Electronic Supplementary information (ESI) for

CO_2 Conversion by High-Dose Rate Electron Beam Irradiation: One Step, Metal-Free, Simultaneous, and Accelerated Production of H_2, CO, CH_4, C_2H_6 and Organic Acid from Acid-Decomposed $CaCO_3$/Additive EtOH Mixture

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Table S1. Results of experiments performed under identical conditions for reproducibility confirmation ($CaCO_3$/1 N HCl/EtOH, 100 kGy × 1, n = 3). Primary data of GC/CE analysis and averages/standard deviations.

Number	GC-TCD (%)		GC-MS (ppm)							CE (μg/mL)		
			CH_4			CO			C_2H_6			
	H_2	CO_2	m/z 16 ^{12}C	m/z 17 ^{13}C	$^{13}C/^{12}C$ ratio	m/z 28 ^{12}C	m/z 29 ^{13}C	$^{13}C/^{12}C$ ratio	m/z 30 ^{12}C	Formate	Acetate	Propionate
1	10	81	1200	14	0.0117	220	1200	5.45	90	94	17	<10
2	11	78	1300	15	0.0115	250	1200	4.80	98	92	19	<10
3	10	80	1300	15	0.0115	240	1200	5.00	100	93	17	<10
Average	10	80	1267	15	0.0116	237	1200	5.08	96	93	18	<10
STDEV	0.69	1.29	57.74	0.58	0.00	15.28	0.00	0.27	5.29	1.00	1.15	0.00

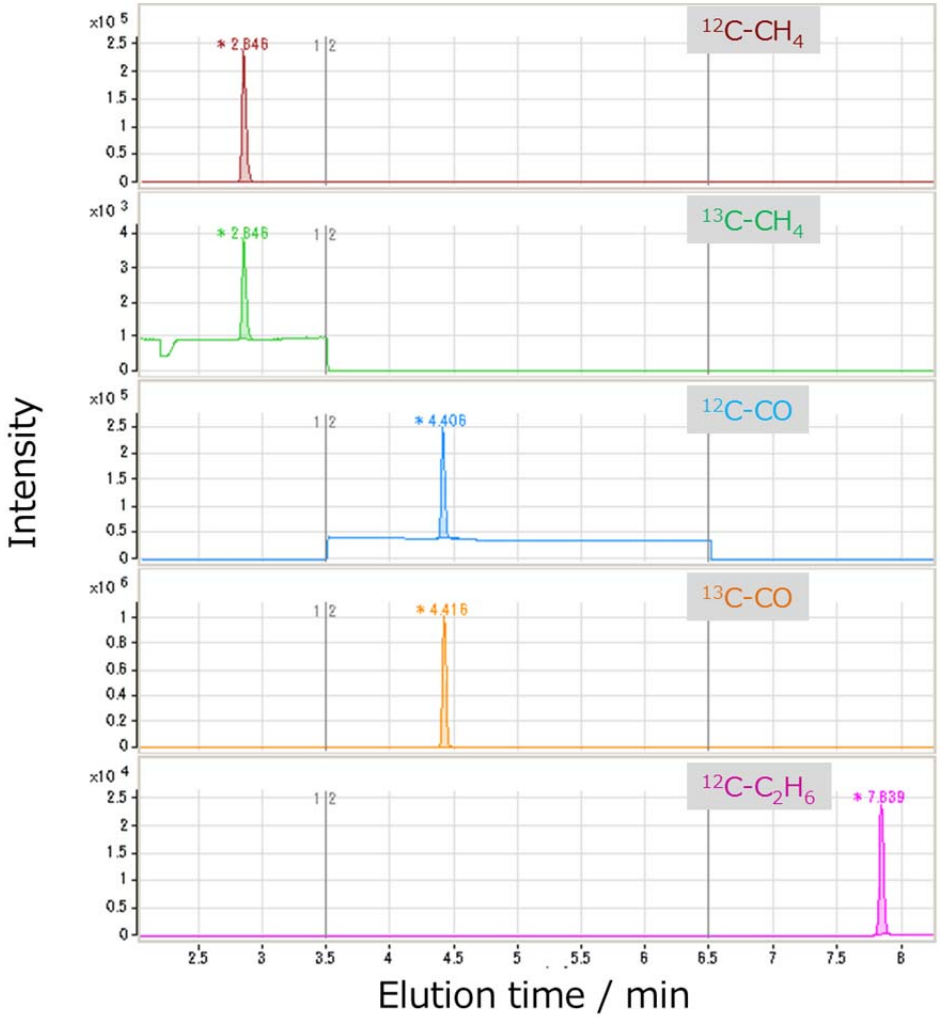


Fig. S1. Typical GC-MS charts of CO, CH_4, and C_2H_6 (100 kGy × 1).

