Supporting information

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High performance, but low cost and environmental impact? Integrated techno-economic and life cycle assessment of Polyoxazolidinone as a novel high-performance polymer

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1. Data sources for life cycle inventory

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

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

Table S 1 summarizes all chemicals and data sources and includes potential exceptions from the hierarchy.

Table S 1: Summary of chemicals, production technologies, locations, and data sources of the Life Cycle Inventory of HPT production.

Name of chemical	Production technologies	Location	Source	Comment
Acetic acid	Catalytic reaction of methanol and carbon monoxide	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Acetone	Hock process	N/A	NexantECA.[3]	Allocated by mass allocation, allocation factor = 0.3809
Allyl chloride	Chlorination of propylene	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Ammonia	Haber-Bosch process, without CO_2 recovery	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Aniline	Catalytic hydrogenation of nitrobenzene	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
	Fermentation and catalytic decarbonization	N/A	Winter et al. 2020[4]	Aggregated process
Benzene	Technology mix	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
	Methanol-to-aromatics	N/A	IHS Markit[5]	Methodology as described in Meys et al. 2021[6]
Benzonitrile	Sohio process	N/A	Ullmann's Encyclopedia of Industrial Chemistry[7]	Process modeled based on stoichiometry
Bisphenol A	Sinopec/Lummus process	N/A	NexantECA.[8]	
Bisphenol A diglycidyl ether (BADGE)	Continuous Caustic Coupling Process of Epichlorohydrin and Bisphenol A	N/A	NexantECA.[9]	Modeled as liquid epoxy resin
p-tert-Butylphenyl glycidyl ether (PBPGE)	-	N/A	-	BADGE used as proxy
Calcium chloride	Solvay process	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.5046
Calcium hydroxide	Technology mix	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Carbon dioxide	CO_2 capture from ammonia plant	N/A	Von der Assen el al.[10]	Modeled as monoethanolamine absorption
Carbon monoxide	Cryogenic air separation of synthesis gas	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
	Partial condensation of synthesis gas from biomass gasification	N/A	IHS Markit[5]	Methodology as described in Meys et al. 2021[6]
Chlorine	Technology mix	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Chlorobenzene	Benzene chlorination	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.9105
Cooling water	Tap water from surface water	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
o-Dichlorobenzene	Benzene chlorination	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent, allocated by mass allocation, allocation factor = 0.0380
4,4'-Dichlorodiphenyl sulfone	Sulfonation of chlorobenzene using sulfur trioxide and thionyl chloride	N/A	NexantECA.[11] and Patent[12]	For details see section 4
Dihydroxydiphenyl sulfone (Bisphenol S)	Sulfonation of phenol using oleum (65 %)	N/A	NexantECA.[11] and Patent[12]	For details see section 4
Electricity	Grid mix 2019	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
	From wind power	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Epichlorohydrin	Allyl chloride hypochlorination and alkaline epoxidation	N/A	NexantECA.[13]	
	Glycerol hypochlorination and alkaline epoxidation	N/A	NexantECA.	
Ethanol	Fermentation, from sugar beet	EU-28	Sphera – GaBi Version 2021.2[1]	Aggregated process
Formaldehyde	Oxidation of methanol	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Glycerine	By product from rapeseed methyl ester via extraction, refining, transesterification	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process, 2014 price allocated
Hydrochloric acid (100 %)	Technology mix	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Hydrogen	Steam reforming of natural gas	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process

Name of chemical	Production technologies	Location	Source	Comment
Light fuel oil	From crude oil	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Methanol	Technology mix	EU-28	Sphera – GaBi Version 2021.2[1]	Aggregated process
	From synthesis gas	N/A	Andersson et al.[14]	For details see section 3
Methyl chloride	Reaction of methane and chlorine	N/A	Ullmann's Encyclopedia of Industrial Chemistry[7]	Process modeled based on stoichiometry
Methylene diphenyl diisocyanate (MDI)	Chematur condensation of aniline	N/A	NexantECA.[15]	
Momomethylamine	Reaction of methanol and ammonia	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Natural gas	Consumption mix	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Nitric acid, dilute (60 %)	Oxidation of ammonia	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Nitric acid (100 %)	Oxidation of ammonia	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Nitrogen	Cryogenic air separation	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
Nitrous dioxide	Ostwald process	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Nitrous oxide	Ostwald process	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Oleum (65 %)	Mixing of sulfuric acid and sulfur trioxide	N/A	Ullmann's Encyclopedia of Industrial Chemistry[7]	Process modeled based on stoichiometry
Phenol	Hock process	N/A	NexantECA.[3]	Allocated by mass allocation, allocation factor = 0.6191
m-Phenylenediamine	Diazotization and hydrogenation of aniline	N/A	NexantECA.[16]	p-Phenylenediamine used as proxy
Phthalic anhydride	Oxidation of xylene	DE	Sphera – GaBi Version 2021.2[1]	Aggregated process
N-methyl Phthalimide	Reaction of phthalic anhydride with momomethylamine	RER	ecoinvent 3.7 - undefined[2]	Process modeled based on stoichiometry
Polyethersulfone	Polymerization of DCDPS, Bisphenol S, and potassium carbonate	N/A	NexantECA.[17]	For details see section 4
Polyetherimide	Polymerization of Bisphenol A, phthalic acid, n-methyl phthalimide, and m-phenylenediamine	N/A	NexantECA.[17]	For details see section 4
Polysulfone	Polymerization of DCDPS and Bisphenol A	N/A	NexantECA.[17]	For details see section 4
Polyoxazolidinone	Polymerization of BADGE and MDI	N/A	Covestro Deutschland AG[18]	Details see paper
Potassium carbonate	Reaction of potassium hydroxide and carbon dioxide	GLO	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Potassium chloride	Shaft mining and beneficiation	EU-28	Sphera – GaBi Version 2021.2	Aggregated process
Potassium hydroxide	Electrolysis of potassium chloride brine	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Process steam	From natural gas (95 % efficiency)	DE	Sphera – GaBi Version 2021.2	Aggregated process
	From electricity (95 % efficiency)	N/A	-	An electric boiler efficiency of 95 % is assumed
Process water	From groundwater	EU-28	Sphera – GaBi Version 2021.2	Aggregated process
Propylene	Steam cracker	DE	Sphera – GaBi Version 2021.2	Aggregated process
	Methanol-to-Olefins by the Lurgi process	N/A	IHS Markit[5]	Methodology as described in Meys et al. 2021[6]
Sodium hydroxide (caustic soda)	Technology mix	DE	Sphera – GaBi Version 2021.2	Aggregated process
Sodium nitrite	Reaction of nitrogen oxides with sodium carbonate	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Sulfuric acid (96 %)	Technology mix	DE	Sphera – GaBi Version 2021.2	Aggregated process
Sulfur (elemental)	From crude oil	DE	Sphera – GaBi Version 2021.2	Aggregated process
Sulfur dichloride	Reaction of sulfur and chloride	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Sulfur dioxide	Liquid SO2 production via sulfur combustion	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Sulfur trioxide	From sulfuric acid	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Synthesis gas	Biomass gasification	N/A	Bachmann et al.[19]	For details see section 3

Name of chemical	Production technologies	Location	Source	Comment
Thionyl chloride	Reaction of sulfur dioxide, sulfur dichloride, and chlorine	RER	ecoinvent 3.7 - undefined[2]	Modeled using unit process data from ecoinvent
Toluene	BTX from reformate	DE	Sphera – GaBi Version 2021.2	Aggregated process

