Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

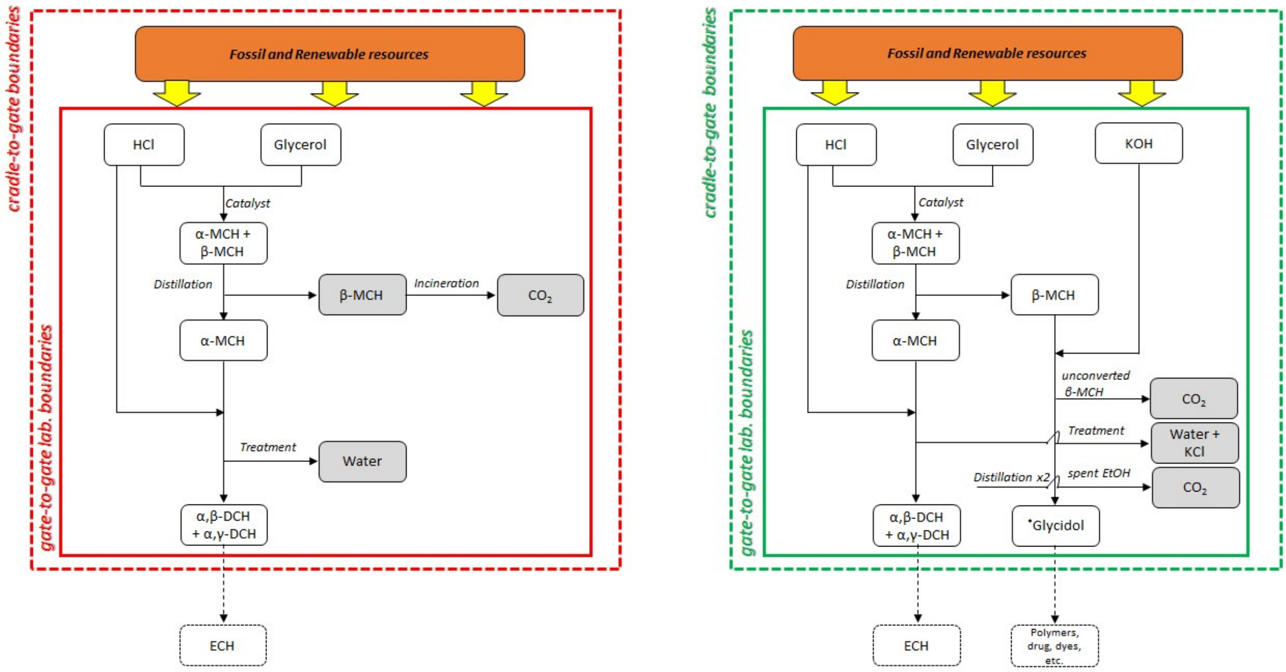

Fig. S1 System boundaries of the traditional (red) and innovative (green) route to chlorohydrins: i) continuous line represents the gate-to-gate boundaries within the laboratory; ii) the dashed box is the entire production chain from the raw materials extraction up to the synthesis of the valuable product(s) (cradle-to-gate approach).

*Glycidol production using renewables (glycerol) implies the avoided production from allyl alcohol according to the system boundaries in **Figure S2**.

