Supporting Information

Revealing the GHG Reduction Potential of an Emerging Biomass-based CO_2 Utilization with Iron Cycle System

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S1. Lab-scale experiments of HR process and BR process

A brief description is given for the experimental setup of the HR and BR processes (Jin et al., 2005). The desired amounts of substrates were loaded in a batch reactor in both HR and BR processes. The reactor was made of stainless steel 316 tubings (9.525 mm (3/8 in) o.d., 1 mm wall thickness and 120 mm length) with fittings sealed at each end, providing the inner volume of 5.7 mL. Then the reactor was immersed in a salt bath with different reaction conditions. After the reaction, the reactor was taken out from the salt bath and put into a cold-water bath. After cooling down to room temperature, the solid, liquid, and gaseous samples were collected for analysis. The produced FA and LA were analyzed using High Performance Liquid Chromatograph (HPLC) and Gas Chromatography-Flame Ionization Detector (GC-FID) equipped with an HP-INNOWAX polyethylene glycol capillary column.

S2. Calculation of the produced H_2

The calculation of the total amount of H_2 in the HR ($m_{\mathrm{H_2-HR}}$) was conducted by combining the main reaction and side reaction according to **eq S5**.

$$m_{\mathrm{H_2-HR}} = \left(C_{Fe} \times n_{\mathrm{Fe-input}} - \frac{1}{4} Y_{\mathrm{HCOONa}} \times n_{\mathrm{CO_2-input}}\right) \times 4 \times 2 \qquad \text{(S5)}$$

where, $n_{\mathrm{Fe-input}}$ and $n_{\mathrm{CO_2-input}}$ are the input of mole number of Fe and CO_2, 2 is the molar mass of H_2.

In the BR process the amount of produced H_2 ($m_{\mathrm{H_2-BR}}$) was calculated according to the main reaction (**eq S3**) and side reaction (**eq S4**), as shown in **eq S6**.

$$m_{\mathrm{H_2-BR}} = \left(Y_{\mathrm{NaL}} \times n_{\mathrm{glycerin-input}} - \frac{4}{3} Y_{\mathrm{Fe}} \times n_{Fe_3O_4\mathrm{-input}}\right) \times 2 \qquad \text{(S6)}$$

where, $n_{\mathrm{glycerin-input}}$ and $n_{\mathrm{Fe_3O_4-input}}$ are the input of mole number of glycerin and Fe_3O_4, 2 is the molar mass of H_2. However, the production of H_2 is from the side reaction, which is not considered in the system boundary.

Table S1. Lab-scale reaction conditions and results in HR process. (Duo et al., 2016) (Reaction temperature of all entries is 300 °C and reaction time of all entries is 120 min.)

Entry	Reaction conditions		Input/g				Yield		Output/g		
	$NaHCO_3$ concentration (mol/L)	Water filling (%)	Fe	CO_2	H_2O	NaOH	Formate [a] (%)	Conversion of Fe into Fe_3O_4 [b](%)	Fe_3O_4	H_2	HCOONa
H1	0.3	55	0.672	0.041	3.135	0.038	33	38.6	0.358	0.012	0.021
H2	0.7	55	0.672	0.097	3.135	0.088	52	59.9	0.556	0.017	0.078
H3	1	55	0.672	0.138	3.135	0.125	62	74.3	0.69	0.02	0.132
H4	1.3	55	0.672	0.179	3.135	0.163	64	81.9	0.76	0.021	0.177
H5	1.7	55	0.672	0.234	3.135	0.213	67	88.6	0.822	0.021	0.243
H6	2	55	0.672	0.276	3.135	0.251	66	90.2	0.837	0.021	0.281
H7	0.7	55	0.224	0.097	3.135	0.088	11	90.2	0.278	0.009	0.016
H8	0.7	55	0.336	0.097	3.135	0.088	19	90.2	0.418	0.014	0.028
H9	0.7	55	0.448	0.097	3.135	0.088	30	90.2	0.557	0.018	0.045
H10	0.7	55	0.672	0.097	3.135	0.088	40	90.2	0.835	0.027	0.06
H11	0.7	55	0.896	0.097	3.135	0.088	70	90.2	0.974	0.031	0.104
H12	0.7	55	1.12	0.097	3.135	0.088	75	90.2	1.114	0.035	0.112
H13	0.7	55	1.344	0.097	3.135	0.088	92	90.2	1.392	0.044	0.137