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

Name of chemical	Production technology	Limiting compound	Process yield in %
Bisphenol A diglycidyl ether (BADGE)	Continuous Caustic Coupling Process of epichlorohydrin and bisphenol A	Bisphenol A	99.9
Bisphenol A	Sinopec/Lummus process	Phenol	98.6
Phenol and Acetone	Hock process	Benzene	96.6
Benzene	Technology mix - aggregated process	Not provided	-
	Methanol-to-aromatics	Methanol	71.5
Propylene	Steam cracker - aggregated process	Not provided	-
	Methanol-to-olefins	Methanol	66.0
Methanol	Technology mix – aggregated process	Not provided	-
	From biomass gasification	Biomass	40.1*
Epichlorohydrin	Allyl chloride hypochlorination and alkaline epoxidation	Allyl chloride	95.0
	Glycerol hypochlorination and alkaline epoxidation	Glycerine	90.0
Allyl chloride	Chlorination of propylene – aggregated process	Not provided	-
Glycerine	By product from rapeseed methyl ester via extraction, refining, transesterification – aggregated process	Not provided	-
Methylene diphenyl diisocyanate (MDI)	Chematur condensation of aniline	Aniline	99.6
Aniline	Catalytic hydrogenation of nitrobenzene – aggregated process	Not provided	-
	Fermentation and catalytic decarbonization	Sugar beet	confidential
Formaldehyde	Oxidation of methanol	Methanol	83.3
Carbon monoxide	Cryogenic air separation of synthesis gas – aggregated process	Not provided	-
	Partial condensation of synthesis gas from biomass gasification	Biomass	46.9*
N-methyl phthalimide	Reaction of phthalic anhydride with momomethylamine	Stoichiometry	100
m-Phenylenediamine	Diazotization and hydrogenation of aniline	Aniline	75.9
Dihydroxydiphenyl sulfone (Bisphenol S)	Sulfonation of phenol using oleum (65 %)	Phenol	93.7
4,4‘-Dichlorodiphenyl sulfone	Sulfonation of chlorobenzene using sulfur trioxide and thionyl chloride	Chlorobenzene	75.0
Chlorobenzene	Benzene chlorination	Chlorine	79.2

2. Material properties of high-performance thermoplastic polymers

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

	POX	PEI	PES	PSU	PE
		Ultem 1000	Ultrason E2010	Ultrason S3010	100
Tensile modulus [MPa]	2740	3236	2656	2516	1100[20]
Stress at yield [MPa]	80	115	90	75	25[20,21]
Strain at yield [%]	6	7	7	6	9[20] - 10[21]
Stress at break [MPa]	84	90	62	64	40[21]
Strain at break [%]	92	80	82	118	1500[21]
Flexural modulus [MPa]	2623	3437	2704	2767	1090[21] - 1150[22]
Flexural strength [MPa]	121	162	125	113	24[20]
Ball indentation hardness HB [MPa]	165	202	154	136	46[20]
Vicat B [°C]	159	211	214	182	77[20] - 125[21]

3. Life Cycle Inventory for POX supply chain

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

Bisphenol A diglycidyl ether

We modeled bisphenol A digylcidyl ether (BADGE) production based on process data for the continuous caustic coupling of epichlorohydrin and bisphenol A.[9] Epichlorohydrin is produced conventionally by chlorohydrination of allyl chloride with chlorine.[7] Alternatively, epichlorohydrin can be produced from glycerol and hydrochloric acid.[13] Since glycerol is a by-product of biodiesel production, the availability of glycerol has increased, and the price has decreased sharply in recent years.[23] Thus, production via bio-based glycerol may offer a low-cost and environmentally beneficial pathway to epichlorohydrin. We modeled the production of epichlorohydrin by using process data for the conventional and alternative pathways from NexantECA.[13] The conventional production via allyl chloride produces calcium chloride as a by-product. We give a credit for avoiding the conventional production of calcium chloride from the Solvay process. Process data for the Solvay process were taken from ecoinvent. Since the Solvay process produced soda ash, calcium chloride, and sodium bicarbonate, we used mass allocation with an allocation factor of 0.51 to allocate the environmental impacts to calcium chloride. An economic allocation based on Ecoinvent prices would result in an allocation factor of 0.57, leading to similar environmental impacts. The alternative production via bio-based glycerol produces sodium chloride and fuel residues as by-products. To give a credit for the avoided conventional production of sodium chloride, we used the aggregated dataset from the LCA database GaBi (GaBi).[24] For the fuel residues, we give a credit based on the “light fuel oil at refinery” process from GaBi. To account for the environmental impact of bio-based glycerol, we used the price-allocated dataset from GaBi since no mass-allocated dataset is available.

Bisphenol A is mainly produced by reacting acetone with phenol.[7] Therefore, bio-based phenol would enable the production of bio-based bisphenol A and, thus, increase the share of bio-based reactants for POX. However, a direct route to bio-based phenol is not yet commercialized.[25] Therefore, we only consider an indirect pathway to bio-based phenol and acetone via the Hock process using bio-based benzene and propylene.[3] Bio-based benzene and propylene, in turn, are produced via the methanol-to-aromatics and methanol-to-olefins processes using bio-based methanol from biomass gasification.[5] The

gasification process uses wood pellets as feedstock. We adapted the LCI for wood pellet gasification from Bachmann et al.[19] and integrated the production of methanol in the LCI.[14] The fossil-based production of phenol and acetone uses benzene and propylene from the aggregated GaBi datasets.

Methylene diphenyl diisocyanate

Methylene diphenyl diisocyanate (MDI) is commercially produced in a two-step synthesis using aniline, formaldehyde, and phosgene as feedstock. We modeled the production of MDI based on process data from NexantECA.[15] We considered two alternatives for the supply of aniline: First, fossil-based aniline based on an aggregated dataset from GaBi, and second, bio-based aniline from Winter et al.[4] For formaldehyde production, we included oxidation of methanol from ecoinvent. Methanol can either be taken from a biomass gasification plant or steam reforming of natural gas (aggregated GaBi dataset). We assume that phosgene is produced on-site, and thus, only carbon monoxide and chlorine are required as inputs in addition to aniline. Carbon monoxide is produced by separating either fossil- or bio-based synthesis gas.

p-tert-Butylphenyl glycidyl ether

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

Catalyst

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

Benzonitrile

Benzonitrile is produced commercially by vapor-phase ammoxidation of toluene with ammonia and air.[7] Since no process data is available for benzonitrile production, we used stoichiometry to generate the

LCI. The reaction is carried out with a ratio of ammonia to toluene of 4:1. The selectivity of toluene to benzonitrile is 87.4 %, and the conversion of toluene and ammonia is 97 % and 30 %, respectively.[7] We assumed that unreacted ammonia is neutralized with sulfuric acid (37 %), resulting in ammonium sulfate production. The assumption for ammonia neutralization is based on the acrylonitrile process, where acrylonitrile is produced by the ammoxidation of propylene.[26] We assume that all by-products from benzonitrile production are treated by incineration. For energy requirements of the benzonitrile process, we use data from a large chemical plant site in Gendorf, Germany.[27]

Benzonitrile is also produced commercially from benzoic acid and urea.[28] However, no process data for the benzoic acid-based production are available. Yet, the higher environmental impact of the reactants suggests that the benzoic acid pathway may also have higher environmental impacts.

4. Life Cycle Inventory for reference HPT production and supply chain

The following section explains the main steps in the production of the reference products polyetherimide (PEI), polyethersulfone (PES), and polysulfone (PSU). Process data and energy requirements for production are taken from the Technoeconomics Report Amorphous High Temperature Engineering Thermoplastics from NexantECA.[17] The process data do not contain any information about the amounts of solvents or precipitation and washing agents used in the HPT production. Therefore, we neglect all solvents and other materials for the production of the reference HPTs. Neglecting all solvents and other materials corresponds to a 100 % solvent and material recovery rate, resulting in a best-case assumption for the reference HPT and a corresponding worst-case assumption for POX. Thus, we conduct a conservative assessment for POX.

Furthermore, the amount of chain stopper for polymerization is not included in the NexantECA process data. Thus, we calculate the minimum amount of chain stopper to set the active chain ends of the reaction to zero using the Carothers equation.[29] To calculate the active chain ends, we assumed a polymer molecular weight of 15000 g/mol resulting in a stoichiometric monomer ratio of about 0.97. Calculating the minimum amount of chain stopper also corresponds to a conservative assessment for POX.

Polyetherimide

Polyetherimide (PEI) is produced in a four-step synthesis based on bisphenol A, phthalic acid, n-methyl phthalimide, and m-phenylenediamine (see Figure S 1).[17]

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

In the second step, sodium nitrate by-product and o-dichlorobenzene are removed from bis-ether phthalimide by extraction and evaporation, respectively. Water with 1% sodium hydroxide is used as extraction solvent. The bis-ether phthalimide is mixed with aqueous phthalic acid and dehydrated to form bis(ether phthalic dianhydride). As a catalyst, an imide-anhydride exchange catalyst such as triethylamine is used. However, the process data do not provide any information about the amount of

catalyst used per unit of PEI. Therefore, we did not consider the catalyst in the assessment. The reactor effluent, containing bis(ether phthalic dianhydride), unreacted bis-ether phthalimide, catalyst, and N-methylphalimide by-product, is separated by extraction. For the extraction, o-dichlorobenzene is used as extraction solvent.

