Electronic Supplementary Material (ESI) for Green Chemistry.

Life Cycle Assessment of CO_2-based C1-Chemicals

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Supporting Information

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S1. Overview of process concepts for C1-chemicals from CO_2

Table S1: CO_2-based processes for C1-chemicals (processes in italics are not considered in main text due to missing data, the products of the processes in italics are used as input for Fischer-Tropsch reaction); PC-process concept, PS-process simulation

Product	ID	Reaction	Product separation	Comment
HCOOH	**Ia**	@ 93 °C and 105 bar	The stripping is performed at 3 bar before formic acid (purity: 85 wt %) is recovered at the top of the reactive distillation column.	REF 1
	Ib	@ 50 °C and 94 bar	First, methanol, water and residual carbon monoxide are removed by distillation. Then, the amine-formic-acid adduct is decomposed in a reactive distillation at 200 mbar and 180 °C to liberate the pure formic acid, which is recovered at the top of the reactive distillation column.	PC: REF 2 PS: REF 3
CO via rWGS	**II**	in electrically heated reactor; heterogeneous catalyst	CO_2 removal by amine scrubbing; H_2 removal by liquid methane washing; recycling of CO_2 and H_2	REF 4
		@ 230 °C and 25 bar in fixed bed reactor with WGS catalyst and water sorbent	*Water is removed in reactor; CO is only product; no product separation required*	*PC: REF 5* *PS: REF 6*
Syngas *via rWGS*		*@ 650 °C and 1 bar; $ZnAl_2O_4$ catalyst*	*Partial removal of H_2 by PSA*	*REF 7*
		@ 900 °C and 25 bar; additional use of steam; recycle from FT	*H_2O removal*	*REF 8*
CO & H_2 via DRM	**III**	in electrically heated reactor; heterogeneous catalyst	CO_2 removal by amine scrubbing; H_2 removal by liquid methane washing; purification of H_2 by PSA; CO_2 recycling	REF 4
Syngas *via DRM*		*@ 1000 °C and 4 bar*	-	*REF 9*
Methanol	**IVa**	@ 220 °C and 50 bar	Separation of gaseous (CO, CO_2 and H_2) and condensable (CH_3OH, H_2O) compounds by flash; Recycling of gaseous compounds; separation of CH_3OH and H_2O in distillation	REF 10
	IVb	@ 210 °C and 78 bar in fixed bed adiabatic reactor	Similar to IVa	REF 11
	IVc	@ 250 °C and 50 bar	Similar to IVa, but additional stripping unit after flash: feed hydrogen (saturated with water) flows in counter-current with the condensed mixture from flash (CH_3OH, H_2O)	REF 12
Methane	**Va**	@ 280 °C and 8 bar with heterogeneous catalyst	Condensation of water	REF 13
	Vb	@ 300 °C and 5 bar	CO_2 removal by amine scrubbing; H_2 removal by membranes; recycling of CO_2 and H_2 to reactor	REF 14

S2. Input and output data for processes analyzed in main text

Data of all processes is presented for CO_2 and hydrogen inlet pressures of 1 bar. If data of original process simulations refers to other inlet pressures, the electricity demand is adjusted. In this case, the original electricity demand is presented in parentheses.

The CO_2 emissions include the CO_2 that is not converted during the reaction and the CO_2 that is produced during the combustion of carbon-containing by-products. The CO_2 emissions do not include indirect CO_2 emissions, e.g., from electricity and heat supply.

Table S2: CO_2-based formic acid production (values per kg pure formic acid)

Process	Inputs				Emissions
	H_2 kg	CO_2 kg	Electricity kWh	Steam kWh	CO_2 kg
Ia (Pérez-Fortes et al.)[1]	0.071	0.988	0.48 (0.35)	3.27	0.032
Ib (Jens et al.)[3]	0.045	0.985	0.53	2.51	0.029

Ia) original inlet pressures: p H_2 = 30 bar & p CO_2 = 1 bar
Ib) see Section S8 for further information

The process of Perez-Fortes and co-workers produces formic acid with a purity of 85 wt% and the process of Jens and co-workers produces 99 mol% formic acid. For the comparison, the results of both processes simulations are converted to "per kg pure formic acid".