[a] The yield of formate was defined as the percentage of formate and the initial $NaHCO_3$ on a carbon basis.(Duo et al., 2016)
[b] The conversion of Fe is defined as the percentage of the amount of oxidized iron divided by the initial iron atom, which was quantified by MDI jade software based on XRD patterns.

Table S2. Lab-scale reaction conditions and results in BR process

Entry	Input/mg			Reaction Conditions		Yield	Output/mg		
	Fe_3O_4	Glycerin	NaOH	T(ºC)	Time (min)	Fe [a] (%)	Fe	H_2	Lactate （85% Yield）
B1	100	920	400	250	5	54	44.766	17.862	952.51
B2	100	920	400	250	10	76	58.9	17.187	952.51
B3	100	920	400	250	20	80	61.275	17.074	952.51
B4	100	920	400	250	30	81	61.86	17.046	952.51
B5	100	920	400	250	60	60	48.812	17.669	952.51
B6	100	920	200	250	30	18	16.842	19.196	952.51
B7	100	920	600	250	30	93	68.622	16.723	952.51
B8	100	920	800	250	30	78	60.094	17.13	952.51
B9	100	920	1000	250	30	33	29.306	18.601	952.51

[a] The yield of Fe was defined as the percentage of Fe and the initial Fe_3O_4 on an iron basis.

S3. Workflow of the up-scale ED process by Aspen Plus®

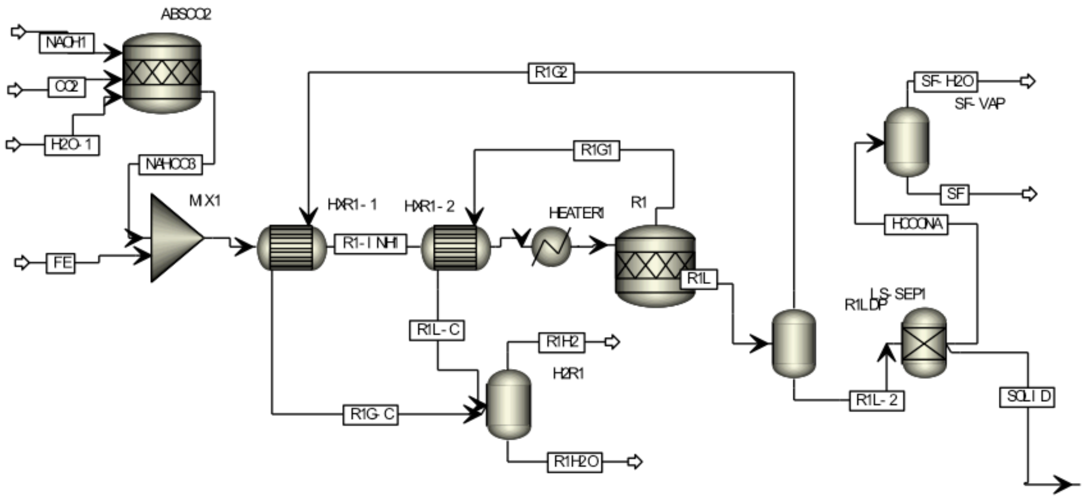

Figure S1. The workflow sheet of the simulation on the HR process in the BCU system.