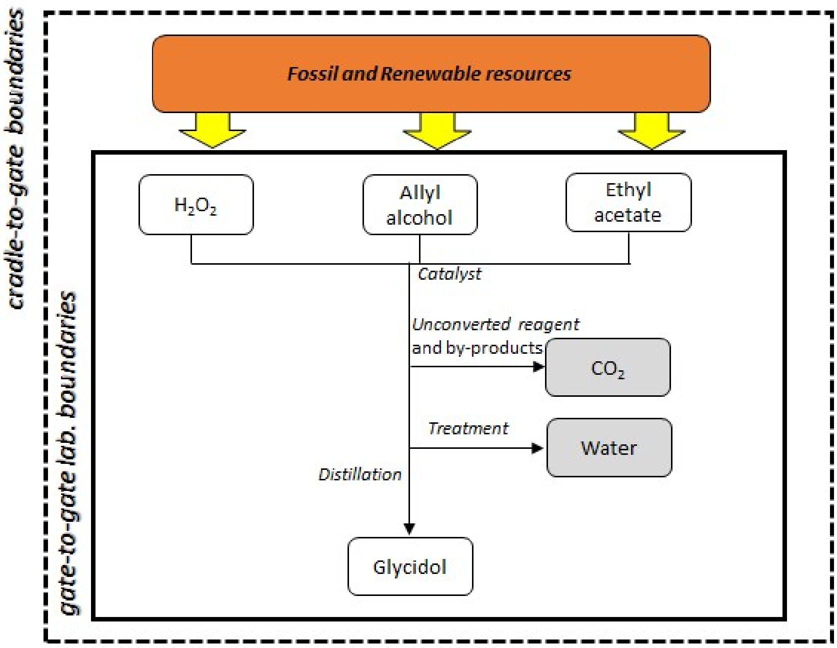

Fig. S2 System boundaries of the traditional fossil-route from allyl alcohol.

System input (for the first chlorination)	Unit	Amount	
Glycerol	g	150.0	
HCl_g	g	119	
Acetic acid (catalyst)	g	7.8	
System outputs - products		*Traditional*	*Innovative*
α,β-DCH	g	188.0	188.0
α,γ-DCH	g	5.0	5.0
Glycidol	g	-	8.1
System outputs – environmental releases			
(β-MCH)	g	(13.5)	-
CO_2 from β-MCH incineration	g	16.1	-
Water	g	0.2	1.6
KCl**	g	-	6.0
Distillation procedures			
N° of steps		1	3
Steam***	MJ	1.4E-02	7.2E-02
Cooling***	MJ	1.2E-02	6.3E-02
EtOH***	g	-	6.4
CO_2 from unrecovered EtOH incineration***	g	-	18.4

**deriving from KOH input (4.5g) used to facilitate the chlorine elimination

*** evaluated on the basis of the methodology reported in literature.[75]

Tab. S1 Inventories for both scenarios: traditional and innovative, derived from experimental data.

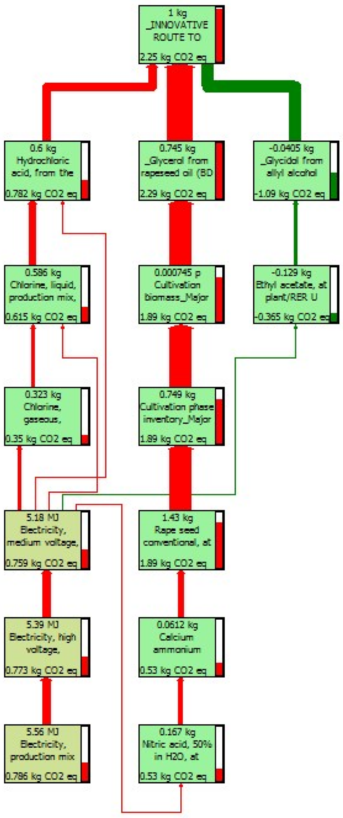

Fig. S3 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the CF index.

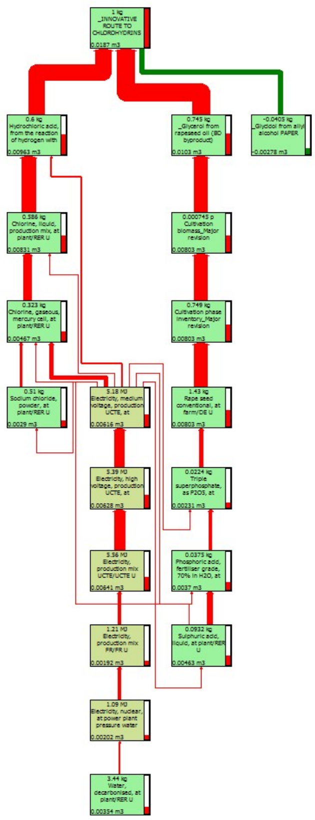

Fig. S4 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the WF index.

