Electronic Supplementary Material (ESI) for Faraday Discussions.

- Supplementary Information -

Renewable Carbon Feedstock for Polymers: Environmental Benefits from the Synergistic Use of Biomass and CO_2

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1 Data sources for life cycle inventory

Table S1: Summary of flows, production technologies and literature sources of the bottom-up model of the polyurethane supply chain.

name of flow	**production technologies**	**source**	**comment**
ammonia	European market for ammonia	ecoinvent 3.5 - cut-off[1]	
ash	European market for wood ash mixture, pure	ecoinvent 3.5 - cut-off[1]	
butane	global market for butane	ecoinvent 3.5 - cut-off[1]	
calcium dioxide	European market for quicklime, milled, packed	ecoinvent 3.5 - cut-off[1]	
carbon dioxide	by direct air capture	von der Assen et al. (2016)[2]	Details see below
	from cement plant	von der Assen et al. (2016)[2]	Details see below
carbon monoxide	reverse water gas shift	Sternberg et al. (2015)[3]	
	dry reforming	CO2RRECT[4]	
	separation of syngas via partial condensation	IHS PEP Yearbook[5]	
caustic soda	global market for sodium hydroxide, without water, in 50 % solution state	ecoinvent 3.5 - cut-off[1]	
chlorine	European market for chlorine	ecoinvent 3.5 - cut-off[1]	
cooling water	global market for water, decarbonized, at user	ecoinvent 3.5 - cut-off[1]	
deionized water	European market for water, deionized, from tap water, at user	ecoinvent 3.5 - cut-off[1]	
diammonium phosphate	European diammonium phosphate production	ecoinvent 3.5 - cut-off[1]	
dinitrotoluene	From toluene by nitration	IHS PEP Yearbook[5]	
dimethyl carbonate	from vapor-phase oxidative carbonylation	IHS PEP Yearbook[5]	
	from liquid-phase oxidative carbonylation	IHS PEP Yearbook[5]	
	from methanol and urea	IHS PEP Yearbook[5]	
electricity	European grid mix	Müller et al.[6]	
electricity, renewable	Depends on scenario	Müller et al.[6], ecoinvent 3.5 - cut-off[1]	For all other environmental impacts except climate change in the full decarbonized scenario, the ecoinvent data set "electricity production, wind, >3MW turbine, onshore, RoW" was used.
ethanol	from fermentation of Miscanthus, carbon dioxide from fermentation is captured, flue gas is released to environment		Details see below
	from fermentation of Miscanthus, carbon dioxide from fermentation and flue gas is captured		Details see below
ethylbenzene	European market for ethylene	ecoinvent 3.5 - cut-off[1]	
ethylene	global market for ethylene	ecoinvent 3.5 - cut-off[1]	

name of flow	production technologies	source	comment
	from ethanol by adiabatic fixed-bed catalytic dehydration	IHS PEP Yearbook[5]	
	from methanol by MTO process	IHS PEP Yearbook[5]	Details see below
	from natural gas by oxidative coupling	IHS PEP Yearbook[5]	
ethylene oxide	from ethylene by oxidation	IHS PEP Yearbook[5]	
ethylene glycol	global market for ethylene glycol	ecoinvent 3.5 - cut-off[1]	
excess heat	European market for heat, district or industrial, natural gas	ecoinvent 3.5 - cut-off[1]	
fuel oil	European market for light fuel oil	ecoinvent 3.5 - cut-off[1]	
glucose	global market for glucose	ecoinvent 3.5 - cut-off[1]	
glycerol	European market for glycerine	ecoinvent 3.5 - cut-off[1]	
hydrochloric acid	European market for hydrochloric acid, without water, in 30% solution state	ecoinvent 3.5 - cut-off[1]	
hydrogen	from steam reforming of natural gas	ecoinvent 3.5 - cut-off[1]	
	from electrolysis	U.S. Department of Energy[7]	
inert gas	European market for nitrogen, liquid	ecoinvent 3.5 - cut-off[1]	
methane	German market for natural gas, high pressure	ecoinvent 3.5 - cut-off[1]	no data for global or European market available
	from carbon dioxide (Sabatier reaction)	Müller et al. (2013)[8]	
methanol	global market for methanol	ecoinvent 3.5 - cut-off[1]	
	from syngas via JM/ICI/DPT technology	IHS PEP Yearbook[5]	
	from natural via JM/ICI/DPT technology	IHS PEP Yearbook[5]	
	from carbon dioxide and hydrogen (direct hydrogenation)	Rihko-Struckmann (2010)[9]	
miscanthus, at farm gate	global market for Miscanthus, chopped	ecoinvent 3.5 - cut-off[1]	
miscanthus, at refinery	miscanthus transportation, average of 300 km	Styles et al. (2008)[10]	
miscanthus, stored at refinery	miscanthus storage, ambient storage	Rentizelas et al. (2009)[11]	
natural gas	German market for natural gas, high pressure	ecoinvent 3.5 - cut-off[1]	no datat for global or European market available
nitric acid	European market for nitric acid, without water, in 50% solution state	ecoinvent 3.5 - cut-off[1]	
nitric oxide	global market for nitric oxide	ecoinvent 3.5 - cut-off[1]	
nitrogen	European market for nitrogen, liquid	ecoinvent 3.5 - cut-off[1]	
oxygen	European market for oxygen, liquid	ecoinvent 3.5 - cut-off[1]	
pentane	global market for pentane	ecoinvent 3.5 - cut-off[1]	
polyol (PO)	from propylene oxid, glycerol as starter	von der Assen et al. (2015)[12]	
polyol (PO/CO_2)	from propylene oxide and carbon dioxide, glycerol as starter	Covestro Deutschland AG (2018)[13]	
polyol (PO/EO)	from propylene oxide and ethylene oxide, glycerol as starter	Ionescu (2016)[14]	
polyurethane, flexible foam	from polyol and TDI	Ecoinvent 3.5 - UPR[1]	
process water	global market for water, decarbonised, at user	ecoinvent 3.5 - cut-off[1]	
propane	global market for propane	ecoinvent 3.5 - cut-off[1]	
propylene	European market for propylene	ecoinvent 3.5 - cut-off[1]	
	from ethylene via dimerization and olefin conversion technology by Lummus Technology	IHS PEP Yearbook[5]	
propylene dichloride	technical chlorination of propane	stoichiometric calculation, hydrochloric acid as co-product	
propylene oxide	from conventional chlorohydrin process	IHS PEP Yearbook[5]	

