Maleic anhydride from bio-based 1-butanol and furfural: a life cycle assessment at pilot scale

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Electronic supporting information (ESI)

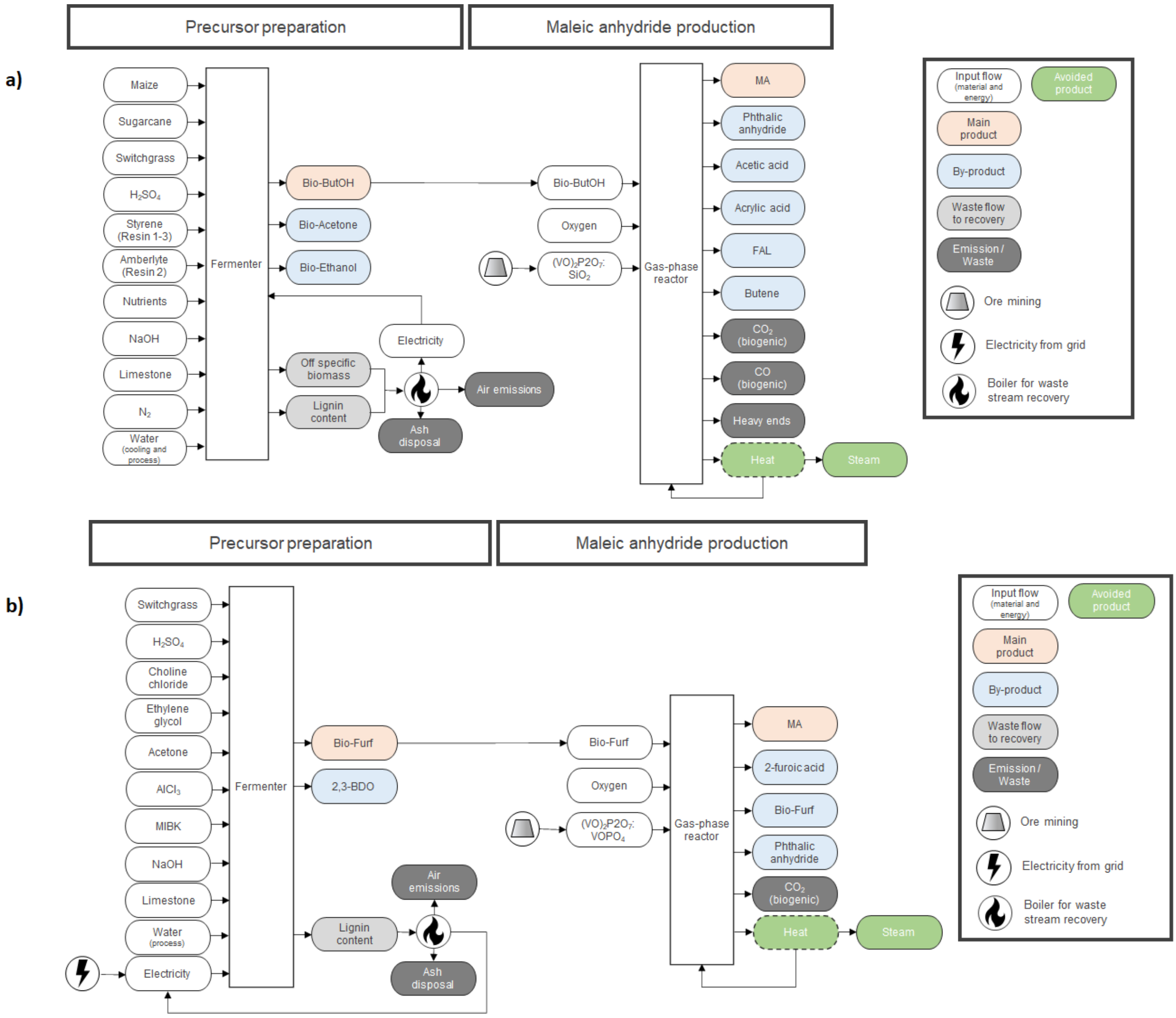


Figure S 1 – System boundaries of the MA production from different biobased precursors, a) Bio-ButOH and b) Bio-Furf, with considering the energy recovery from vessel. Flows related to by-products recovery were not included in the system boundaries due to the mass allocation.

Table S 1 – Calculation setup for E_f.

MA from Bio-ButOH	**Level I E_f**	**Level II E_f**
Maleic anhydride	Product	Product
Carbon dioxide	Waste	Waste
Phthalic anhydride	Waste	Co-product
Carbon monoxide	Waste	Waste
Acetic acid	Waste	Co-product
Acrylic acid	Waste	Co-product
Formaldehyde	Waste	Co-product
Butene	Waste	Co-product
Others	Waste	Waste
	1.2E+00	2.6E-01

MA from Bio-Furf	**Level I E_f**	**Level II E_f**
Maleic anhydride	Product	Product
Carbon dioxide	Waste	Waste
2-furoic acid	Waste	Co-product
Others	Waste	Waste
	8.2E-02	3.0E-03

Table S 2 – LCI MA from Bio-ButOH in the case of none energy recovery from the reaction vessel. Values were allocated in mass on software, respect to the main product (MA, 56.7%).

	C	S	Y	Amount	Unit
Input					
Bio-butanol	100%	-	-	1938.1	kg
Oxygen (O_2)	-	-	-	280.3	kg
$(VO)_2P_2O_7$:SiO_2 (90:10) - Catalyst	-	-	-	19.4	kg
Electricity				1.2E+02	kWh
Total				*2218.4*	*kg*
Output					
Maleic anhydride	-	39.0%	39.0%	1000.0	kg
Carbon dioxide	-	18.0%	18.0%	207.1	kg
Phthalic anhydride	-	12.0%	12.0%	464.7	kg
Carbon monoxide	-	12.0%	12.0%	87.9	kg
Acetic acid	-	8.0%	8.0%	125.6	kg
Acrylic acid	-	8.0%	8.0%	150.7	kg
Formaldehyde	-	1.0%	1.0%	7.9	kg
Butene	-	1.0%	1.0%	14.7	kg
Others*	-	1.0%	1.0%	159.8	kg
Heat waste	-	-	-	7.3 E+03	kWh
Total		*100.0%*	*100.0%*	*2218.4*	*kg*

*Heavy end, according to Aresta, Michele, Dibenedetto, Angela and Dumeignil, Franck. Biorefineries: An Introduction, Berlin, München, Boston: De Gruyter, 2015. https://doi.org/10.1515/9783110331585.[1]

Table S 3 - Breakdown catalyst, MA from Bio-ButOH.

Molecule		Composition %	Amount (kg)	MM tot (kg/kmol)	
$(VO)_2P_2O_7$		90%	17.4	307.82	
		MA (kg/kmol	n° atom per molecule	% atom per molecule	kg atom per molecule
	V	50.94	2	33%	5.8
	O	16.00	9	47%	8.2
	P	30.97	2	20%	3.5
			Amount (kg)	MM tot (kg/kmol)	
SiO_2		10%	1.9	80.08	

Table S 4 – LCI MA from Bio-Furf in the case of none energy recovery from the reaction vessel. Values were allocated in mass on software, respect to the main product (MA, 92.9%).

	C	S	Y	Amount	Unit
Input					
Furfural	99.2%	-	-	1008.9	kg
Oxygen (O_2)	-	-	-	81.4	kg
$(VO)_2P_2O_7$:$VOPO_4$ - VPO Catalyst	-	-	-	10.1	kg
Electricity				1.3E+02	kWh
Total				*1090.3*	*kg*
Output					
Maleic anhydride	-	97.9%	97.1%	1000.0	kg
Carbon dioxide	-	0.7%	0.7%	3.2	kg
2-furoic acid	-	0.5%	0.5%	5.8	kg
Phthalic anhydride*		0.9%	0.9%	73.2	kg
Furfural**	0.8%	-	0.8%	8.1	kg
Heat waste	-	-	-	3.8E+03	kWh
Total		*100.0%*	*100.0%*	*1090.3*	*kg*

* In the manuscript reported as "Others (include possible polymerized products and other unidentified products)". Here in the simulation, it was assumed to be phthalic anhydride: according to literature[2] MA can react with furan to produce phthalic anhydride.