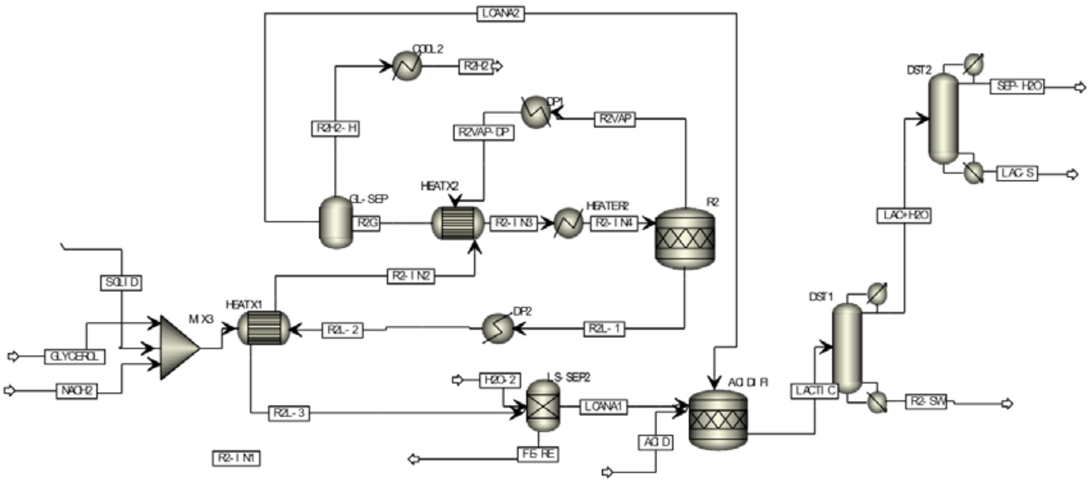

Figure S2. The workflow sheet of the simulation on the BR process in the BCU system.

Table S3. Designing parameters of heat exchangers in Aspen Plus®

Heat exchanger	**HXR1-1**	**HXR1-2**	**HeatX-1**	**HeatX-2**
Specifications	Hot outlet-cold inlet temperature difference	Hot inlet-cold outlet temperature difference	Hot outlet-cold inlet temperature difference	Hot outlet-cold inlet temperature difference
Value	10 ºC	10 ºC	50 ºC	10 ºC
Minimum temperature difference	1 ºC	1 ºC	1 ºC	1 ºC