Table S3: CO_2-based carbon monoxide production via rWGS (values per kg carbon monoxide)

Process	Inputs				Emissions
	H_2 kg	CO_2 kg	Electricity kWh	Steam kWh	CO_2 kg
IIa – electrically heated reactor (CO_2RRECT)[4]	0.072	1.581	1.54	0.71	0.010
IIb – reactor heated by steam	0.072	1.581	1.13	1.11	0.010

Table S4: CO_2-based carbon monoxide production via DRM (values per kg carbon monoxide)

Process	Inputs				Outputs	Emissions
	CH_4 MJ	CO_2 kg	Electricity kWh	Steam kWh	H_2 kg	CO_2 kg
IIIa – electrically heated reactor (CO_2RRECT)[4]	13.02	0.910	1.98	--	0.050	0.053
IIIb – reactor heated by steam	13.02	0.910	0.76	1.22	0.050	0.053

Table S5: CO_2-based methanol production (values per kg methanol)

Process	Inputs				Emissions
	H_2 kg	CO_2 kg	Electricity kWh	Steam kWh	CO_2 kg
IVa (Rihko-Struckmann et al.)[10]	0.197	1.436	1.34	--	0.062
IVb (Van-Dal et al.)[11]	0.204	1.484	0.69 (0.30)	--	0.112
IVc (Kiss et al.)[12]	0.189	1.376	0.67 (0.55)	0.37	0.002

IVb) original inlet pressures: p H_2 = 30 bar & p CO_2 = 1 bar;
IVc) original inlet pressures p H_2 = 1.1 bar & p CO_2 = 100 bar

Table S6: CO_2-based methane production (values per GJ SNG based on LHV)

Process	Inputs			Emissions
	H_2 kg	CO_2 kg	Electricity kWh	CO_2 kg
Va (Müller et al.)[13]	9.97	57.53	19.31 (6.38)	3.79
Vb (De Saint Jean et al.)[14]	10.04	55.46	54.14 (40.41)	0.90

Va) original inlet pressures: p H_2 = 30 bar & p CO_2 = 1 bar;
Vb) original inlet pressures: p H_2 = 7.4 bar & p CO_2 = 100 bar

Both CO_2-based processes for methane produce so-called substitute natural gas (SNG). The main component of SNG is methane (> 85 vol-%). Furthermore, SNG contains H_2 and CO_2. The H_2 contributes to the energy content of SNG. The CO_2 is considered as emission.

Table S7: Fossil-based production of C1-chemicals (values per kg C1-chemical)

Process	Inputs				Outputs	Emissions	Comment
	CH_4 MJ	CO kg	Electricity kWh	Heat kWh	Hydrogen kg	CO_2 kg	
HCOOH (REF[15])[a)]	--	0.614	0.13	5.35[c)]	--	0.010	
CO (REF[4])	36.20	--	0.89	2.38[d)]	0.216	0.414	H_2/CO = 3
CO [b)]	40.43	--	0.41	6.60[d)]	0.317	0.646	H_2/CO = 4.4
CH3OH (Ref[16])	25.00	--	0.43	0.97[d)]	--	--	High-efficiency
CH3OH (Ref[16])	25.00	--	--[e)]	3.25[d)]	--	--	Low-efficiency

a) purity of formic acid is not mentioned in reference; carbon balance indicates that results are presented per kg pure formic acid

b) data for syngas production from Baltrusaitis and Luyben,[9] and energy demand for carbon monoxide separation from Lyke and Moore[17]

c) value represents steam demand

d) value represents natural gas demand

e) required electricity is internally produced from excess steam

S3. LCA data

In Table S8 the considered LCA data sets are presented.

Table S8: Considered LCA data sets

Product	Name of data set	Year	Database
Heat	steam from natural gas (efficiency 90 %) [EU-27]	2012	GaBi ts
Heat	steam from natural gas (efficiency 90 %) [NL]	2012	GaBi ts
Heat	steam from natural gas (efficiency 90 %) [PT]	2012	GaBi ts
Natural gas	natural gas mix [EU-27]	2012	GaBi ts
Natural gas	natural gas mix [NL]	2012	GaBi ts
Natural gas	natural gas mix [PT]	2012	GaBi ts
Hydrogen	hydrogen from steam reforming - natural gas [DE]	2012	GaBi ts
Electricity	electricity from wind power [EU-27]	2012	GaBi ts
Electricity	electricity from photovoltaics [DE]	2012	GaBi ts
Electricity	electricity generation mix [all countries of EU-27]	2012	GaBi ts
Electricity	electricity mix 2020 (average power plant) [EU-27]	2015	GaBi ts
Electricity	electricity mix 2040 (average power plant) [EU-27]	2015	GaBi ts
Electricity	electricity mix 2050 (average power plant) [EU-27]	2015	GaBi ts