name of flow	production technologies	source	comment
	from BASF-DOW HPPO process	IHS PEP Yearbook[5]	
	from Lyondell Oxirane process with styrene as by-product	IHS PEP Yearbook[5]	Details see below
rapeseed oil methyl ester	global market for vegetable oil methyl ester	ecoinvent 3.5 - cut-off[1]	
steam	global market for steam, in chemical industry	ecoinvent 3.5 - cut-off[1]	
styrene	global market for styrene	ecoinvent 3.5 - cut-off[1]	
sulfuric acid	European market for sulfuric acid	ecoinvent 3.5 - cut-off[1]	
syngas (molar hydrogen-to-carbon monoxide ratio of 2:1)	from natural gas by partial oxidation	IHS PEP Yearbook[5]	
	from natural gas by steam reforming with carbon dioxide import	IHS PEP Yearbook[5]	
	from gasification of Miscanthus in pressurized direct oxygen-steam blown circulating fluidized bed gasifier		Details see below
	from gasification of Miscanthus in dual fluidized bed gasifier		Details see below
toluene	European market for toluene, liquid	ecoinvent 3.5 - cut-off[1]	
	$9\ CO_2 + 26\ H_2 \rightarrow C_7H_8 + 18\ H_2O + 2\ CH_4$	Low-TRL CCU technology[15,16]	
	methanol-to-aromatics	High-TRL CCU technology[17]	
toluene diisocyanate	from phosgenation	IHS PEP Yearbook[5]	
	from dinitrotoluene	IHS PEP Yearbook[5]	
transportation of miscanthus	European market for transport, freight, lorry >32 metric ton, EURO5	ecoinvent 3.5 - cut-off[1]	
urea	from mitsui toatsu process	IHS PEP Yearbook[5]wan	

1.1 Carbon dioxide capture and transportation

For carbon dioxide (CO_2) supply, we consider biomass utilization technologies, cement plants, and ambient air. In both biomass utilization technologies, namely fermentation and gasification, CO_2 is obtained in high concentrations at ambient pressure. In all cases, to use CO_2 as feedstock, it is compressed to 110 bar and then transported to the production site. We account for the energy demand for compression, according to Farla et al.[18], and neglected all other environmental impacts of compression and transportation. Excess CO_2 from biomass utilization technologies, which is not used in CCU processes, is released into the environment. For the supply of CO_2 from cement plants and ambient air by direct air capture, we use average values from von der Assen et al..[2]