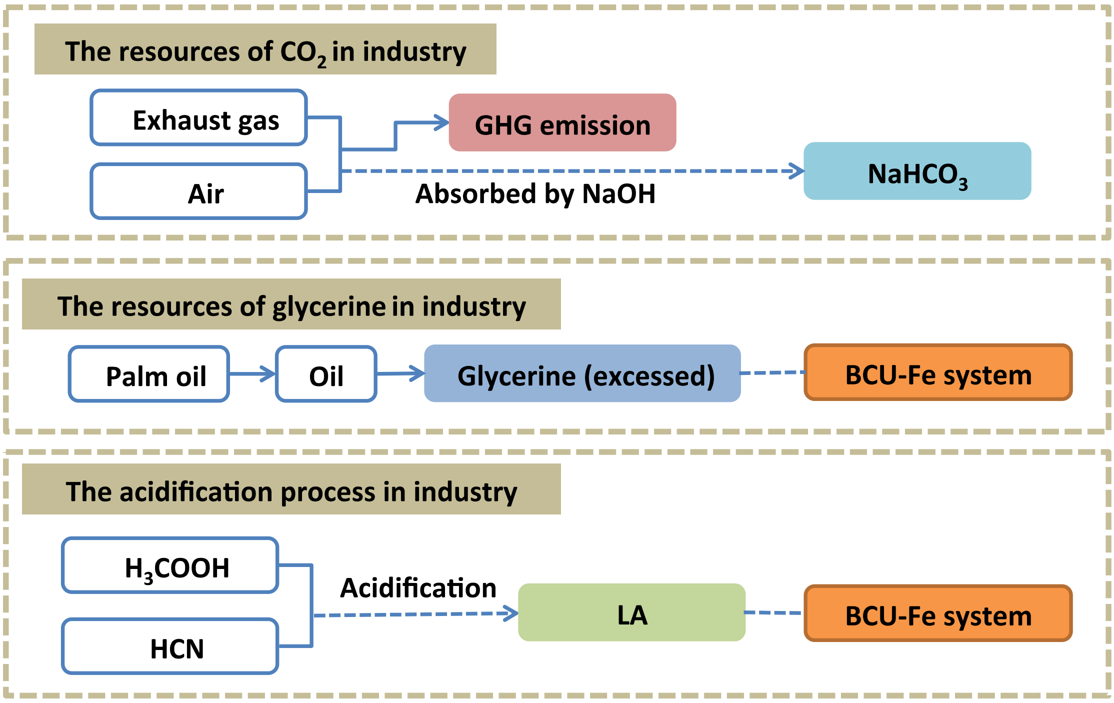

Figure S3. The background system in industry of the resources of CO_2 and glycerin and the acidification process

S4. Calculation of GHG emissions of HR process and BR process in BCU system

Table S4. Database of GHG emissions for the LCA on the CO_2 utilization by the BCU system

Inventory	Database	Geography
Electricity production	Ecoinvent: electricity, high voltage, production mix | electricity, high voltage | Cutoff, S	CN-SGCC[a]
Glycerin production	Ecoinvent: esterification of palm oil | glycerine | Cutoff, S	RoW[b]
Hydrogen production	Hydrogen production, gaseous, petroleum refinery operation | hydrogen, gaseous | Cutoff, S	RoW
Lactic acid production	Ecoinvent: lactic acid production | lactic acid | Cutoff, S	RoW
NaOH production	Ecoinvent: chlor-alkali electrolysis, membrane cell | sodium hydroxide, without water, in 50% solution state | Cutoff, S	RoW
Sodium formate production	Ecoinvent: sodium formate production | sodium formate | Cutoff, S	GLO[c]
Sulfuric acid production	Ecoinvent: sulfuric acid production | sulfuric acid | Cutoff, S	RoW

[a] CN-SGCC: China-State Grid Corporation of China
[b] RoW: Rest of World
[c] GLO: Global

S5. Calculation of material input and output inventory data of HR process and BR process in BCU system

Table S5. Material input and output inventory data of HR process and BR process with various reaction conditions in lab-scale HR process.

Entry	Results of lab-scale experiments			Input of HR process/kg			Input of BR process/kg			Output of HR process/kg			Output of BR process/kg	
	Y_{NaFA} (%)	C_{Fe} (%)	Y_{Fe} (%)	Fe	CO_2	NaOH	Glycerin	NaOH	H_2SO_4	Fe_3O_4	H_2	HCOONa	LA	Na_2SO_4
H1	33	38.6	80	672	41	38	653	284	348	89	0.07	21	553	436
H2	52	59.9	80	672	97	88	1014	440	540	139	0.10	78	858	676
H3	62	74.3	80	672	138	125	1257	546	670	172	0.11	132	1064	839
H4	64	81.9	80	672	179	163	1386	602	738	190	0.12	177	1173	925
H5	67	88.6	80	672	234	213	1499	651	798	205	0.12	243	1269	1000
H6	66	90.2	80	672	276	251	1527	663	813	209	0.12	281	1292	1018
H7	11	90.2	80	224	97	88	323	140	172	44	0.03	16	273	216
H8	19	90.2	80	336	97	88	491	213	261	67	0.05	28	415	327
H9	30	90.2	80	448	97	88	665	289	354	91	0.06	45	563	444
H10	40	90.2	80	672	97	88	1014	440	540	139	0.10	78	858	676
H11	70	90.2	80	896	97	88	1353	588	721	185	0.13	104	1145	903
H12	75	90.2	80	1120	97	88	1662	722	885	227	0.16	112	1407	1109
H13	92	90.2	80	1344	97	88	2000	869	1065	274	0.19	137	1692	1334

Table S6. Material input and output inventory data of HR process and BR process with various reaction conditions in lab-scale BR process.

