Supplementary information

S1) The avoided burden approach

If the system investigated in an LCA study provides more than one product, the system is called "multi-functional." The ISO standards define a clear priority order of approaches to deal with multi-functionality in LCA.[1,2] Following this order, the favored approach in ESTIMATe is the avoided burden approach.

The avoided burden approach assumes that the co-production of a given product replaces the benchmark production route of that product. Hence, the environmental burden of the benchmark is assumed to be avoided. Figure S1 shows the application of the avoided burden approach to determine product-specific environmental impacts for CO_2-based methanol production. The CO_2-based system provides two functions: electricity production and methanol production from captured CO_2. In order to compare CO_2-based and fossil-based methanol, a mono-functional system that provides solely the electricity production, i.e., a power plant without CO_2 capture, is subtracted from the multi-functional system (cf. Figure S1).

While the avoided burden approach is commonly used in LCA, results must be interpreted carefully to avoid misinterpretation. Specifically, the avoided environmental burdens depend on the assumption that by-products actually replace the benchmark process, and on the choice of benchmark process, which might improve or change in the future. Furthermore, assumed avoided emissions could be misinterpreted as true emission removal from the environment. For a broader discussion on allocation in the context of CCU, please refer to von der Assen et al.[3]

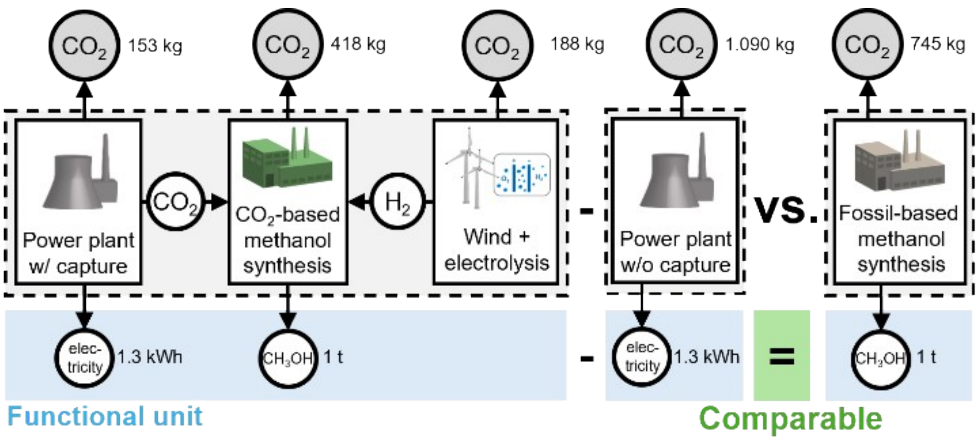

Figure S1: The avoided burden approach: Quantitative flow sheet from a methanol producer perspective. Calculation of product-specific results for methanol. Adapted from von der Assen et al.[3]

S2) Estimation methods included in the ESTIMATe tool

Table S1: Estimation methods available in ESTIMATe. TRL refers to recommendations in the CCU guidelines [4]