Table S2. GC primary data for EB-irradiated samples treated under different conditions.

Entry	Sample Contents	Dose / kGy (kGy/s × Pass)	GC-TCD (%)		GC-MS (ppm)						
					CH_4			CO			C_2H_6
			H_2	CO_2	^{12}C	^{13}C	$^{13}C/^{12}C$	^{12}C	^{13}C	$^{13}C/^{12}C$	^{12}C
1	$CaCO_3$/1 N HCl/EtOH	25 (25 × 1)	3	68	230	2.5	0.0109	35	220	6.29	15
2		100 (25 × 4)	13	71	1300	14	0.0108	180	980	5.44	85
3		100 (100 × 1)	10	80	1300	15	0.0115	240	1200	5.00	100
4		300 (100 × 3)	21	65	390	4.1	0.0105	84	320	3.81	28
R1	$CaCO_3$/1 N HCl	100 (100 × 1)	1	91	2.1	N.D.	N.D.	13	420	32.31	N.D.
R2	$CaCl_2/H_2O$/EtOH		6	0.03	630	6.9	0.0110	52	0.7	0.01	150
R3	H_2O/EtOH		6	0.04	800	8.8	0.0110	64	0.8	0.01	180
R4	$CO_2/CaCl_2/H_2O$/EtOH		8	23	460	5.2	0.0113	84	170	2.02	40
R5	$CO_2/CaCl_2/H_2O$		0	34	2.4	0.2	0.0833	6.7	70	10.45	N.D.
R6	CO_2/H_2O/EtOH		7	31	420	4.7	0.0112	74	200	2.70	32
R7	CO_2/H2O		0	30	3.0	0.2	0.0667	7.0	65	9.29	N.D.

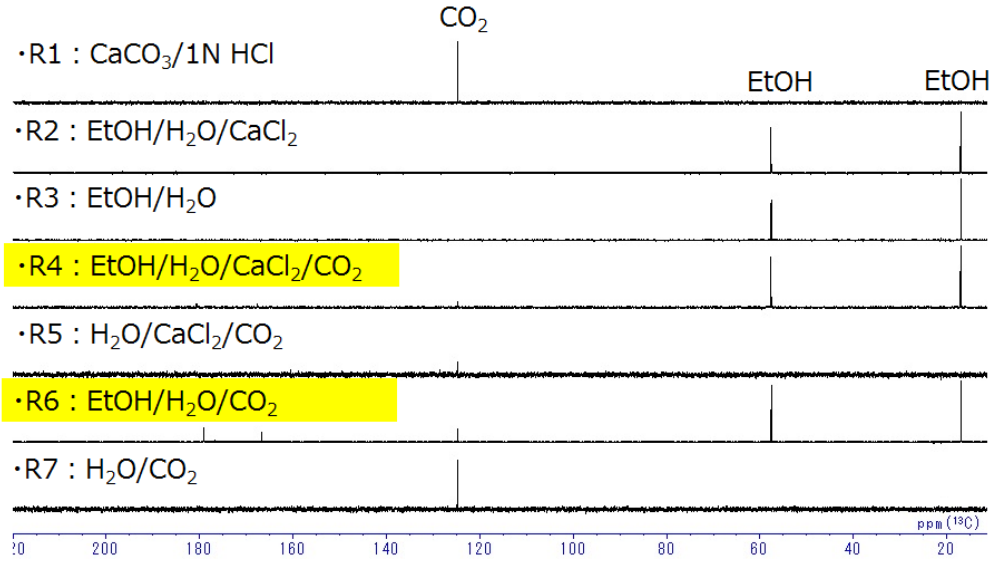


Fig. S2. ^{13}C NMR (400 MHz, D_2O) spectra of reference samples [0.4 mL irradiated solution/0.2 mL D_2O mixtures] after EB irradiation (100 kGy × 1).