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

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

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

Furthermore, to the best of the author's knowledge, no data sets for n-methyl phthalimide and m-phenylenediamine are publically or commercially available. For n-methyl phthalimide, we used process data for phthalimide production from ecoinvent as a proxy. For m-phenylenediamine, the energy demand for production from ecoinvent seems unusually and unjustifiably high. Thus, we modeled the production of p-phenylenediamine as a proxy for m-phenylenediamine based on the process data from the Aromatic Polyamides (Polyaramids) PERP Report from NexantECA.[16] To model the production of trimethylamine, we used process data from ecoinvent.

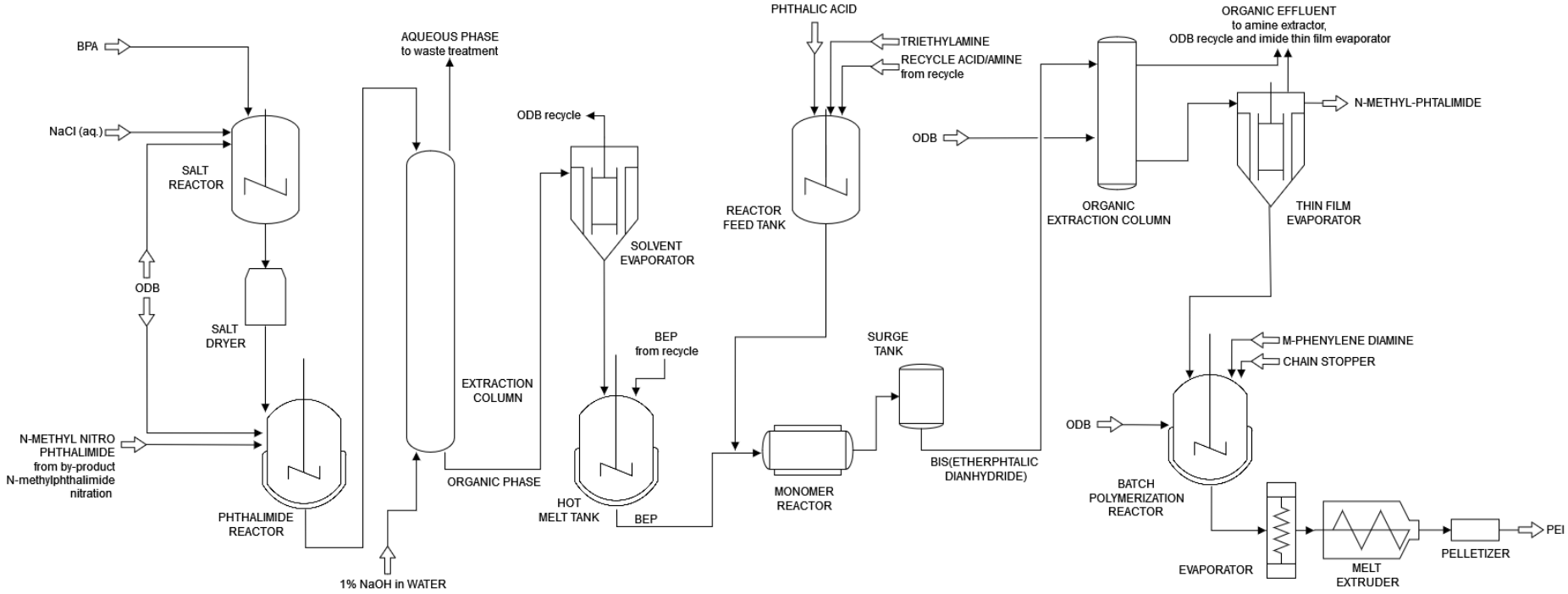

Figure S 1: Simplified process flowsheet of polyetherimide (PEI) production adapted from NexantECA. Not shown: Amine extractor for phtalic acid and amine recycle, solvent thin film evaporator for ODB recycle, imide thin film evaporator for BEP recycle and the separation of N-methylphtalimide for the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

Polyethersulfone

The production of polyethersulfone (PES) consists of polymerization, followed by polymer and solvent recovery (see Figure S 2). The typical production of PES is solely based on 4,4'-dichlorodiphenyl sulfone (DCDPS). However, we considered the alternative production based on DCDPS and 4,4'-dihydroxydiphenyl sulfone (bisphenol S) with faster reaction rates and lower temperature since the alternative production is more likely to be applied industrially.[17] For the polymerization, DCDPS, bisphenol S, and potassium carbonate are charged to the reactor with dimethyl sulfoxide (DMSO) as the reaction solvent.

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

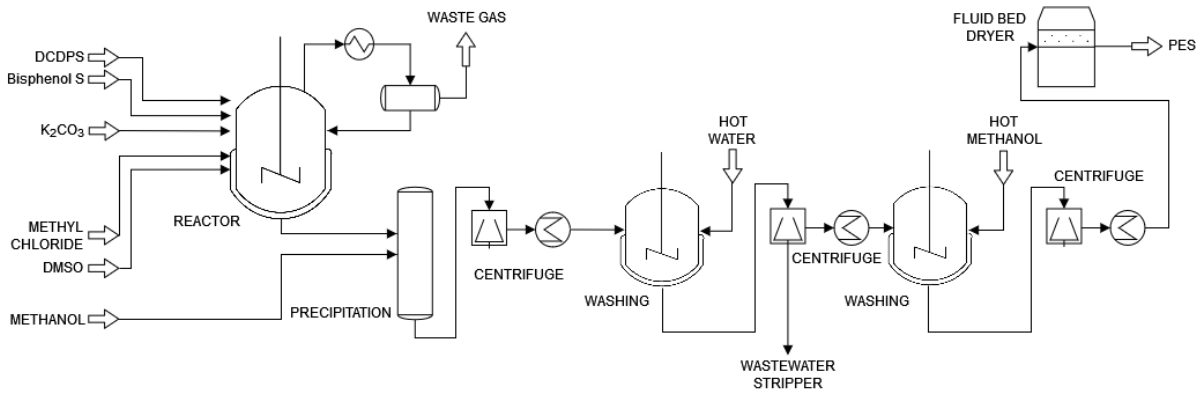

Figure S 2: Simplified process flowsheet of polyethersulfone (PES) production adapted from NexantECA. Abbreviations: DCDPS = 4,4′-Dichlorodiphenyl sulfone, DMSO = dimethyl sulfoxide, K_2CO_3 = potassium carbonate.

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

The Life Cycle Inventory for producing 4,4'-dichlorodiphenyl sulfone (DCDPS) was derived from the Process Evaluation/Research Planning (PERP) Report for Amorphous High Temperature Engineering Thermoplastics from NexantECA.[11] The PERP Report includes detailed information about energy and material requirements for DCDPS production. However, it does not include the amount of caustic soda needed for off-gas scrubbing of sulfur dioxide and hydrochloric acid. Consequentially, we calculated the amount of caustic soda based on stoichiometry as a conservative assumption.

Furthermore, the PERP Report does not include any process data for 4,4'-dihydroxydiphenyl sulfone (bisphenol S production). Thus, we modeled the production based on the patent EP0489788B1, which proposes a procedure for producing bisphenol S.[12] We chose example 4 of the patent using phenol and oleum (65%) as reactants and o-dichlorobenzene as reaction solvent. The bisphenol S yield from phenol is 93%. Since the patent does not include any information about energy requirements for production, we used the energy requirements from DCDPS as a proxy for bisphenol S.