Entry	Results of lab-scale experiments			Input of HR process/kg			Input of BR process/kg			Output of HR process/kg			Output of BR process/kg	
	Y_{NaFA} (%)	C_{Fe} (%)	Y_{Fe} (%)	Fe	CO_2	NaOH	Glycerin	NaOH	H_2SO_4	Fe_3O_4	H_2	HCOONa	LA	Na_2SO_4
B1	66	90	54	672	97	251	653	668	819	712	0.12	592	1292	1018
B2	66	90	76	672	97	251	1014	664	814	264	0.12	592	1292	1018
B3	66	90	80	672	97	251	1257	663	813	209	0.12	592	1292	1018
B4	66	90	81	672	97	251	1386	663	813	196	0.12	592	1292	1018
B5	66	90	60	672	97	251	1499	667	818	557	0.12	592	1292	1018
B6	66	90	18	672	97	251	1527	675	828	3806	0.12	592	1292	1018
B7	66	90	93	672	97	251	323	661	810	63	0.12	592	1292	1018
B8	66	90	78	672	97	251	491	663	813	236	0.12	592	1292	1018
B9	66	90	33	672	97	251	665	672	824	1696	0.12	592	1292	1018

S6. Calculation of energy consumption of HR process and BR process in BCU system

Table S7. Details of energy consumption of HR process and BR process with various reaction conditions in lab-scale HR process.

Entry	Reaction conditions and results		Energy consumption (EC, kWh)								
	Yield (HR-NaFA)	Yield (BR-Fe)	HR Heater	HR Reactor	HR Evaporation	BR Heater	BR Reactor	BR Distillation 1	BR Distillation 2	Allocation	Total EC
H1	0.33	0.8	1223.944	902.9249	12.62124	452.3506	1546.948	1011.386	1577.954	0.1580447	2864.7
H2	0.52	0.8	955.8705	576.2531	47.43603	701.0101	1532.656	1576.16	2448.875	0.1580447	2568.714
H3	0.62	0.8	753.3512	363.7931	79.53926	869.1212	1522.993	1958.01	3037.681	0.1580447	2364.287
H4	0.64	0.8	549.9493	230.0008	105.2458	957.8474	1517.893	2159.551	3348.443	0.1580447	2146.983
H5	0.67	0.8	277.7743	118.3773	143.1129	1036.066	1513.398	2337.225	3622.405	0.1580447	1884.081
H6	0.66	0.8	73.043	66.82239	165.9553	1054.746	1512.324	2379.651	3687.828	0.1580447	1670.465
H7	0.11	0.8	954.9442	153.5711	6.582279	223.5291	511.468	502.3299	780.7666	0.1580447	1434.046
H8	0.19	0.8	955.1741	287.7989	15.0193	339.2968	766.972	762.5946	1185.172	0.1580447	1740.666
H9	0.3	0.8	955.4062	404.6559	26.33971	459.8678	1022.2	1033.775	1606.404	0.1580447	2037.901
H10	0.52	0.8	955.8705	576.2531	47.43603	701.0102	1532.656	1576.16	2448.875	0.1580447	2568.714
H11	0.7	0.8	956.3317	663.9611	62.02302	935.7477	2043.479	2104.038	3268.925	0.1580447	3002.335
H12	0.75	0.8	956.7828	660.709	62.5275	1149.669	2555.5	2584.681	4016.082	0.1580447	3308.817
H13	0.92	0.8	957.2432	608.1156	70.27421	1382.806	3066.415	3108.966	4830.536	0.1580447	3593.605

Table S8. Details of energy consumption of HR process and BR process with various reaction conditions in lab-scale BR process.