S4. Breakdown of fossil depletion impacts for CO_2-based processes

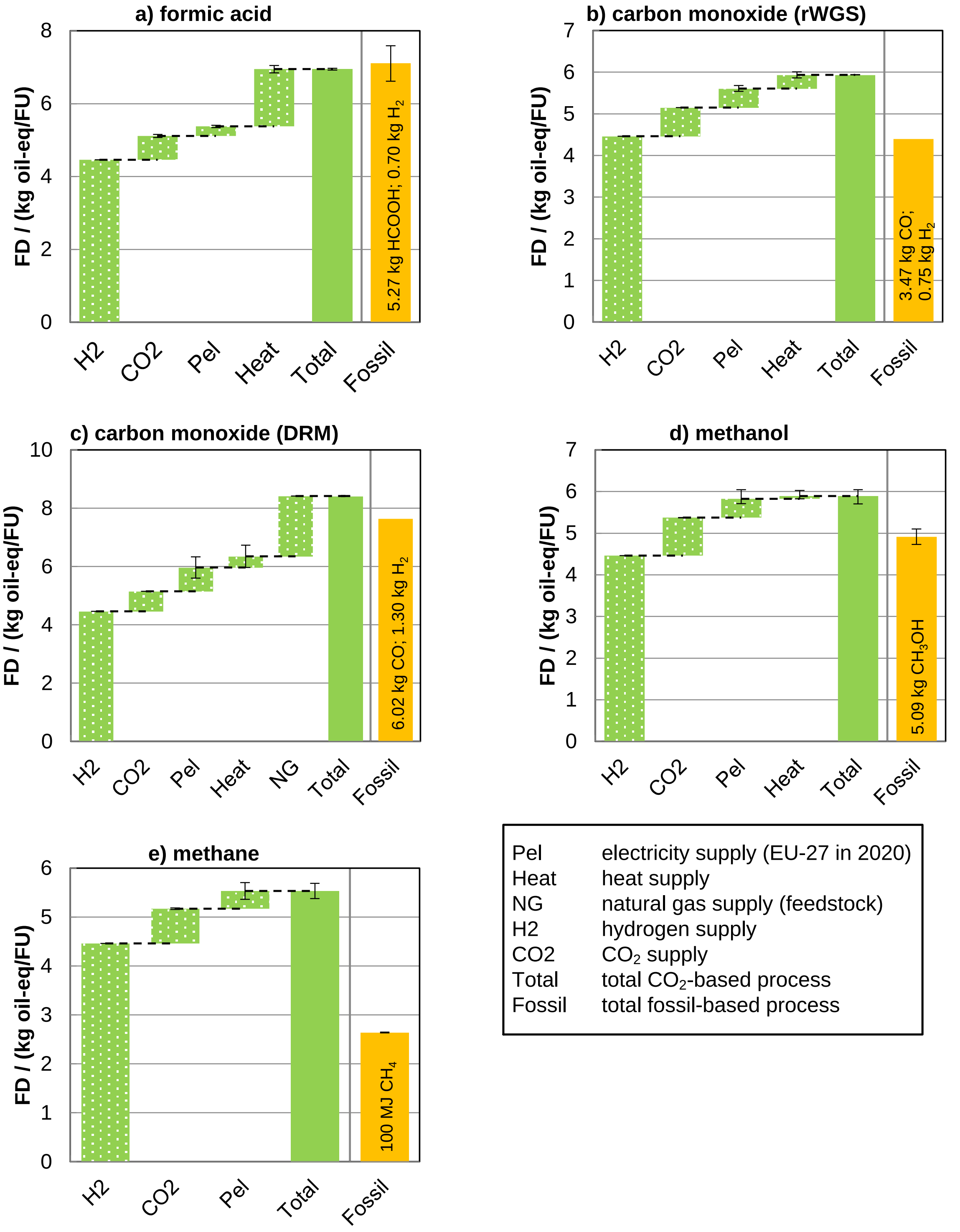

Figure S1: Breakdown of fossil depletion (FD) impacts per functional unit (FU = use of 1kg hydrogen) for CO_2-based processes for a) formic acid, b) carbon monoxide via rWGS, c) carbon monoxide via DRM, d) methanol and e) methane. For CO_2 supply, a fossil depletion impact of 0.13 kg Oil-eq/kg CO_2 is considered. The hydrogen is supplied by fossil-based steam-methane-reforming. The error bars of the CO_2-based processes represent the range of considered process concepts. The right bar represents fossil-based processes with an upper bound of fossil depletion impacts (worst case). The range of the fossil-based processes is due to different yields of C1-chemicals from the considered CO_2-based processes. The average yield is shown in the right bar.

S5. Breakdown of global warming and fossil depletion impacts for fossil-based processes

In this section, the breakdown of global warming and fossil depletion impacts is shown for fossil-based processes per functional unit. For formic acid, methanol and methane, the average yield of C1-chemicals from Table S9 is considered. The average yield of each considered C1-chemical is presented in Figure S1.

