dry biomass (final moisture content at gate)	10%	percentage	
Conversion factor wet biomass to dry	Woody biomass	1.4	dimensionless	Calculations
	Grasses	1.2	dimensionless	Calculations
	Agricultural residues	1.3	dimensionless	Calculations
Energy content biomass	Woody biomass	18.4	MJ/kg dbm	Phyllis, 2023
	Grasses	18.6	MJ/kg dbm	Phyllis, 2023
	Agricultural residues	17.95	MJ/kg dbm	Phyllis, 2023
Drying energy	Drying energy	2.3	MJ/kg H_2O	Calculation based on Piccinno et al. (2016)
Transport GHG emissions	Truck (0.55 tkm) and barge (0.5 tkm)	0.053	kg CO_2-eq/kg wbm	Calculations
	Freight	0.098	kg CO_2-eq/kg chemical	Calculations
Number of operational petroleum refineries:	Asia & pacific	324	refineries	Statista, 2023
	North-America	190	refineries	Statista, 2023
	Europe	156	refineries	Statista, 2023
	Latin America	62	refineries	Statista, 2023
	Asia & pacific	324	refineries	Statista, 2023
Land surface	North-America	44579000	km^2	
	Europe	24709000	km^2	
	Latin America	10180000	km^2	
	Asia & pacific	20111457	km^2	
		Chemical processes		
Methanol				
Input	Dry biomass (straw)	3.23	kg	Galán-Martín et al. (2021) based on Liu et al. (2019), adjusted with Puig-Gamero et al. (2021) & Ecoinvent 3.7 & Afzal et al. 2023. *Heat demand covered by steam produced internally (Oliveira et al., 2020)
	Electricity	0.61	MJ	
	Electricity, cooling	3.10	MJ	
	Heat, steam	3.02	MJ	
	Oxygen	1.05	kg	
	Zinc (removing sulphur substances) | Cu/Zn/Al	0.0003	kg	
	Dolomite (removing tar)	0.07	kg	
	Zeolite powder	0.015	kg	
Output	Methanol	1	kg	
	Heat	3.02	MJ	Re-used internally
	Wastewater	0.05	kg	
	Solid waste	0.07	kg	
Input	Dry biomass (woody biomass)	2.27	kg	Yadav et al. (2020), adjusted with Ecoinvent 3.8 & Afzal et al. 2023 & Liu et al. (2020). Heat demand covered by steam produced internally (Oliviera et al. 2019)
	Electricity	3.70	MJ	
	Heat, steam	3.02	MJ	
	Water, cooling	22.87	MJ	
	Oxygen	1.051	kg	
	Zinc (removing sulphur substances)	0.0003	kg	
	Dolomite	0.07	kg	

	Zeolite powder	0.015	kg	
Output	Methanol	1	kg	
	Heat	3	MJ	Re-used internally
	Wastewater	0.05	kg	
	Solid waste	0.07	kg	
Methanol-to-olefins (MTO)				
Input	Methanol	2.92	kg	Dutta et al. (2019)
	Electricity	1.54	MJ	
	Electricity, cooling	1.61	MJ	
	Steam	0.25	kg	
	Zeolite	0.008	kg	
	Water, cooling	2.6	m3	
Output	Ethylene	0.61	kg	
	Propylene	0.39	kg	
	Sales gas	0.04	kg	Re-used internally
	Pentane	0.02	kg	Substitution
	Butene	0.11	kg	Substitution
	Ethane	0.01	kg	
	Hydrogen	0.01	kg	Substitution
Methanol-to-aromatics (MTO)				
Input	Methanol	6.05	kg	Jiang et al. (2020); Yang et al. (2022)
	Electricity (cooling)	1.03	MJ	
	Electricity	0.30	MJ	
	Steam	4.89	MJ	
	Heat	2.75	MJ	
Output	Benzene	0.09	kg	
	Toluene	0.30	kg	
	Xylene	0.61	kg	
	LPG	1.19	kg	Re-used internally
	Dry gas	0.30	kg	Re-used internally
	Pentane	0.23	kg	
	C9+	0.17	kg	Substitution as diesel
	Wastewater	0.003	m3	
Syngas production				
Input	Woody biomass	1.7	kg	Bachmann et al. (2022)
	Electricity	0.76	MJ	
	Steam (MP)	0.00	kg	
	Oxygen	0.87	kg	
	Water, process	1.22	kg	
Output	Syngas	1	kg	
	Heat	2.27	kg	Substitution
	Solid waste	0.04	Kg	
Input	Lignocellulosic	1.95	kg	
	Electricity	0.74	MJ	
	Steam (MP)	0.00	kg	
	Oxygen	0.54	kg	
	Water, process	1.23	kg	
Output	Syngas	1	kg	
	Heat	5.03	kg	Substitution
	Solid waste	0.05	kg	
FT syngas to naphtha				
Input	Syngas (2:1)	2.3	kg	Van Der Giesen et al. (2014), updated with work from Liu et al. (2020).
	Cobalt catalyst (as cobalt)	0.00017	kg	
	Energy (self-sufficient)*			* The remaining hydrocarbon chains that

				are too short to convert into fuels but are sufficient to generate energy to run the plant.
Output	Synthetic fuel	3.83	kg	
	Of which: naphtha C5-C11	1	kg	
	Jet fuel C9–C16 (paraffin’s)	1.80	kg	Substitution as kerosene
	Diesel	1.03	kg	Substitution
Steam cracking (naphtha)				
Input	Naphtha	1.13	kg	Ren et al. (2006)
	Energy (heat from steam	16	MJ	
Output	Ethylene	0.67	kg	
	Propylene	0.33	kg	
	Aromatics	0.31	kg	
	Butadiene	0.11	kg	Substitution
	H2	0.02	kg	Substitution
Fermentation to ethanol				
Biomass input	Sugarcane	5.20	kg wbm	Ecoinvent
	Woody biomass	3.80	kg dbm	Ecoinvent
	Grasses / lignocellulosic biomass	3.90	kg dbm	*Same process (SSF) is required
GHG emissions gate-to-gate	Ethanol (sugarcane)	0.03	kg CO_2-eq/kg ethanol	Ecoinvent
	Ethanol (woody biomass)	0.43	kg CO_2-eq/kg ethanol	Ecoinvent
	Ethanol (grasses)	0.31	kg CO_2-eq/kg ethanol	Ecoinvent
Catalytic dehydration				
Input	Ethanol	1.71	kg	Bazzanella and Ausfelder, (2017); Nitzsche et al. (2016)
	Electricity	0.83	MJ	
	NaOH (50% solution)	0.005	kg	
	H2SO4 solution	0.017	kg	
	Water	0.45	kg	
Output	Ethylene	1	kg	
	C4-hydrocarbon	0.01	kg	Substitution
	Wastewater		m3	
Dimerization & metathesis				
Input	Ethylene	1.21	kg	Kikuchi et al. (2017)
	H2	0.00068	kg	
	Electricity	10.01	MJ	
	Heavy oil	0.21	kg	* by-products are used to replace the heavy oil input
Output	Propylene	1	kg	
	C5H12, C6H14, C3H8	0.21	Kg	Re-used internally
Pyrolysis to aromatics				
Input	Biomass (woody biomass)	5.05	Kg	Yang et al. (2022)
	Electricity	*self-sufficient*	MJ	** “Onsite steam and electricity are generated from coke, NGCs, humins, and unreacted biomass. The remaining electricity (4.2MJ) is exported.”*
	Catalyst (Zeolite)	0.10	kg	
	Heat, distillation	0.61	MJ	
Output	Aromatics	1	kg	
	Electricity	4.20	MJ	Substitution
	Heat from steam	11.61	MJ	Substitution
	Wastewater	0.0013	m3	

	Solid waste	0.03	kg	
		Energy		
GHG emissions	Electricity, current mix	0.14	kg CO2 eq./MJ	(Ecoinvent, 2020; Galán-Martín et al., 2021)
	Electricity, renewables mix	0.04	kg CO2 eq./MJ	(Ecoinvent, 2020; Galán-Martín et al., 2021)
	Heat, natural gas or district	0.04	kg CO2 eq./MJ	Ecoinvent
	Heat from steam	0.10	kg CO2-eq/MJ	Ecoinvent
Gas to electricity	Natural gas LHV	47.1	MJ/kg	
	LPG LHV	48.5	MJ/kg	
	Simple cycle gas turbine	16.5	MJ electricity/kg natural gas	Efficiency 20-35%
	CHP	20.7	MJ electricity/kg natural gas	Efficiency 44 %
Production volume (2022)	Methanol	171.84	million metric tons	Statista, 2023
	Ethylene	225.52	million metric tons	Statista, 2023
	Propylene	150.3	million metric tons	Statista, 2023
	Aromatics	116.68	million metric tons	Straits Research, 2023

1.2 Conversion efficiencies table

Table 18: Conversion efficiencies per route, depending on product and feedstock. Minimum and maximum values are used in the sensitivity analysis. These values are also used in the sensitivity analysis on conversion efficiencies.