Entry	Reaction conditions and results		Energy consumption (EC, kWh)								
	Yield (HR-NaFA)	Yield (BR-Fe)	HR Heater	HR Reactor	HR Evaporation	BR Heater	BR Reactor	BR Distillation 1	BR Distillation 2	Allocation	Total EC
B1	0.66	0.54	74.2695	168.8985	165.9553	1568.039	1847.781	3648.527	5404.742	0.107508	1749.656
B2	0.66	0.76	73.17707	77.9805	165.9553	1110.888	1549.093	2518.865	3875.265	0.150321	1678.132
B3	0.66	0.8	73.043	66.82239	165.9553	1054.745	1512.324	2379.651	3687.828	0.158045	1670.465
B4	0.66	0.81	73.01155	64.20505	165.9553	1041.574	1503.694	2346.968	3643.874	0.159973	1668.717
B5	0.66	0.6	73.89211	137.4904	165.9553	1410.146	1744.734	3258.975	4876.048	0.11924	1723.548
B6	0.66	0.18	81.81716	797.0589	165.9553	4723.72	3901.691	11405.29	15994.91	0.036226	2349.881
B7	0.66	0.93	72.68692	37.1874	165.9553	905.5684	1414.462	2008.818	3190.528	0.183022	1652.04
B8	0.66	0.78	73.10832	72.25839	165.9553	1082.098	1530.241	2447.497	3779.132	0.154185	1674.158
B9	0.66	0.33	76.67103	368.7677	165.9553	2572.377	2502.089	6120.382	8772.534	0.066114	1931.522

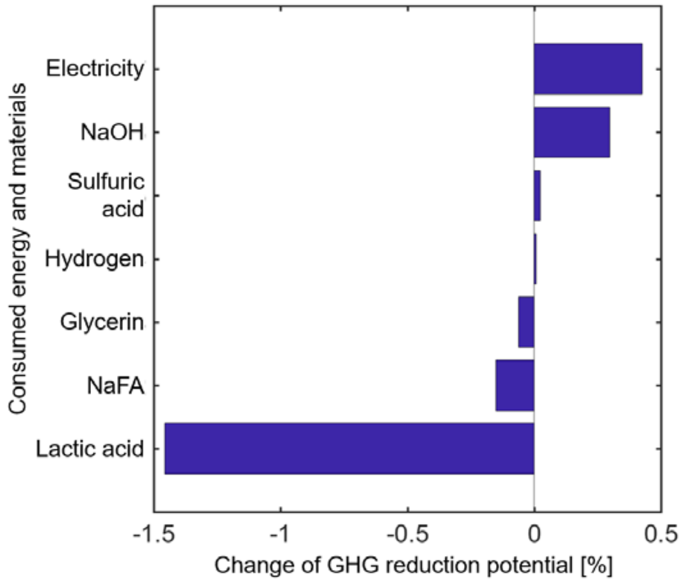

Figure S4. Sensitivity analysis on the change of GHG reduction potential when applying 1% increase on the cradle-to-gate GHG emissions of the consumed energy and materials.