Estimation of	TRL	Source	Automation within ESTIMATe	Comment
Environmental impact	1	Wernet et al. (2009)[5]	Not automated	EstiMol database, available online. Information and link are given in ESTIMATe.
Reactant & water mass flows	2-3	Althaus et al. (2007), Hischier et al. (2005)[6,7]	Calculation and scaling to functional unit	Consistent with ecoinvent database.
Minimum energy demand	2 - 3	Roh et al. (2020)[8]	Calculation and scaling to functional unit	
Electricity and heat demand	2-3	Althaus et al. (2007)[6]	Calculation and scaling to functional unit	Guidelines also recommend Kim et al. (2003)[9]. We use Althaus to be consistent with the source for reactant mass flows.
Emissions to air and water	2	Hischier et al. (2005)[7]	Calculation and scaling to functional unit	While guidelines also recommend method by Jimenez-Gonzalez et al. (2000)[10], we use Hischier to be consistent with the source for reactant mass flows.
Energy for separation and recycling	3	Roh et al. (2020)[8]	Calculation	
Energy demand for reactor	3	Parvatker et al. (2019)[11]	Calculation	
Energy demand for distillation	3	Parvatker et al. (2019)[11]	Calculation	
Energy demand for dryer	3	Parvatker et al. (2019)[11]	Calculation	
Energy demand for liquid batch reactor	4	Piccinno et al. (2016)[12]	Calculation	
Energy demand for drying	4	Piccinno et al. (2016)[12]	Calculation	
Energy demand for distillation	4	Piccinno et al. (2016)[12]	Calculation	
Energy demand for pumping	4	Piccinno et al. (2016)[12]	Calculation	
Energy demand for pressurizing	4	Perry et al. (2008)[13]	Calculation	
Fugitive emissions	4	Ng et al. (2017), Hassim et al. (2010)[14,15]	No	Hybrid approach for fugitive emissions from process modules, e.g., tanks, valves, etc. Not automatable, information & link given in ESTIMATe.
Energy demand of separation	N/A	Lange (2017)[16]	Calculation	Applicable to separation of organic chemicals. Not included in guideline.

S3) Process inventory data used for case studies

In the process inventories listed below, linked processes from the ecoinvent database are referred to by their reference product, process name, and location following the format [reference product], from [process name] [location]. The location codes used are RoW for Rest of World and GLO for Global.

S3.1) Best-Case Assessment

Table S2: Process inventory of the Best-Case Assessment of CO_2 reduction to ethylene

reference product	amount	unit	type	linked process
ethylene (g)	**1**	kg	main product	ethylene, from market for ethylene [RoW]
carbon dioxide (g)	**3.14**	kg	input	ESTIMATe feedstock carbon dioxide
water (l)	**1.28**	kg	input	water, deionised, from market for water, deionised [RoW]
oxygen (g)	**3.42**	kg	emission	oxygen (g)
electricity	**13.18**	kWh	input	ESTIMATe electricity

S3.2) Hotspot Assessment at laboratory scale

Table S3: Process inventory of the laboratory-scale Hotspot Assessment of CO_2 reduction to ethylene without recycle assumption

reference product	amount	unit	type	linked process
ethylene (g)	**1**	kg	main product	ethylene, from market for ethylene [RoW]
carbon dioxide (g)	**18.03**	kg	input	ESTIMATe feedstock carbon dioxide
water (l)	**6.76**	kg	input	water, deionised, from market for water, deionised [RoW]
carbon dioxide (g)	**13.52**	kg	emission	carbon dioxide (g)
water (l)	**5.07**	kg	emission	water (l)
carbon monoxide (g)	**0.373**	kg	emission	carbon monoxide (g)
oxygen (g)	**4.39**	kg	emission	oxygen (g)
ethanol (l)	**0.236**	kg	emission	ethanol (l)
methane (g)	**0.0066**	kg	emission	methane (g)
acetic acid (l)	**0.0615**	kg	emission	acetic acid (l)
formic acid (l)	**0.0892**	kg	emission	formic acid (l)
propanol (l)	**0.0410**	kg	emission	propanol (l)
electricity	**37.82**	kWh	input	ESTIMATe electricity

Table S4: Process inventory of the laboratory-scale Hotspot Assessment of CO_2 reduction to ethylene with recycle assumption

reference product	amount	unit	type	linked process
ethylene (g)	**1**	kg	main product	ethylene, from market for ethylene [RoW]
carbon dioxide (g)	**5.01**	kg	input	ESTIMATe feedstock carbon dioxide
water (l)	**6.76**	kg	input	water, deionised, from market for water, deionised [RoW]
carbon dioxide (g)	**0.50**	kg	emission	carbon dioxide (g)
water (l)	**5.07**	kg	emission	water (l)
carbon monoxide (g)	**0.373**	kg	emission	carbon monoxide (g)
oxygen (g)	**4.39**	kg	emission	oxygen (g)
ethanol (l)	**0.236**	kg	emission	ethanol (l)
methane (g)	**0.0066**	kg	emission	methane (g)
acetic acid (l)	**0.0615**	kg	emission	acetic acid (l)
formic acid (l)	**0.0892**	kg	emission	formic acid (l)
propanol (l)	**0.0410**	kg	emission	propanol (l)
electricity	**37.82**	kWh	input	ESTIMATe electricity
minimum separation electricity	**2.25**	kWh	input	ESTIMATe electricity