1.2 Methanol-to-Olefins processes

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

1.3 Propylene oxide production

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

1.4 Miscanthus gasification for syngas production

We consider two technologies for the gasification of Miscanthus to syngas: a pressurized direct oxygen-steam blown circulating fluidized bed (CFB) gasifier and an atmospheric indirect air-blown dual fluidized bed (DFB) gasifier. The CFB gasifier model is based on a concept by Hannula et al.[19] and the associated process layout by Isaksson et al.[20]. The dryer and the gasifier models are taken from Arvidsson et al..[21] The reformer model is based on data published by the National Renewable Energy Laboratory.[22] LCI data for the DFB gasifier were generated using a model developed by Arvidsson et al., based on the technology used in the Gothenburg Biomass Gasification project.[23] Both gasification models are modified to account for Miscanthus's higher ash content compared to wood chips and wood pellets conventionally used for gasification. The produced syngas has a hydrogen to carbon monoxide ratio of 2:1. Additional CO_2 from syngas upgrading is captured and can be used in the foreground system. We modeled a simplified heat integration using a Grand Composite Curve. Excess heat substitutes district or industrial heat. Matthias Hermesmann performed the modeling of the gasification process under the supervision of Johan Ahlström, Stavros Papadokonstantakis, and Harvey Simon at the Chalmers University of Technology.

1.5 Miscanthus fermentation for ethanol production

The ethanol production from Miscanthus is based on the 2011 design report by the National Renewable Energy Laboratory[24] and the associated aspen model. The aspen model only considers corn stover as feedstock for ethanol production. We modified the lignocellulosic feedstock's composition in the aspen model to reflect the composition of Miscanthus. Miscanthus is used to supply both feedstock for fermentation and process heat. Excess heat is used to produce electricity, which can be used in other processes within the foreground system or substitutes grid electricity. The fermentation vents a high concentrated CO_2 stream that can be compressed and used in the foreground system.

In addition to CO_2 released during the fermentation, additional CO_2 is released as flue gas during lignin and other combustibles' incineration. However, the flue gas has a much lower CO_2 concentration than the fermentation CO_2 steam and is thus harder to purify. Therefore, we added another data set for the fermentation process, where we added CO_2 capture from flue gas. For CO_2 capture from flue gas, we assumed the same heat and electricity requirements as for the CO_2 capture from cement plants[2], since both flue gases have similar CO_2 concentrations. The heat required for CO_2 capture is supplied by excess heat of the fermentation process. The modified model, therefore, does not produce any excess electricity. The captured CO_2 can be compressed and used in the foreground system.

1.6 Biomass-to-heat efficiency

We calculated the biomass-to-steam efficiency with a steam boiler efficiency of 95 % and an energy content of steam of 2.75 MJ/kg. We used a carbon footprint of Miscanthus of -1.5 $kg_{CO2\text{-}eq}/kg_{Biomass}$ for calculation and assumed an average heating value of 20 $MJ/kg_{Biomass}$[25]. GHG emissions of fossil-based steam is taken from ecoinvent 3.5 - cut-off[1]. We neglect the transportation and storage of Miscanthus in this calculation.

2 Miscanthus as a feedstock

With Miscanthus as perennial energy crop, this study considers only one possible biomass feedstock for polymer production. Perennial energy crops have great potential to serve as a supplier of energy and carbon feedstock in the future.[26] However, the availability of perennial energy crops is still limited today. The actual potential varies greatly between studies[26,27] since it depends on many factors such as the availability and type of marginal land used for cultivation. Therefore, large-scale implementation of bio-based production also consider other lignocellulosic biomass. Consequently, we discuss the potential use of other lignocellulosic biomass for the considered processes.

For gasification, various lignocellulosic biomass feedstocks are suitable.[28] The type of lignocellulosic biomass influences the characteristics of the gasification process, such as the operating conditions and the gasifying agent.[29] The syngas yield and quality depend on moisture content, particle size, and particle density of the biomass feedstock.[29] Furthermore, the heating value of the biomass feedstock ranges between 18 and 22 MJ/kg for most lignocellulosic biomass and has a significant impact on the syngas yield and process efficiency.[28]

For fermentation of lignocellulosic biomass to ethanol, various feedstocks can be used as well. Here, the biomass composition, which consists of cellulose, hemicellulose, and lignin, has a significant impact on the ethanol yield.[30] The higher the lignin content of the biomass, the lower the ethanol yield. Since the share of lignin is particularly high for lignocellulosic biomass, the conversion process requires efficient pretreatment processes to degrade the crystallinity of cellulose fibers and remove lignin from biomass.[30] However, the use of other lignocellulosic biomass feedstocks leads to product yields similar to those obtained with the technologies employed in this study.[31]

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

Savings of renewable resources from the combined utilization of biomass and CO_2

Synergies from combined utilization save renewable resources compared to the utilization of either biomass or CO_2. In the paper, we analyze the GHG reduction from 7.6 $kg_{CO2\text{-}eq}/kg_{PUR}$ to 4.5 $kg_{CO2\text{-}eq}/kg_{PUR}$ for the carbon footprint of -1.7 $kg_{CO2\text{-}eq}$ per kg biomass and 3 $g_{CO2\text{-}eq}$ per MJ renewable electricity. The reduction requires 2 kg of biomass and 45 MJ of renewable electricity used in separate production facilities (linear combination in Figure S1). In combined utilization, the same GHG reduction is achieved using only 1.6 kg of biomass and 33 MJ of renewable electricity.