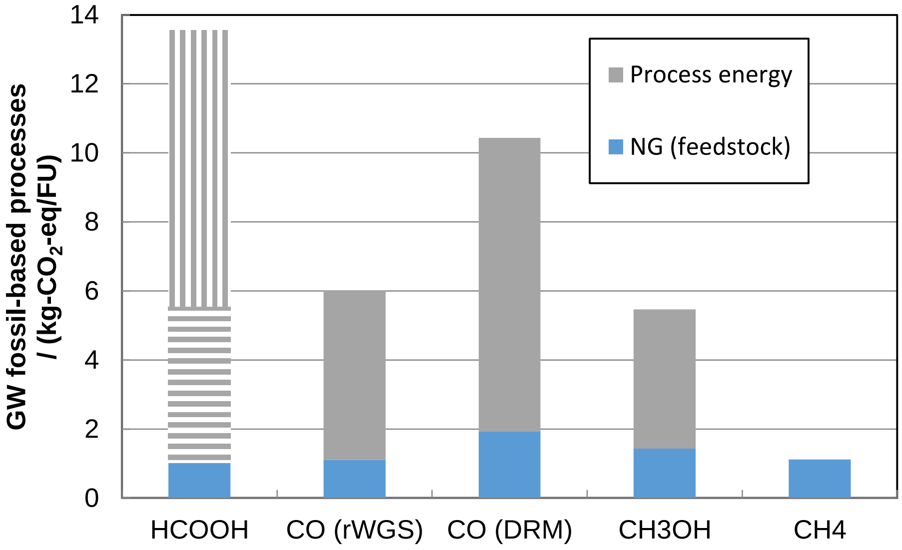

Figure S2: Breakdown of global warming impacts (GW) for fossil-based processes per functional unit (FU). For formic acid, the process energy (heat and electricity) demand is divided in production of the precursor carbon monoxide (horizontal lines) and the conversion of carbon monoxide to formic acid (vertical lines). The global warming impacts of NG (feedstock) include upstream processes such as transportation and natural gas purification. For fossil-based carbon monoxide, the difference between CO (rWGS) and CO (DRM) is due to different product yields of the CO_2-based processes (rWGS and DRM).

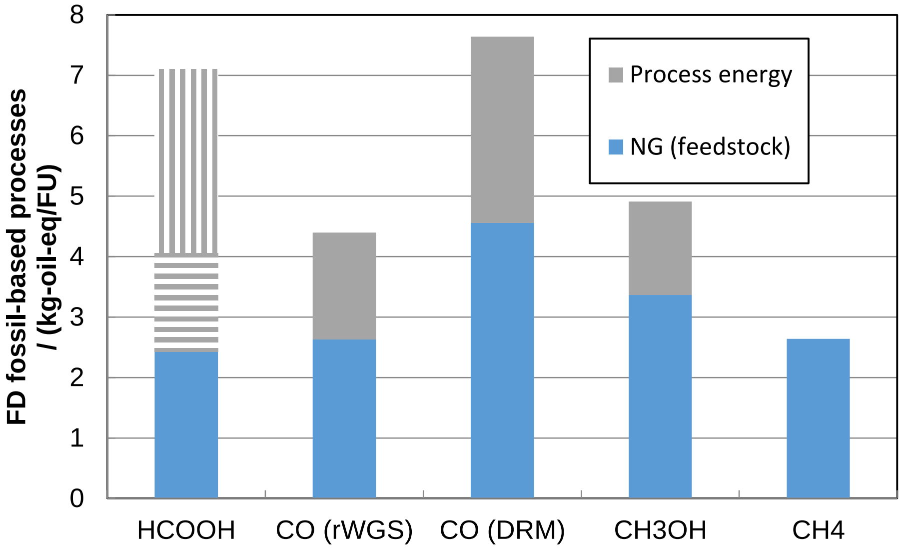

Figure 3: Breakdown of fossil depletion impacts (FD) for fossil-based processes per functional unit (FU). For formic acid (HCOOH), the process energy (heat and electricity) demand is divided in production of the precursor carbon monoxide (horizontal lines) and the conversion of carbon monoxide to formic acid (vertical lines). The fossil depletion impacts of NG (feedstock) include upstream processes such as transportation and natural gas purification.

Table S9: Yield of chemicals for considered CO_2-based processes per functional unit (use of 1 kg hydrogen)

	C1-chemical in kg	Hydrogen in kg	C1-chemical in mol	Hydrogen in mol
Formic acid	4.91-5.63	0.65-0.75	107-122	323-370
Carbon monoxide (rWGS)	3.47	0.75	124	372
Carbon monoxide (DRM)	6.02	1.30	215	645
Methanol	4.90-5.29	--	153-165	--
Methane [a)]	1.97-1.99	0.004-0.017	123-124	2-8

a) Corresponds to 99.6-100.3 MJ based on lower heating value (LHV)

Table S10: Input and output (negative values) of hydrogen in mol for CO_2-based and fossil-based processes of C1-chemicals based on process simulations (data from Tables S2 - S7) and stoichiometric data (see Figure 2 in main text). For the CO_2-based production of CO via DRM, the production of 2 mol CO is considered because thereby we ensure that all CO_2-based processes use 1 mol CO_2 and substitute 1 mol fossil-based methane. The CO_2-based production of CO via DRM substitutes 2 mol fossil-based CO but requires 1 mol methane as feedstock. For the fossil-based production of methanol (process data), the hydrogen output is 0 because the co-produced hydrogen is not purified in the considered process concepts and thus not available as by-product.