S3.3) Hotspot Assessment at process design scale

Table S5: Process inventory of the process design-scale Hotspot Assessment of CO_2 reduction to ethylene

reference product	amount	unit	type	linked process
ethylene (g)	**1**	kg	main product	ethylene, from market for ethylene [RoW]
carbon dioxide (g)	**3.15**	kg	input	ESTIMATe feedstock carbon dioxide
water (l)	**1.79**	kg	input	water, deionised, from market for water, deionised [RoW]
electricity (electrolyzer)	**40.14**	kWh	input	ESTIMATe electricity
electricity (compression & auxiliaries)	**0.28**	kWh	input	ESTIMATe electricity
KOH	**0.0382**	kg	input	potassium hydroxide, from market for potassium hydroxide [GLO]
hydrogen (g)	**0.0348**	kg	by-product	ESTIMATe hydrogen
oxygen (g)	**3.70**	kg	by-product	oxygen, liquid, from market for oxygen, liquid [RoW]
wastewater	**0.0001**	m3	waste	wastewater, average, from treatment of wastewater, average, capacity 1E9l/year [RoW]

S3.4) Hotspot Assessment of methanol at process design scale (for Mitigation Potential Assessment)

Table S6: Process inventory of the process design-scale Hotspot Assessment of CO_2 hydrogenation to methanol. This assessment was used in the Mitigation Potential Assessment case study.

reference product	amount	unit	type	linked process
methanol (l)	**1**	kg	main product	methanol, from market for methanol [GLO]
electricity	**0.144**	kWh	input	ESTIMATe electricity
carbon dioxide (g)	**1.45**	kg	input	ESTIMATe feedstock carbon dioxide
hydrogen (g)	**0.201**	kg	input	ESTIMATe hydrogen
steam	**3.32**	MJ	input	ESTIMATe steam
argon (g)	**0.0010**	kg	emission	[not characterized]
carbon dioxide (g)	**0.1016**	kg	emission	carbon dioxide (g)
hydrogen (g)	**0.0001**	kg	by-product	ESTIMATe hydrogen
nitrogen (g)	**0.0951**	kg	emission	nitrogen (g)
oxygen (g)	**0.225**	kg	by-product	oxygen, liquid, from market for oxygen, liquid [RoW]
water (l)	**1179.75**	kg	emission	water (l)