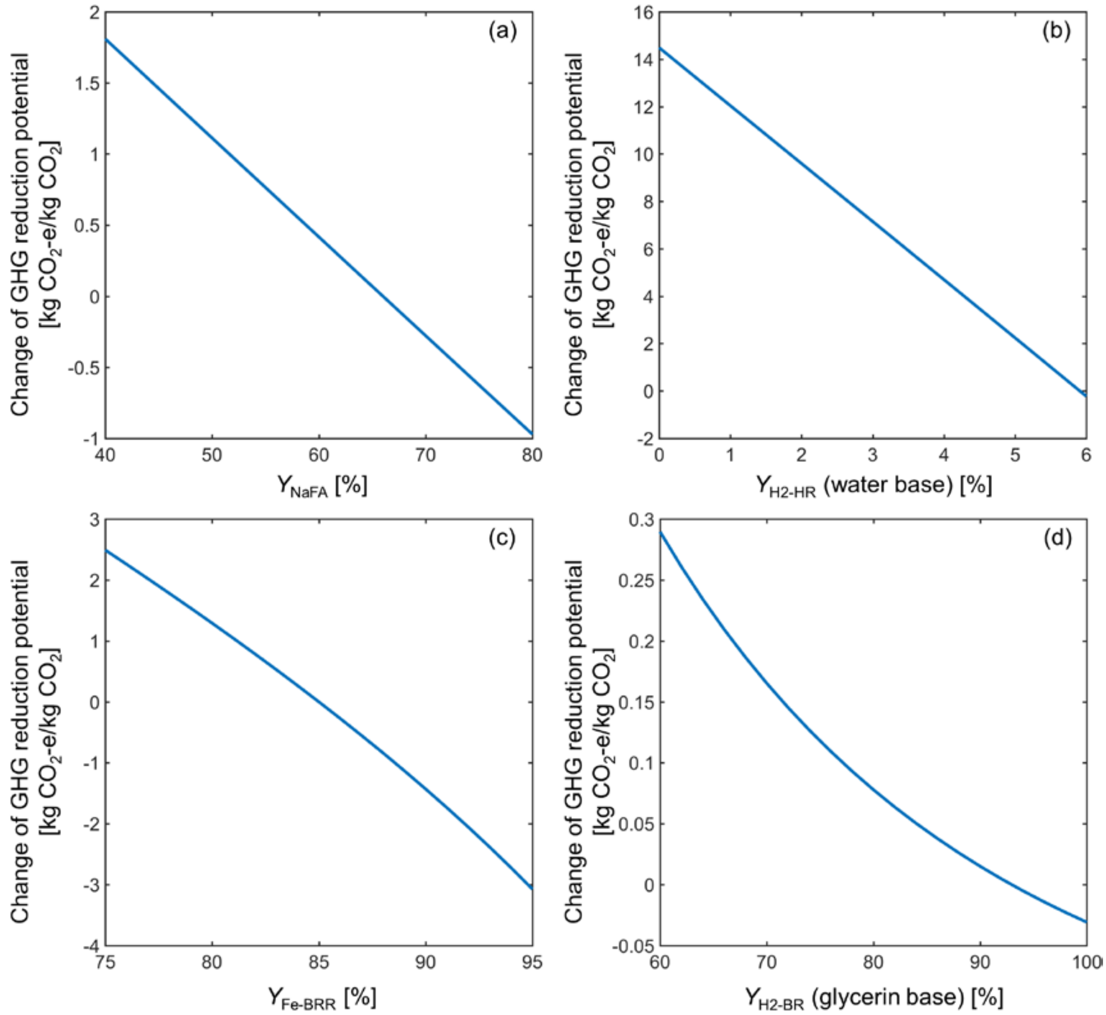

Figure S5. Sensitivity analysis on the change of GHG reduction potential with the key yields obtained from the experiments.

Table S9. Life-cycle impact assessment and the contribution analysis based on ReCiPe 2016 (H) method for the fixed conditions of Entry H13.