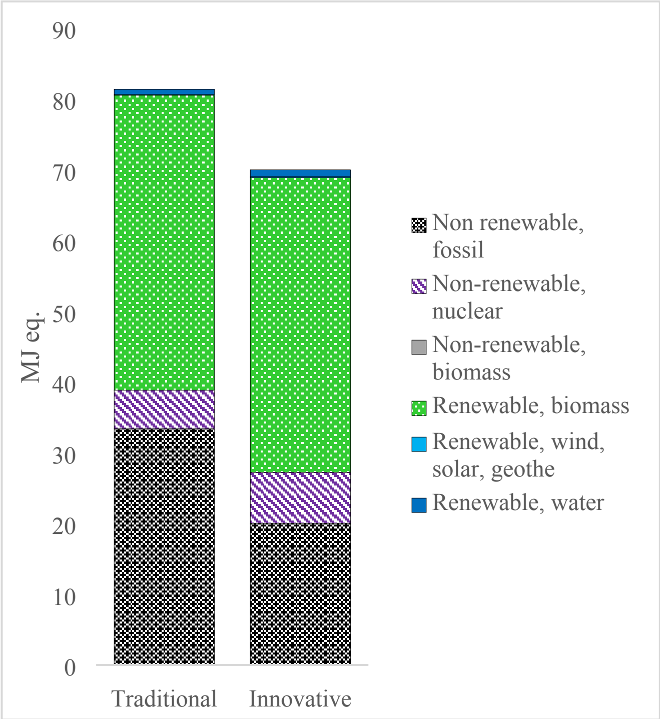

Fig. S5 Contribution to CED indicator.

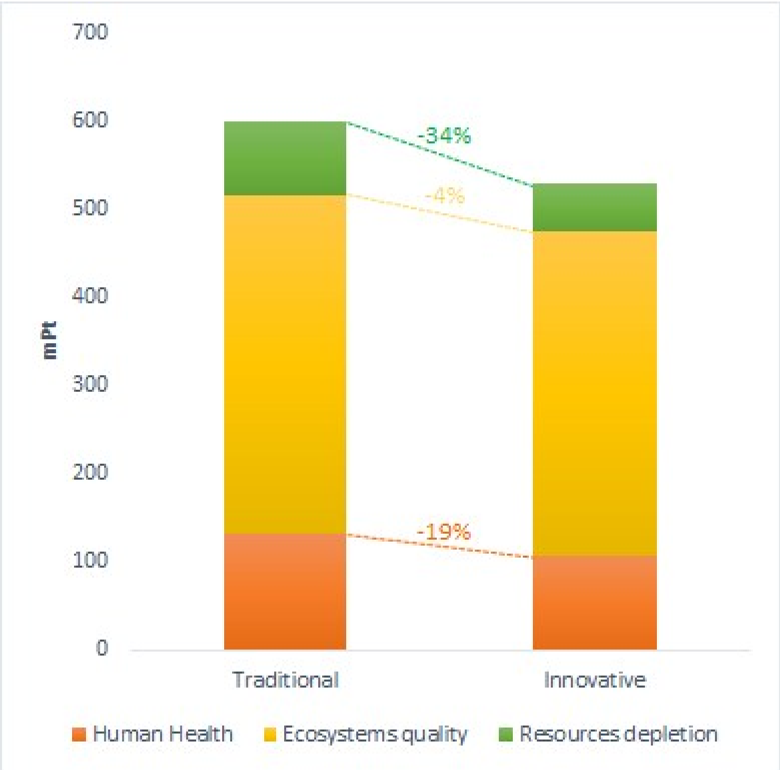

Fig. S6 Effect of the improvements on the ReCiPe receptors.