Product	Feedstock	Route	Conversion efficiency (default)	Conversion efficiency (max)	Conversion efficiency (min)
methanol	woody	MeOH-BASED, woody	0.44	0.70	0.38
ethylene	woody	MeOH-BASED, woody	0.15	0.31	0.13
propylene	woody	MeOH-BASED, woody	0.15	0.31	0.13
aromatics	woody	MeOH-BASED, woody	0.07	0.16	0.06
ethylene	woody	EtOH BASED, woody	0.15	0.22	0.09
propylene	woody	EtOH BASED, woody	0.13	0.18	0.03
ethylene	woody	NAPHTHA-BASED, woody	0.23	0.28	0.10
propylene	woody	NAPHTHA-BASED, woody	0.23	0.28	0.10
aromatics	woody	NAPHTHA-BASED, woody	0.23	0.28	0.10
aromatics	woody	BIO-OIL-BASED, woody	0.20	0.20	0.14
methanol	grassy	MeOH-BASED, grassy	0.31	0.45	0.31
ethylene	grassy	MeOH-BASED, grassy	0.11	0.20	0.11
propylene	grassy	MeOH-BASED, grassy	0.11	0.20	0.11
aromatics	grassy	MeOH-BASED, grassy	0.05	0.10	0.05
ethylene	grassy	EtOH BASED, grassy	0.15	0.45	0.08
propylene	grassy	EtOH BASED, grassy	0.12	0.37	0.03
ethylene	grassy	NAPHTHA-BASED, grassy	0.20	0.33	0.10
propylene	grassy	NAPHTHA-BASED, grassy	0.20	0.33	0.10
aromatics	grassy	NAPHTHA-BASED, grassy	0.20	0.33	0.10
methanol	residues	MeOH-BASED, residues	0.31	0.53	0.31
ethylene	residues	MeOH-BASED, residues	0.11	0.23	0.11
propylene	residues	MeOH-BASED, residues	0.11	0.23	0.11
aromatics	residues	MeOH-BASED, residues	0.05	0.12	0.05
ethylene	residues	NAPHTHA-BASED, residues	0.20	0.33	0.17
propylene	residues	NAPHTHA-BASED, residues	0.20	0.33	0.17
aromatics	residues	NAPHTHA-BASED, residues	0.20	0.33	0.17
ethylene	residues	EtOH BASED, residues	0.15	0.20	0.08
propylene	residues	EtOH BASED, residues	0.12	0.17	0.03
ethylene	sugarcane	EtOH BASED, sugarcane	0.11	0.17	0.08

propylene	sugarcane	EtOH BASED, sugarcane	0.09	0.14	0.03

1.3 Process descriptions

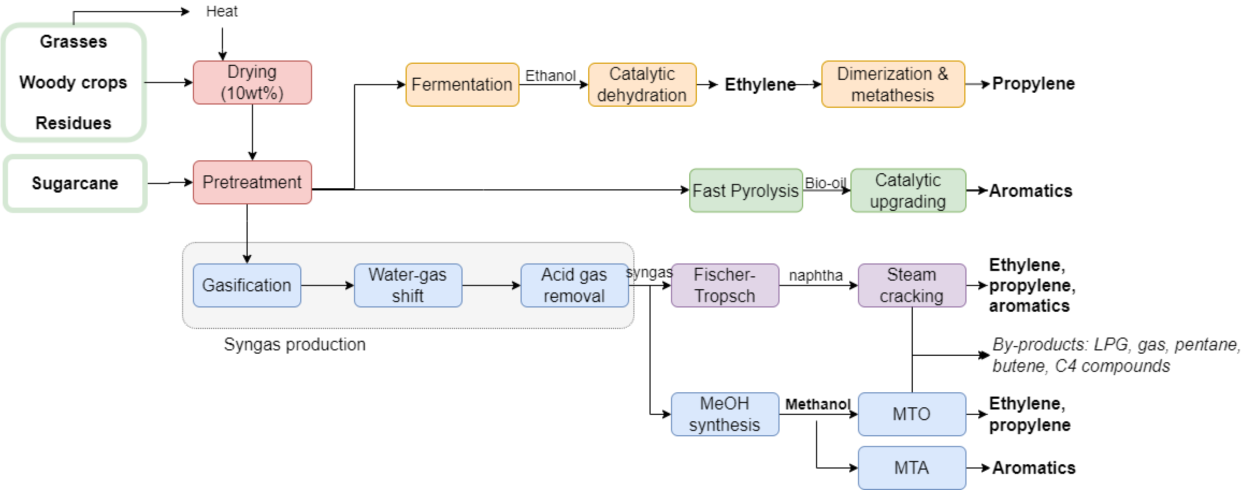


Figure 4: overview of chemical production routes from (i) grasses, (ii) woody crops, (iii) agricultural residues and (iv) sugarcane. Orange: ethanol-based routes; Blue: methanol-based routes via syngas production; Purple: naphtha-based routes; Green: bio-oil based routes. Down below, technical description of part of the route is given.

Gasification to methanol

Inventory data is based on work of Galán-Martín et al. (2021), based on a simulated process (Liu et al., 2020). The biomass-to-methanol process includes a raw material pretreatment unit, water-gas conversion unit, acid-gas removal unit, methanol synthesis and refining unit. After dried biomass is treated in the first two units, a water-gas shift reaction follows. The WGS unit is to adjust the H_2/CO proportion to improve the methanol yield and conversion rate. Next is the acid-gas removal, before the syngas enters this unit, it is cooled to 40°C by a low pressure waste heat boiler. The acid gas is then removed from syngas. Last step is to convert syngas into methanol. It is mixed with hydrogen and pressurized, followed by a methanol purification step (Lui et al., 2020).

Fermentation to ethanol

Data is based on the following processes:

- Sugarcane: This industrial process converts 50% of the sugarcane juice for raw sugar and the other 50%, along with the by-product molasses, into ethanol. Wet biomass is first crushed in crushing mills, then fed in the reactor to extract sugars, after which an ethanol fermentation process follows. In a final step, the ethanol is dehydrated to a 95% solution state (Ecoinvent, 2023).

Optimized features related to a modern plant are included, such as reduced steam consumption, efficient high-pressure boilers and molecular sieves for ethanol dehydration, leading to an electricity surplus (Chagas et al., 2016).

- Grasses/lignocellulosic: Includes a pretreatment with steam and a Saccharification and Simultaneous Fermentation process (SSF). By-products are fibers and proteins from grass, these are allocated based on economic value (Ecoinvent, 2023).
- Woody biomass: Includes a dilute acid pre-hydrolysis and a SSF process. Process heat and electricity supply is covered by combustion of unconverted biomass (Ecoinvent, 2023)

Gasification & Fisher-Tropsch process to naphtha

The gasification of biomass to syngas process is modelled according to the LCI from Bachmann et al. (2022), based on a circulating fluidized bed gasifier. Gasification involves no pretreatment but requires a biomass moisture content of less than 15% (Bachmann et al., 2022), which was managed by a previous drying step (Piccinno et al., 2016) that was applied to the biomass feedstock.

The Fischer-Tropsch process was modelled based on data from Van Der Giesen et al. (2014), updated with work from Liu et al. (2020). The syngas input has a H:CO ratio of 2:1. The process takes place in a fixed bed reactor over a cobalt-based catalyst, with a pressure between 20-60 bar and at a temperature between 180-250°C (Boerrigter et al., 2004). The process is exothermic and produces heat, which is re-used in the process itself leading to a self-sufficient process. The process produces diesel and paraffins (jet fuel) as by-products.

Fast pyrolysis to aromatics

The life cycle modelling is based on work from Yang et al. (2022). The fast pyrolysis step requires no pretreatment except drying, producing bio-oil (~25wt%) from woody biomass (Huang et al., 2020), the vapors are passed over a zeolite-based catalyst to obtain aromatics with a selectivity of 85% (Zheng et al., 2017), and including a distillation step at the end (Yang et al., 2022).