** Assuming to be recovered (100% efficiency) for the next run.

Table S 5 - Breakdown catalyst, MA from Bio--Furf.

Molecule			**Amount (kg)**	**MM tot (kg/kmol)**	
$(VO)_2P_2O_7$		50%	5.0	307.82	
		MA	n° atom per molecule	% atom per molecule	kg atom per molecule
	V	50.94	2	33%	1.7
	O	16.00	9	47%	2.4
	P	30.97	2	20%	1.0
			Amount (kg)	MM tot (kg/kmol)	
$VOPO_4$		50%	5.0	161.91	
		MA	n° atom per molecule	% atom per molecule	kg atom per molecule
	V	50.94	1	17%	0.8
	O	16.00	5	26%	1.3
	P	30.97	1	10%	0.5

Table S 6 – LCI Bio-ButOH production. Values allocated in mass (79.3%) respect to the original extrapolated from literature.[52]

Stage	Material/Substance	Amount	Unit
Input			
Feedstock handling	Maize	4346.3	kg
	Sugarcane	4346.3	kg
	Switchgrass	4346.3	kg
Pretretment and hydrolysis	Sulphuric acid (75%)	644.1	kg
	Resin (001) - styrene	9.8	dm^3
Fermentation	Nutrients (glucose:ammonium sulphate, 99:1)	1074.2	kg
	Sodium hydroxide (1M)	42.3	kg
Separation and purification	Resin (002) - amberlyte	10.8	dm^3
	Resin (003) - styrene	4.6E-02	dm^3
Waste Water Tratment	Sodium hydroxide	228.5	kg
Co-generator	Limestone for FGD (flue-gas desulfurization)	136.2	kg
Utilities	Sulphuric acid (pH adjuster)	0.3	kg
	Nitrogen (N_2 gas)	0.1	dm^3
	Electricity[1]	-	kWh
	Process water	4845.2	kg
	Cooling water	4845.2	kg
Output			
Feedstock handling	Off specific biomass (sent to boiler)[2]	822.1	kg
Pretretment and hydrolysis	Lignin content (sent to boiler)[3]	3952.0	kg
Final product	Butanol	1938.1	kg
Co-generator	Ash disposal from boiler	871.2	kg
Air emissions	Amount and type derived from ecoinvent process "Heat, district or industrial, other than natural gas {ASCC}| heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | APOS, U"		
Avoided products			
Energy recovery	Electricity produced from steam[4]	-5.7 E+01	kWh

[1] Not requested since able to recover energy from boiler.

[2] Approximately 5% of the total fed biomass is screened (as off-spec).

[3] Estimated as 25.3 % of the inlet biomass.

[4] Derived from incineration of lignin and off specific biomass.

Table S 7 – LCI Bio-Furf production. Values allocated in mass (31.5%) respect to the original extrapolated from literature.[53,54]

Stage	Material/Substance	Amount	Unit
Input			
Feedstock Handling	Switchgrass	3661.8	kg
DES pretratment	Sulphuric acid Choline chloride - $[(CH_3)_3NCH_2CH_2OH]Cl$ Ethylene glycol Acetone	80.1 34.5 61.4 171.9	kg kg kg kg
Furfural production and distillation	Aluminium chloride ($AlCl_3$) methyl isobutyl ketone (MIBK)	7.9 172.7	kg kg
Wastewater treatment	Sodium hydroxide	73.9	kg
Boiler and stream	Limestone for flue-gas desulfurization (FGD)	18.5	kg
Utilities	Sulphuric acid (pH adjuster) as Cooling Tower chemical Process water Electricity	0.1 1360.7 1360.7 322.4	kg kg kg kWh
Output			
Final product	Furfural	1008.9	kg
Boiler to treat waste	Lignin content	342.6	kg
Boiler to treat waste	Ash disposal, from lignin combustion[1]	62.5	kg
Boiler to treat waste	Air emissions. Amount and type derived from ecoinvent process "Heat, district or industrial, other than natural gas {ASCC}| heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | APOS, U"		
Avoided products			
Energy recovery	Electricity produced from steam[2]	-4.1 E+00	kWh

[1] Assuming the same amount of ash produced per mass of combusted biomass of the bio-ButOH scenario.

[2] Derived from incineration of lignin, assuming the same energy content of the bio-ButOH scenario.

Eq. 1 was applied to the stoichiometric reactions to estimate the enthalpy of reaction ($\Delta rH°$). Both routes are extremely exothermic. Two scenarios were simulated. One without energy recovery (Level I_{EN}) and in the second the heat released was assumed to be 100% recovered to pre-heat reagents and generate steam for further plant usages (Level II_{EN}). Energy requirements to heat reagents was calculated using equations (3,4,5,7) already reported in literature.[51] The difference between the total heat requirements for heating reagents (q tot reaction) and the enthalpy of reaction ($\Delta rH°$) represents the net energy input.

$$\Delta rH° = \sum \nu{\cdot}\Delta fH°p - \sum \nu{\cdot}\Delta fH°r$$

Eq. 1 – Enthalpy of reaction

Table S 8 - MA from Bio-ButOH enthalpy of reaction.

Stoichiometric reaction	$C_4H_{10}O + 3O_2 \rightarrow C_4H_2O_3 + 4H_2O$	
Input	$\Delta_fH°r$ (kJ/mol)	ν
Bio-butanol	-274.9	1
Oxigen (O_2)	498.4	3
∑ ν·ΔfH°r	1220.3	
Output	$\Delta_fH°r$ (kJ/mol)	ν
Maleic anhydride	-398.3	1
Water	-241.8	4
∑ ν·ΔfH°p	-1365.5	
ΔrH°	-2585.8	MJ/kmol
	-7304.4	kWh/FU

Table S 9 - MA from Bio-Furf enthalpy of reaction.

Stoichiometric reaction	$C_5H_4O_2 + 2O_2 \rightarrow C_4H_2O_3 + CO_2 + H_2O$	
Input	ΔfH°r (kJ/mol)	ν
Furfural	-274.9	1
Oxigen (O_2)	498.4	2
∑ ν·ΔfH°r	721.9	
Output	ΔfH°r (kJ/mol)	ν
Maleic anhydride	-398.3	1
Carbon dioxide	-393.5	1
Water	-241.8	1
∑ ν·ΔfH°p	-640.1	
ΔrH°	-1362.0	MJ/kmol
	-3847.4	kWh/FU

Table S 10 - MA from Bio-ButOH: full energy balance.

***q* bio-ButOH (liquid → gas)**					
Cp liq (J/mol K)		**A + BT + CT^2 + DT^3 + ET^4**			
Source:*	A	B	C	D	E
bio-ButOH (liquid)	83.877	5.66E-01	-0.0017208	2.28E-06	-
T1(=Tenv)	298	H at T1	3.95E-02	kJ/mol	
T2(=Tb)	391	H at T2	5.51E-02	kJ/mol	
		ΔH	1.57E-02	kJ/mol	
Cp gas (J/mol K)		**A + B[(C/T)/sinh(C/T)]^2+ D[(E/T)/cosh(E/T)]^2**			
Source:*	A	B	C	D	E
bio-ButOH (gas)	8.16E+00	4.10E-01	-2.26E-04	6.04E-08	-6.28E-12
T1(=Tb)	391	H at T1	3.35E-03	kJ/mol	
T2(=Tr)	613	H at T2	5.25E-03	kJ/mol	
		ΔH	1.90E-03	kJ/mol	
ΔH_{vap} (Source**)	43.29	kJ/mol	390.9	K	
q_{tot} bio-ButOH	4.33E+01	kJ/mol			

***q* oxygen (gas)**					
Cp gas (J/mol K)		**A + B[(C/T)/sinh(C/T)]^2+ D[(E/T)/cosh(E/T)]^2**			
	A	B	C	D	E
	29.526	-8.90E-03	3.81E-05	-3.26E-08	8.86E-12
T1(=Tenv)	298	H at T1	8.80E-03	kJ/mol	
T2(=Tr)	613	H at T2	1.81E-02	kJ/mol	
		ΔH	9.30E-03	kJ/mol	

q* tot reaction**				
q_{tot} bio-ButOH + q oxygen	4.33E+01	kJ/mol	4.33E+04	kJ/kmol
			4.42E+05	kJ/FU
			1.22E+02	kWh/FU

Net energy input = *q* tot reaction - ΔrH°			
Net energy input	-7.2E+03	kWh/FU	Since negative, it was assumed to be recovered as steam for other processes (9.4E+03 kg steam/FU)

*Ludwig's Applied Process Design for Chemical and Petrochemical Plants, Volume 1, Fourth Edition, A. Kayode Coker Gulf Professional Publishing is an imprint of Elsevier 30 Corporate Drive, Suite 400, Burlington, MA 01803, USA Linacre House, Jordan Hill, Oxford OX2 8DP, UK 2007 Elsevier Inc.[3]

**National Institute of Standards and Technology (NIST) available at https://webbook.nist.gov/cgi/cbook.cgi?ID=C71363&Mask=4 (accessed 22 June 2023).[4]

***It represents the energy requirements to heat reagents according to literature.[51]

Table S 11 - MA from Bio-Furf: full energy balance.