Potassium carbonate

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

Polysulfone

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

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

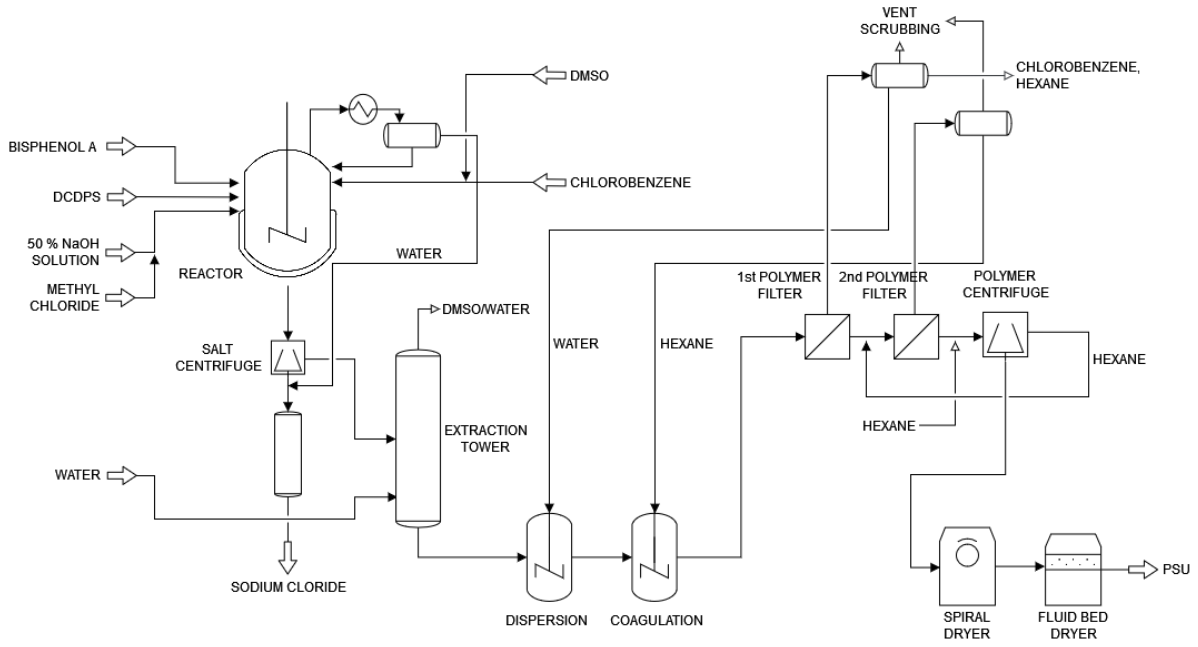

Figure S 3: Simplified process flowsheet of polysulfone (PSU) production adapted from NexantECA. Abbreviations: DCDPS = 4,4′-Dichlorodiphenyl sulfone, DMSO = dimethyl sulfoxide.

Like in PEI production, melt polymerization may also be applied in POX, PES, and PSU production. Melt polymerization may reduce both energy and solvent requirements of HPT production.[29] However, as data for melt polymerization are not available for all HPTs, this study is limited to the conventional production of HPT.

5. Further assumptions in the Life Cycle Assessment

For the process steam, we assumed medium-pressure steam with 13.8 bar (200 psig) according to the NexantECA reports.[17] The specific enthalpy of the medium-pressure steam is 2757 kJ/kg.

We assumed a heating value of 50 MJ/kg for fuel gas demands and by-product credit, corresponding to methane.

6. Land-use change emissions

The cultivation of biomass can change the carbon content of the soil, resulting in so-called land-use change (LUC) emissions. We account for LUC emissions of bio-based products considered in this study, namely ethanol, aniline, glycerol, carbon monoxide, and methanol. The aggregated data sets from GaBi already include LUC emissions.[1] To validate the LUC emissions from GaBi, we compare them with literature data (see Figure S4).

For ethanol and aniline, we used the worst-case assumptions for LUC emissions from Winter et al. corresponding to the values from Al-Riffai et al.[4,30] Glycerol is a by-product from biodiesel production that we modeled using an aggregated and economically allocated data set from GaBi.[1] The aggregated data set does not reveal any information about the amount of biomass consumed. Therefore, we used data on LUC emissions from biodiesel from Malca et al. to calculate the LUC emissions from glycerol.[31] We used the ratio of GHG emissions with and without LUC emissions from Marca et al. and applied it to the aggregated data set from GaBi.

Carbon monoxide and methanol are produced from synthesis gas from wood pellet gasification. According to the literature, wood pellets are mainly produced from softwood pine, which has either no or even negative direct LUC emissions.[32] In addition, indirect LUC emissions from wood pellets are considered small.[33] Assuming no LUC emissions is consistent with the general assumption that second-generation biomass and biofuels have lower LUC emissions than first-generation biomass and biofuels.[34] Furthermore, wood pellets are often produced from waste materials such as forest residues or sawdust from sawmills, so that potential LUC emissions could also be allocated to the main product.[2]

Overall, we assume that bio-based carbon monoxide and methanol from wood pellet gasification does not lead to LUC emission.

Overall, LUC emissions are small compared to the total product emissions of HPTs (see Figure S4). POX has higher LUC emissions than the reference HPTs since more aniline and glycerol are used in POX production. In contrast, the reference products rely mainly on methanol (and PEI on ethanol) as a biogenic carbon source.

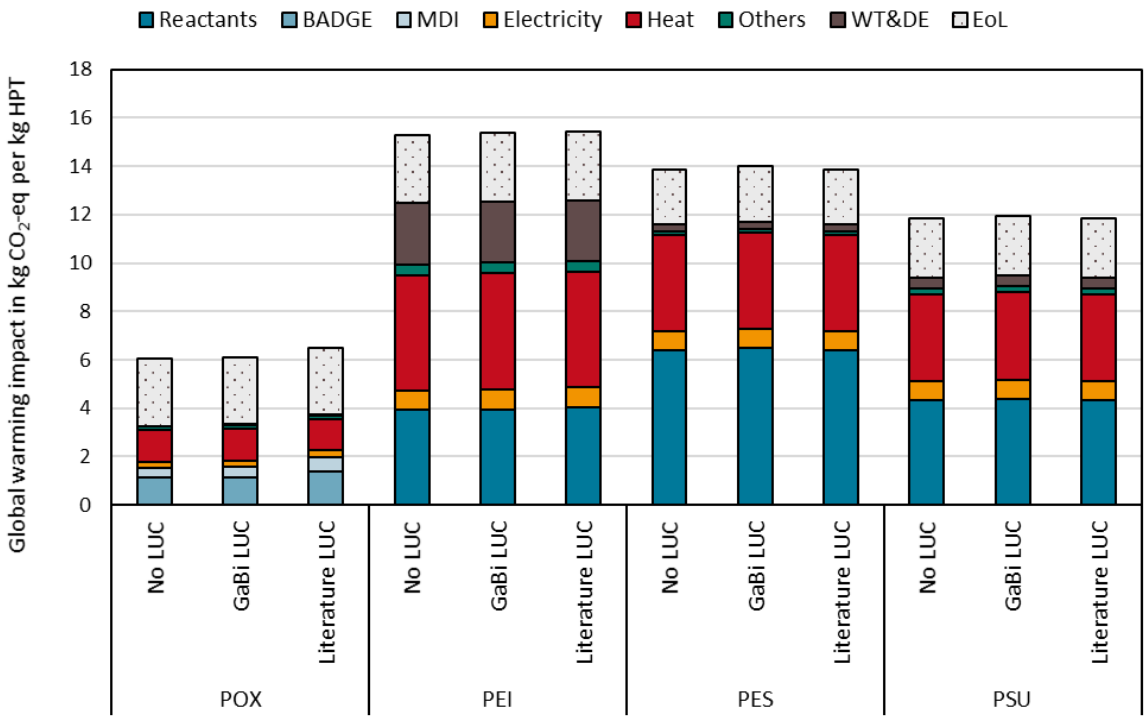

Figure S 4: Global warming impact of high-performance thermoplastic polymer excluding LUC emissions (No LUC) and including LUC emissions from GaBi (GaBi LUC) or literature values (Literature LUC).

7. Sensitivity analysis on the climate change impact of fossil-based HPT

The analysis of HPT production incorporates uncertainties. To address these uncertainties, we vary the demands of electricity, steam, and fuel gas (only reference HPT) and the process yields for key chemical intermediates in reasonable ranges in a sensitivity analysis (Figure S 5 - Figure S 8). For POX, the process yield of BADGE production, which is set to 99.9 % and, thus, close to stoichiometric conditions, has the most significant influence on GHG emissions. Changing the process yield of BADGE production to 80 % results in about 1.2 kg CO2-eq higher GHG emissions per kg POX, corresponding to an increase of about 13 %. The parameters with the next largest sensitivity for the GHG emissions of POX are the MDI process yield and the steam demand for POX production.

For the reference HPTs, steam demands in HPT production also strongly influence GHG emissions. Increasing or decreasing the steam demand by 50 % increases or decreases the GHG emissions of the reference HPTs by 1.8 - 2.2 kg CO2-eq, which corresponds to a change of about 13 %. Furthermore, the process yield of DCDPS production, which is set to 75 %, can change the GHG emissions of PES and PSU by about -1.7 - 3.3 kg CO2-eq (-10 % to 23 %).