Catalytic dehydration to ethylene

This process catalytically dehydrates ethanol to ethylene at 300-450°C in a fluidized bed reactor over a 1% H_2SO_4 solution as catalyst (Nitzsche et al., 2016). A gas separation removes the gaseous hydrocarbon by-products (Bazzanella and Ausfelder, 2017), the dehydration reactor effluent is quenched to a temperature of 40°C and pressurized, remaining water is removed with NaOH. Finally, the effluent is sent to an ethylene purification unit, where it is separated (Yang et al., 2018). The process is highly selective to ethylene (97%) and endothermic (Bazzanella and Ausfelder, 2017).

Dimerization & metathesis to propylene

Inventory data is taken from Kikuchi et al. (2017). Ethylene can be converted into propylene in a metathesis reaction at 200°C and 1 atm along with butane (Takai et al., 2006), which can be obtained through dimerization of ethylene, a process at 400°C and 1 atm (Kikuchi et al., 2013).

Methanol-To-Olefins & Methanol-To-Aromatics

Data on the MTO process was taken from work by Dutta et al. (2019), and MTA processes were based on work by Jiang et al. (2020). Methanol is dehydrated in a catalytic reactor to olefins (450°C), over a zeolite catalyst. The product stream is then compressed using cooling water, after which it is treated with CO_2 before the olefins are separated by distillation. The by-products are sales gas, pentane, butane, ethane, hydrogen (Dutta et al., 2019). In regard to the MTA process, methanol is first fed into an aromatization reactor and heated to 455°C. The product stream is cooled and water is removed, after which it is pressurized and fed into a train of distillation columns to separate the aromatics. The by-products are LPG, dry gas, pentane, C9+ (Jiang et al., 2020).

Steam cracking

Inventory data is taken from research of Ren et al. (2006) on naphtha steam cracking, which is partly based *The Handbook of Petrochemicals and Processes* (Wells, 1991). The (bio-)naphtha is fed into a pyrolysis furnace and preheated to 650°C, after which the pyrolysis takes place in a reactor at temperatures up to 1100°C. The cracked gas is then quenched, condensed and fractionated. In the last phase the fractionate is separated through distillation, refrigerated and extracted into olefins, aromatics, and the (by-)products butadiene, H_2. The other products - fuel oil, C4 and C8+ fractions - flow back to the refinery (Ren et al., 2006).

Table 19: Overview of each core process in terms of feedstock, product and by-product. Descriptions are given above.

Main process	Feedstock	Main product	By-products
Gasification	Biomass	Methanol	Heat
Fermentation	Biomass	Ethanol	Electricity
Fast Pyrolysis	Biomass	Aromatics	Heat, electricity
Gasification	Biomass	Syngas	Heat
Fischer-Tropsch synthesis	Syngas	Naphtha	Synthetic fuel, jet fuel (C_9-

			C_{16}; paraffin's), diesel
Steam cracking	Naphtha	Olefins, aromatics	Butadiene, H_2
Catalytic dehydration	Ethanol	Ethylene	C_4-hydrocarbons
Dimerization & metathesis	Ethylene	Propylene	Hydrocarbons (C_5H_{12}, C_6H_{14}, C_3H_8)
Methanol-to-Olefins (MTO)	Methanol	Product gas (olefin-rich)	Sales gas, pentane, butane, ethane, hydrogen
Methanol-to-Aromatics (MTA)	Methanol	Reformate (BTX-rich)	LPG, dry gas, pentane, C_{9+}

1.4 Allocation methods

The default allocation method substitutes the emissions of the by-products (Table 4). In the sensitivity analysis, allocation based on calorific value is applied. Calorific values of products and by-products are shown in Table 5.

Table 20: Overview of by-products in terms of chemicals and energy, their emissions and database names.

By-products	GHG emission	Unit	Name
Pentane	0.74	kg CO2-eq/kg	Pentane {GLO}| market for | APOS, U
Butene	1.69	kg CO2-eq/kg	Butene, mixed {RoW}| market for butene, mixed | APOS, U
Kerosene	0.42	kg CO2-eq/kg	Kerosene {RoW}| market for | APOS, U
Diesel	0.43	kg CO2-eq/kg	Diesel {GLO}| market group for | APOS, U
Hydrogen	1.44	kg CO2-eq/kg	H2 {RoW}| market for | APOS, U
C6 alkanes	0.60	kg CO2-eq/kg	Average of: Hexane {GLO}| market for | APOS, U & 2-methylpentane {GLO} market for | APOS, U
Butadiene	1.23	kg CO2-eq/kg	Butadiene {RoW}| market for butadiene | APOS, U
Electricity, current	0.14	kg CO2 eq./MJ	Electricity, Europe based | APOS, U
Heat from steam	0.10	kg CO2-eq/MJ	Heat, from steam, in chemical industry {RER}| market for heat, from steam, in chemical industry | APOS, U
Steam	0.28	kg CO2-eq/kg	Steam, in chemical industry {RER}| market for steam, in chemical industry | APOS, U

Table 21: Calorific values of (by-)products to allocate emissions (calorific-value based allocation method).

Products	Calorific value (MJ/kg)
Methanol	22.7
Ethylene	47.2
Propylene	45.8
BTX (benzene)	41.8
Pentane	45.4
Butene	45.3
LPG	46.1

Dry gas (methane)	55.5
Pentane	48.6
Diesel	44.8
Kerosine	46.4
Butadiene	44.6
Paraffin	46.0
Ethane	51.9
Hydrogen	141.8
Syngas	5
Naphtha	45
Ethanol	26.7
Toluene	40.6
Xylene	40.9

1.5 Sensitivity Analysis: Cultivation emissions

Table 22: Overview of emissions related to biomass cultivation applied in sensitivity analysis regarding cultivation emissions.

Feedstock	**Type**	**GHG emissions (kg CO_2-eq/kg wbm)**	**GHG emissions (kg CO_2-eq/kg dbm)**	**Location**	**Source**
Grasses	Cultivation and harvest emissions	0.047	0.062	NA	Default
Grasses	Fertillizer emissions	0.009	0.012	CH	Grass, organic {CH}| grass production, permanent grassland, organic, extensive | APOS, U - excl. transport, harvest, etc.
Grasses	Fertillizer emissions	0.009	0.012	RoW	Grass, organic {RoW}| grass production, permanent grassland, organic, extensive | APOS, U - excl., transport, harvest etc.
Grasses	Cultivation and harvest emissions	0.083	0.110	RoW	Grass, organic {RoW}| grass production, organic, intensive | APOS, U - excl. transport, harvest etc.
Grasses	Cultivation and harvest emissions	0.039	0.052	Mediterranean	Zucaro et al., 2014
Grasses	Fertillizer emissions	0.054	0.072	NA	Hamelinck & Hoogwijk, 2007
Grasses	Fertillizer emissions	0.030	0.040	NA	Tadele et al. (2019)
Grasses	Fertillizer emissions	0.030	0.040	NA	Tadele et al. (2019)
Sugarcane	Cultivation and harvest emissions	0.072	0.072	NA	Default
Sugarcane	Fertillizer emissions	0.151	0.151	RoW	Hanssen et al., (2020): Smeets et al., 2009
Sugarcane	Fertillizer emissions	0.073	0.073	South America	Hanssen et al., (2020): Smeets et al., 2009
Sugarcane	Cultivation and harvest emissions	0.080	0.080	Australia	Renouf et al., 2010
Sugarcane	Cultivation and harvest emissions	0.11	0.110	NA	Edwards et al. (2011)
Sugarcane	Cultivation and harvest emissions	0.118	0.118	India	Powar et al., 2021
Sugarcane	Cultivation and harvest emissions	0.040	0.040	Brazil	Kikuchi et al. (2013)