***q* bio-Furf (liquid → gas)**					
Cp liq (J/mol K)			**A + BT + CT^2 + DT^3 + ET^4**		
Source:*	A	B	C	D	E
bio-Furf (liquid)	73.9	0.2994	-	-	-
T1(=Tenv)	298	H at T1	3.53E-02	kJ/mol	
T2(=Tb)	435	H at T2	6.05E-02	kJ/mol	
		ΔH	2.52E-02	kJ/mol	
Cp gas (J/mol K)			**A + B[(C/T)/sinh(C/T)]^2+ D[(E/T)/cosh(E/T)]^2**		
Source:*	A	B	C	D	E
bio-Furf (gas)	47.3	198.3	1040.6	109	472.6
T1(=Tb)	435	H at T1	1.89E-01	kJ/mol	
T2(=Tr)	633	H at T2	2.20E-01	kJ/mol	
		ΔH	3.03E-02	kJ/mol	
ΔH_{vap} (Source**)	44.7	kJ/mol	range 357-435	K	
q_{tot} bio-Furf	4.48E+01	kJ/mol			

***q* oxygen**					
Cp gas (J/mol K)			**A + B[(C/T)/sinh(C/T)]^2+ D[(E/T)/cosh(E/T)]^2**		
	A	B	C	D	E
	29.526	-8.90E-03	3.81E-05	-3.26E-08	8.86E-12
T1	298	H at T1	8.80E-03	kJ/mol	
T2(=Tr)	633	H at T2	1.87E-02	kJ/mol	
		ΔH	9.89E-03	kJ/mol	

q tot reaction* **				
q_{tot} bio-Fur + q oxygen	4.48E+01	kJ/mol	4.48E+04	kJ/kmol
			4.57E+05	kJ/FU
			1.26E+02	kWh/FU

Net energy input = *q* tot reaction - ΔrH°			
Net energy input	-3.7E+03	kWh/FU	Since negative, it was assumed to be recovered as steam for other processes (4.9 E+03 kg steam/FU)

*TransFurans Chemicals bvba. Available at: https://pdf4pro.com/amp/view/physical-properties-of-furfural-483595.html (accessed 22 June 2023).[5]

**National Institute of Standards and Technology (NIST). Available at: https://webbook.nist.gov/cgi/cbook.cgi?ID=C98011&Mask=4 (accessed 22 June 2023).[6]

***It represents the energy requirements to heat reagents according to literature.[51]

Table S 12 – LCI MA from Bio-ButOH in the case of 100% energy recovery from the reaction vessel to produce steam. Values were allocated in mass on software, respect to the main product (MA, 56.7%).

	C	S	Y	Amount	Unit
Input					
Bio-butanol	100%	-	-	1938.1	kg
Oxygen (O_2)	-	-	-	280.3	kg
$(VO)_2P_2O_7$:SiO_2 (90:10) - Catalyst	-	-	-	19.4	kg
Electricity				0.0	kWh
Total				*2218.4*	*kg*
Output					
Maleic anhydride	-	39.0%	39.0%	1000.0	kg
Carbon dioxide	-	18.0%	18.0%	207.1	kg
Phthalic anhydride	-	12.0%	12.0%	464.7	kg
Carbon monoxide	-	12.0%	12.0%	87.9	kg
Acetic acid	-	8.0%	8.0%	125.6	kg
Acrylic acid	-	8.0%	8.0%	150.7	kg
Formaldehyde	-	1.0%	1.0%	7.9	kg
Butene	-	1.0%	1.0%	14.7	kg
Others*	-	1.0%	1.0%	159.8	kg
Heat waste	-	-	-	0.0	kWh
Total		*100.0%*	*100.0%*	*2218.4*	*kg*
Avoided product					
Steam	-	-	-	-9.4E+3	kg

*Heavy end, according to Aresta, Michele, Dibenedetto, Angela and Dumeignil, Franck. Biorefineries: An Introduction, Berlin, München, Boston: De Gruyter, 2015. https://doi.org/10.1515/9783110331585. [1]

Table S 13 – LCI MA from Bio-Furf in the case of 100% energy recovery from the reaction vessel to produce steam. Values were allocated in mass on software, respect to the main product (MA, 92.9%).

	C	S	Y	Amount	Unit
Input					
Furfural	99.2%	-	-	1008.9	kg
Oxygen (O_2)	-	-	-	81.4	kg
$(VO)_2P_2O_7$:$VOPO_4$ - VPO Catalyst	-	-	-	10.1	kg
Electricity				0.0	kWh
Total				*1090.3*	*kg*
Output					
Maleic anhydride	-	97.9%	97.1%	1000.0	kg
Carbon dioxide	-	0.7%	0.7%	3.2	kg
2-furoic acid	-	0.5%	0.5%	5.8	kg
Phthalic anhydride*		0.9%	0.9%	73.2	kg
Furfural**	0.8%	-	0.8%	8.1	kg
Heat waste	-	-	-	0.0	kWh
Total		*100.0%*	*100.0%*	*1090.3*	*kg*
Avoided product					
Steam	-	-	-	-4.9E+3	kg

* In the manuscript reported as "Others (include possible polymerized products and other unidentified products)". Here in the simulation, it was assumed to be phthalic anhydride: according to literature[61] MA can react with furan to produce phthalic anhydride.

** Assuming to be recovered (100% efficiency) for the next run.

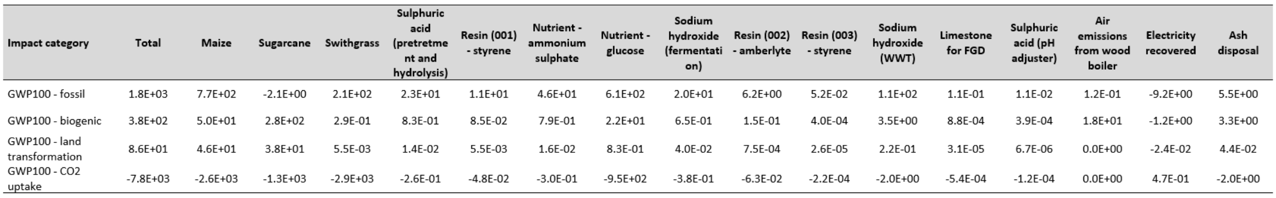
Table S 14 – Carbon footprint (in kgCO_2eq.) of the bio-based MA routes, with and w/o the energy recovery IPCC 2021 GWP100 (incl. CO_2 uptake), v.1.01.

Impact category	Bio-ButOH MA	Bio-Furf MA	Bio-ButOH MA+En.Recov.	Bio-Furf MA+En.Recov.
GWP100 - fossil	1999.2	839.9	478.0	-471.2
GWP100 - biogenic	537.0	28.0	491.7	-13.4
GWP100 – CO_2 uptake	94.3	0.6	94.1	0.3
GWP100 - land use and transf.	-8606.5	-2321.8	-8575.8	-2294.6

Table S 15 – Resources consumption (in GJ eq.) of the bio-based MA routes, with and w/o the energy recovery. Absolute values using CED method (v.1.11).