S4) Additional case study result figures

S4.1) Best-Case Assessment

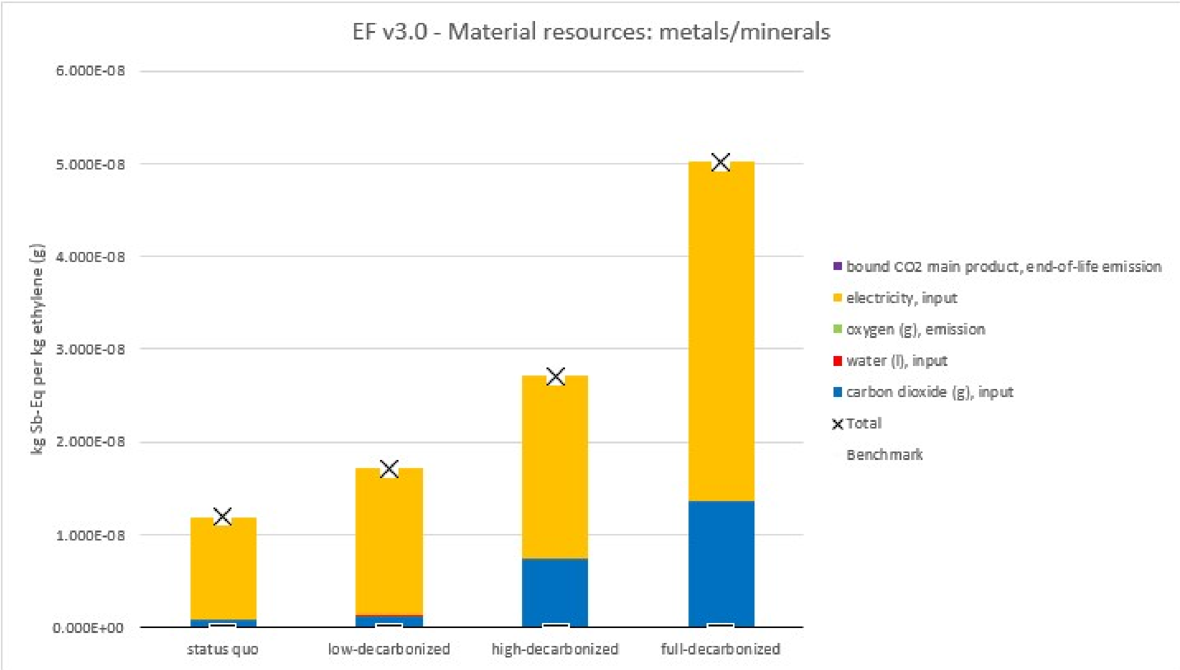

Figure S2: Material resources: metals/minerals impacts for the Best-Case Assessment of CO_2 reduction to ethylene in the ESTIMATe tool. The different bars correspond to the different background system scenarios defined in the methods section. An increase in renewable electricity production leads to increasing metals consumption for electricity supply and electricity-using processes.

S4.2) Hotspot Assessment at laboratory scale

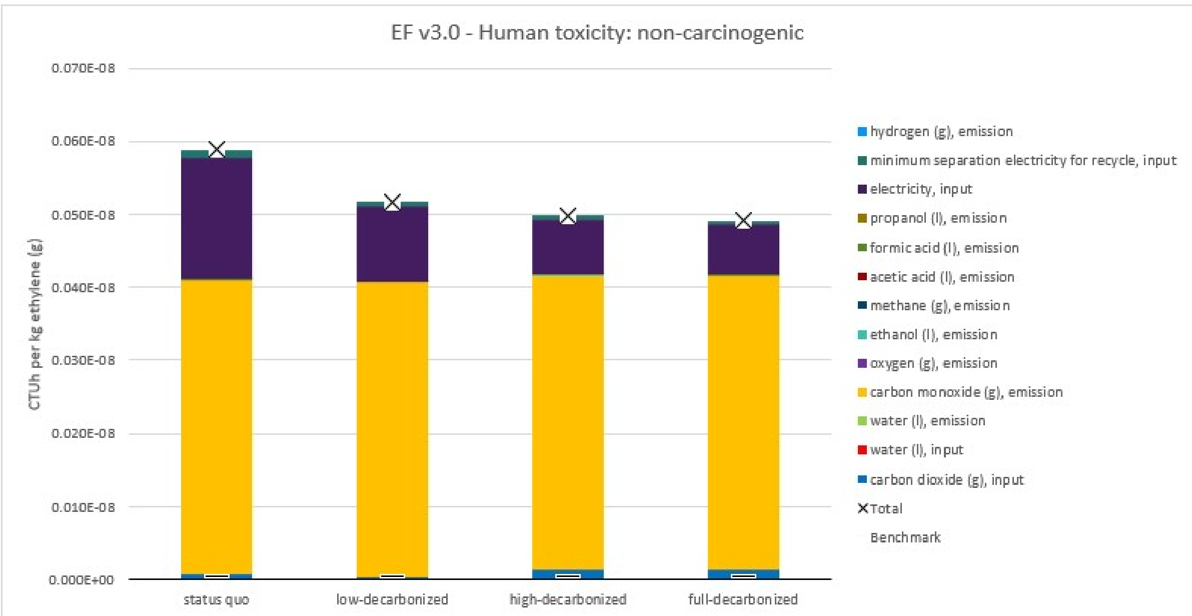

Figure S3: Human toxicity: non-carcinogenic impacts for the laboratory-scale Hotspot Assessment of CO_2 reduction to ethylene in the ESTIMATe tool. The different bars correspond to the different background system scenarios defined in the methods section. Carbon monoxide emissions are the major contributor to the overall impact.