	Formic acid 1 mol	CO (rWGS) 1 mol	CO (DRM) 2 mol	Methanol 1 mol	Methane 1 mol
Data based on process simulations					
CO_2-based	1.03-1.62	1.00	-1.39	3.01-3.24	4.00-4.03
Fossil-based	-3.02	-3.00	-6.00	0.00	0.00
Total (CO_2-based – Fossil-based)	**4.05-4.64**	**4.00**	**4.61**	**3.01-3.24**	**4.00-4.03**
Stoichiometric data					
CO_2-based	1	1	-2	3	4
Fossil-based	-3	-3	-6	1	0
Total (CO_2-based – Fossil-based)	**4**	**4**	**4**	**4**	**4**

S6. Maximum impact reductions for global warming including CO_2 supply from CCS

In the main text (Figure 5), a range of global warming impacts for CO_2 supply is considered from –0.42 to –0.99 kg CO_2-eq/kg CO_2. In Figure S4, a range of global warming impacts for CO_2 supply is considered from 0 to –1 kg CO_2-eq/kg CO_2. A global warming impact of zero for CO_2 supply corresponds to the utilization of CO_2 that otherwise would be stored in the underground (CCS).

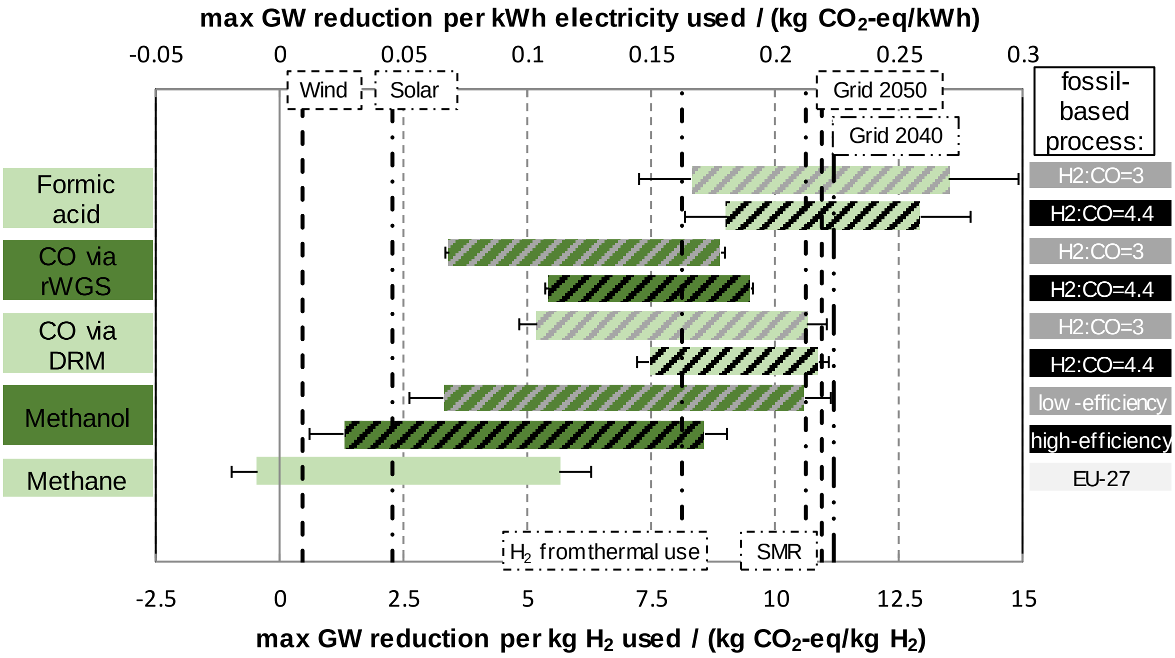

Figure S4: Maximum global warming (GW) impact reductions including CO_2 supply from CCS. For further explanation of the Figure, see caption of Figure 5 in main text.

S7. Maximum environmental impact reductions for alternative natural gas supply

In the main text, the maximum environmental impact reductions for global warming and fossil depletion are determined by considering the natural gas supply mix in the EU-27. In this section, the maximum environmental impact reductions for global warming and fossil depletion are presented for natural gas mixes of countries with highest (Portugal) and lowest (The Netherlands) environmental impacts in the EU-27.

