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Supplementary information

Eco-friendly and techno-economic conversion of CO_2 into calcium formate, a valuable resource

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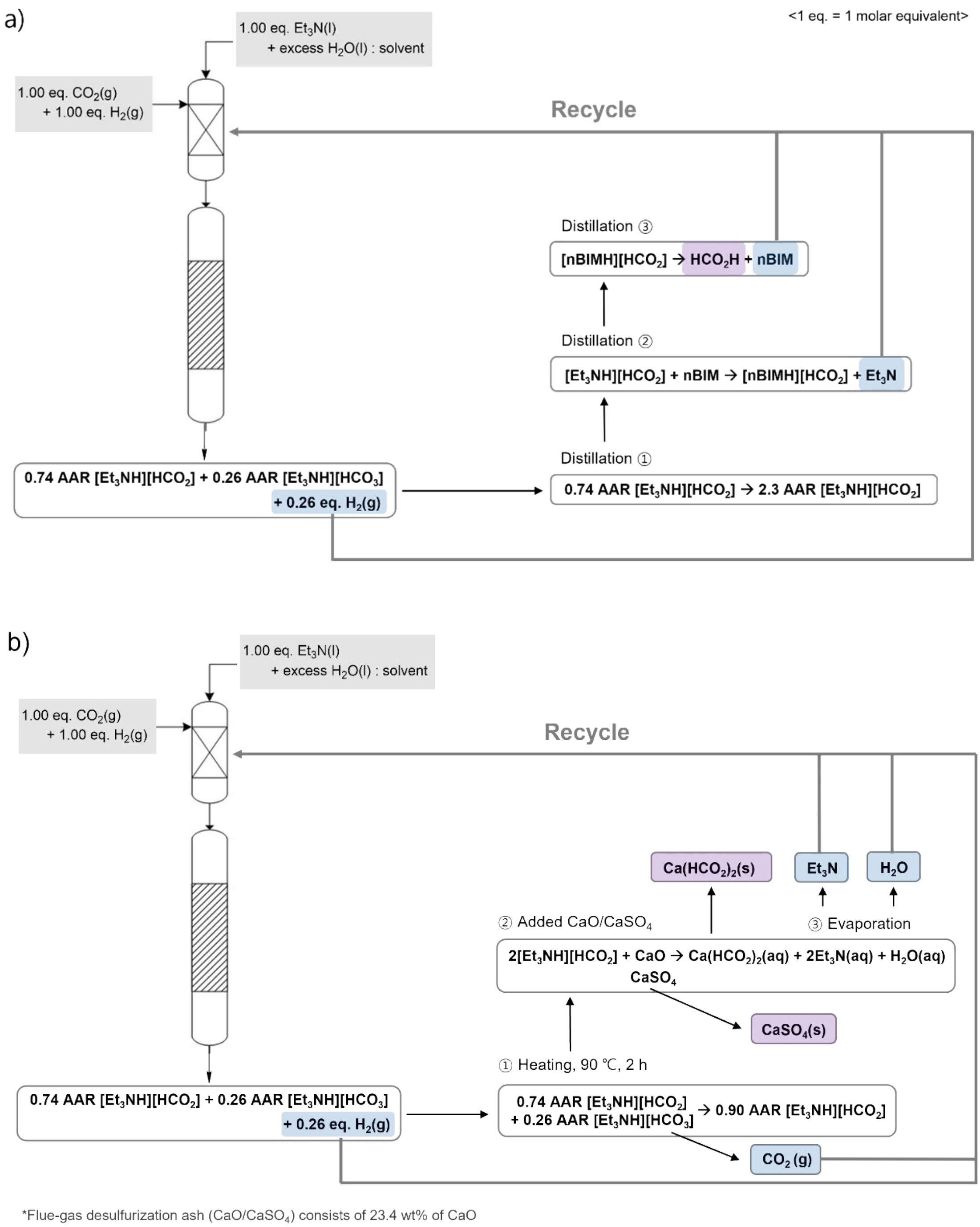

Figure S1. Detailed schematics of CO_2 conversion into value-added chemicals: a) conventional HCO_2H production process and b) proposed $Ca(HCO_2)_2$ production process. (AAR: acid to amine ratio)

2. composition analysis of CO_2 hydrogenation adduct

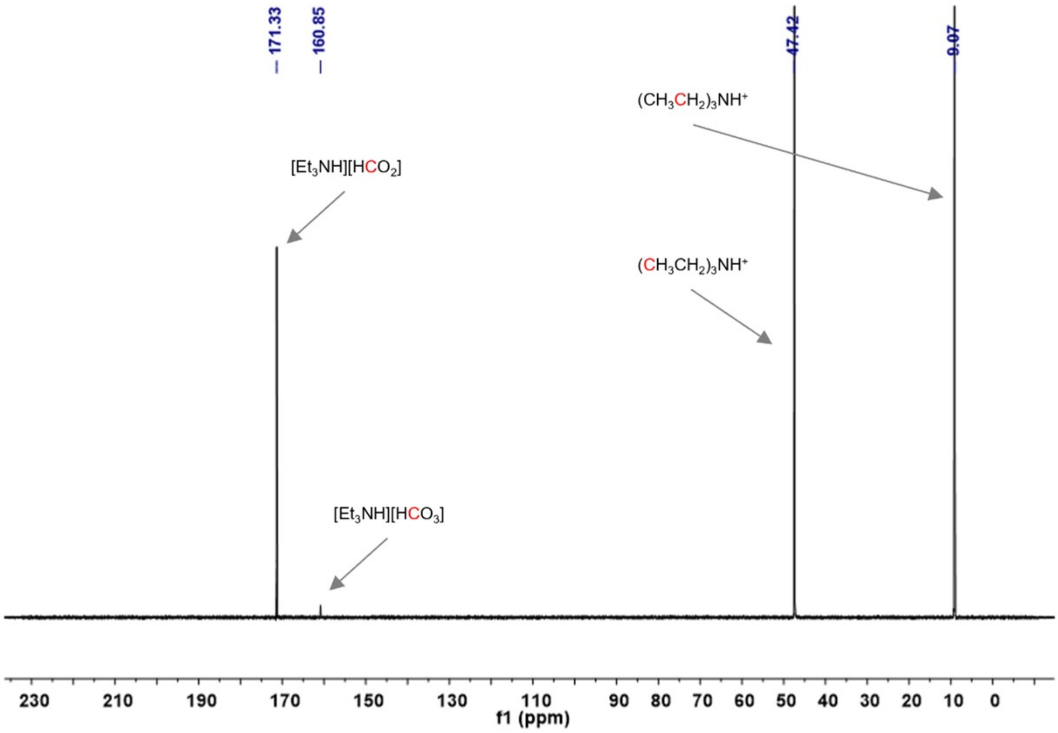

Figure S2. ^{13}C NMR analysis of the $[Et_3NH][HCO_2]$ adduct generated by CO_2 hydrogenation.