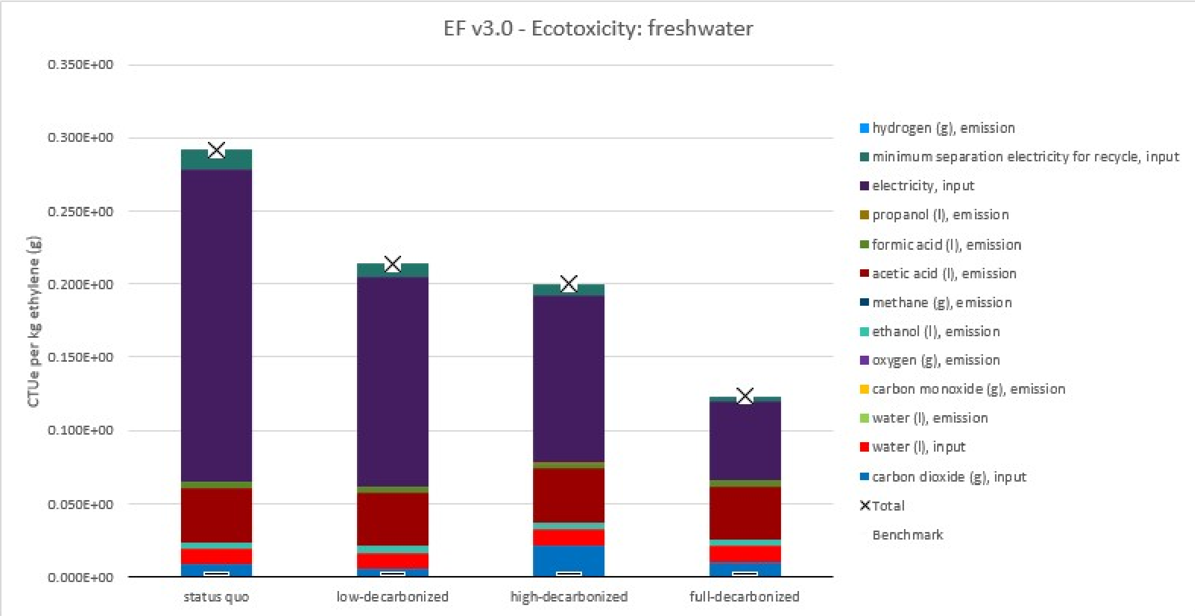

Figure S4: Ecotoxicity: freshwater impacts for the laboratory-scale Hotspot Assessment of CO_2 reduction to ethylene in the ESTIMATe tool. The different bars correspond to the different background system scenarios defined in the methods section. Electricity use and emissions of organic substances contribute most to the overall impact.