Sugarcane	Fertillizer emissions	0.041	0.041	RoW	Sugarcane {RoW}| production | APOS, U - excl. transport, harvesting etc.
Sugarcane	Cultivation and harvest emissions	0.044	0.044	Australia	Renouf et al., 2018
Sugarcane	Cultivation and harvest emissions	0.046	0.046	RoW	Sugarcane {RoW}| production | APOS, U
Sugarcane	Fertillizer emissions	0.047	0.047	Brazil	Sugarcane {BR-SP}| sugarcane production | APOS, U - excl. transport, harvesting etc.
Woody crops	Cultivation and harvest emissions	0.052	0.075	NA	Default
Woody crops	Cultivation and harvest emissions	0.050	0.072	RoW	Ecoinvent, wood chips
Woody crops	Cultivation and harvest emissions	0.018	0.026	DE	Wood chips and particles, willow {DE}| willow production, short rotation coppice | APOS, U - excl. transport etc.
Woody crops	Fertillizer emissions	0.020	0.029	RoW	Wood chips and particles, willow {RoW}| willow production, short rotation coppice | APOS, U - excl. transport etc.
Woody crops	Fertillizer emissions	0.020	0.029	RoW	Wood chips and particles, willow {RoW}| willow production, short rotation coppice | APOS, U - excl. transport etc.
Woody crops	Fertillizer emissions	0.055	0.079	NA	Hanssen et al., (2020)
Woody crops	Cultivation and harvest emissions	0.070	0.101	NA	Therasme et al. (2021)
Woody crops	Cultivation and harvest emissions	0.090	0.129	NA	IEA, 2013
Woody crops	Cultivation and harvest emissions	0.100	0.144	NA	Njakou Djomo et al. (2010)
Woody crops	Cultivation and harvest emissions	0.110	0.158	NA	Caputo et al. (2014)
Woody crops	Cultivation and harvest emissions	0.018	0.026	DE	Wood chips and particles, willow {DE}| willow production, short rotation coppice | APOS, U - excl. transport etc.
Agricultural residues	Cultivation and harvest emissions	0.000	0.000	NA	No cultivation impact
Agricultural residues	Cultivation and harvest emissions	0.07	0.080619	USA	GREET
Agricultural residues	Cultivation and harvest emissions	0.03	0.032831	RoW	Default, allocated share of ecoinvent corn

2. Results

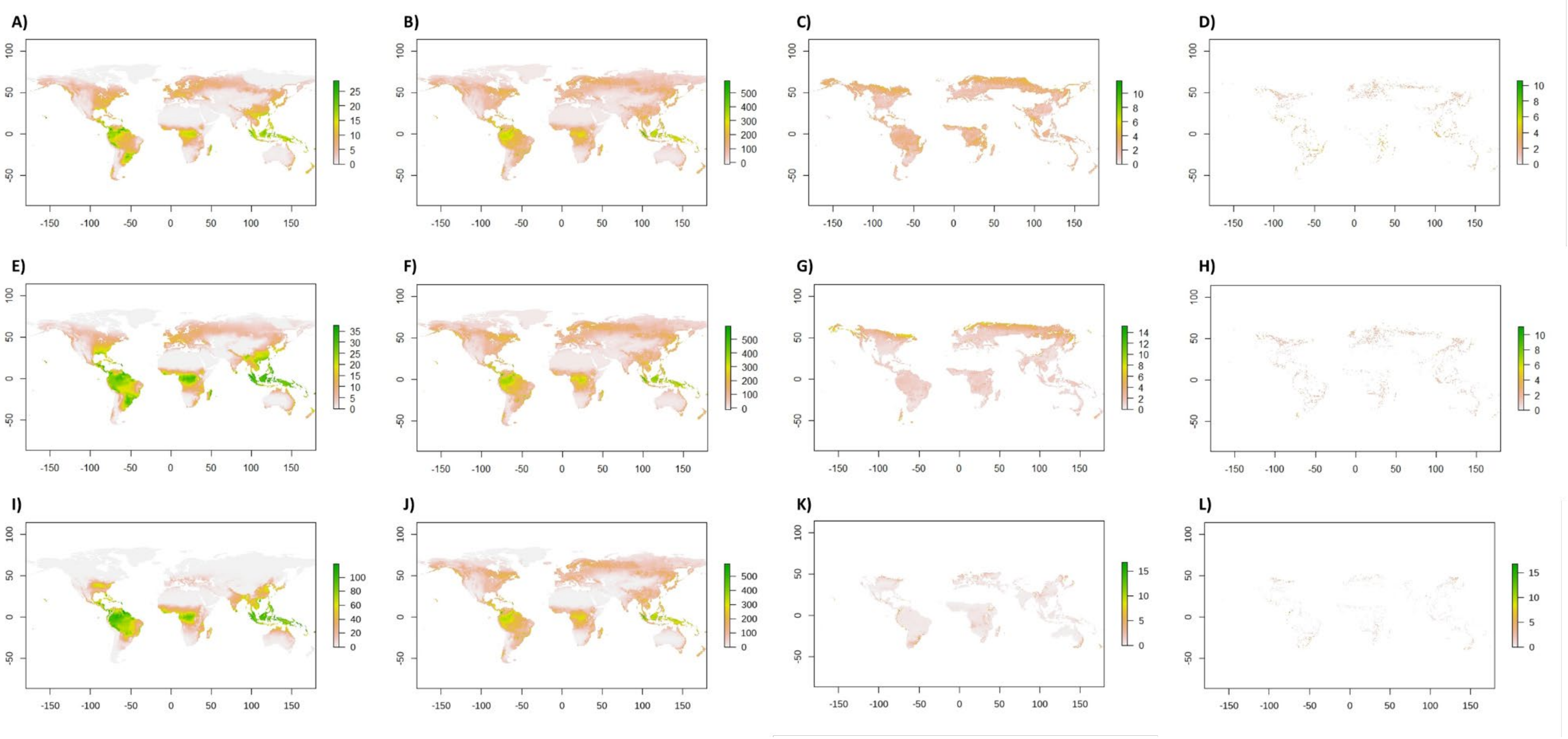


Figure 5: Maps of crop-specific yield estimates, carbon stocks, calculated LUC emissions including global all cover types and LUC emissions including abandoned and marginal land and degraded and managed forests, over a 30-year evaluation period (from left to right), of the feedstocks; (A-D) Woody crops; (E-H) Grasses; and (I-L) Sugarcane. Data is derived from the IMAGE integrated assessment model (Stehfest et al., 2014) coupled to the global vegetation and hydrological model LPJml (Schaphoff et al., 2018; Sitch et al., 2003).