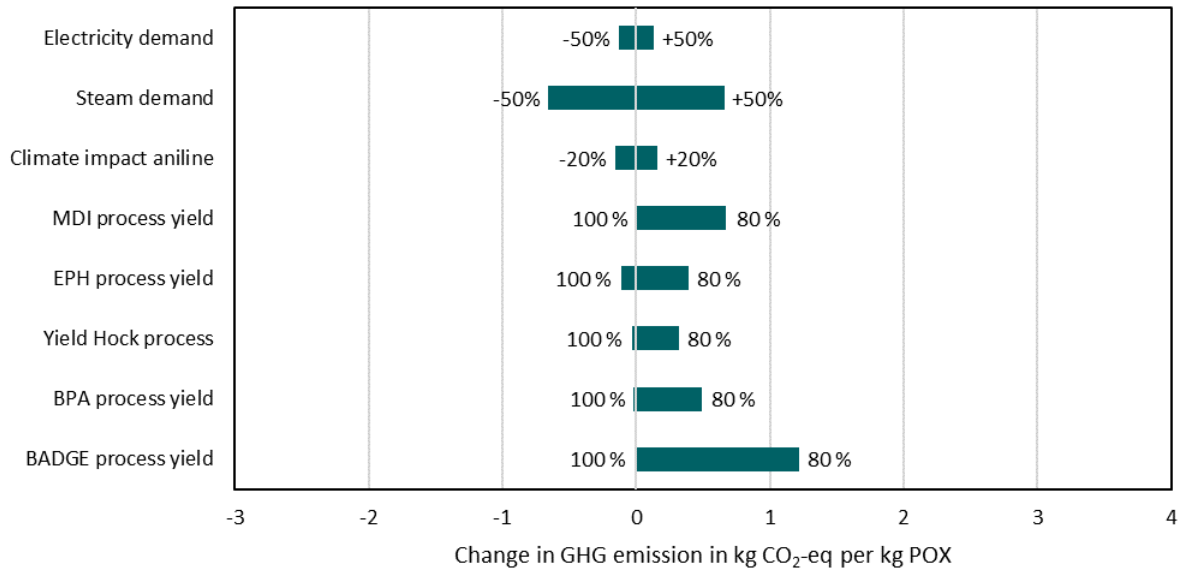

Figure S 5: Change in GHG emissions for polyoxazolidinone (POX) depending on utility demands, GHG emissions of the aggregated aniline process, and process yields in the POX supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in the main article. The percentages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

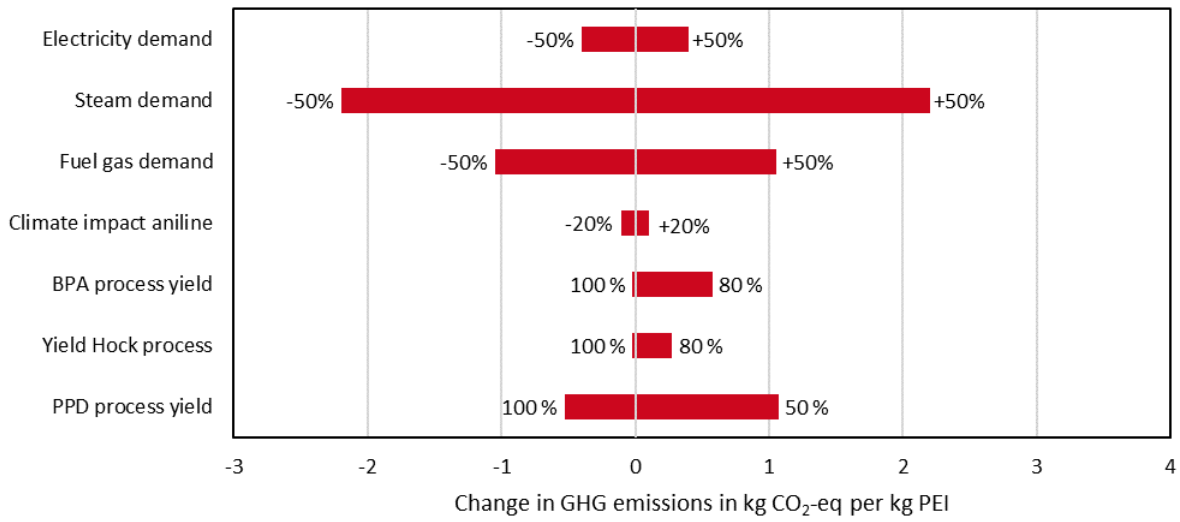

Figure S 6: Change in GHG emissions for polyetherimide (PEI) depending on utility demands, GHG emissions of the aggregated aniline process, and process yields in the PEI supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in the main article. The percentages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

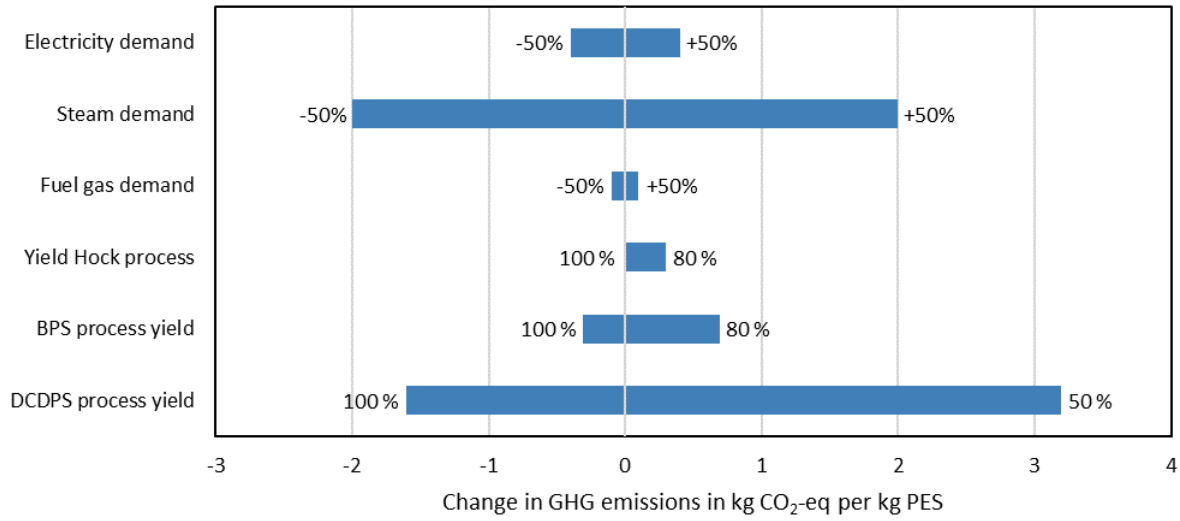

Figure S 7: Change in GHG emissions for polyethersulfone (PES) depending on utility demands and process yields in the PES supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in the main article. The percentages next to the bars refer to the minimum and maximum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

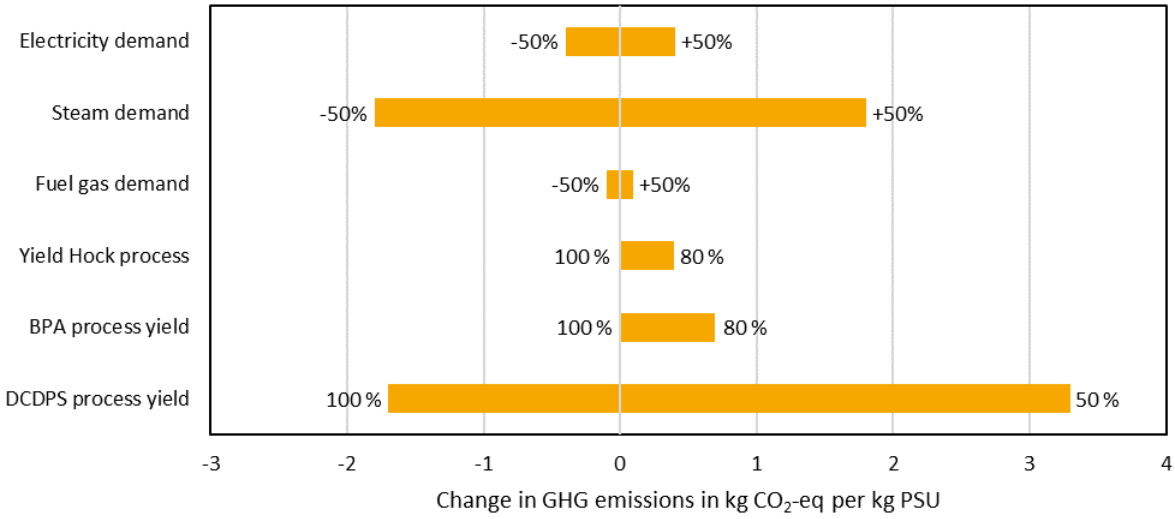

Figure S 8: Change in GHG emissions for polysulfone (PSU) depending on utility demands and process yields in the PSU supply chain. Parameters for this sensitivity analysis were chosen based on the hot-spot analysis in the main article. The percentages next to the bars refer to the minimum and maximum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

8. Further impact categories

Table S 4: Cradle-to-grave environmental impacts of HPTs for the conventional scenario. The color code shows the highest (red) and lowest (green) value in each category.