S4.3) Hotspot Assessment at process design scale

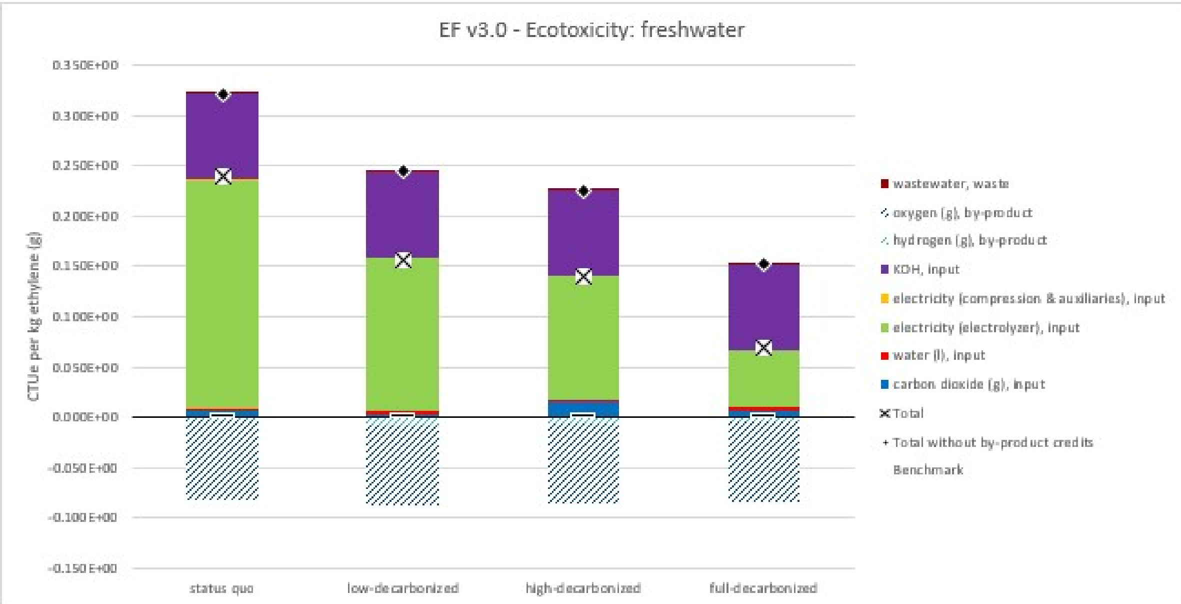

Figure S5: Ecotoxicity: freshwater impacts for the process design-scale Hotspot Assessment of CO_2 reduction to ethylene in the ESTIMATe tool. The different bars correspond to the different background system scenarios defined in the methods section. Electricity use and potassium hydroxide production contribute most to the overall impact.

S5) Modeled process inventories for scenario processes

Table S7: Process inventory for electric boiler, assuming an efficiency of 95%

Name	Amount	Unit	Linked ecoinvent process
Products			
Heat	1	megajoule	
Flows to/from technosphere			
Electricity	0.292	kilowatt hour	ESTIMATe electricity, GLO

Table S8: Process inventory for alkaline water electrolysis, from Koj et al. (2017)[17]

Name	Amount	Unit	Linked ecoinvent process
Products			
Hydrogen	1	kilogram	
Flows to/from technosphere			
Electrolyser cell	0.00000015	pcs.	Cell Production, GLO
Cell Stack Framework	0.000000037	pcs.	Cell Stack Framework Production, GLO
electricity	50	kilowatt hour	ESTIMATe electricity, GLO
market for nitrogen, liquid	0.00029	kilogram	market for nitrogen, liquid, RoW
market for potassium hydroxide	0.0019	kilogram	market for potassium hydroxide, GLO
market for water, deionised	10	kilogram	market for water, deionised, RoW
steam	0.3025	megajoule	ESTIMATe steam, GLO

Table S9: Process inventory for cell stack framework production for alkaline water electrolysis, from Koj et al. (2017)[17]

Name	Amount	Unit	Linked ecoinvent process
Products			
cell stack framework	1	pcs.	
Flows to/from technosphere			
copper, cathode	2000	kilogram	market for copper, cathode, GLO
reinforcing steel	200000	kilogram	market for reinforcing steel, GLO

Table S10: Process inventory for electrolyser cell production for alkaline water electrolysis, from Koj et al. (2017)[17]