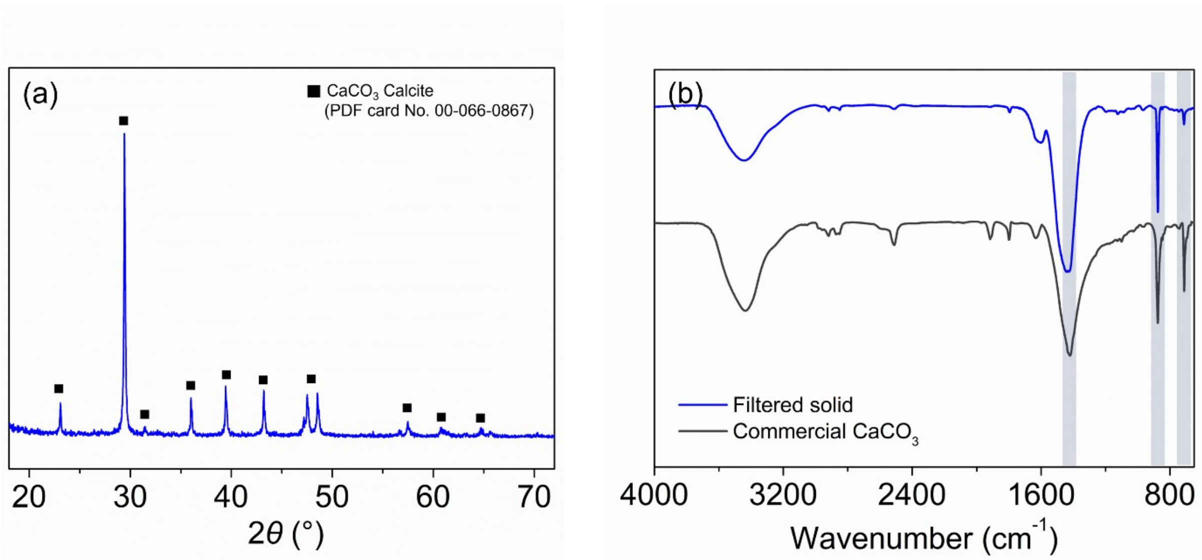

Figure S3. (a) XRD and (b) FT-IR analyses of filtered solid (blue) and commercial $CaCO_3$ (black) in a stirred solution obtained by adding CaO to the adduct containing bicarbonate.

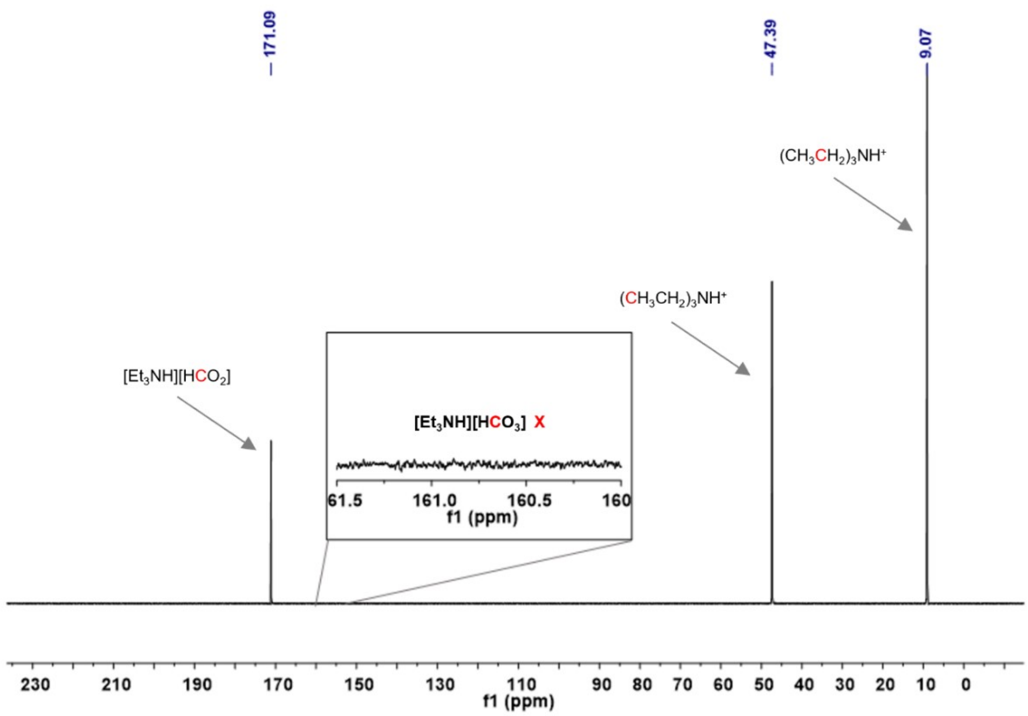

Figure S4. ^{13}C NMR analysis of the adduct produced by CO_2 hydrogenation after degassing at 90 °C for 2 h.