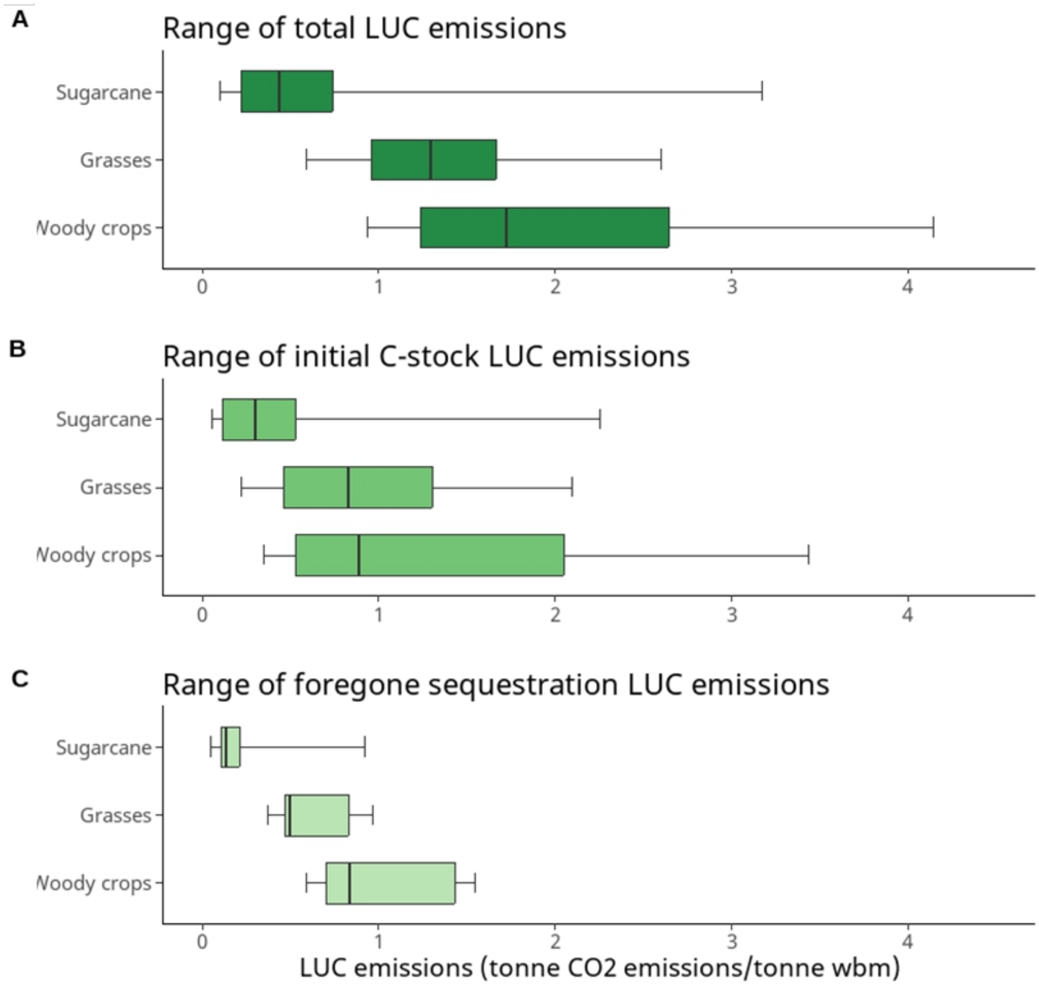


Figure 6: Boxplots (5,25,50,75,95 percentiles) of default LUC emissions: (A) Total LUC emissions (= initial C-stock emissions + foregone sequestration emissions); (B) Initial C-stock LUC emissions; (C) LUC emissions related to foregone sequestration.

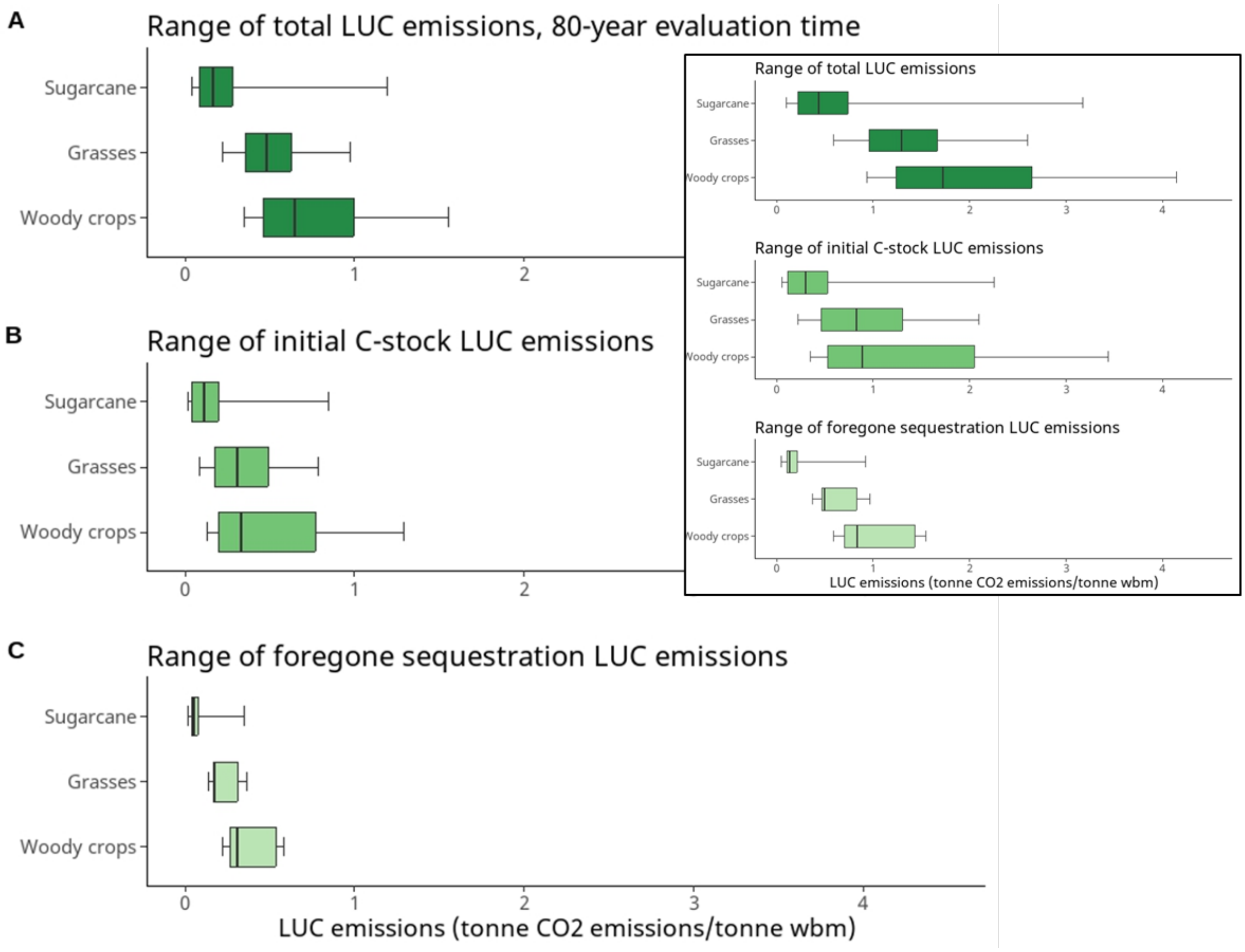


Figure 7: Boxplots (5,25,50,75,95 percentiles) of LUC emissions over a 80-year evaluation time instead of the default of 30-years: (A) Total LUC emissions (= initial C-stock emissions + foregone sequestration emissions); (B) Initial C-stock LUC emissions; (C) LUC emissions related to foregone sequestration. The smaller plot is Figure S.1, for comparison.

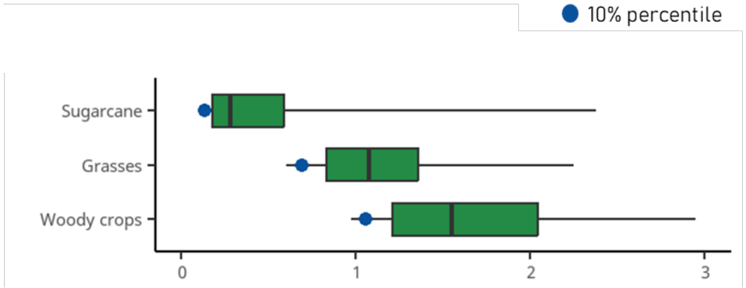
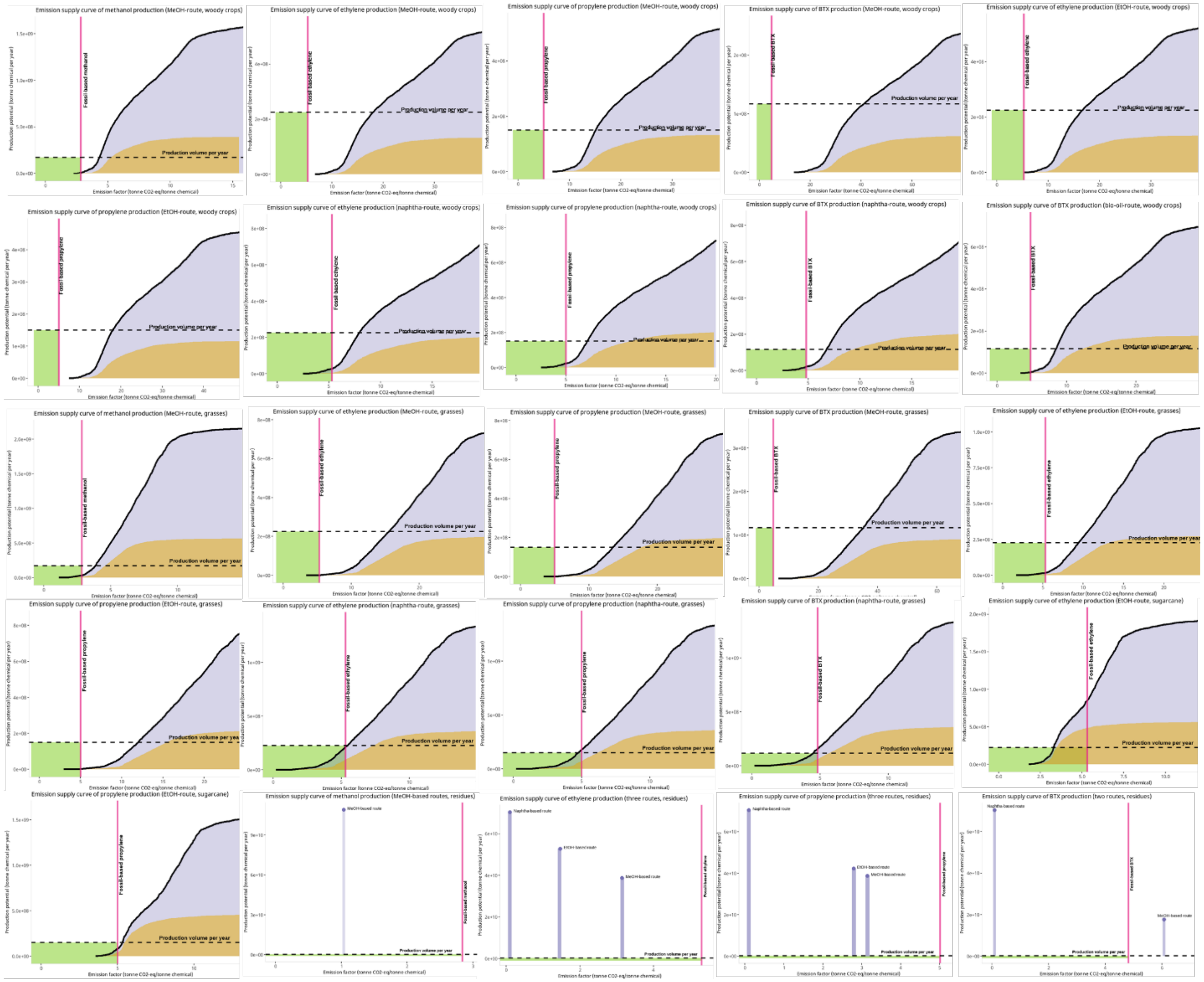