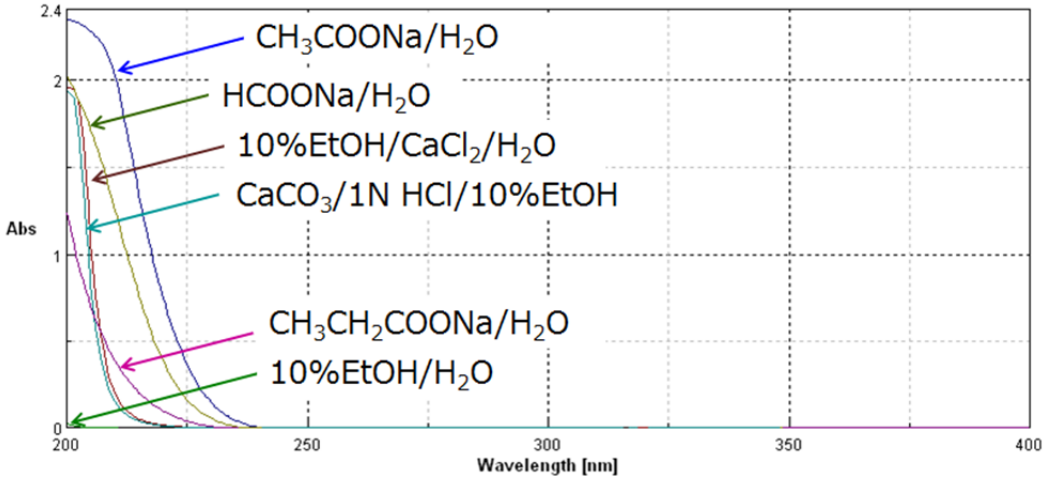
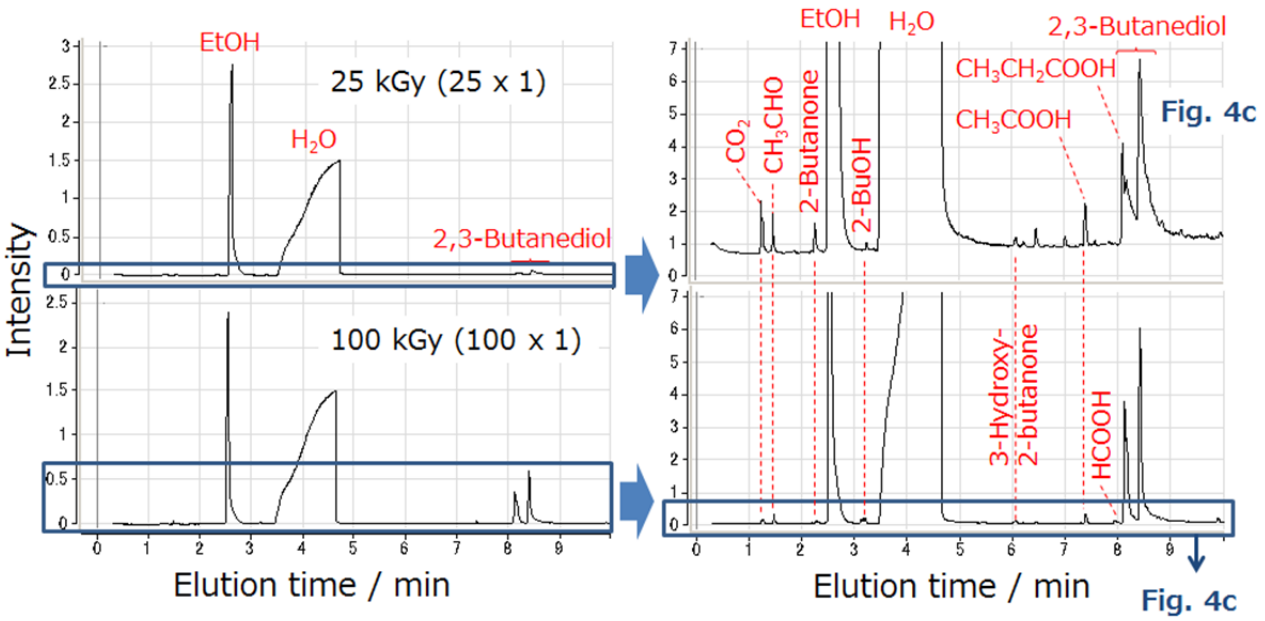


Fig. S3. Qualitative UV spectra of reference samples and of the reaction solution before EB irradiation.

a)



b)