Conventional scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0242	0.0173	0.0148	0.00679
EF 3.0 Climate Change [kg CO2 eq.]	13.9	13.8	11.9	6.57
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	188	202	211	107
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	180	192	202	108
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	7.89	9.07	9.11	-1.44
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	0.355	0.374	0.37	0.283
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.0000261	0.0000269	0.0000257	0.0000391
EF 3.0 Eutrophication, marine [kg N eq.]	0.0143	0.00485	0.00425	0.00286
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.117	0.0524	0.0461	0.0255
EF 3.0 Human toxicity, cancer - total [CTUh]	2.61E-09	3.05E-09	2.63E-09	1.58E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	2.37E-19	1.59E-19	1.31E-19	8.7E-20
EF 3.0 Human toxicity, cancer metals [CTUh]	1.77E-09	1.87E-09	1.71E-09	1.06E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	8.43E-10	1.18E-09	9.16E-10	5.18E-10
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.83E-07	1.93E-07	1.71E-07	9.68E-08
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.63E-08	4.05E-08	4.09E-08	2.33E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.46E-07	1.53E-07	0.00000013	7.33E-08
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.34E-09	1.42E-09	1.2E-09	7.35E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.273	0.307	0.254	0.156
EF 3.0 Land Use [Pt]	16.1	21.7	18.1	10.7
EF 3.0 Ozone depletion [kg CFC-11 eq.]	8.05E-14	1.31E-13	1.02E-13	7.39E-10
EF 3.0 Particulate matter [Disease incidences]	1.25E-07	1.33E-07	1.19E-07	6.06E-08
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0281	0.02	0.0185	0.00829
EF 3.0 Resource use, fossils [MJ]	251	283	237	137
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000186	0.0000283	0.0000172	0.00000182
EF 3.0 Water use [m³ world equiv.]	1.49	3.15	2.9	1.04

Table S 5: Cradle-to-grave environmental impacts of HPTs for the biomass scenario. The color code shows the highest (red) and lowest (green) value in each category.

Biomass scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0273	0.0207	0.0188	0.0159
EF 3.0 Climate Change [kg CO2 eq.]	12.5	11.7	9.47	3.32
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	165	175	181	77
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	161	164	169	75.2
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	5.27	11.1	11.4	2.68
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	-1.29	0.195	0.164	-0.877
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.0000533	0.0000324	0.000032	0.000162
EF 3.0 Eutrophication, marine [kg N eq.]	0.0152	0.00635	0.00596	0.00525
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.135	0.0687	0.0646	0.072
EF 3.0 Human toxicity, cancer - total [CTUh]	2.15E-09	2.8E-09	2.34E-09	2.13E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	7.55E-19	3.29E-19	3.26E-19	8.13E-19
EF 3.0 Human toxicity, cancer metals [CTUh]	1.19E-09	1.34E-09	1.1E-09	1.56E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	9.56E-10	1.46E-09	1.24E-09	5.62E-10
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.66E-07	1.81E-07	1.57E-07	2.98E-07
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.58E-08	4.02E-08	4.05E-08	1.99E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	0.00000013	1.41E-07	1.16E-07	2.78E-07
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.17E-09	1.33E-09	1.1E-09	4.09E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.364	0.488	0.46	0.222
EF 3.0 Land Use [Pt]	24.1	110	119	67.2
EF 3.0 Ozone depletion [kg CFC-11 eq.]	-1.59E-08	1.81E-13	1.59E-13	-2.31E-08
EF 3.0 Particulate matter [Disease incidences]	1.82E-07	2.55E-07	2.59E-07	1.59E-07
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0318	0.0237	0.0227	0.0121
EF 3.0 Resource use, fossils [MJ]	232	262	213	88.3
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	1.12E-07	0.0000288	0.0000177	-3.59E-07
EF 3.0 Water use [m³ world equiv.]	0.179	3.49	3.3	-0.575

Table S 6: Cradle-to-grave environmental impacts of HPTs for the renewable energy scenario. The color code shows the highest (red) and lowest (green) value in each category.

Renewable energy scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0319	0.0257	0.01868446	0.00489
EF 3.0 Climate Change [kg CO2 eq.]	6.98	3.45	4.08685028	3.55
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	249	276	254.12265	105
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	242	269	246.066198	107
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	6.76	6.44	7.27264926	-2.14
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	0.932	1.09	0.78380317	0.272
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.000182	0.000221	0.00013835	0.0000374
EF 3.0 Eutrophication, marine [kg N eq.]	0.0166	0.00719	0.00512212	0.00199
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.137	0.0709	0.05145796	0.016
EF 3.0 Human toxicity, cancer - total [CTUh]	9.59E-09	1.31E-08	1.0281E-08	4.54E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	1.97E-19	7.27E-20	7.1304E-20	6.55E-20
EF 3.0 Human toxicity, cancer metals [CTUh]	1.89E-09	2.04E-09	1.8474E-09	1.12E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	7.71E-09	1.11E-08	8.4333E-09	3.42E-09
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.95E-07	2.09E-07	1.8207E-07	9.96E-08
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	4.02E-08	4.38E-08	4.2036E-08	2.18E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.54E-07	1.64E-07	1.3936E-07	7.76E-08
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.5E-09	1.5E-09	1.0995E-09	4.87E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.178	0.113	0.11962094	0.109
EF 3.0 Land Use [Pt]	194	242	145.380721	7.43
EF 3.0 Ozone depletion [kg CFC-11 eq.]	2.42E-13	3.49E-13	2.8218E-13	7.39E-10
EF 3.0 Particulate matter [Disease incidences]	1.91E-07	2.06E-07	1.5642E-07	4.99E-08
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.03	0.0209	0.0176314	0.00587
EF 3.0 Resource use, fossils [MJ]	118	90	94.0398396	85.2
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000876	0.0000379	2.4224E-05	0.00000423
EF 3.0 Water use [m³ world equiv.]	2.65	4.81	4.2247356	1.62

Table S 7: Cradle-to-grave environmental impacts of HPTs for the renewable carbon & energy scenario. The color code shows the highest (red) and lowest (green) value in each category.

Renewable carbon & energy scenario	**PEI**	**PES**	**PSU**	**POX**
EF 3.0 Acidification [Mole of H+ eq.]	0.0339	0.0278	0.0211	0.0131
EF 3.0 Climate Change [kg CO2 eq.]	4.76	-0.137	-0.0453	-0.461
EF 3.0 Ecotoxicity, freshwater - total [CTUe]	226	246	220	72.6
EF 3.0 Ecotoxicity, freshwater inorganics [CTUe]	223	238	211	72.5
EF 3.0 Ecotoxicity, freshwater metals [CTUe]	3.67	7.31	8.26	1.08
EF 3.0 Ecotoxicity, freshwater organics [CTUe]	-0.727	0.897	0.562	-0.899
EF 3.0 Eutrophication, freshwater [kg P eq.]	0.000185	0.000223	0.000141	0.000158
EF 3.0 Eutrophication, marine [kg N eq.]	0.0171	0.00817	0.00624	0.00408
EF 3.0 Eutrophication, terrestrial [Mole of N eq.]	0.15	0.0816	0.0637	0.0593
EF 3.0 Human toxicity, cancer - total [CTUh]	9.68E-09	1.41E-08	1.13E-08	5.59E-09
EF 3.0 Human toxicity, cancer inorganics [CTUh]	6.93E-19	2.09E-19	2.27E-19	7.65E-19
EF 3.0 Human toxicity, cancer metals [CTUh]	1.32E-09	1.53E-09	1.25E-09	1.63E-09
EF 3.0 Human toxicity, cancer organics [CTUh]	8.36E-09	1.25E-08	1.01E-08	3.96E-09
EF 3.0 Human toxicity, non-cancer - total [CTUh]	1.78E-07	1.96E-07	1.67E-07	0.0000003
EF 3.0 Human toxicity, non-cancer inorganics [CTUh]	3.85E-08	4.2E-08	3.99E-08	1.73E-08
EF 3.0 Human toxicity, non-cancer metals [CTUh]	1.38E-07	1.53E-07	1.27E-07	2.83E-07
EF 3.0 Human toxicity, non-cancer organics [CTUh]	1.27E-09	1.3E-09	8.67E-10	1.02E-10
EF 3.0 Ionising radiation, human health [kBq U235 eq.]	0.222	0.222	0.245	0.12
EF 3.0 Land Use [Pt]	198	325	240	60.1
EF 3.0 Ozone depletion [kg CFC-11 eq.]	-1.6E-08	4.12E-13	3.54E-13	-2.31E-08
EF 3.0 Particulate matter [Disease incidences]	2.39E-07	0.00000032	2.86E-07	1.42E-07
EF 3.0 Photochemical ozone formation, human health [kg NMVOC eq.]	0.0328	0.0233	0.0203	0.00894
EF 3.0 Resource use, fossils [MJ]	86.2	45.4	42.4	25.3
EF 3.0 Resource use, mineral and metals [kg Sb eq.]	0.00000855	0.0000392	0.0000257	0.0000023
EF 3.0 Water use [m³ world equiv.]	1.42	5.34	4.84	0.064