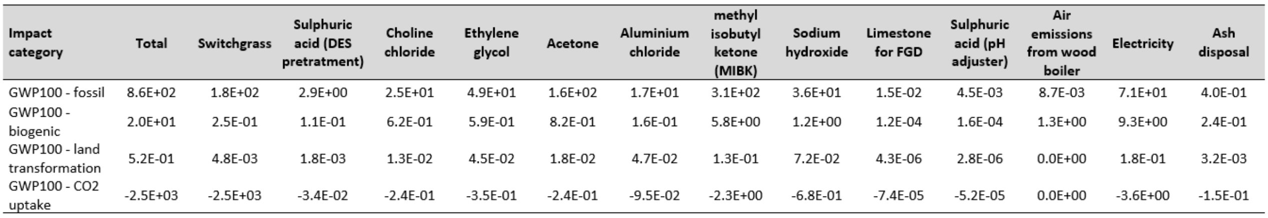
Impact category	Bio-ButOH MA	Bio-Furf MA	Bio-ButOH MA+En.Recov.	Bio-Furf MA+En.Recov.
Total	*1.2E+02*	*4.4E+01*	*9.2E+01*	*2.2E+01*
Non-renewable, fossil	2.2E+01	1.6E+01	-1.7E+00	-4.1E+00
Non-renewable, nuclear	1.6E+00	1.8E+00	6.9E-01	8.3E-01
Non-renewable, biomass	2.3E-01	2.3E-04	2.3E-01	9.6E-05
Tot. Non-renewables	*2.4E+01*	*1.8E+01*	*-7.5E-01*	*-3.3E+00*
Renewable, biomass	9.2E+01	2.6E+01	9.2E+01	2.5E+01
Renewable, wind, solar, geothe	2.1E-01	1.8E-01	9.9E-02	6.2E-02
Renewable, water	5.9E-01	3.4E-01	4.2E-01	1.6E-01
Tot. Renewables	*9.3E+01*	*2.6E+01*	*9.3E+01*	*2.6E+01*

Table S 16 – Carbon footprint (in kgCO_2eq.) of the production of 1ton of bio-ButOH, IPCC 2021 GWP100 (incl. CO_2 uptake), v.1.01.



Impact category	Total	Maize	Sugarcane	Swithgrass	Sulphuric acid (pretretment and hydrolysis)	Resin (001) - styrene	Nutrient - ammonium sulphate	Nutrient - glucose	Sodium hydroxide (fermentation)	Resin (002) - amberlyte	Resin (003) - styrene	Sodium hydroxide (WWT)	Limestone for FGD	Sulphuric acid (pH adjuster)	Air emissions from wood boiler	Electricity recovered	Ash disposal
GWP100 - fossil	1.8E+03	7.7E+02	-2.1E+00	2.1E+02	2.3E+01	1.1E+01	4.6E+01	6.1E+02	2.0E+01	6.2E+00	5.2E-02	1.1E+02	1.1E-01	1.1E-02	1.2E-01	-9.2E+00	5.5E+00
GWP100 - biogenic	3.8E+02	5.0E+01	2.8E+02	2.9E-01	8.3E-01	8.5E-02	7.9E-01	2.2E+01	6.5E-01	1.5E-01	4.0E-04	3.5E+00	8.8E-04	3.9E-04	1.8E+01	-1.2E+00	3.3E+00
GWP100 - land transformation	8.6E+01	4.6E+01	3.8E+01	5.5E-03	1.4E-02	5.5E-03	1.6E-02	8.3E-01	4.0E-02	7.5E-04	2.6E-05	2.2E-01	3.1E-05	6.7E-06	0.0E+00	-2.4E-02	4.4E-02
GWP100 - CO2 uptake	-7.8E+03	-2.6E+03	-1.3E+03	-2.9E+03	-2.6E-01	-4.8E-02	-3.0E-01	-9.5E+02	-3.8E-01	-6.3E-02	-2.2E-04	-2.0E+00	-5.4E-04	-1.2E-04	0.0E+00	4.7E-01	-2.0E+00

Table S 17 – Carbon footprint (in kgCO_2eq.) of the production of 1ton of bio-Furf, IPCC 2021 GWP100 (incl. CO_2 uptake), v.1.01.



Impact category	Total	Switchgrass	Sulphuric acid (DES pretratment)	Choline chloride	Ethylene glycol	Acetone	Aluminium chloride	methyl isobutyl ketone (MIBK)	Sodium hydroxide	Limestone for FGD	Sulphuric acid (pH adjuster)	Air emissions from wood boiler	Electricity	Ash disposal
GWP100 - fossil	8.6E+02	1.8E+02	2.9E+00	2.5E+01	4.9E+01	1.6E+02	1.7E+01	3.1E+02	3.6E+01	1.5E-02	4.5E-03	8.7E-03	7.1E+01	4.0E-01
GWP100 - biogenic	2.0E+01	2.5E-01	1.1E-01	6.2E-01	5.9E-01	8.2E-01	1.6E-01	5.8E+00	1.2E+00	1.2E-04	1.6E-04	1.3E+00	9.3E+00	2.4E-01
GWP100 - land transformation	5.2E-01	4.8E-03	1.8E-03	1.3E-02	4.5E-02	1.8E-02	4.7E-02	1.3E-01	7.2E-02	4.3E-06	2.8E-06	0.0E+00	1.8E-01	3.2E-03
GWP100 - CO2 uptake	-2.5E+03	-2.5E+03	-3.4E-02	-2.4E-01	-3.5E-01	-2.4E-01	-9.5E-02	-2.3E+00	-6.8E-01	-7.4E-05	-5.2E-05	0.0E+00	-3.6E+00	-1.5E-01

Table S 18 – Total resources consumption (in GJ eq.) of the bio-based MA routes, with and w/o the energy recovery. Pairwise comparison using CED method (v.1.11).

	Bio-ButOH AM	Bio-Furf AM	Bio-ButOH AM+En.Recov.	Bio-Furf AM+En.Recov.
Bio-ButOH AM	0.0	72.7	25.0	94.5
Bio-Furf AM	-72.7	0.0	-47.7	21.8
Bio-ButOH AM+En.Recov.	-25.0	47.7	0.0	69.5
Bio-Furf AM+En.Recov.	-94.5	-21.8	-69.5	0.0

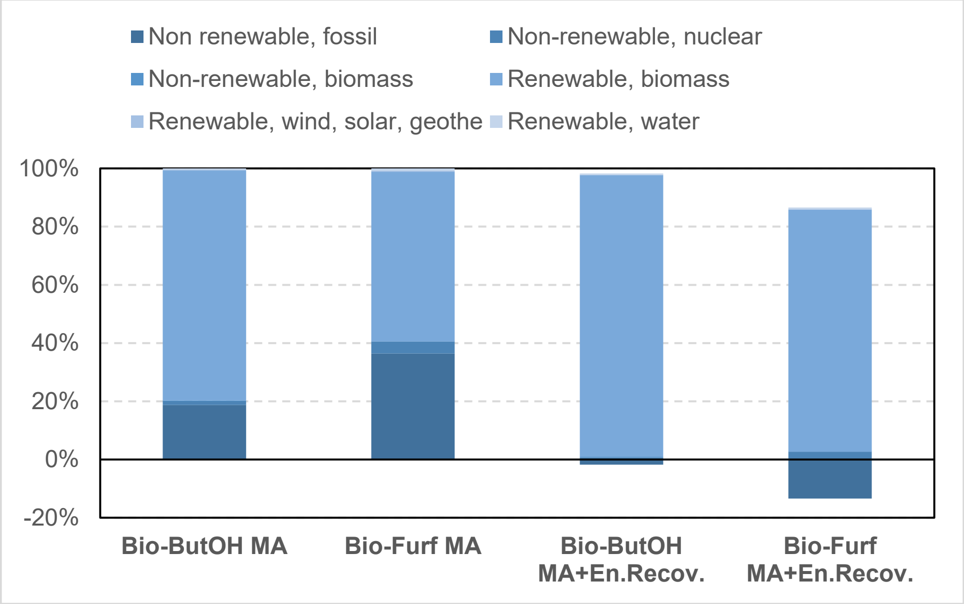


Figure S 2 – Resources consumption of the bio-based MA routes, with and w/o the energy recovery. Contribution analysis using CED method (v.1.11).