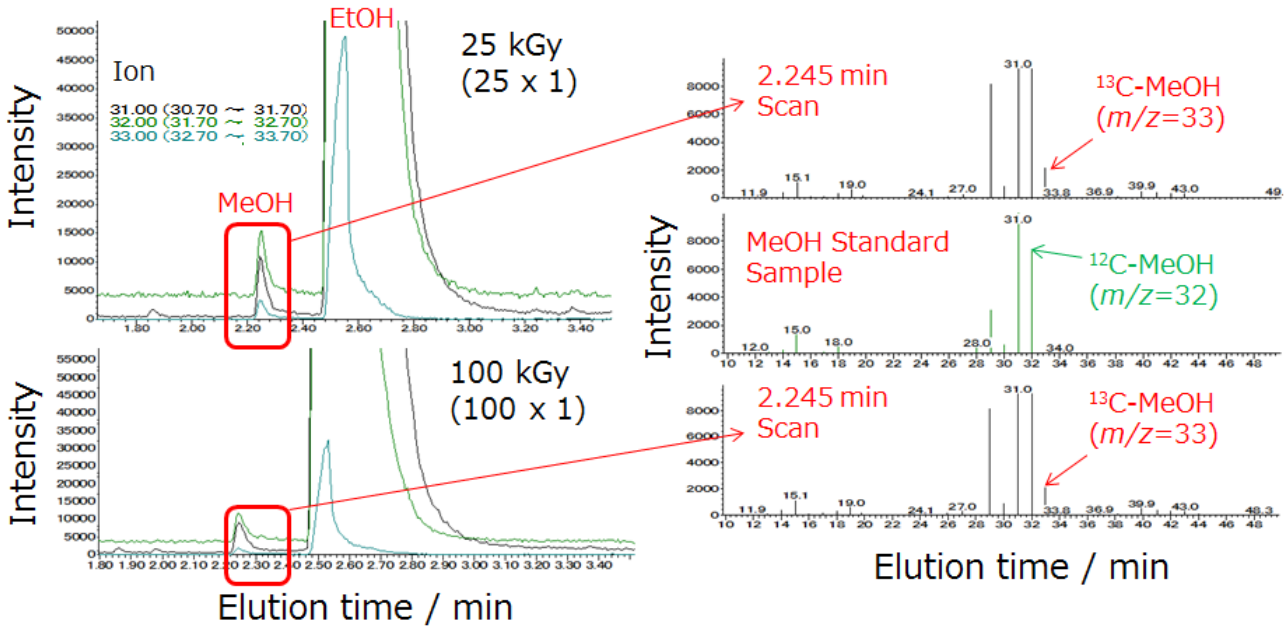


Fig. S4. Selected GC-MS charts of aqueous phases. (a) Complete charts [different intensity scales], (b) MeOH analysis chart.