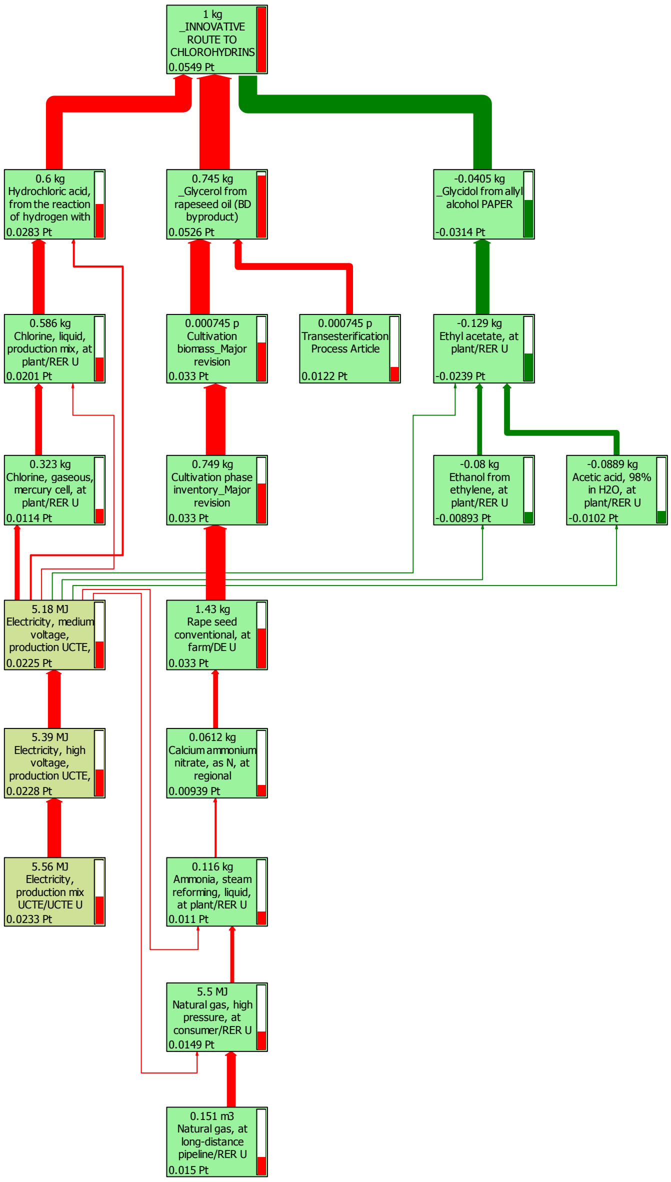

Fig. S7 SimaPro network tool: SS-resources depletion receptor.

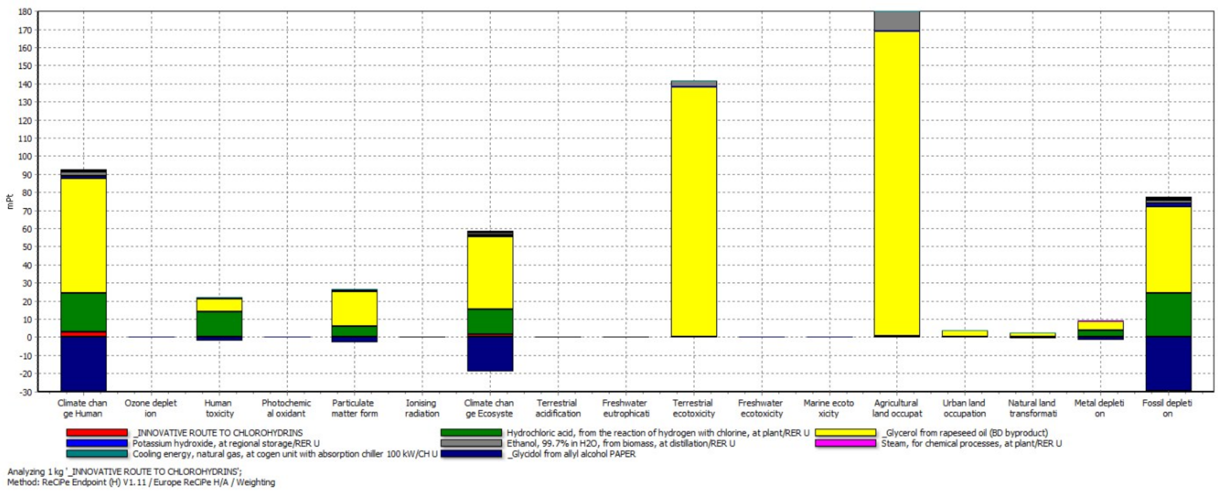

Fig. S8 SimaPro weighting tool: contribution of each category to cumulative SS.