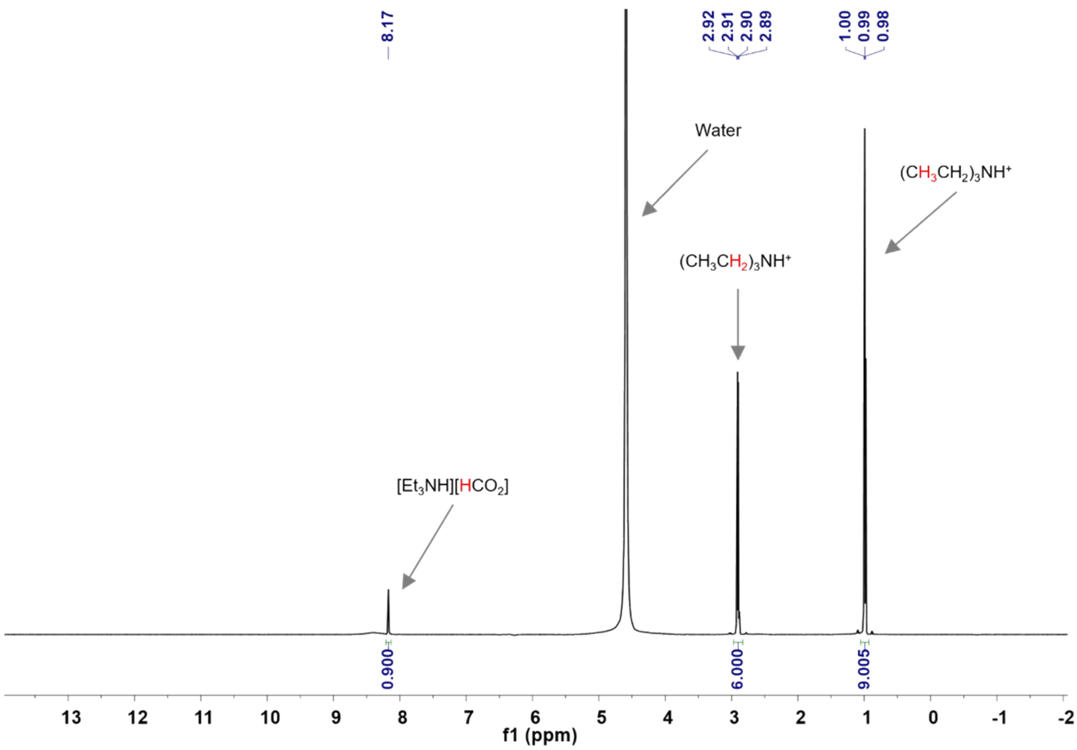

Figure S5. ^{1}H NMR analysis of the adduct produced by CO_2 hydrogenation after degassing at 90 °C for 2 h.

3. Analysis of substances generated during separation of $Ca(HCO_2)_2$ production

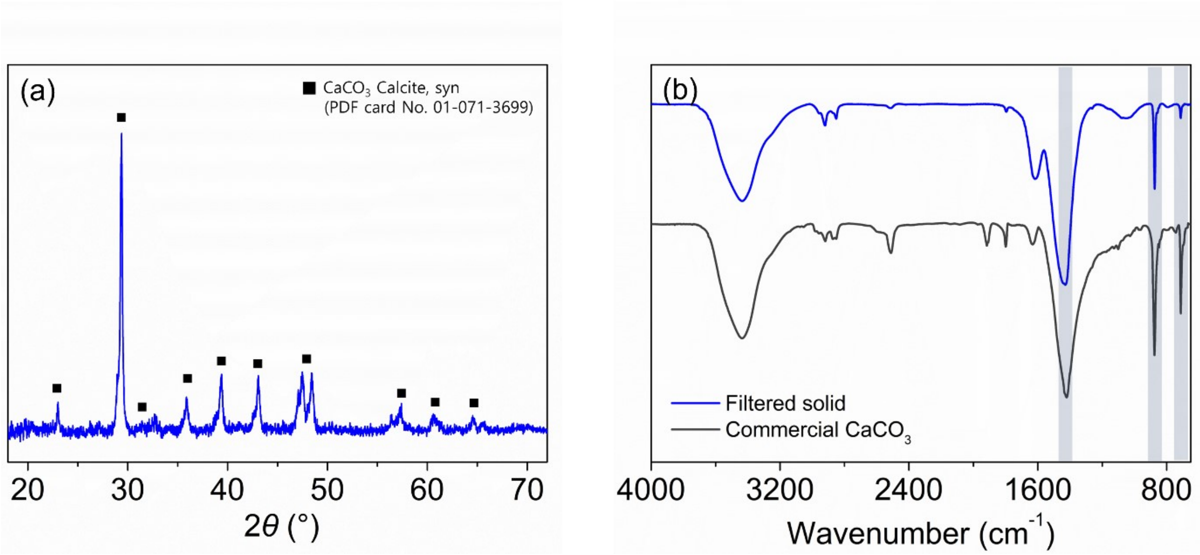

Figure S6. (a) XRD and (b) FT-IR analyses of the filtered solid produced during the synthesis of $Ca(HCO_2)_2$ from $[Et_3NH][HCO_2]$ by using CaO.

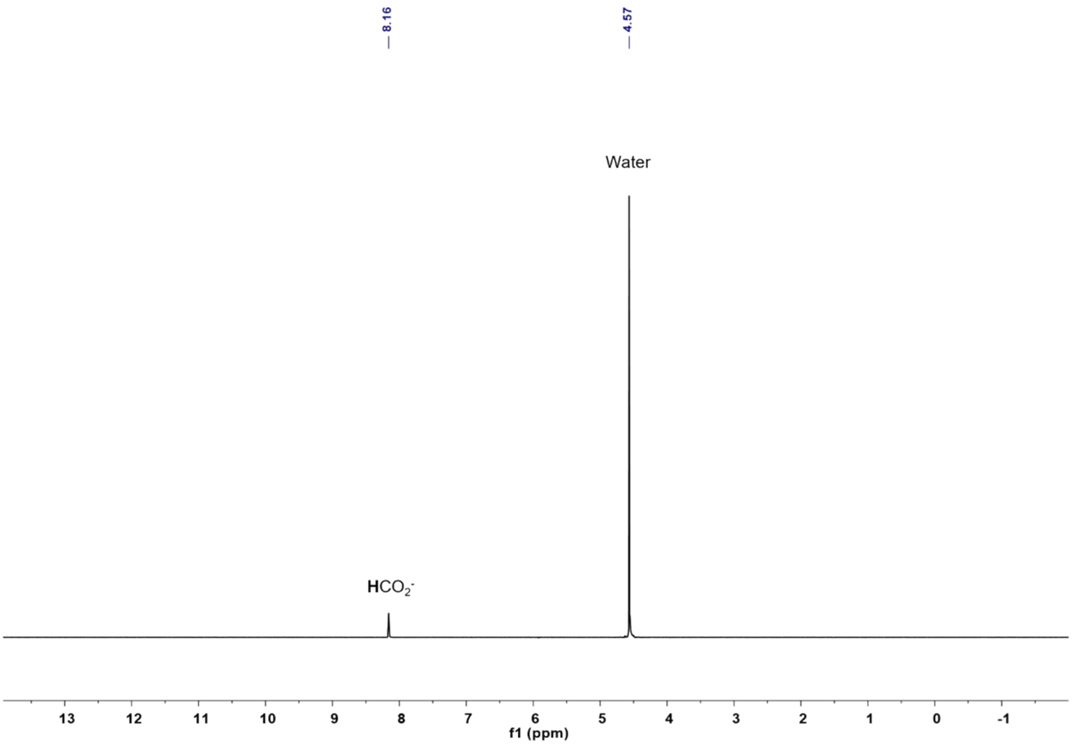

Figure S7. ^1H NMR analysis of the evaporated solid produced during the synthesis of $Ca(HCO_2)_2$ from $[Et_3NH][HCO_2]$ by using CaO.