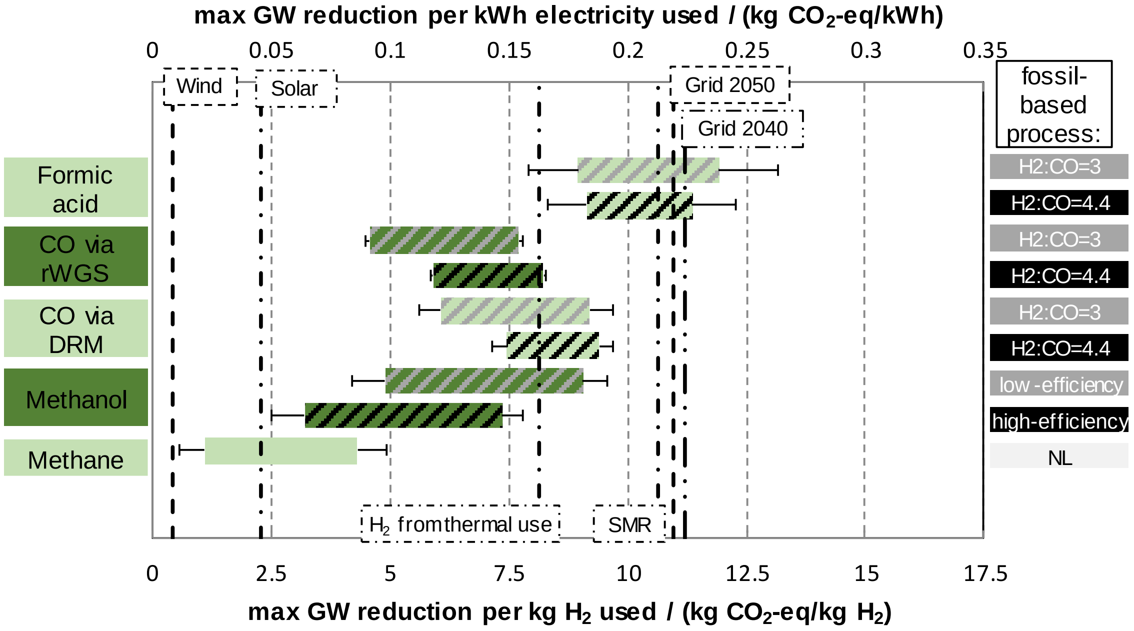

Figure S5: Maximum global warming (GW) impact reductions for the Dutch natural gas mix. For further explanation of the Figure, see caption of Figure 5 in main text.

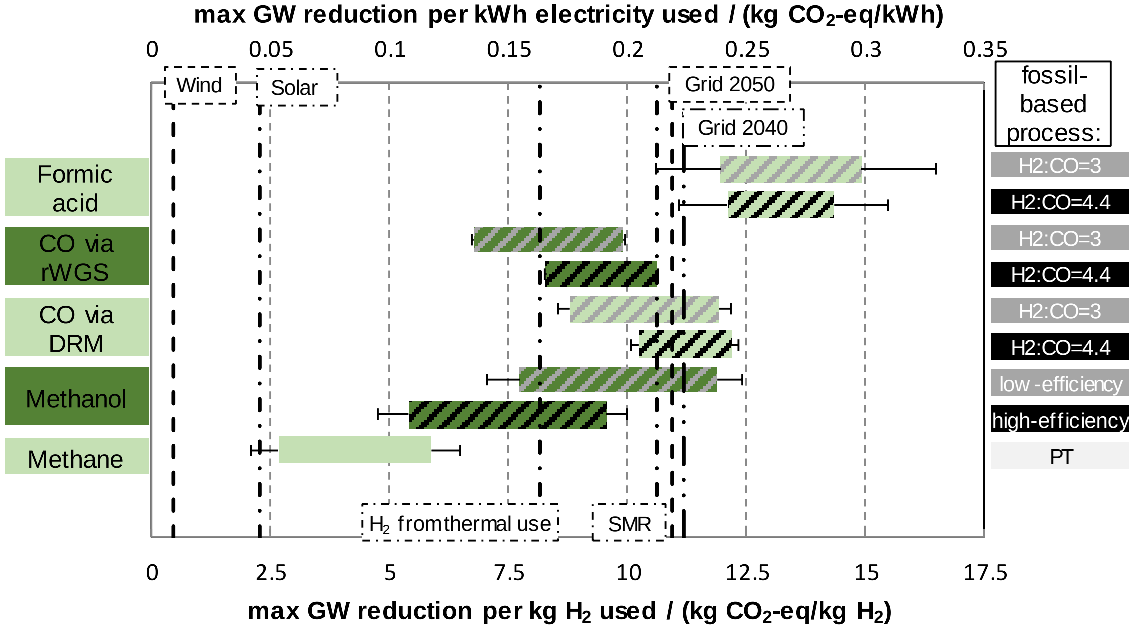

Figure S6: Maximum global warming (GW) impact reductions for the Portuguese natural gas mix. For further explanation of the Figure, see caption of Figure 5 in main text.