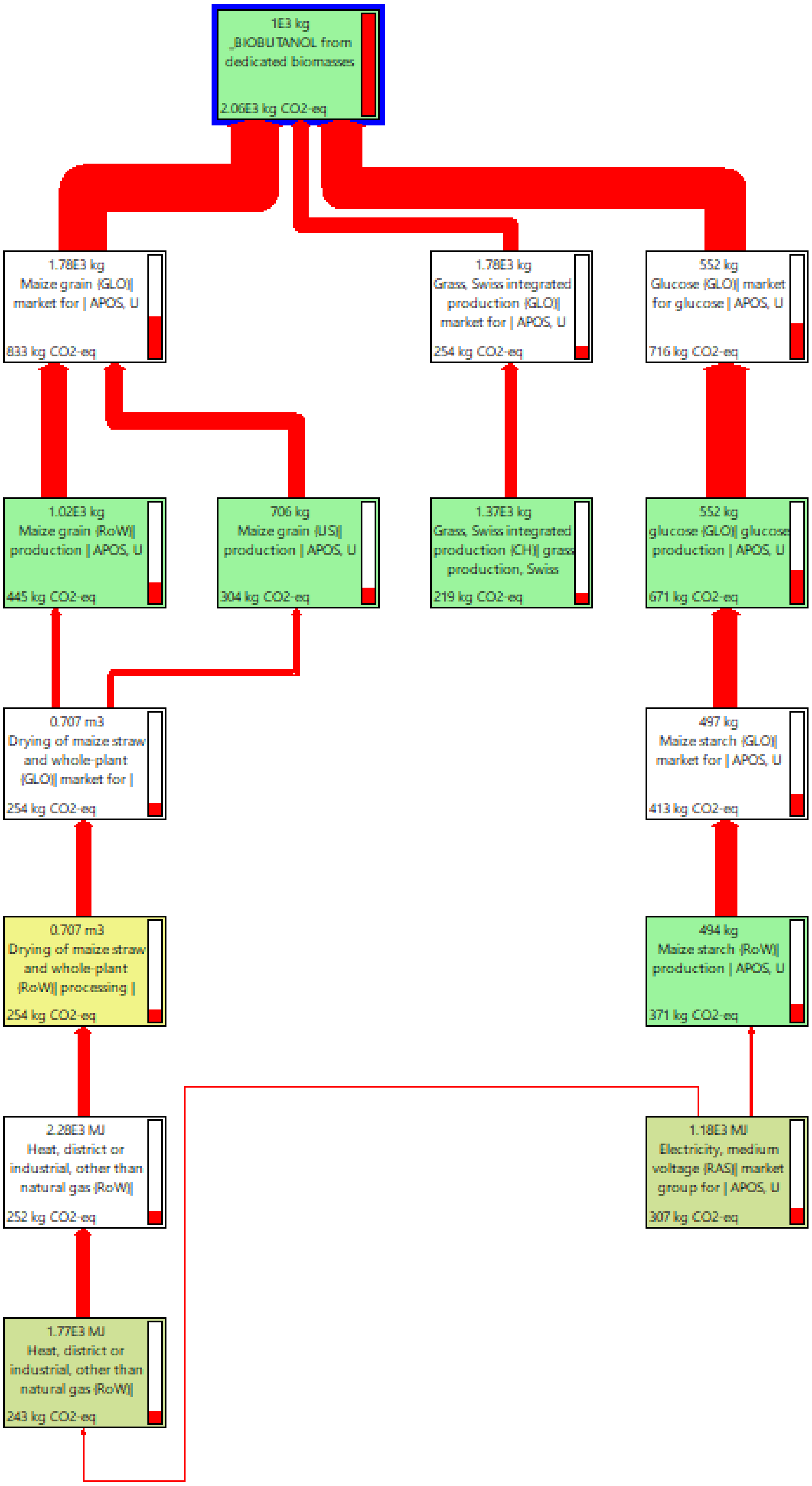


Figure S 3 – Bio-ButOH production (1 ton): Sankey-based diagram for the fossil indicator IPCC 2021 GWP100 (incl. CO_2 uptake), v.1.01.

Table S 19 – Contribution analysis of the bio-ButOH MA+En.Recov. (A) and bio-Furf MA+En.Recov. (B) using ReCiPe 2016 method (v.1.07).

A)

Impact category	**Unit**	**Total**	**bio-ButOH**	**Catalyst**	**Steam recovery**
GW	kg CO$_2$ eq	6.4E+02	2.2E+03	4.6E-02	-1.5E+03
SOD	kg CFC11 eq	2.1E-02	2.1E-02	1.5E-08	-3.7E-04
IR	kBq Co-60 eq	3.6E+01	7.2E+01	3.1E-04	-3.5E+01
OF HH	kg NO$_x$ eq	4.7E+00	6.4E+00	2.4E-04	-1.7E+00
FPMF	kg PM$_{2.5}$ eq	6.2E+00	7.3E+00	9.2E-05	-1.1E+00
OF TE	kg NO$_x$ eq	4.7E+00	6.4E+00	2.4E-04	-1.7E+00
TA	kg SO$_2$ eq	3.2E+01	3.5E+01	2.3E-04	-3.4E+00
FWEu	kg P eq	8.7E-01	1.1E+00	1.2E-05	-1.9E-01
MEu	kg N eq	4.3E+00	4.3E+00	5.0E-07	-9.7E-03
TEu	kg 1,4-DCB	3.0E+03	5.1E+03	3.1E-01	-2.2E+03
FWEc	kg 1,4-DCB	1.8E+02	1.8E+02	3.6E-04	-4.7E+00
MEc	kg 1,4-DCB	2.3E+02	2.4E+02	6.5E-04	-7.6E+00
HCT	kg 1,4-DCB	2.7E+01	3.7E+01	6.9E-04	-1.1E+01
HNCT	kg 1,4-DCB	5.5E+03	5.7E+03	2.3E-02	-2.4E+02
LU	m^{2}a crop eq	3.3E+03	3.4E+03	1.3E-02	-2.7E+01
MRS	kg Cu eq	1.6E+01	2.4E+00	1.3E+01	-8.4E-02
FRS	kg oil eq	-3.8E+01	4.7E+02	1.1E-02	-5.1E+02
WC	m^3	3.7E+02	3.8E+02	3.5E-04	-1.6E+00

B)

Impact category	**Unit**	**Total**	**bio-Furf**	**Catalyst**	**Steam recovery**
GW	kg CO$_2$ eq	-4.5E+02	8.3E+02	0.0E+00	-1.3E+03
SOD	kg CFC11 eq	4.1E-03	4.4E-03	0.0E+00	-3.1E-04
IR	kBq Co-60 eq	2.4E+01	5.4E+01	0.0E+00	-3.0E+01
OF HH	kg NO$_x$ eq	8.8E-01	2.3E+00	0.0E+00	-1.4E+00
FPMF	kg PM$_{2.5}$ eq	1.4E+00	2.3E+00	0.0E+00	-9.5E-01
OF TE	kg NO$_x$ eq	1.1E+00	2.5E+00	0.0E+00	-1.4E+00
TA	kg SO$_2$ eq	9.9E+00	1.3E+01	0.0E+00	-2.9E+00
FWEu	kg P eq	1.8E+00	1.9E+00	0.0E+00	-1.6E-01
MEu	kg N eq	1.0E+00	1.0E+00	0.0E+00	-8.3E-03
TEu	kg 1,4-DCB	-1.2E+03	6.7E+02	0.0E+00	-1.9E+03
FWEc	kg 1,4-DCB	1.2E+01	1.6E+01	0.0E+00	-4.0E+00
MEc	kg 1,4-DCB	1.5E+01	2.2E+01	0.0E+00	-6.4E+00
HCT	kg 1,4-DCB	8.9E+00	1.8E+01	0.0E+00	-8.9E+00
HNCT	kg 1,4-DCB	5.6E+02	7.6E+02	0.0E+00	-2.0E+02
LU	m^{2}a crop eq	8.7E+02	9.0E+02	0.0E+00	-2.3E+01
MRS	kg Cu eq	9.7E+00	3.4E-01	9.4E+00	-7.1E-02
FRS	kg oil eq	-9.0E+01	3.4E+02	0.0E+00	-4.3E+02
WC	m^3	1.1E+01	1.2E+01	0.0E+00	-1.3E+00