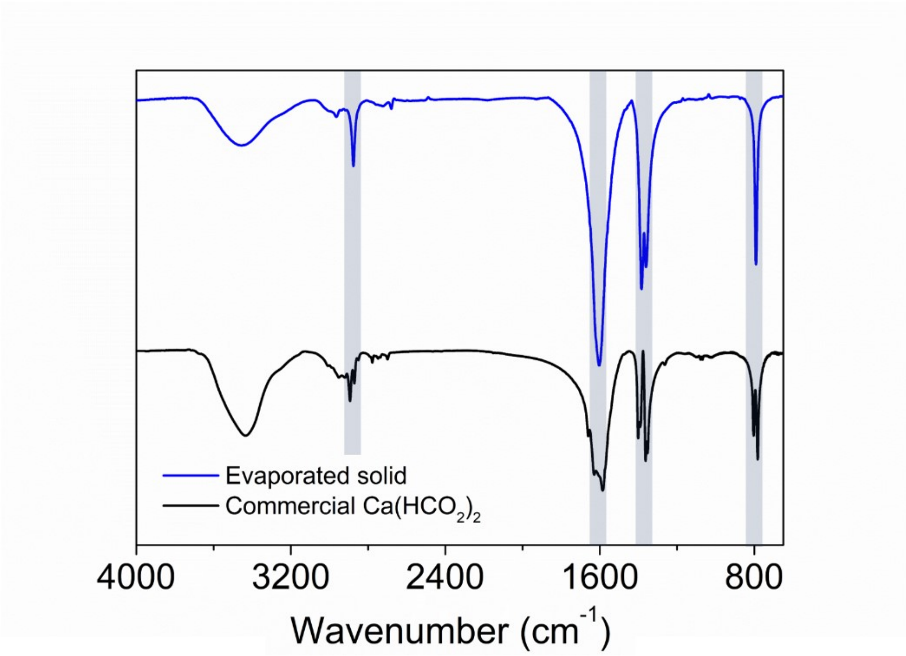

Figure S8. FT-IR analysis of the evaporated solid produced during the synthesis of $Ca(HCO_2)_2$ from $[Et_3NH][HCO_2]$ by using CaO.

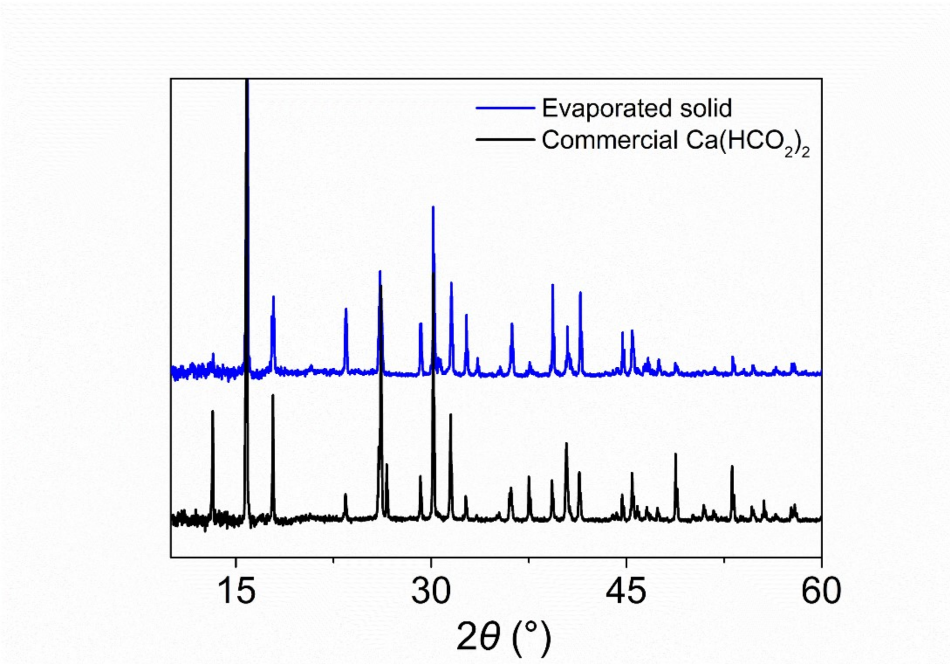

Figure S9. XRD image of $Ca(HCO_2)_2$ obtained from $[Et_3NH][HCO_2]$ by using CaO.