Name	amount	unit	linked ecoinvent process
Products			
electrolyser cell	1	pcs.	
Flows to/from technosphere			
acetic anhydride	54	kilogram	market for acetic anhydride, GLO
acrylonitrile-butadiene-styrene copolymer	160	kilogram	market for acrylonitrile-butadiene-styrene copolymer, GLO
aluminium, cast alloy	450	kilogram	market for aluminium, cast alloy, GLO
Aniline	49	kilogram	market for aniline, RoW
carbon monoxide	150	kilogram	market for carbon monoxide, RoW
decarbonized water	11000	kilogram	market for water, decarbonised, RoW
electricity	10000	kilowatt hour	ESTIMATe electricity, GLO
graphite	430	kilogram	market for graphite, GLO
Heat	88000	megajoule	ESTIMATe heat, GLO
hydrochloric acid, without water, in 30% solution state	433.33	kilogram	market for hydrochloric acid, without water, in 30% solution state, RoW
industrial machine production	0.16	kilogram	industrial machine production, heavy, unspecified, RoW
lubricating oil	0.48	kilogram	market for lubricating oil, RoW
nickel, class 1	19000	kilogram	market for nickel, class 1, GLO
nitric acid, without water, in 50% solution state	33	kilogram	market for nitric acid, without water, in 50% solution state, RoW
N-methyl-2-pyrrolidone	1300	kilogram	market for N-methyl-2-pyrrolidone, GLO
plaster mixing	780	kilogram	market for plaster mixing, GLO
polyphenylene sulfide	340	kilogram	market for polyphenylene sulfide, GLO
polysulfone	260	kilogram	market for polysulfone, GLO
purified terephthalic acid	88	kilogram	market for purified terephthalic acid, GLO
steam	700	megajoule	ESTIMATe steam, GLO
tetrafluoroethylene	78	kilogram	market for tetrafluoroethylene, GLO
water, deionised	86000	kilogram	market for water, deionised, RoW
zirconium oxide	1100	kilogram	market for zirconium oxide, GLO

Table S11: Process inventory for methanation, from Müller et al. (2011)[18]

Name	Amount	Unit	Linked ecoinvent process
Products			
natural gas	1	kilogram	
Flows to/from technosphere			
feedstock carbon dioxide	2.94	kilogram	ESTIMATe feedstock carbon dioxide, GLO
electricity	0.330	kilowatt hour	ESTIMATe electricity, GLO
hydrogen	0.511	kilogram	ESTIMATe hydrogen, GLO
Flows to/from biosphere			
Carbon dioxide	0.197	kilogram	

Table S12: Process inventory for direct air capture, from von der Assen et al. (2013)[3]

Name	Amount	Unit	Linked ecoinvent process
Products			
feedstock carbon dioxide	1	kilogram	
Flows to/from technosphere			
electricity	0.358	kilowatt hour	ESTIMATe electricity, GLO
heat	4.19	megajoule	ESTIMATe heat, GLO
Flows to/from biosphere			
Carbon dioxide	-1	kilogram	

Table S13: Process inventory for carbon dioxide captured from a coal-fired power plant, from Schreiber et al. (2009)[19]

Name	Amount	Unit	Linked ecoinvent process
Products			
feedstock carbon dioxide	1	kilogram	
Flows to/from technosphere			
Electricity	0.339	kilowatt hour	ESTIMATe electricity, GLO
Flows to/from biosphere			
Carbon dioxide	-1	kilogram	

Table S14: Process inventory for steam production, assuming 85% efficiency and an energy content of 2.75 MJ steam/kg steam[6]

Name	Amount	Unit	Linked ecoinvent process
Products			
steam	1	kilogram	
Flows to/from technosphere			
heat	3.24	megajoule	ESTIMATe heat, GLO

Name	Amount	Unit	Linked ecoinvent process
Products			
steam	1	megajoule	
Flows to/from technosphere			
heat	1.18	megajoule	ESTIMATe heat, GLO

Table S15: Process inventory for hydrogen production from steam methane reforming, from Mehmeti et al. (2018)[20]. Assumed density of natural gas is 0.92 kg/cubic meter.[21]

Name	Amount	Unit	Linked ecoinvent process
Products			
hydrogen	1	kilogram	
Flows to/from technosphere			
electricity	1.11	kilowatt hour	ESTIMATe electricity, GLO
water, deionised	21.869	kilogram	market for water, deionised, RoW
natural gas	3.929	cubic meter	ESTIMATe natural gas, GLO
Flows to/from biosphere			
carbon dioxide	9.2565	kilogram	

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