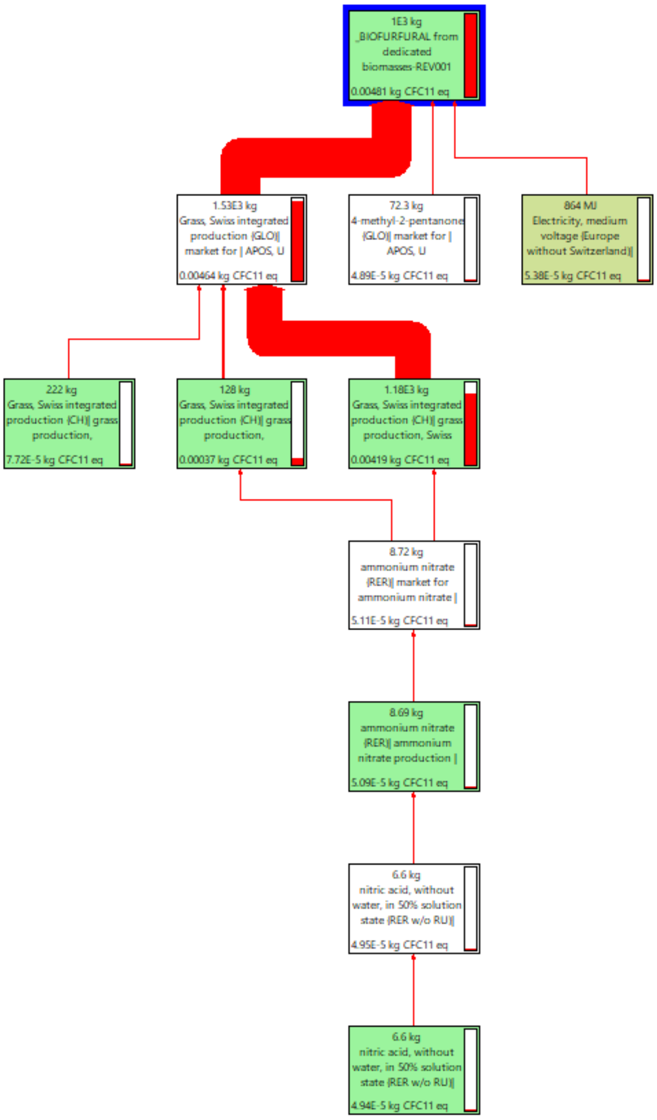


Figure S 4 - Bio-Furf production (1 ton): Sankey-based diagram for the SOD category ReCiPe 2016 method (v.1.07).

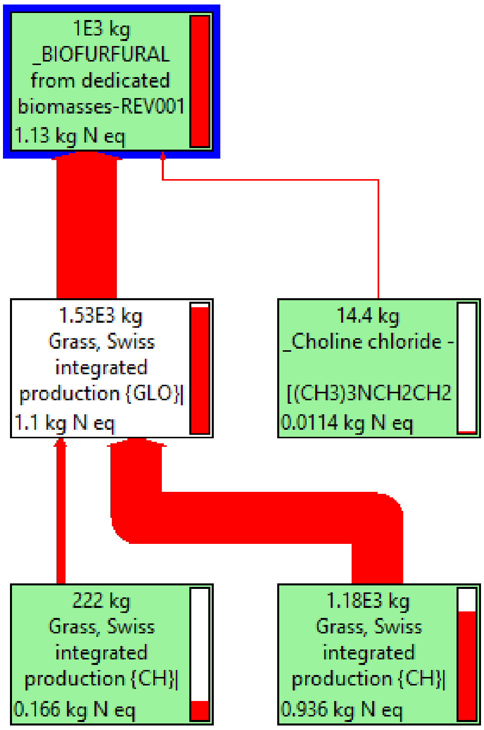


Figure S 5- Bio-Furf production (1 ton): Sankey-based diagram for the MEu category ReCiPe 2016 method (v.1.07).

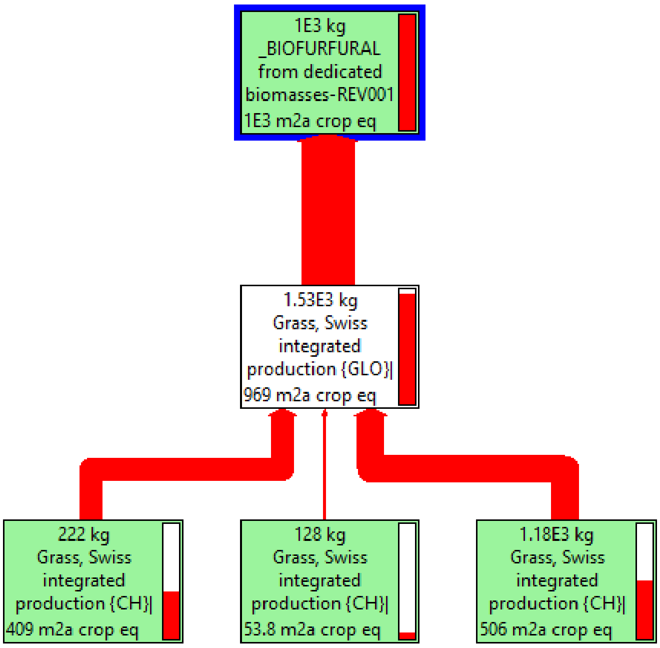


Figure S 6 - Bio-Furf production (1 ton): Sankey-based diagram for the LU category ReCiPe 2016 method (v.1.07).

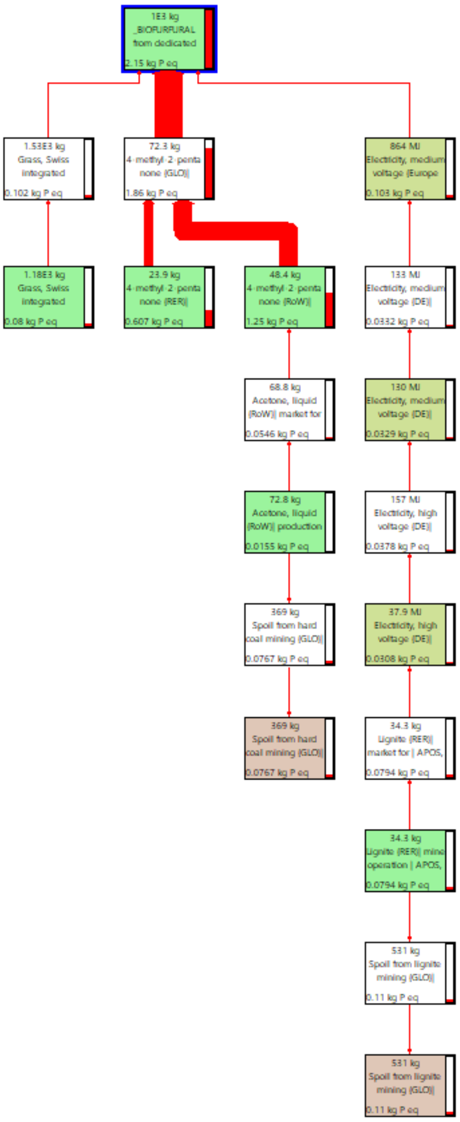


Figure S 7 - Bio-Furf production (1 ton): Sankey-based diagram for the FWEu category ReCiPe 2016 method (v.1.07).