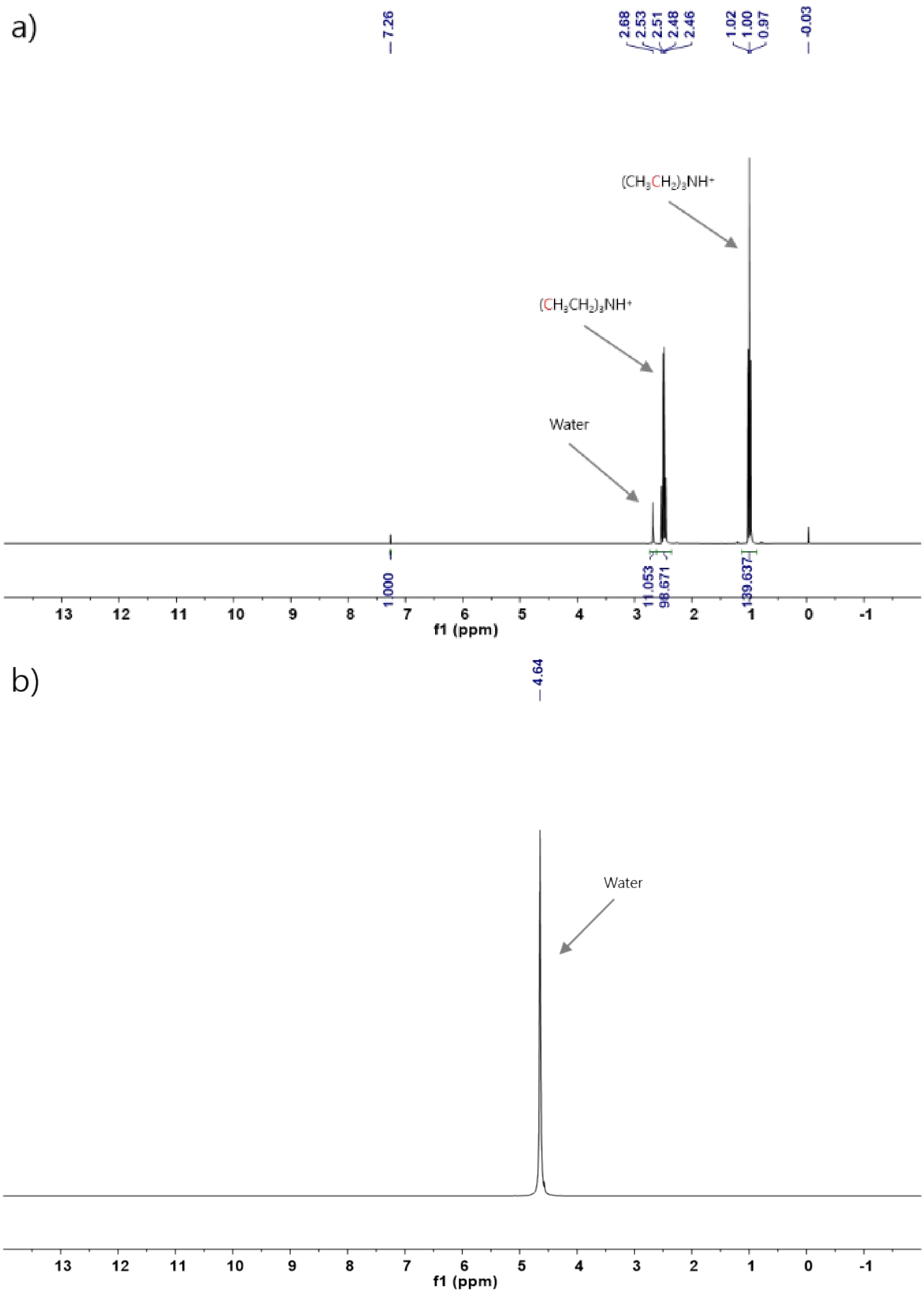

Figure S10. ^{1}H-NMR data of a) Et_3N and b) H_2O obtained by evaporating the filtrate at 100 and 130 °C.

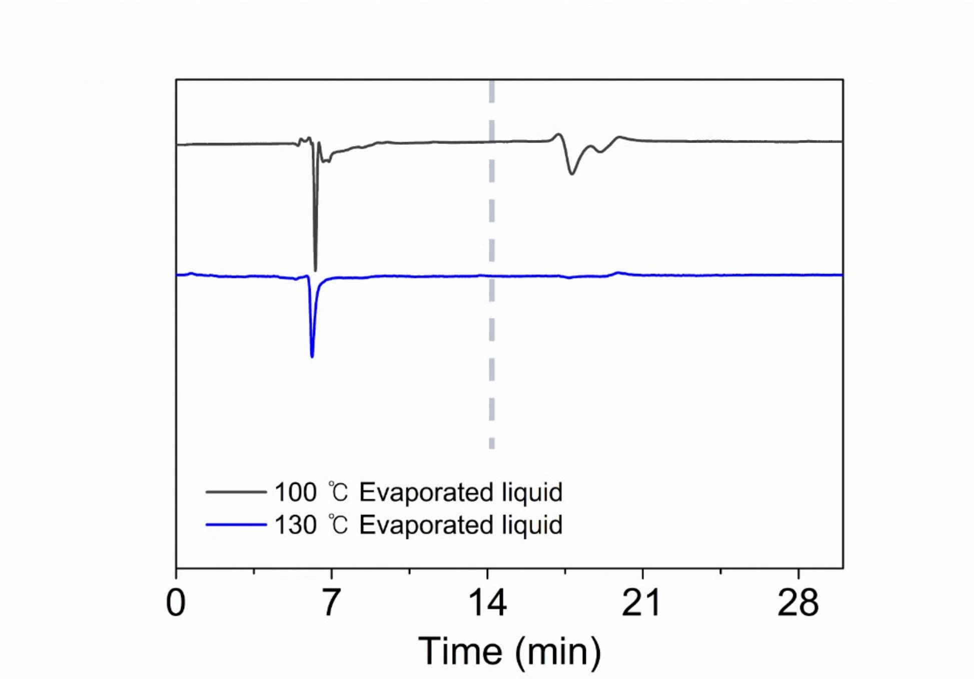

Figure S11. HPLC data of Et_3N (black) and H_2O (blue) obtained by evaporating the filtrate at 100 and 130 °C.