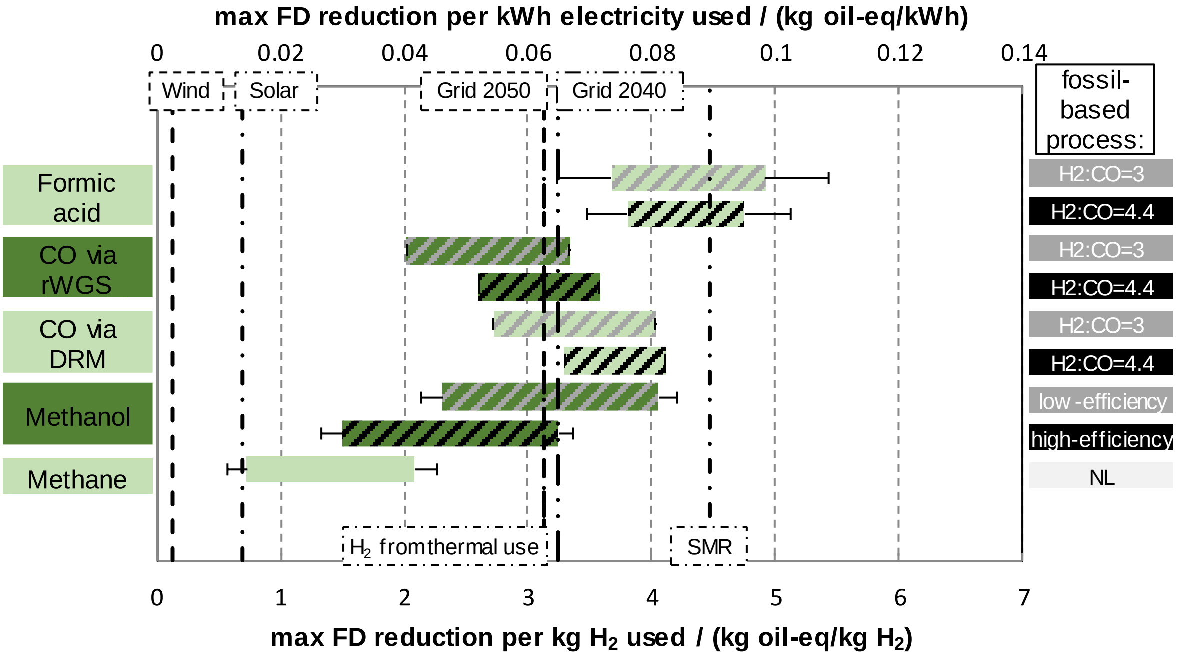

Figure S7: Maximum fossil depletion (FD) impact reductions for the Dutch natural gas mix. For further explanation of the Figure, see caption of Figure 6 in main text.