Impact name	Unit	Electricity production	Glycerin production	Hydrogen production	Lactic acid production	NaOH production	Sodium formate production	Sulfuric acid production	Absorbed CO_2	Net balance
Water consumption, Terrestrial ecosystem	species.yr	1.34E-09	1.04E-08	4.29E-12	-1.46E-08	3.70E-09	-6.03E-10	3.11E-09	0.00E+00	3.35E-09
Water consumption, Human health	DALY	2.20E-07	1.71E-06	7.06E-10	-2.40E-06	6.09E-07	-9.92E-08	5.12E-07	0.00E+00	5.51E-07
Water consumption, Aquatic ecosystems	species.yr	5.98E-14	4.66E-13	1.92E-16	-6.54E-13	1.66E-13	-2.70E-14	1.39E-13	0.00E+00	1.50E-13
Terrestrial ecotoxicity	species.yr	2.06E-10	5.90E-10	2.38E-11	-1.19E-09	2.16E-10	-5.30E-11	5.10E-11	0.00E+00	-1.53E-10
Terrestrial acidification	species.yr	2.78E-08	2.67E-08	1.03E-09	-5.20E-08	9.63E-09	-2.32E-09	1.92E-08	0.00E+00	3.00E-08
Stratospheric ozone depletion	DALY	3.20E-09	8.70E-08	4.91E-10	-9.87E-09	7.26E-09	-1.16E-09	2.45E-10	0.00E+00	8.71E-08
Ozone formation, Terrestrial ecosystems	species.yr	1.40E-08	8.57E-09	2.77E-10	-1.99E-08	4.09E-09	-9.63E-10	4.47E-10	0.00E+00	6.52E-09
Ozone formation, Human health	DALY	9.83E-08	5.45E-08	1.84E-09	-1.34E-07	2.86E-08	-6.69E-09	3.01E-09	0.00E+00	4.57E-08
Mineral resource scarcity	USD2013	2.08E-03	1.20E-02	1.23E-04	-4.80E-02	9.21E-03	-2.29E-03	3.53E-03	0.00E+00	-2.33E-02
Marine eutrophication	species.yr	7.83E-13	1.20E-10	6.69E-15	-2.56E-11	1.10E-12	-2.03E-13	7.23E-14	0.00E+00	9.64E-11
Marine ecotoxicity	species.yr	5.46E-11	6.87E-11	8.26E-13	-4.38E-10	9.60E-11	-2.31E-11	2.94E-11	0.00E+00	-2.12E-10
Land use	species.yr	6.86E-10	2.69E-07	3.28E-11	-6.55E-09	1.54E-09	-3.77E-10	2.89E-10	0.00E+00	2.64E-07
Ionizing radiation	DALY	4.77E-09	2.56E-09	2.58E-10	-2.08E-08	8.71E-09	-2.91E-09	6.12E-10	0.00E+00	-6.81E-09
Human non-carcinogenic toxicity	DALY	3.89E-06	9.87E-07	2.99E-08	-1.40E-05	3.35E-06	-7.79E-07	7.25E-07	0.00E+00	-5.77E-06
Human carcinogenic toxicity	DALY	4.43E-06	3.21E-06	7.64E-08	-1.44E-05	3.34E-06	-8.08E-07	7.67E-07	0.00E+00	-3.35E-06
Global warming, Terrestrial ecosystems	species.yr	1.09E-07	-1.19E-07	1.58E-09	-2.25E-07	3.64E-08	-8.52E-09	3.69E-09	-2.80E-09	-2.05E-07
Global warming, Human health	DALY	3.61E-05	-3.95E-05	5.24E-07	-7.45E-05	1.21E-05	-2.82E-06	1.22E-06	-9.28E-07	-6.78E-05
Global warming, Freshwater ecosystems	species.yr	2.98E-12	-3.26E-12	4.32E-14	-6.14E-12	9.95E-13	-2.33E-13	1.01E-13	-7.65E-14	-5.59E-12
Freshwater eutrophication	species.yr	4.67E-09	2.12E-09	1.84E-11	-1.28E-08	4.02E-09	-9.52E-10	3.78E-10	0.00E+00	-2.57E-09
Freshwater ecotoxicity	species.yr	2.60E-10	3.88E-10	2.62E-12	-2.24E-09	4.88E-10	-1.17E-10	1.52E-10	0.00E+00	-1.06E-09
Fossil resource scarcity	USD2013	7.41E-01	1.13E+00	5.14E-01	-1.03E+01	6.06E-01	-3.40E-01	4.31E-01	0.00E+00	-7.24E+00
Fine particulate matter formation	DALY	3.71E-05	3.14E-05	1.02E-06	-6.54E-05	1.80E-05	-3.95E-06	1.71E-05	0.00E+00	3.53E-05

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