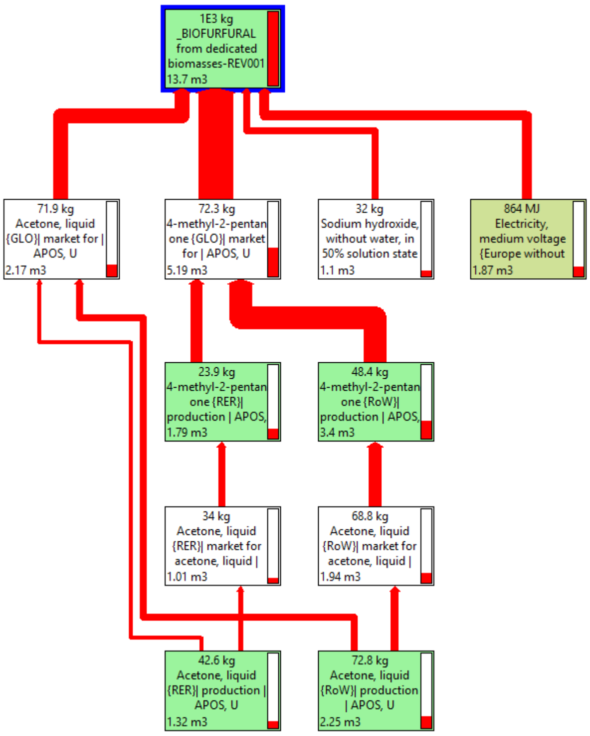


Figure S 8 - Bio-Furf production (1 ton): Sankey-based diagram for the WC category ReCiPe 2016 method (v.1.07).

Table S 20 - BioButOH production using ReCiPe 2016 method (v.1.07): contribution analysis.

Impact category	Unit	Cooling and process water	Maize	Sugarcane	Swithgrass	Sulphuric acid (pretretment and hydrolysis)	Resin (001) - styrene	Nutrient - ammonium sulphate	Nutrient - glucose	Sodium hydroxide (fermentation)	Resin (002) - amberlyte	Resin (003) - styrene	Sodium hydroxide (WWT)	Limestone for FGD	Sulphuric acid (pH adjuster)	Air emissions from wood boiler	Electricity recovered	Ash disposal
GW	kg CO$_2$ eq	0.0E+00	1.6E+03	9.6E+01	4.3E+02	4.6E+01	2.2E+01	9.0E+01	1.2E+03	4.0E+01	1.3E+01	1.0E-01	2.2E+02	2.1E-01	2.2E-02	2.7E-01	-1.8E+01	1.1E+01
SOD	kg CFC11 eq	0.0E+00	1.8E-02	3.4E-03	1.0E-02	1.7E-05	3.4E-06	2.3E-05	5.7E-03	4.5E-05	1.4E-06	1.6E-08	2.5E-04	4.6E-07	8.1E-09	9.3E-06	-9.8E-06	1.6E-05
IR	kBq Co-60 eq	0.0E+00	2.5E+01	1.3E+00	2.2E+00	5.2E+00	5.4E-01	5.9E+00	6.5E+01	4.5E+00	7.7E-01	2.5E-03	2.4E+01	2.2E-03	2.4E-03	0.0E+00	-9.5E+00	5.5E-01
OF$_{HH}$	kg NO$_x$ eq	0.0E+00	4.6E+00	1.2E+00	1.7E+00	1.3E-01	7.7E-02	9.5E-02	2.7E+00	1.0E-01	1.9E-02	3.6E-04	5.4E-01	4.9E-03	6.0E-05	5.5E-02	-3.2E-02	6.0E-02
FPMF	kg PM$_{2.5}$ eq	0.0E+00	3.5E+00	1.5E+00	3.4E+00	1.2E+00	3.4E-02	2.5E-01	2.5E+00	8.6E-02	1.5E-02	1.6E-04	4.6E-01	1.9E-03	5.5E-04	1.6E-02	-2.7E-02	2.5E-02
OF$_{TE}$	kg NO$_x$ eq	0.0E+00	4.6E+00	1.2E+00	1.7E+00	1.3E-01	1.0E-01	9.6E-02	2.7E+00	1.0E-01	2.0E-02	4.7E-04	5.4E-01	4.9E-03	6.0E-05	5.5E-02	-3.2E-02	6.0E-02
TA	kg SO$_2$ eq	0.0E+00	1.5E+01	5.5E+00	2.5E+01	4.0E+00	6.2E-02	9.9E-01	1.0E+01	1.4E-01	4.8E-02	2.9E-04	7.7E-01	3.1E-03	1.9E-03	2.2E-02	-6.8E-02	5.7E-02
FWEu	kg P eq	0.0E+00	6.9E-01	5.8E-02	1.7E-01	1.5E-02	7.9E-03	1.3E-02	4.1E-01	2.0E-02	1.3E-03	3.7E-05	1.1E-01	3.2E-05	7.2E-06	0.0E+00	-1.9E-02	4.0E-01
MEu	kg N eq	0.0E+00	2.8E+00	9.2E-01	2.5E+00	1.2E-03	4.1E-04	1.2E-01	1.3E+00	2.1E-03	1.2E-04	1.9E-06	1.1E-02	1.7E-06	5.4E-07	0.0E+00	-1.4E-03	2.3E-04
TEu	kg 1,4-DCB	0.0E+00	2.6E+03	6.8E+02	1.7E+02	1.6E+03	2.0E+01	3.3E+02	3.1E+03	5.5E+01	1.8E+01	9.2E-02	3.0E+02	2.2E-01	7.6E-01	2.6E+01	-1.2E+01	1.0E+02
FWEc	kg 1,4-DCB	0.0E+00	2.4E+01	5.6E+00	3.0E-01	1.5E+00	2.0E-01	2.8E+00	1.6E+01	6.0E-01	8.7E-02	9.5E-04	3.2E+00	7.1E-04	6.9E-04	7.1E-04	-5.2E-01	2.6E+02
MEc	kg 1,4-DCB	0.0E+00	2.0E+01	3.5E+00	3.7E-01	3.3E+00	2.9E-01	1.1E+00	1.6E+01	8.5E-01	1.3E-01	1.4E-03	4.6E+00	1.1E-03	1.5E-03	1.7E-02	-7.2E-01	3.7E+02
HCT	kg 1,4-DCB	0.0E+00	2.2E+01	2.6E+00	1.2E-01	8.1E-01	5.8E-01	7.2E-01	2.1E+01	1.4E+00	1.9E-01	2.7E-03	7.5E+00	2.5E-03	3.8E-04	6.1E-03	-1.0E+00	9.4E+00
HNCT	kg 1,4-DCB	0.0E+00	-3.0E+00	3.7E+02	3.8E+02	1.4E+02	8.7E+00	3.7E+01	-8.7E+02	2.9E+01	3.0E+00	4.1E-02	1.5E+02	2.9E-02	6.5E-02	1.2E+00	-2.3E+01	9.9E+03
LU	m^{2}a crop eq	0.0E+00	2.4E+03	6.2E+02	2.1E+03	1.7E+00	1.8E-01	1.9E+00	7.2E+02	1.1E+00	1.2E-01	8.3E-04	6.2E+00	8.8E-03	7.7E-04	0.0E+00	-3.1E+00	1.0E+01
MRS	kg Cu eq	0.0E+00	2.2E+00	4.9E-01	3.4E-02	2.3E-02	3.6E-03	6.3E-02	1.2E+00	1.1E-02	2.8E-03	1.7E-05	6.1E-02	1.7E-04	1.1E-05	0.0E+00	-1.5E-02	7.9E-02
FRS	kg oil eq	0.0E+00	2.7E+02	2.7E+01	4.7E+01	5.6E+01	1.3E+01	3.8E+01	3.1E+02	1.0E+01	5.8E+00	6.0E-02	5.4E+01	6.2E-02	2.6E-02	0.0E+00	-5.0E+00	4.8E+00
WC	m^3	7.7E+00	5.8E+02	2.3E+01	8.9E-01	1.0E+01	2.3E-01	3.2E+00	2.9E+01	1.1E+00	2.3E-01	1.1E-03	6.1E+00	2.8E-03	4.8E-03	0.0E+00	-3.5E-01	-1.5E-01

Table S 21 - BioFurf production using ReCiPe 2016 method (v.1.07): contribution analysis.