9. Major assumptions for TEA

Table S 8: Process assumptions and financial assumption for POX and reference HPTs.

Parameter	Applies to	Assumption
Depreciation	POX, PEI, PES, PSU	linear depreciation of fixed capital investment over 10 years
Annual capacity	POX, PEI, PES, PSU	8 kt/a at 8000 h/a
Operating rate	POX, PEI, PES, PSU	100%
Material of construction	POX	304 stainless steel
Base year plant construction	POX, PEI, PES, PSU	2021
Base year material	POX, PEI, PES, PSU	2020, when available
Plant lifetime	POX, PEI, PES, PSU	10 years

10.Variable costs of production input price data

Table S 9: Material input price data.

Input	Price [€/kg]	Source	Comment
Bisphenol A	1.16	UN Comtrade[35], HS290723	reporter Germany; import average (world); 2020
Bisphenol-A-diglycidylether	3.68	UN Comtrade[35], HS291090	reporter Germany; import average (world); 2020
Methylendiphenylisocyanat	2.38	UN Comtrade[35], HS292910	reporter Germany; import average (world); 2020
para-Tertbutylphenolglycidylether	3.04	UN Comtrade[35], HS291090	see BADGE
Catalyst	25.00	Assumption	Assumption based on communication with Covestro
Benzonitrile	4.77	UN Comtrade[35], HS292690	reporter Germany; import average (world); 2020
4,4′-Dichlorodiphenyl sulfone	3.50	Alibaba[36], Made-in-China[37]	Search "bisphenol S" (>1t); exchange rate $ to € Q1 2021, 0.75·lower bound + 0.25·upper bound of all prices available to account for bulk pricing; accessed 11/2021
4,4- Dihydroxy diphenyl sulphone	3.50	*see DCDPS*	
Potassium Carbonate	0.73	UN Comtrade[35], HS283640	reporter Germany; import average (world); 2019
Methyl chloride	0.62	UN Comtrade[35], HS290311	reporter Germany; import average (world); 2019
Caustic soda	0.18	UN Comtrade[35], HS281512	reporter Germany; import average (world); 2020
Phthalic anhydride	0.73	UN Comtrade[35], HS291735	reporter Germany; import average (world); 2020
n-Methyl phthalimide	5.06	UN Comtrade[35], HS292519	reporter Germany; import average (world); 2020
m-Phenylenediamine	1.87	UN Comtrade[35], HS292151	reporter Germany; import average (world); 2020
Nitric acid	0.14	UN Comtrade[35], HS280800	reporter Germany; import average (world); 2020
Triethylamine	2.82	UN Comtrade[35], HS292129	Exchange rate $ to € for 2018, 2019, 2020, Reporter Germany; import average of 2018, 2019 and 2020 (world)
Dilute nitric acid	0.07	Assumption	half the price of nitric acid (see above)

Table S 10: Utility price data.

Utility	Price [€/Unit]	Unit	Source	Comment
Electricity	0.11	kWh	Statista 2021[38,39]	Germany; 2020; including taxes; excluding EEG
Medium pressure steam	0.03	kg	Turton et al. 2013[40]	Process steam: latent heat only
Cooling water	3.78E-05	kg	NexantECA 2021[41]	
Fuel gas	5.51	GJ	NexantECA 2021[41]	Modelled as natural gas
Inert gas	73.19	m3	NexantECA 2021[41]	Modelled as nitrogen

Table S 11: Material input price data.

Product	Input	Costs [€/kg product]
POX	Bisphenol-A-diglycidylether	2.02
	Methylendiphenylisocyanat	1.00
	para-Tertbutylphenolglycidylether	0.10
	Catalyst	0.08
	Benzonitrile	0.05
	TOTAL	3.25
PEI	Bisphenol A	0.48
	Phthalic anhydride	0.40
	n-Methyl phthalimide	0.35
	m-Phenylenediamine	0.36
	Nitric acid	0.35
	Caustic soda	0.05
	Triethylamine	0.03
	Catalyst	0.10
	Dilute nitric acid	-0.17
	TOTAL	1.95
PES	4,4′-Dichlorodiphenyl sulfone	2.21
	4,4- Dihydroxy diphenyl sulphone	1.93
	Potassium Carbonate	0.21
	Methyl chloride	0.00
	Catalyst	0.10
	TOTAL	4.45
PSU	Bisphenol A	0.61
	4,4′-Dichlorodiphenyl sulfone	2.32
	Caustic soda	0.02
	Methyl chloride	0.00
	Catalyst	0.10
	TOTAL	3.05

Table S 12: Utility price data.

Utility	Price [€/Unit]	Unit	Source	Comment
Electricity	0.11	kWh	Statista 2021[38,39]	Germany; 2020; including taxes; excluding EEG
Medium pressure steam	0.03	kg	Turton et al. 2013[40]	Process steam: latent heat only
Cooling water	3.78E-05	kg	NexantECA 2021[41]	
Fuel gas	5.51	GJ	NexantECA 2021[41]	Modelled as natural gas
Inert gas	73.19	m3	NexantECA 2021[41]	Modelled as nitrogen

11. Fixed costs of production

Table S 13: Labor cost calculation.

Gross wage per shift/year in €/a			**60,000**
Labour	**Shifts position**	**Operators per shift**	**Total labour costs**
POX	5	5	1,500,000
PSU	5	5	1,500,000
PES	5	5	1,500,000
PEI	5	6	1,800,000

Table S 14: Fixed costs of production estimation factors. Abbrevations: ISBL = inside battery limited, OSBL = outside battery limits, FCI = fixed capital investment.

No.	**Item**	**Reference**	**Factor**	**Comment**	**Source**
1	Operating Labour (L)	-	-	see labour calculation	Assumption
2	Supervision (S)	L	0.25		Sinnott, Towler 2020[42]
3	Direct salary overhead	L+S	0.50		Sinnott, Towler 2020[42]
4	Maintenance (materials and labour)	ISBL costs	0.04	mean value within range	Sinnott, Towler 2020[42]
5	Property taxes & insurance	FCI	0.02	mean value within range	Sinnott, Towler 2020[42]
6	Rent of land/building	ISBL + OSBL	0.01	lower value since assumed to be company owned	Sinnott, Towler 2020[42]
7	General plant overhead (HR, R&D, IT, finance, legal etc.)	1+2+3+4	0.65		Sinnott, Towler 2020[42]
8	Allocated environmental charges	ISBL + OSBL	0.01	e.g. REACH in EU	Sinnott, Towler 2020[42]
9	Running license fees and royalty payments	-	-	Assumed to be proprietary for R&D project	Assumption
10	Capital charges (interest payments (dept or loans))	-	-	Neglected, in line with reference product calculation	NexantECA 2021[41]
11	Sales & marketing costs	-	-	Neglected, in line with reference product calculation	NexantECA 2021[41]

Table S 15: Fixed costs of production in €/kg product.