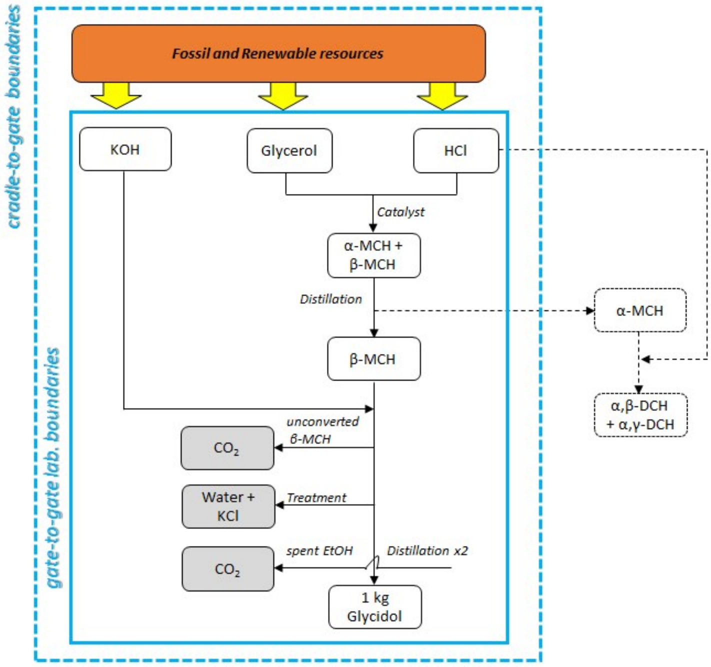

Fig. S9 System boundaries of the innovative route to produce 1kg of glycidol.

System input	**Unit**	
Allyl alcohol	kg	1.8
Ethyl acetate	kg	3.1
H_2O_2	kg	3.5
(Catalyst)	kg	0.2
Molar yield to glycidol	%	43
Selectivity to glycidol	%	93
System outputs – environmental releases		
Water	kg	4.3
CO_2 from unconverted allyl alcohol incineration	kg	1.0
CO_2 from by-products incineration	kg	0.2
CO_2 from unrecovered ethyl acetate incineration	kg	3.1
Distillation procedures		
N° of steps		1
Steam***	MJ	2.6
Cooling***	MJ	2.1

*** evaluated on the basis of the methodology reported in literature. [75]

Tab. S2 Cradle-to-gate inventories and allocation for the innovative route to produce 1kg of glycidol.

System input	**Unit**	
Glycerol	kg	18.4
HCl_g	kg	14.6
Acetic acid (catalyst)	kg	1.0
Co-products (not included in the boundaries)	kg	
(α,γ-DCH)	kg	23.1
(β,γ-DCH)	kg	0.6
System outputs – environmental releases	kg	
Water	kg	0.2
KCl****	kg	0.7
CO_2 from unrecovered β-MCH	kg	0.2
Distillation procedures		
N° of steps		3
Steam***	MJ	8.8
Cooling***	MJ	7.7
EtOH***	kg	0.8
CO_2 from unrecovered EtOH incineration***	kg	2.3
Allocation to be applied	%	4

*** evaluated on the basis of the methodology reported in literature. [75]

**** deriving from KOH input (0.6kg) used to facilitate the chlorine elimination.

Tab. S3 Cradle-to-gate inventories for the traditional route to produce 1kg of glycidol. Based on data reported in literature.[36]

Performance index	***from allyl alcohol***	***from glycerol***
CF (kg $CO_{2\ eq.}$)	27.0	3.3
WF (m^3)	7.0E-02	2.0E-02
CED ($MJ_{eq.}$)	349.1	83.0
SS (Pt)	2.1	0.6

Tab. S4 Cradle-to-gate analysis for the synthesis of 1kg of glycidol: results for the traditional route (from allyl alcohol) and the innovative pathway (from glycerol).