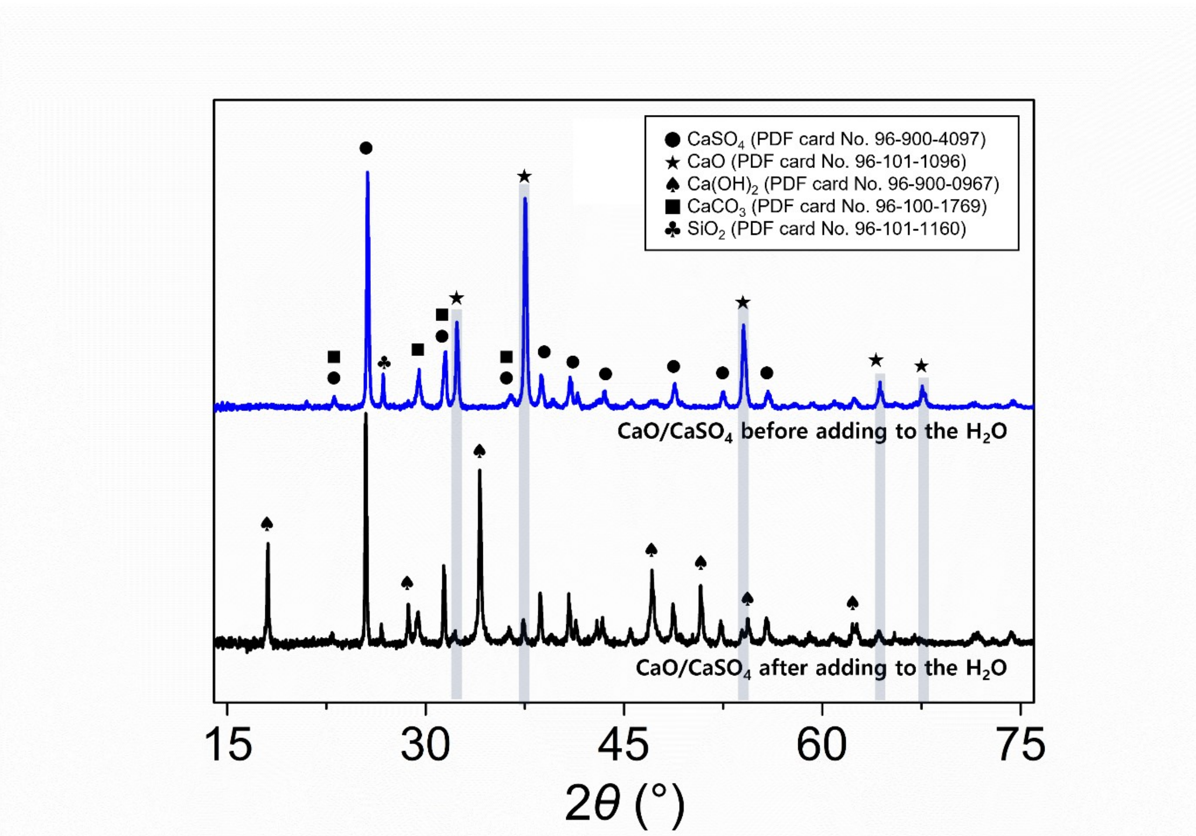

Figure S12. XRD image before and after adding $CaO/CaSO_4$ to the H_2O.

4. $Ca(HCO_2)_2$ yield and amine loss according to the change of additives containing CaO

Table S1. $Ca(HCO_2)_2$ yields from the reaction between $[Et_3NH][HCO_2]$ and CaO for various reaction times and temperatures.

Entry	**Temp.**	**Time**	**Et_3N**	**HCO_2H**	**Added CaO**	**Reacted CaO**	**Reacted CaO**	**Produced $Ca(HCO_2)_2$**	**Produced $Ca(HCO_2)_2$**
	[°C]	[h]	[M]	[M]	[M]	[M]		[M]	
1	30	0.0833	1.9008	1.7107	0.8554	0.8547	99.93%	0.8434	98.60%
2	30	0.0833	1.9008	1.7107	0.8554	0.8518	99.58%	0.8559	100.06%
3	30	0.5	1.9008	1.7107	0.8554	0.8510	99.50%	0.8551	99.97%
4	30	0.5	1.9008	1.7107	0.8554	0.8516	99.56%	0.8453	98.83%
5	30	2	1.9008	1.7107	0.8554	0.8526	99.68%	0.8735	102.13%
6	30	2	1.9008	1.7107	0.8554	0.8521	99.62%	0.8618	100.75%
7	30	15	1.9008	1.7107	0.8554	0.8543	99.88%	0.8677	101.44%
8	30	15	1.9008	1.7107	0.8554	0.8484	99.19%	0.8603	100.58%
9	30	60	1.9008	1.7107	0.8554	0.8395	98.15%	0.8394	98.13%
10	30	60	1.9008	1.7107	0.8554	0.8171	95.53%	0.8329	97.37%
11	45	0.0833	1.9008	1.7107	0.8554	0.8539	99.83%	0.8584	100.36%
12	45	0.0833	1.9008	1.7107	0.8554	0.8521	99.62%	0.8411	98.33%
13	60	0.0833	1.9008	1.7107	0.8554	0.8521	99.62%	0.8664	101.29%
14	60	0.0833	1.9008	1.7107	0.8554	0.8527	99.69%	0.8432	98.57%
15	75	0.0833	1.9008	1.7107	0.8554	0.8520	99.61%	0.8536	99.79%
16	75	0.0833	1.9008	1.7107	0.8554	0.8536	99.79%	0.8657	101.21%
17	90	0.0833	1.9008	1.7107	0.8554	0.8536	99.79%	0.8217	96.06%
18	90	0.0833	1.9008	1.7107	0.8554	0.8533	99.76%	0.8210	95.98%

Table S2. $Ca(HCO_2)_2$ yields from the reaction between $[Et_3NH][HCO_2]$ and the CaO-$CaSO_4$ mixture for various reaction times and temperatures.

Entry	Temp.	Time	Et_3N	HCO_2H	Added $CaSO_4$	Added CaO	Reacted CaO	Reacted CaO	Produced $Ca(HCO_2)_2$	Produced $Ca(HCO_2)_2$
	[°C]	[h]	[M]	[M]	[M]	[M]	[M]		[M]	
1	30	0.0833	1.9008	1.7107	0.8554	0.8554	0.9034	105.62%	0.8852	103.49%
2	30	0.0833	1.9008	1.7107	0.8554	0.8554	0.9014	105.38%	0.8606	100.61%
3	30	0.5	1.9008	1.7107	0.8554	0.8554	0.8959	104.74%	0.8464	98.96%
4	30	0.5	1.9008	1.7107	0.8554	0.8554	0.8821	103.13%	0.8310	97.16%
5	30	2	1.9008	1.7107	0.8554	0.8554	0.8993	105.14%	0.8396	98.16%
6	30	2	1.9008	1.7107	0.8554	0.8554	0.8864	103.63%	0.8553	99.99%
7	30	15	1.9008	1.7107	0.8554	0.8554	0.8987	105.06%	0.8727	102.03%
8	30	15	1.9008	1.7107	0.8554	0.8554	0.8332	97.41%	0.8530	99.72%
9	30	60	1.9008	1.7107	0.8554	0.8554	0.9183	107.36%	0.8859	103.57%
10	30	60	1.9008	1.7107	0.8554	0.8554	0.8946	104.59%	0.8676	101.43%
11	45	0.0833	1.9008	1.7107	0.8554	0.8554	0.8819	103.11%	0.8474	99.07%
12	45	0.0833	1.9008	1.7107	0.8554	0.8554	0.8736	102.14%	0.8634	100.94%
13	60	0.0833	1.9008	1.7107	0.8554	0.8554	0.8973	104.90%	0.8629	100.89%
14	60	0.0833	1.9008	1.7107	0.8554	0.8554	0.8899	104.04%	0.8540	99.84%
15	75	0.0833	1.9008	1.7107	0.8554	0.8554	0.9084	106.20%	0.9053	105.84%
16	75	0.0833	1.9008	1.7107	0.8554	0.8554	0.8887	103.89%	0.8722	101.97%
17	90	0.0833	1.9008	1.7107	0.8554	0.8554	0.9037	105.65%	0.8669	101.35%
18	90	0.0833	1.9008	1.7107	0.8554	0.8554	0.8843	103.39%	0.8650	101.12%