Figure 8: Boxplots (5,10,25,50,75,95 percentiles) of LUC emissions (kg CO_2/kg wbm) that only include the land cover type of abandoned and marginal land.


Emission supply curve of methanol production (MeOH-route, woody crops)

Emission supply curve of ethylene production (MeOH-route, woody crops)

Emission supply curve of propylene production (MeOH-route, woody crops)

Emission supply curve of BTX production (MeOH-route, woody crops)

Emission supply curve of ethylene production (EtOH-route, woody crops)

Emission supply curve of propylene production (EtOH-route, woody crops)

Emission supply curve of ethylene production (naphtha-route, woody crops)

Emission supply curve of propylene production (naphtha-route, woody crops)

Emission supply curve of BTX production (naphtha-route, woody crops)

Emission supply curve of BTX production (bio-oil-route, woody crops)

Emission supply curve of methanol production (MeOH-route, grasses)

Emission supply curve of ethylene production (MeOH-route, grasses)

Emission supply curve of propylene production (MeOH-route, grasses)

Emission supply curve of BTX production (MeOH-route, grasses)

Emission supply curve of ethylene production (EtOH-route, grasses)

Emission supply curve of propylene production (EtOH-route, grasses)

Emission supply curve of ethylene production (naphtha-route, grasses)

Emission supply curve of propylene production (naphtha-route, grasses)

Emission supply curve of BTX production (naphtha-route, grasses)

Emission supply curve of ethylene production (EtOH-route, sugarcane)

Emission supply curve of propylene production (EtOH-route, sugarcane)

Emission supply curve of methanol production (MeOH-based routes, residues)

Emission supply curve of ethylene production (three routes, residues)

Emission supply curve of propylene production (three routes, residues)

Emission supply curve of BTX production (two routes, residues)

Figure 9: Emission supply curves of each route per feedstock in 25 panels (residue-based routes are shown in four panels in total, per chemical: methanol, ethylene, propylene and BTX). The dashed line shows the current production volume of the chemical; the pink line represents the fossil-based emissions; the green rectangles indicate the area of mitigation potential; sandy colored curve refers to ‘abandoned and marginal land’ and purple to ‘managed and degraded forests’.

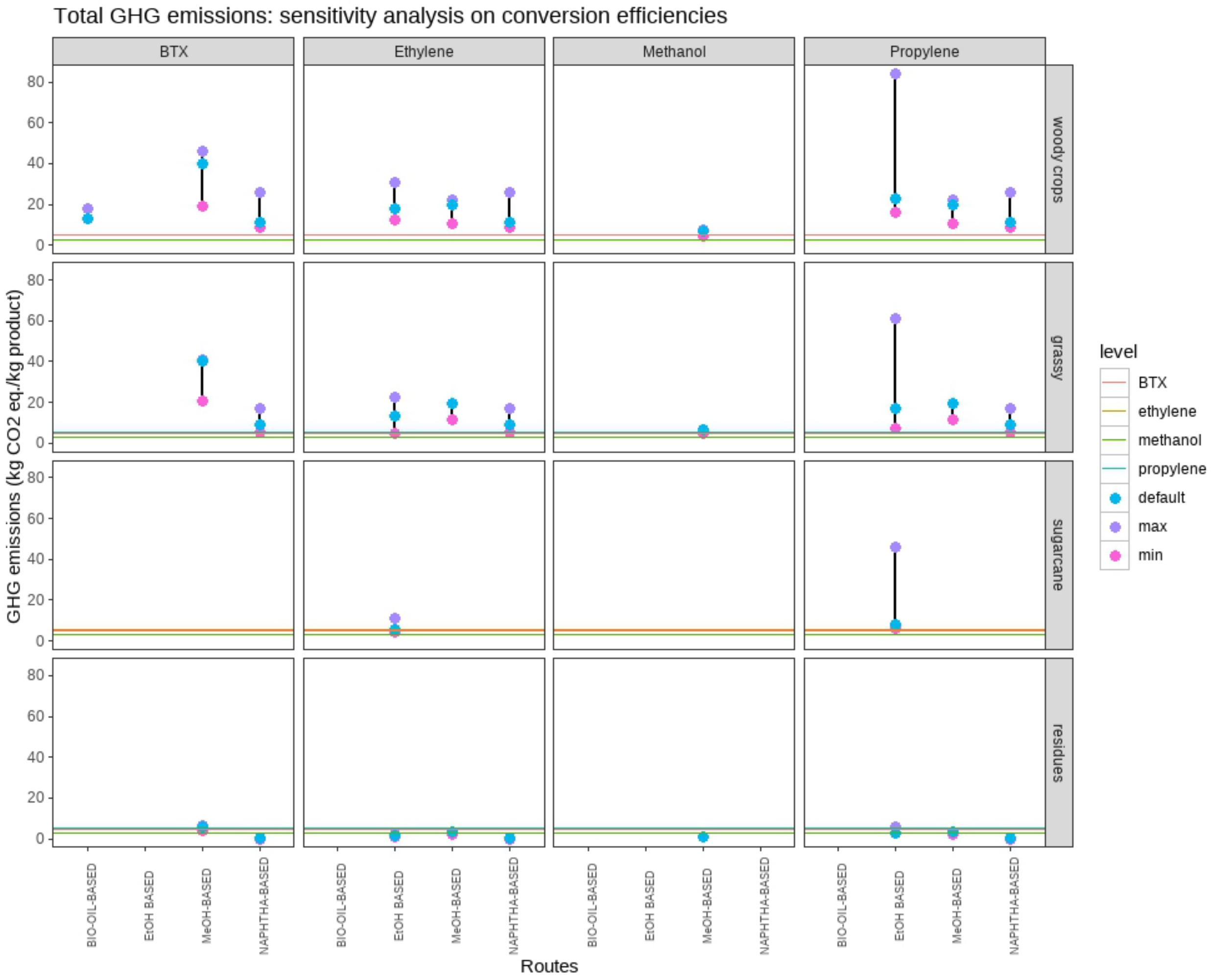


Figure 10: Sensitivity analysis plot on conversion efficiencies. Blue dot: default GHG emissions; Pink dot: GHG emissions based on minimal conversion efficiencies values from literature; Purple dot: GHG emissions based on maximal conversion efficiencies values from literature. Lines indicate fossil-based products' GHG emissions.