No.	**Item**	**POX**	**PEI**	**PES**	**PSU**
1	Operating Labour	0.19	0.23	0.19	0.19
2	Supervision	0.05	0.06	0.05	0.05
3	Direct salary overhead	0.12	0.14	0.12	0.12
4	Maintenance (materials and labour)	0.13	0.49	0.32	0.32
5	Property taxes & insurance	0.09	0.26	0.12	0.12
6	Rent of land/building	0.05	0.17	0.11	0.11
7	General plant overhead	0.31	0.60	0.44	0.44
8	Allocated environmental charges	0.05	0.17	0.11	0.11
9	Running license fees and royalty payments	-	-	-	-
10	Capital charges	-	-	-	-
11	Sales & marketing costs	-	-	-	-
	TOTAL	**0.98**	**2.11**	**1.46**	**1.46**

12.Capital costs estimation method

Table S 16: Fixed capital investment installation factors.

Item	Factor	Reference	Comment	Source
f_{er} Equipment erection	0.5			
f_p Piping	0.6			
f_i Instrumentation and control	0.3			
f_{el} Electrical	0.2	total equipment costs	Fluids-solids process type	Sinnott, Towler 2020[42]
f_c Civil	0.3			
f_s Structures and buildings	0.2			
f_l Lagging and Paint	0.1			
f_m Material Factor	1.8	total equipment costs, piping	material factor for 304 stainless steel	Perry, Green 1999[43]

Table S 17: Capital costs positions and annual capital charge estimation.

Item	Abbreviation	Calculation	Source
Total equipment cost	C	$C = \sum C_e$	Calculation based on equipment list
Inside battery limits costs	ISBL	$\mathrm{ISBL} = C\left(\left(1 + f_p\right) f_m + \left(f_{er} + f_i + f_{el} + f_c + f_s + f_l\right)\right)$	Sinnott, Towler 2020[42]
Outside battery limits costs	OSBL	$\mathrm{OSBL} = 0.4 \cdot \mathrm{ISBL}$	Sinnott, Towler 2020[42]
Design and engineering	D&E	$\mathrm{D\&E} = 0.25 \cdot (\mathrm{ISBL} + \mathrm{OSBL})$	Sinnott, Towler 2020[42]
Contingency	Contin.	$\mathrm{Contin.} = 0.1 \cdot (\mathrm{ISBL} + \mathrm{OSBL})$	Sinnott, Towler 2020[42]
Fixed capital investment	FCI	$\mathrm{FCI} = \mathrm{ISBL} + \mathrm{OSBL} + \mathrm{D\&E} + \mathrm{Conting.}$	Sinnott, Towler 2020[42]
Annual capital charge	ACC	$\mathrm{ACC} = \frac{\mathrm{FCI}}{\text{plant lifetime} \cdot \mathrm{Capacity}}$	Assumption

13.Detailed TEA results

Table S 18: Estimated capital costs of POX and reference HTPs in € 2021. Abbreviation: ISBL = inside battery limits, OSBL = outside battery limits.

	POX	PSU	PES	PEI
ISBL costs	25,959,952	64,219,624	64,219,624	98,703,228
OSBL costs	10,383,981	25,687,850	25,687,850	39,481,291
Design and engineering	9,085,983	incl. in ISBL & OSBL	incl. in ISBL & OSBL	incl. in ISBL & OSBL
Contingency	3,634,393	incl. in ISBL & OSBL	incl. in ISBL & OSBL	incl. in ISBL & OSBL
Fixed capital investment	49,064,310	89,907,473	89,907,473	138,184,519
Working capital	6,467,643	7,807,715	9,716,245	7,796,889
TOTAL	**55,531,953**	**97,715,188**	**99,623,718**	**145,981,408**

Table S 19: Estimated total costs of production of POX and reference HTPs in € per kg product Abbreviation: COP = costs of production.

	POX	PSU	PES	PEI
Material	3.25	3.24	4.62	2.00
Energy & utilities	0.40	0.80	0.80	1.06
Variable COP	3.64	4.04	5.42	3.06
Fixed COP	0.98	1.46	1.46	2.11
Cash COP	4.62	5.49	6.87	5.17
Annual capital charge	0.61	1.12	1.12	1.73
Total COP	**5.24**	**6.62**	**8.00**	**6.90**

14. Sensitivity analysis on HPT's net present value

The net present value (NPV) can determine the economic viability of a project. The NPV is calculated as follows:

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n}$$

Where CF_n is the cash flow in year n, t represents the project life in years, and i the interest rate, i.e., the cost of captial.[42]

To address the uncertainty in economic viability, we determine the range of NPV in a sensitivity analysis (see Table S 20). Therefore, we vary the interest rate and the market prices for POX and the reference HPT. The range of the interest rates corresponds to the minimum, current, and maximum key interest rates defined by the European Central bank from 1999 until today.[44] To determine the market price range, we used the minimum cost of production of all HPT (5.09 euro per kg for POX) and the maximum selling price of all HPT (15 euro per kg for PEI). The medium scenario with about 10 euros per kg is the mean value of both prices.

Overall, the economic viability unlocks the potential to achieve the environmental benefits of POX (see Figure S 9).

Table S 20: Net present value of HPT depending on interest rate and HPT market price.

Interest rate in %	**Product**	**Net present value in Million Euro**		
		Market price in euros per kg HPT		
		5.09	10.05	15.00
0	POX	-21.6	303.4	694.1
	PEI	-161.9	163.2	553.8
	PES	-214.4	110.7	501.3
	PSU	-117.1	208.0	598.6
1.25	POX	-23.9	276.5	637.6
	PEI	-159.8	140.6	501.7
	PES	-205.0	95.4	456.5
	PSU	-115.0	185.4	546.5
4.75	POX	-28.8	214.5	506.8
	PEI	-154.3	88.9	381.3
	PES	-182.8	60.4	352.8
	PSU	-109.7	133.6	425.9

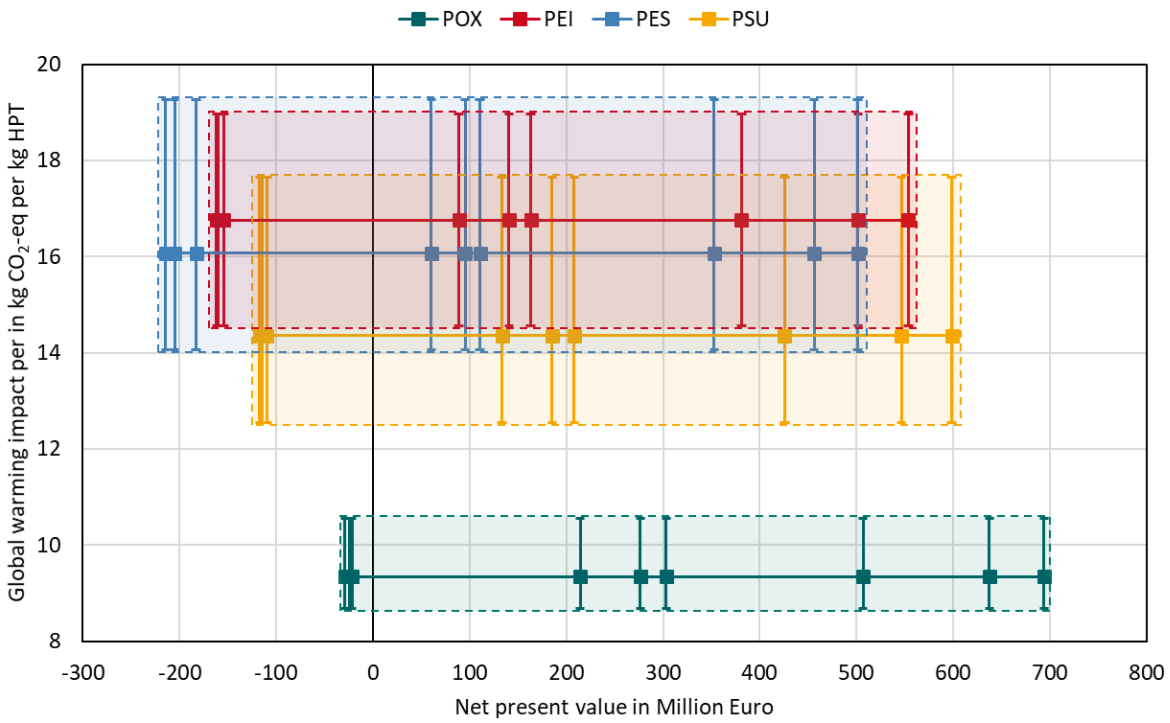

Figure S 9: Ashby plot of HPT's global warming impact and net present value. Error bars for the global warming impact refer to the minimum and maximum global warming impact from the sensitivity analysis (see Figure S 5 – Figure S 8). Ranges for the net present value are based on the sensitivity analysis from Table S 20: Net present value of HPT depending on interest rate and HPT market price.

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