Table S3. Ca(HCO_2)$_2$ yields from the reaction between [Et_3NH][HCO_2] and the ash in the desulfurization process (CaO 23.4wt%).

Temp.	Time	Et_3N	HCO_2H	Added CaO	Reacted CaO	Reacted CaO	Produced Ca(HCO_2)$_2$	Produced Ca(HCO_2)$_2$
[°C]	[min]	[M]	[M]	[M]	[M]		[M]	
30	5	1.9008	1.7107	0.9593	0.8529	99.71%	0.8624	100.83%

Table S4. Amine loss during synthesis of Ca(HCO_2)$_2$ from [Et_3NH][HCO_2] by using (1) CaO, (2) CaO+$CaSO_4$ and (3) ash in desulfurization process.

Entry	HCO_2H	Et_3N	Temp.	Time	Added CaO	Produced Ca(HCO_2)$_2$	Produced Ca(HCO_2)$_2$	Produced amine	Amine loss
	[M]	[M]	[°C]	[min]	[M]	[M]	%		
1	1.7107	1.9008	30	5	0.8554	0.8559	100.06%	100.06%	**0%**
2	1.7107	1.9008	30	5	0.8554	0.8606	100.61%	100.61%	**0%**
3	1.7107	1.9008	30	5	0.8554	0.8624	100.82%	100.82%	**0%**

5. Techno-economic analysis

Table S5. Parameters used and assumptions made for the economic analysis[1, 2]

	Parameter	Value
Assumptions	(1) Annual $Ca(HCO_2)_2$ production (t $Ca(HCO_2)_2$/yr)	38,500
	(2) Economic life of the plant (yr)	20
	(3) Annual operating hours (hr/yr)	8,000
	(4) Interest rate (%)	8
	(5) Tax rate (%)	35
	(5) Depreciation method	Straightforward
	(6) Direct supervisory and clerical labor (% of operating labor cost)	17
	(7) Maintenance and repairs (% of fixed capital investment cost)	6
	(8) Operating supplies (% of maintenance and repairs cost)	15
	(9) Laboratory charges (% of operating labor cost)	15
	(10) Patents and royalties (% of total operating cost)	3
	(11) Taxes and insurance (% of fixed capital investment cost)	2
	(12) Plant overhead costs (% of operating labor, (6) and (7))	60
	(13) Administration costs (% of operating labor, (6) and (7))	15
	(14) Distribution and selling cost (% of total operating cost)	11
	(15) Research and development (% of total operating cost)	5
Utilities	(16) Low-pressure steam (USD/GJ)	13.28
	(17) Electricity (Conventional) (USD/kWh)	0.07
	(18) Electricity (Renewable) (USD/kWh)	0.14
	(19) Cooling water (USD/ton)	0.354

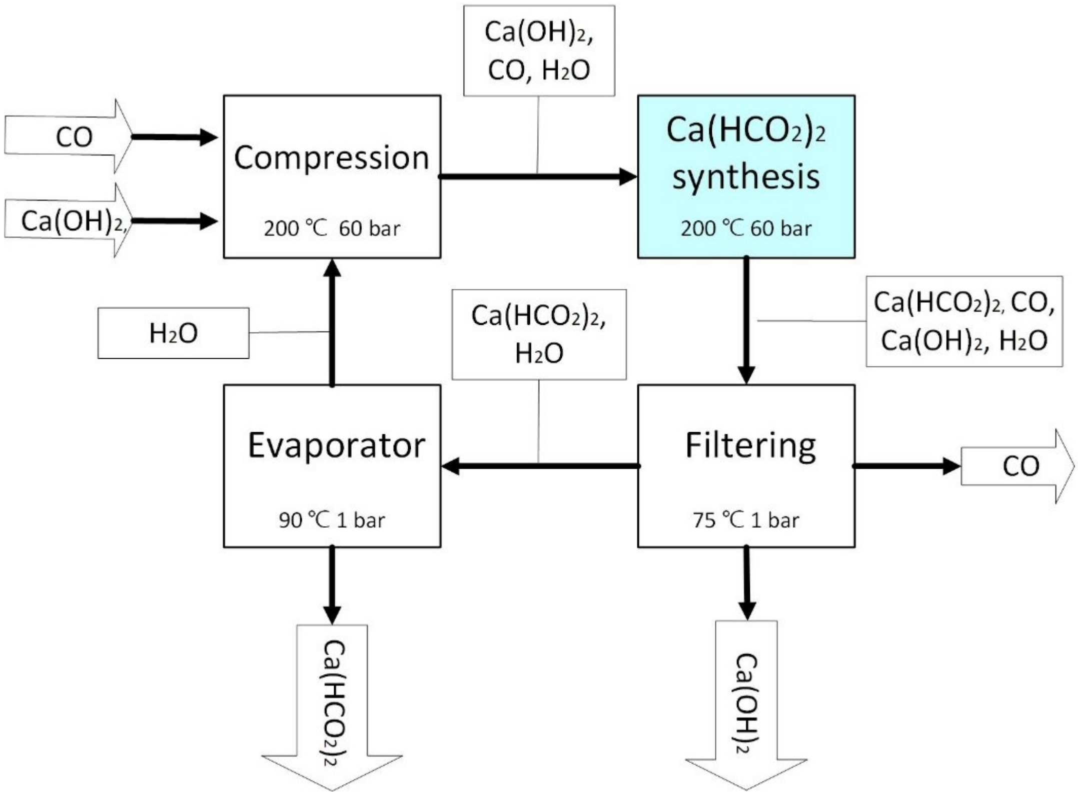

Figure S13. Block flow diagram of the process of $Ca(HCO_2)_2$ production from CO and $Ca(OH)_2$.