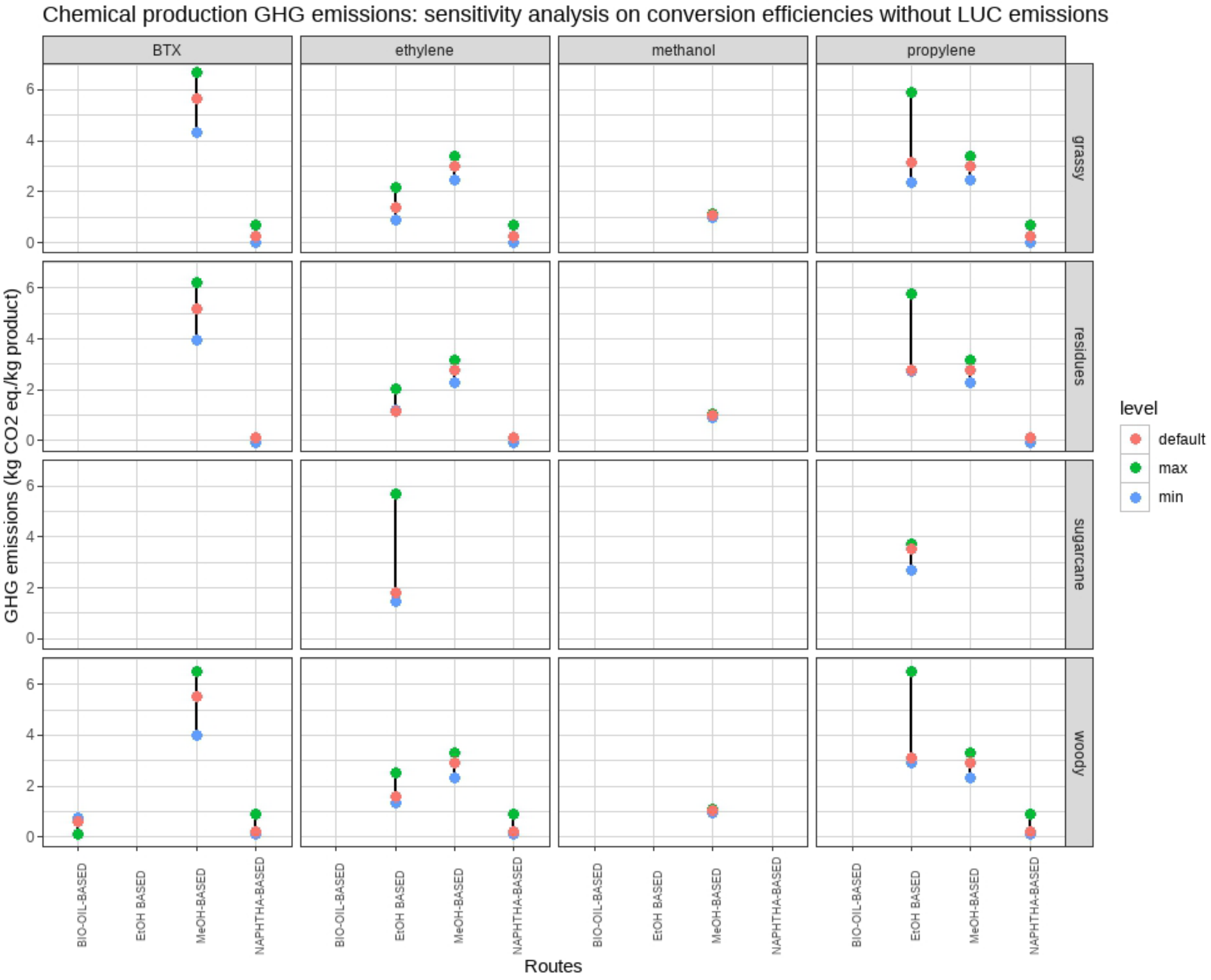


Figure 11: Sensitivity analysis on conversion efficiencies: GHG emissions of the different routes, excluding LUC emissions. Pink dot: default GHG emissions; Blue dot: GHG emissions based on minimal conversion efficiencies values from literature; Green dot: GHG emissions based on maximal conversion efficiencies values from literature.

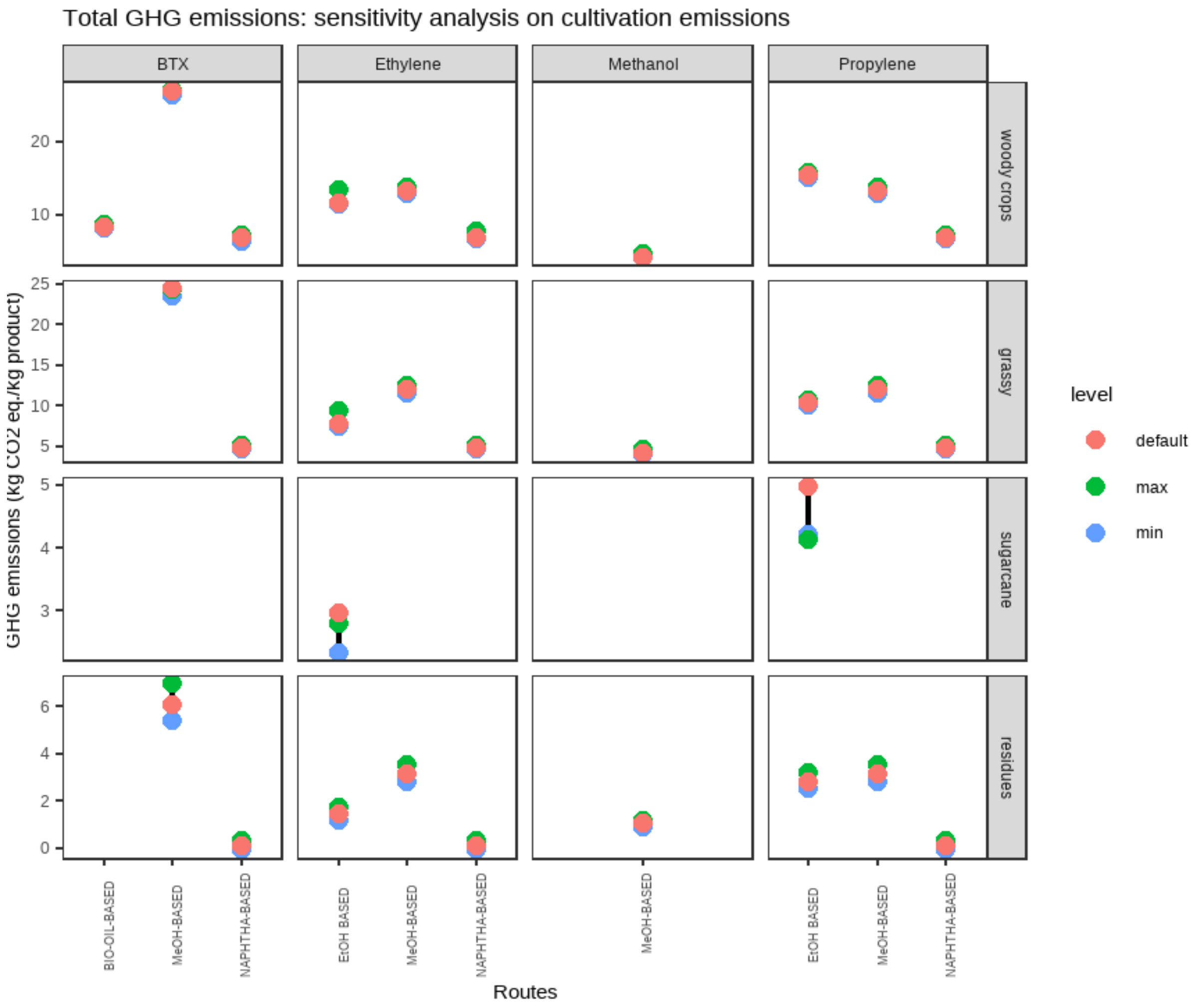


Figure 12: Sensitivity analysis plot on cultivation emissions. Red dot: default GHG emissions; Green dot: GHG emissions based on minimal cultivation emission values from literature; Blue dot: GHG emissions based on maximal cultivation emission values from literature (details in Table S.6).