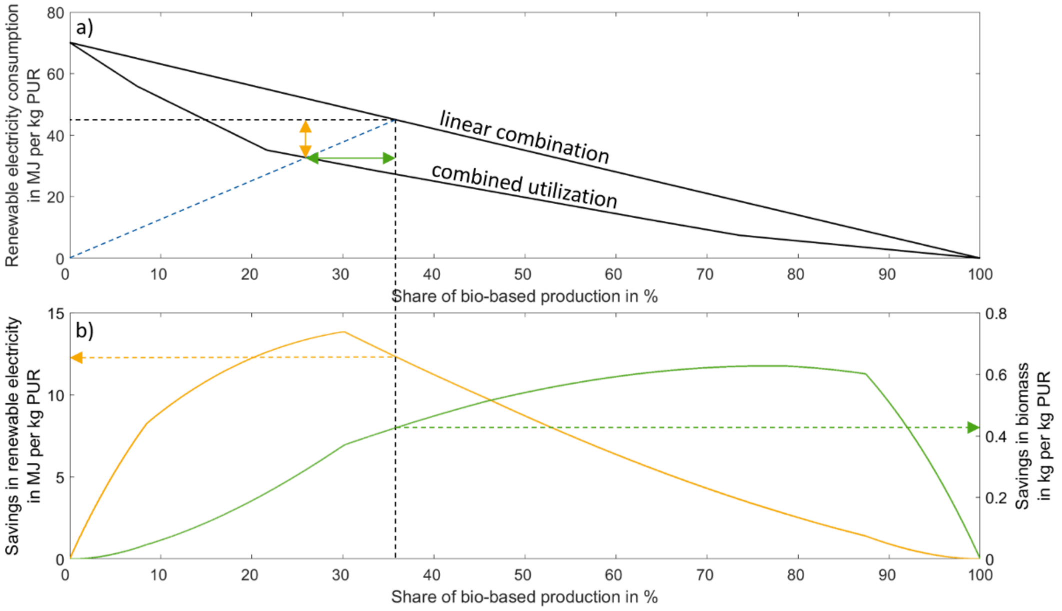

Figure S1a: Renewable electricity consumption for a linear combination of bio- and CCU-based production and combined utilization as a function of the share of the bio-based production for a global warming impact of 4.5 $kg_{CO2\text{-}eq}/kg_{PUR}$.

Figure S1b: Savings of renewable electricity (left y-axis) and biomass (right y-axis) as a function of the share of bio-based production for a global warming impact of 4.5 $kg_{CO2\text{-}eq}/kg_{PUR}$. The savings equal the difference between the linear combination of bio- and CCU-based production and the combined utilization.

3 Sensitivity analysis for the carbon footprint of renewable feedstocks

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

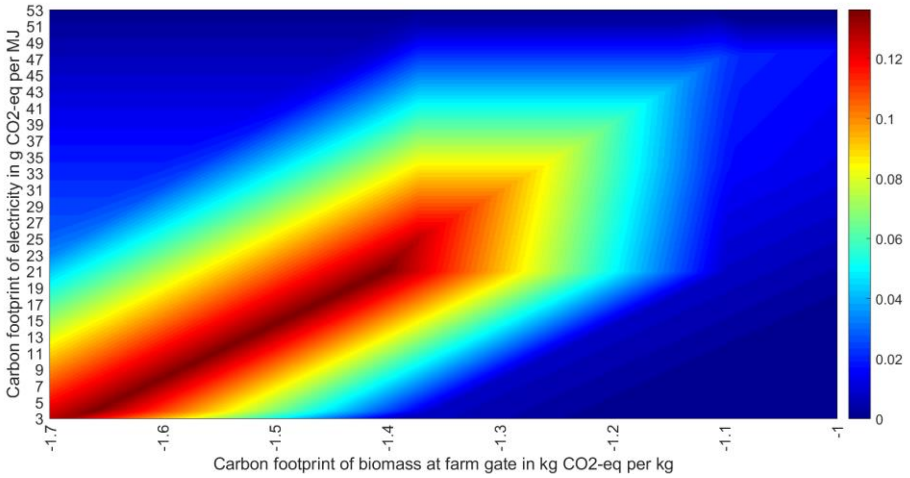

Figure S2: Relative savings in GHG emissions of the combined utilization of biomass and CO_2 compared to individual utilization as a function of the carbon footprint of biomass and CO_2. The relative savings are expressed as the difference between the minimum GHG emissions of the individual utilization and the combined utilization of biomass and CO_2 divided by the minimum GHG emissions of the individual utilization.

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