Impact category	Unit	Cooling and process water	Switchgrass	Sulphuric acid (DES pretratment)	Choline chloride	Ethylene glycol	Acetone	Aluminium chloride	methyl isobutyl ketone (MIBK)	Sodium hydroxide	Limestone for FGD	Sulphuric acid (pH adjuster)	Air emissions from wood boiler	Electricity	Ash disposal
GW	kg CO$_2$ eq	0.0E+00	1.9E+02	3.1E+00	2.6E+01	5.1E+01	1.7E+02	1.8E+01	3.3E+02	3.7E+01	1.5E-02	4.7E-03	1.0E-02	7.3E+01	4.2E-01
SOD	kg CFC11 eq	0.0E+00	4.7E-03	1.2E-06	8.7E-06	9.3E-06	7.3E-06	6.5E-06	4.3E-05	4.2E-05	3.3E-08	1.8E-09	3.5E-07	3.9E-05	6.1E-07
IR	kBq Co-60 eq	0.0E+00	9.7E-01	3.4E-01	1.9E+00	2.2E+00	1.6E+00	6.1E-01	9.2E+00	4.1E+00	1.6E-04	5.3E-04	0.0E+00	3.8E+01	2.1E-02
OF$_{HH}$	kg NO$_x$ eq	0.0E+00	7.4E-01	8.5E-03	4.1E-02	9.7E-02	3.5E-01	4.4E-02	1.0E+00	9.3E-02	3.5E-04	1.3E-05	2.1E-03	1.3E-01	2.3E-03
FPMF	kg PM$_{2.5}$ eq	0.0E+00	1.5E+00	7.8E-02	2.5E-02	6.6E-02	2.0E-01	3.6E-02	4.2E-01	8.0E-02	1.3E-04	1.2E-04	6.0E-04	1.1E-01	9.7E-04
OF$_{TE}$	kg NO$_x$ eq	0.0E+00	7.4E-01	8.5E-03	4.2E-02	9.8E-02	3.7E-01	4.4E-02	1.2E+00	9.3E-02	3.5E-04	1.3E-05	2.1E-03	1.3E-01	2.3E-03
TA	kg SO$_2$ eq	0.0E+00	1.1E+01	2.7E-01	7.1E-02	1.3E-01	5.8E-01	7.5E-02	1.1E+00	1.3E-01	2.2E-04	4.1E-04	8.4E-04	2.7E-01	2.2E-03
FWEu	kg P eq	0.0E+00	7.8E-02	1.0E-03	8.7E-03	1.4E-02	3.4E-02	7.2E-03	1.9E+00	1.8E-02	2.3E-06	1.6E-06	0.0E+00	7.6E-02	1.5E-02
MEu	kg N eq	0.0E+00	1.1E+00	7.6E-05	1.1E-02	8.7E-04	7.7E-04	4.7E-04	3.5E-03	2.0E-03	1.3E-07	1.2E-07	0.0E+00	5.5E-03	8.9E-06
TEu	kg 1,4-DCB	0.0E+00	7.8E+01	1.1E+02	1.8E+01	2.7E+01	8.6E+01	1.3E+01	3.0E+02	5.1E+01	1.6E-02	1.7E-01	9.9E-01	4.7E+01	3.9E+00
FWEc	kg 1,4-DCB	0.0E+00	1.4E-01	9.8E-02	2.3E-01	4.2E-01	6.0E-01	3.4E-01	3.1E+00	5.5E-01	5.1E-05	1.5E-04	2.7E-05	2.1E+00	1.0E+01
MEc	kg 1,4-DCB	0.0E+00	1.7E-01	2.2E-01	3.2E-01	5.9E-01	8.3E-01	4.9E-01	3.3E+00	7.9E-01	7.7E-05	3.3E-04	6.6E-04	2.9E+00	1.4E+01
HCT	kg 1,4-DCB	0.0E+00	5.3E-02	5.4E-02	4.0E-01	1.2E+00	2.8E+00	2.9E+00	6.2E+00	1.3E+00	1.8E-04	8.3E-05	2.3E-04	4.2E+00	3.6E-01
HNCT	kg 1,4-DCB	0.0E+00	1.7E+02	9.2E+00	8.7E+00	1.9E+01	2.0E+01	1.4E+01	9.0E+01	2.7E+01	2.1E-03	1.4E-02	4.4E-02	9.2E+01	3.8E+02
LU	m^{2}a crop eq	0.0E+00	9.6E+02	1.1E-01	6.8E-01	5.1E-01	5.2E-01	1.8E-01	3.8E+00	1.1E+00	6.3E-04	1.7E-04	0.0E+00	1.2E+01	4.0E-01
MRS	kg Cu eq	0.0E+00	1.5E-02	1.5E-03	1.2E-02	1.4E-02	1.6E-02	1.6E-01	7.9E-02	1.0E-02	1.2E-05	2.4E-06	0.0E+00	5.9E-02	3.0E-03
FRS	kg oil eq	0.0E+00	2.1E+01	3.7E+00	1.7E+01	2.8E+01	1.0E+02	3.9E+00	1.7E+02	9.3E+00	4.4E-03	5.7E-03	0.0E+00	2.0E+01	1.9E-01
WC	m^3	1.1E+00	4.0E-01	6.8E-01	4.2E-01	6.6E-01	2.2E+00	1.6E-01	5.1E+00	1.0E+00	2.0E-04	1.0E-03	0.0E+00	1.4E+00	-5.9E-03

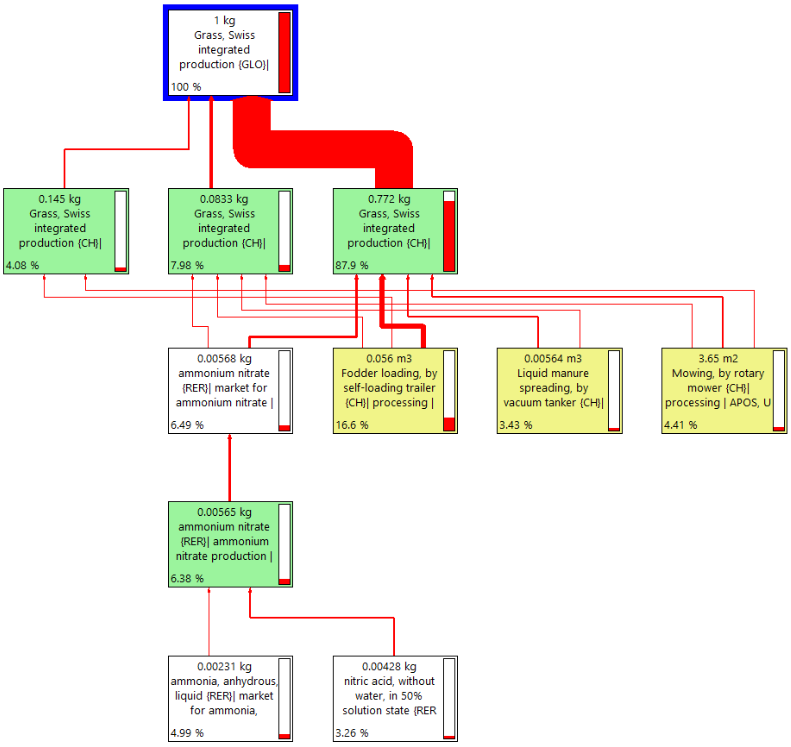


Figure S 9 - Switchgrass production (1kg): Sankey-based diagram for the category climate change ReCiPe 2016 method (v.1.07).

Table S 22 - Weidema's[68] quality pedigree matrix values adopted to estimate uncertainties, in Monte Carlo analysis.

MA Bio-ButOH	**Reliability**	**Completeness**	**Temporal correlation**	**Geographical correlation**	**Further tecnological correlation**
Bio-ButOH	4	5	3	3	4
Oxygen	4	5	3	3	4
Catalyst	4	5	3	3	4
Electricity	4	5	1	1	4
Emission CO2	4	5	3	3	4
Emission CO	4	5	3	3	4
Emission Others (heavy compounds)	4	5	3	3	4
MA Bio-Furf	**Reliability**	**Completeness**	**Temporal correlation**	**Geographical correlation**	**Further tecnological correlation**
Bio-Furf	4	5	2	5	4
Oxygen	4	5	2	5	4
Catalyst	4	5	2	5	4
Electricity	4	5	1	1	4
Emission CO2	4	5	2	5	4
Emission Others (heavy compounds)	4	5	2	5	4

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