3. Discussion

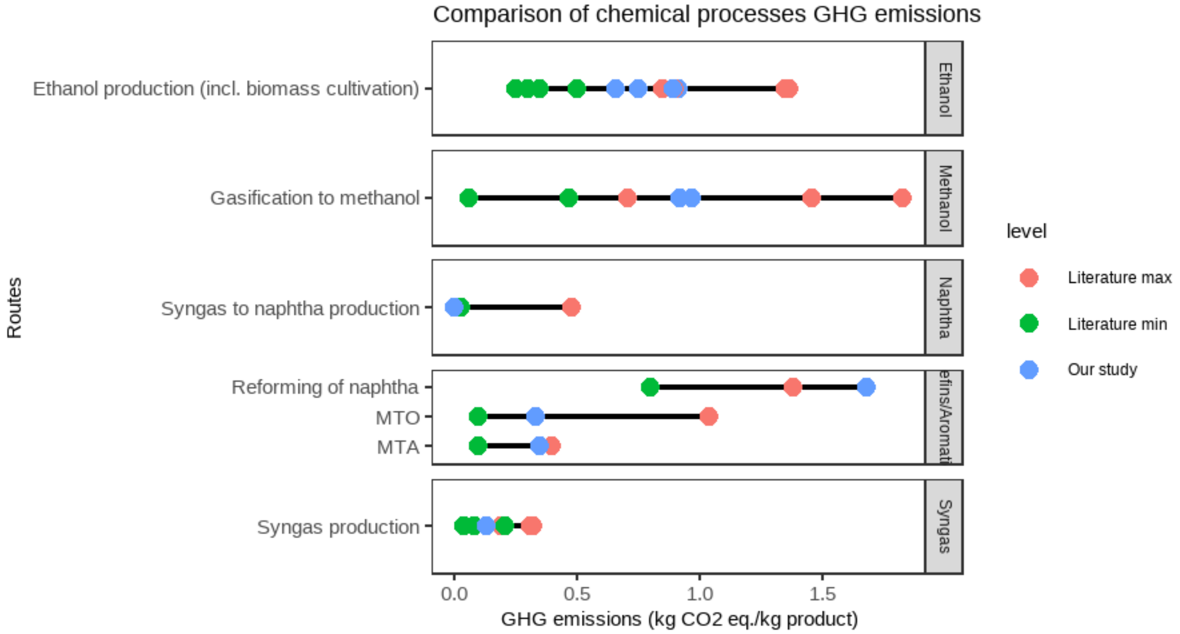


Figure 13: Plots showing chemical processing related GHG emissions from literature and this study. The multiple same coloured dots within one plot represents the same route and product but with different biomass feedstock input.

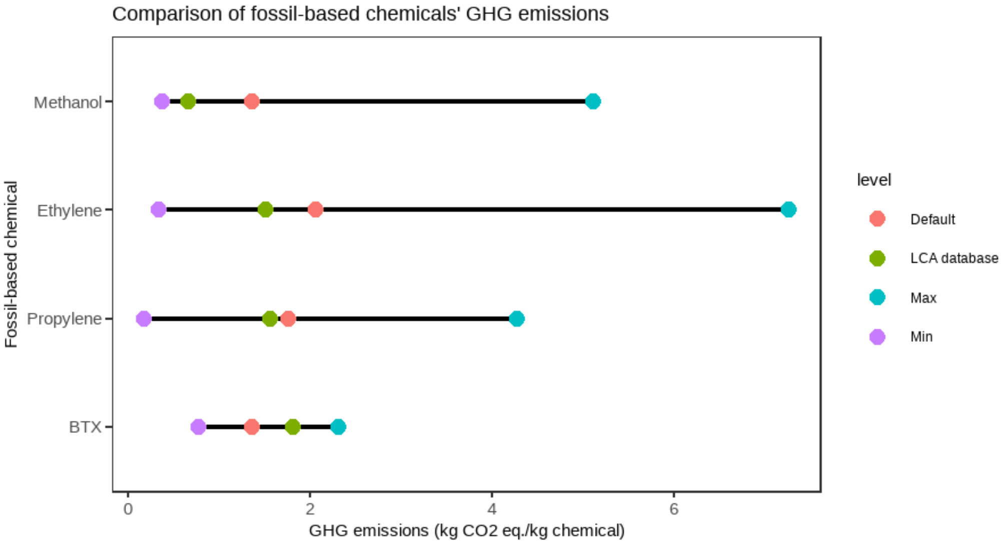


Figure 14: Plot showing cradle-to-gate GHG emissions of fossil-based chemicals; range based on detailed study from Cullen et al., (2024) and LCA datasets of Ecoinvent.

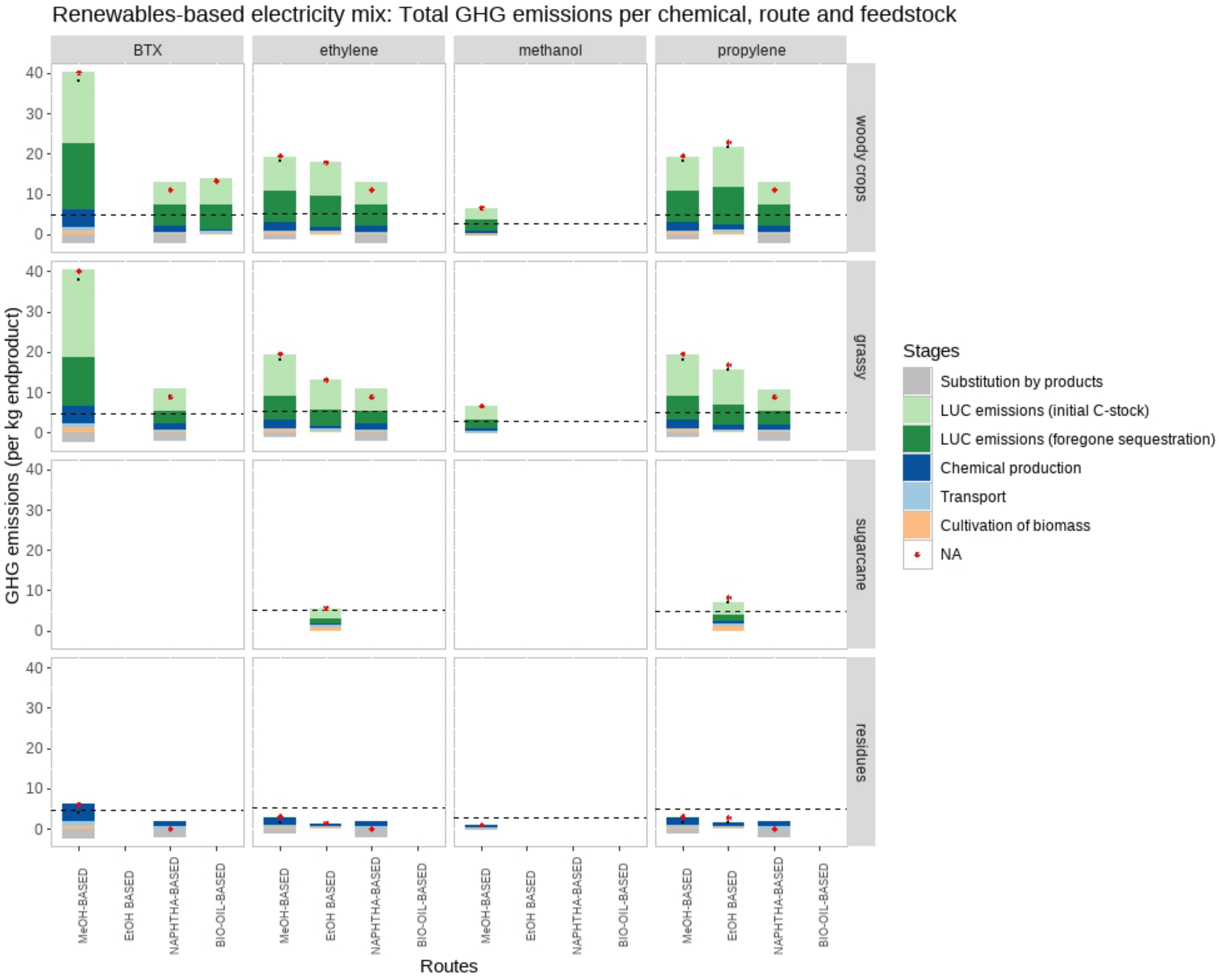


Figure 15: Plots on total GHG emissions per chemical, route and feedstock based on a renewables-based electricity-mix during chemical production. Black dot represents overall total GHG emissions; Red dot represents the default overall GHG emissions (incl. current electricity-mix). Modelling of the cleaner electricity mix was based on the ‘low emissions & carbon-neutral (incl. CCS)’ dataset (Galán-Martín et al., 2021), which was based on projections from IMAGE, assessing external developments for 2050 in the electricity sector. This resulted in 0.04 kg CO2-eq/MJ of electricity, instead of the default of 0.14 kg CO2-eq/MJ.

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