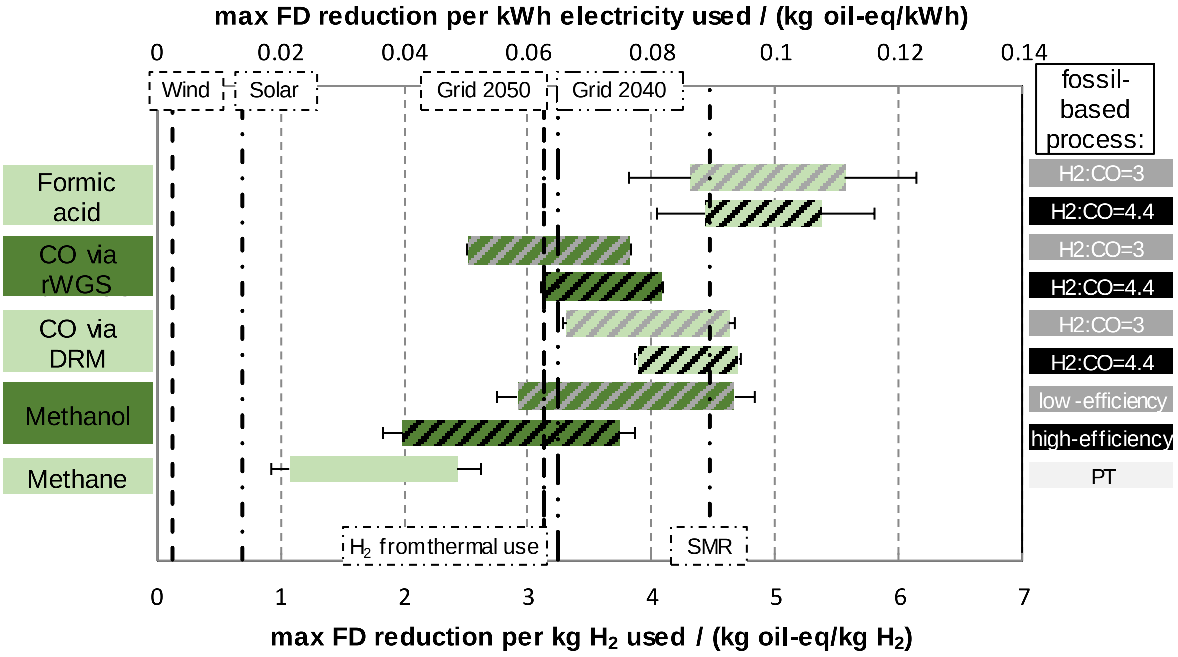

Figure S8: Maximum fossil depletion (FD) impact reductions for the Portuguese natural gas mix. For further explanation of the Figure, see caption of Figure 6 in main text.

S8. Calculation details for CO_2-based process for formic acid (Jens and co-workers)[3]

Simulation was performed with Aspen Plus based on assumptions and physical properties as shown in details below.

Flow sheets

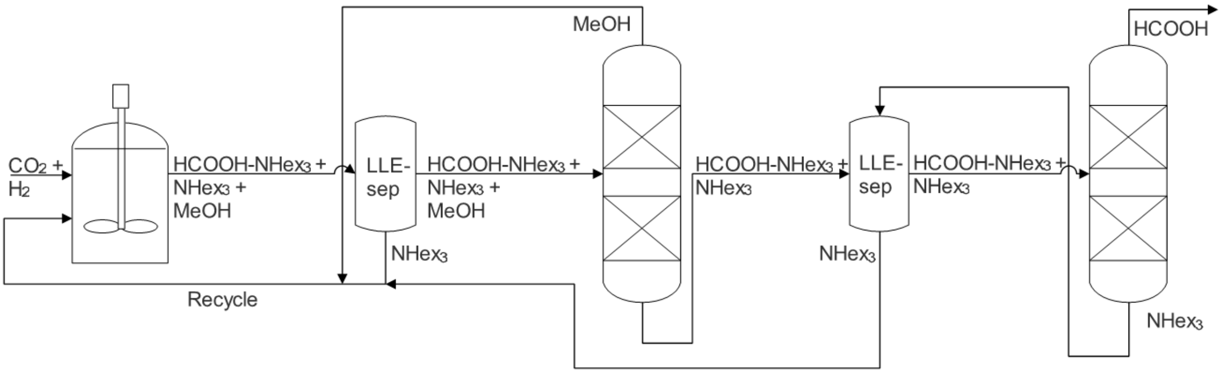

Figure S9: Process flow sheet for $NHex_3$-based process

Physical properties

Table S11: References for physical properties of pure components; COSMO-RS Version: COSMOthermX15 with parameterization TZVPD-FINE

Component	C_p	ΔH_{vap}	p_{vap}	Molar volume
HCOOH	Aspen database	Aspen database	Aspen database	Aspen database
$NHex_3$	Góralski et al.[18]	COSMO-RS	COSMO-RS	Góralski et al.[18]
Methanol	Aspen database	Aspen database	Aspen database	Aspen database
HCOOH-$NHex_3$	Sum of $NHex_3$ and HCOOH	COSMO-RS	COSMO-RS	Same as $NHex_3$

The reference for the physical properties of all considered mixtures is COSMOthermX15 with TZVP-FINE parameterization. The HCOOH-$NHex_3$ complex was implemented with COSMOconfX13.

Assumptions for process simulation

Table S12: Assumptions for process simulation of NHex$_3$-based process and corresponding references

Assumption	Reference
Reactor	
Pressure (CO_2 and H_2), temperature, reaction yields	Patent of Schaub et al.[19]
Enthalpy of reaction	Schaub and Paciello[2]
Solvent effect on the enthalpy of reaction	COSMO-RS
LLE separation	
Partition coefficients are based on:	
• experimental data if available • prediction otherwise	Patent of Schaub et al.[19] COSMO-RS
Distillation	
Temperature and pressure	Patent of Schaub et al.[19]
Reflux ratio; reboiler/condenser heating/cooling	RADFRAC Model in Aspen Plus; Number of stages and feed tray are varied to minimize energy demand
Reactive distillation	Approximated as combination of reactor (with full conversion) at distillation conditions and a RADFRAC distillation.[1] Solvent correction on heat of reaction calculated with COSMO-RS.

S9. References

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