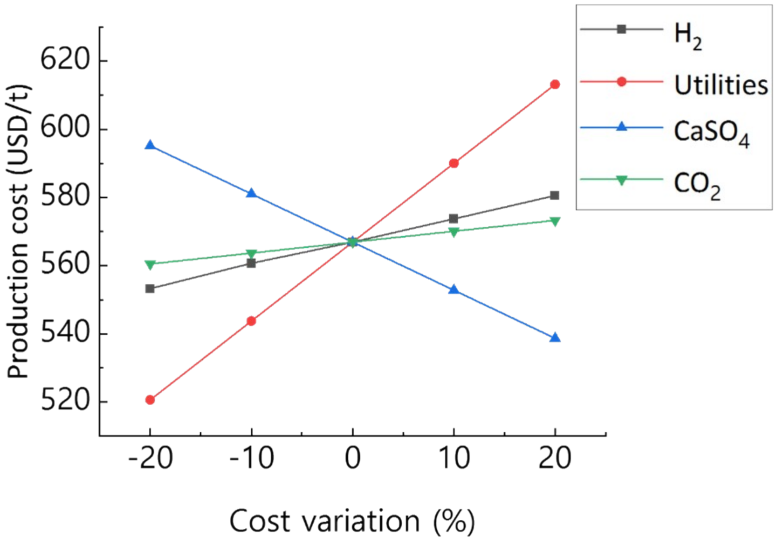

Figure S14. Sensitivity analysis of the $Ca(HCO_2)_2$ production cost for the fluctuation of H_2 from SMR(black), utilities (red), CO_2 (green), and $CaSO_4$ (blue).

6. Life-cycle assessment

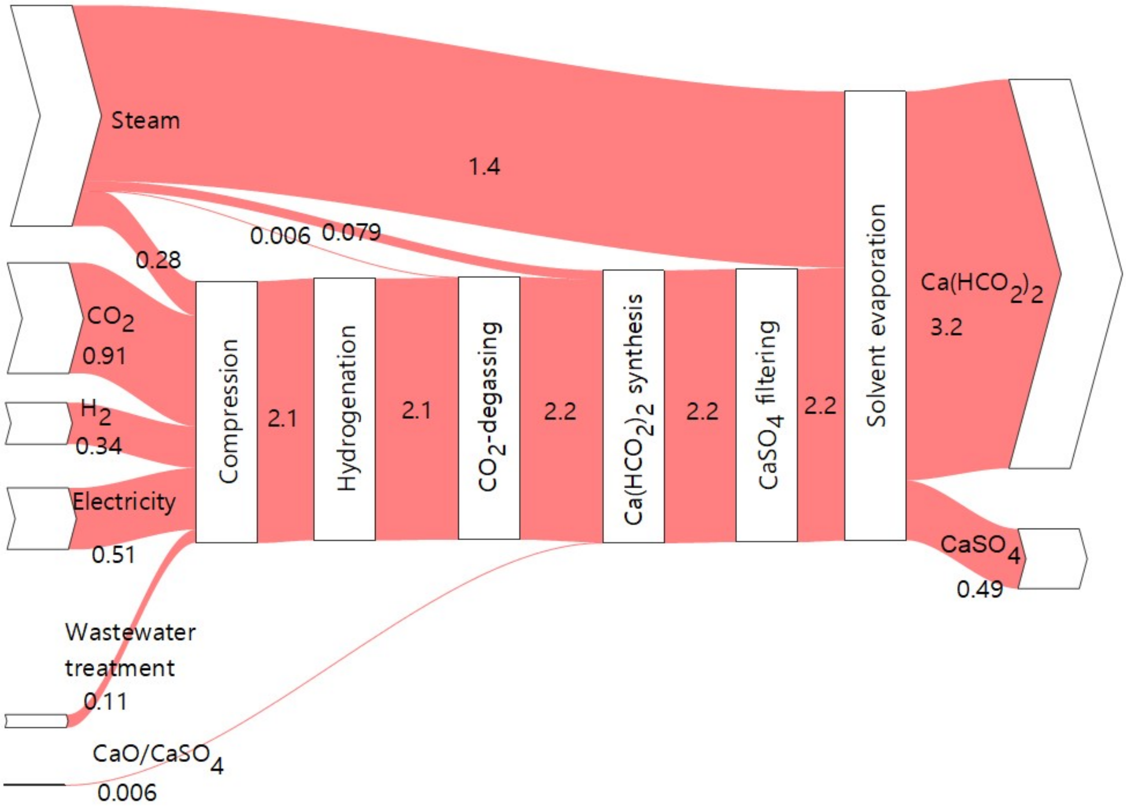

Figure S15. Sankey diagram for the GW index of the proposed process (H_2 from SMR) (unit: kg CO_2-eq/kg $Ca(HCO_2)_2$).

Table S6. Parameters used for the environmental analysis.

Inflows	Database	Note
Material		
H_2[3]	Hydrogen (reformer) E	H_2 from SMR
CO_2[4]	Carbon dioxide, liquid | market for | Cut-off, S	
$CaO/CaSO_4$[4]	Waste gypsum | market for | Cut-off, S	
CO[4]	Carbon monoxide | market for | Cut-off. S	
$Ca(OH)_2$[4]	Lime, hydrated, packed | market for | Cut-off, S	
H_2O[4]	Water, completely softened | market for | Cut-off, S	
Et_3N	Triethyl amine {GLO} | market for | Cut-off, S	
Utilities		
Steam[4]	Heat, from steam, in chemical industry | market for | Cut-off, S	
Electricity[4]	Electricity, high voltage [2]| heat and power co-generation, hard coal | Cut-off, S	
Electricity[4, 5]	Electricity, low voltage [2] | electricity production, photovoltaic, 570kWp open | Cut-off, S	H_2 from Electrolysis
Electricity[4, 5]	Electricity, high voltage [2]| electricity production, wind, >3MW turbine, onshore | Cut-off, S	H_2 from Electrolysis
Outflows		
Wastewater[4]	Wastewater, average | treatment of, capacity 1E9l/year | Cut-off, S	
Inert waste[4]	Inert waste | treatment of, sanitary landfill | Cut-off, S	

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