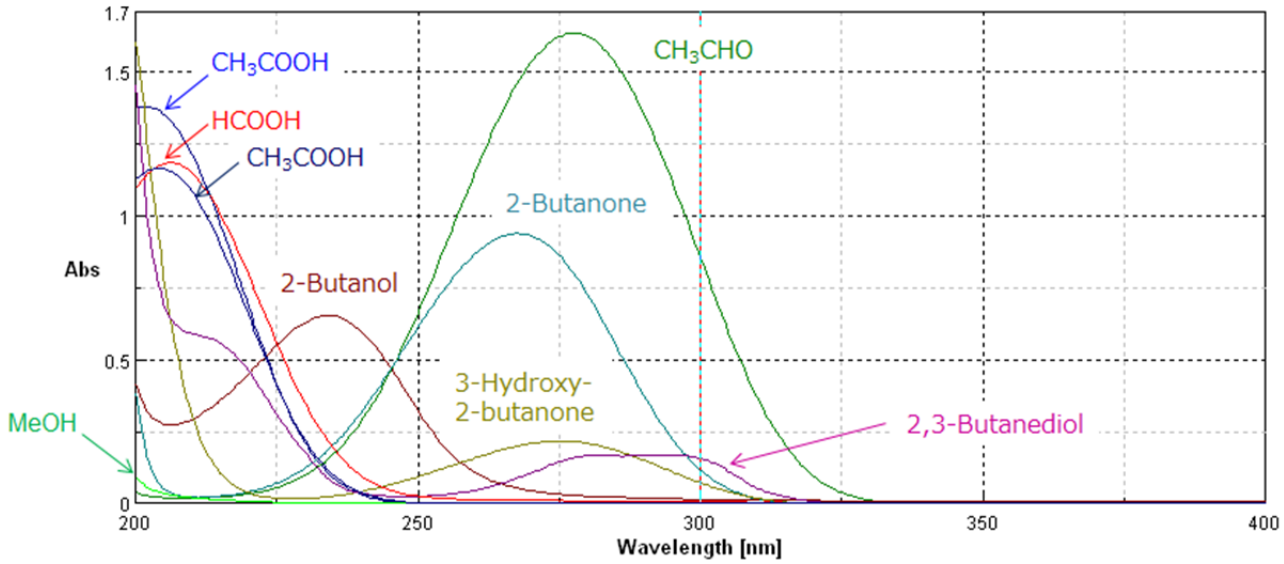


Fig. S5. Qualitative UV spectra (H_2O, 3–10%) of pure compounds observed in MS spectra.

Table S3. Concentrations of organic acids (including all isotopes) in the aqueous phase estimated by CE analysis.

Entry	Dose / kGy (kGy/s × Pass)	Concentration (μg/mL)		
		HCOOH	CH_3COOH	CH_3CH_2COOH
1	25 (25 × 1)	24	<10	<10
3	100 (100 × 1)	94	17	<10
4	300 (100 × 3)	220	69	28

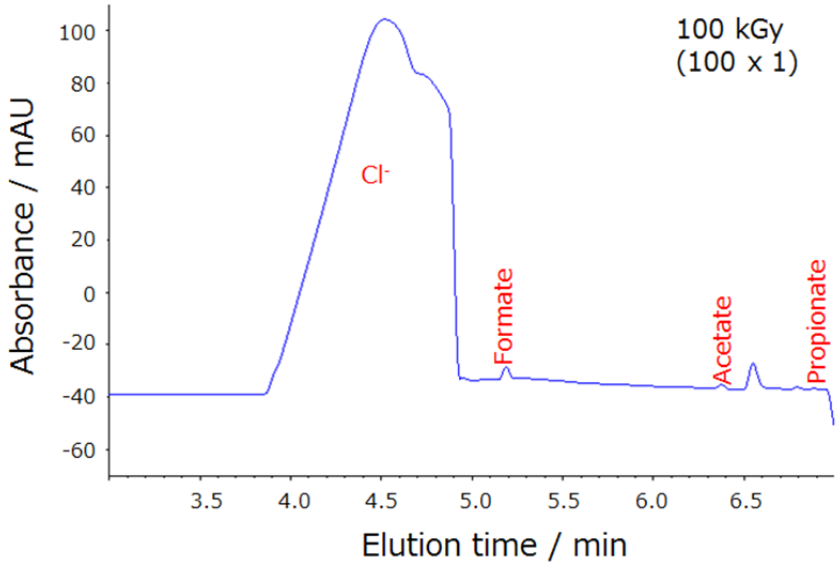


Fig. S6. Typical CE electropherogram of the aqueous solution (100 kGy × 1).

Table S4. Comparison of $^{13}C/^{12}C$ isotope ratio between natural organic acids and experimentally observed organic acids (300 kGy irradiated sample). (a) Formate, (b) acetate, and (c) propionate ratios.

a)

Methyl formate	*m/z*	Isotope ratio (%)	
		Natural	Observed
^{12}C	60	0.989	0.221
^{13}C	61	0.011	0.779

b)

Methyl acetate	*m/z*	Isotope ratio (%)	
		Natural	Observed
^{12}C-^{12}C	74	0.979	0.892
^{12}C-^{13}C	75	0.021	0.101
^{13}C-^{13}C	76	(0.0001)	0.007

c)

Methyl propionate	*m/z*	Isotope ratio (%)	
		Natural	Observed
^{12}C-^{12}C-^{12}C	88	0.968	0.088
^{12}C-^{12}C-^{13}C	89	0.031	0.879
^{12}C-^{13}C-^{13}C	90	(0.000339)	0.024
^{13}C-^{13}C-^{13}C	91	(0.000001)	-

–: Not detected

Table S5. ^{13}C organic acid concentrations estimated by CE and GC-MS analyses.

Entry	Dose / kGy (kGy/s × Pass)	Concentration (μg/mL)				
		HCOOH	CH_3COOH		CH_3CH_2COOH	
		^{13}C	^{12}C-^{13}C	^{13}C-^{13}C	^{12}C-^{12}C-^{13}C	^{12}C-^{13}C-^{13}C
1	25 (25×1)	11	-	-	-	-
3	100 (100×1)	73	1.8	-	-	-
4	300 (100×3)	171	7	0.5	24.6	0.7

–: Not detected