SUPPLEMENTARY INFORMATION

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S.1 Formic acid (FA) production strategies

S.1.1 Conventional FA production strategy

This process consumes fossil-based CO, and produces FA by the hydrolysis of methyl formate obtained from CO [1, 2]. The hydrolysis of methyl formate consists of the following reaction steps:

Methanol is carbonylated by CO at 80 ℃ and 45 bar (Eq. 1).

$$CO + CH_3OH \leftrightarrow HCOOCH_3 \qquad \text{(Eq. 1)}$$

In the conversion of methyl formate and water, the methyl formate is converted by only about 30% (Eq. 2).

$$H_2O + HCOOCH_3 \leftrightarrow HCOOH + CH_3OH \qquad \text{(Eq. 2)}$$

The overall equation of the conventional process is as follows (Eq. 3) and does not require the supply of CO_2.

$$CO + H_2O \leftrightarrow HCOOH \qquad \text{(Eq. 3)}$$

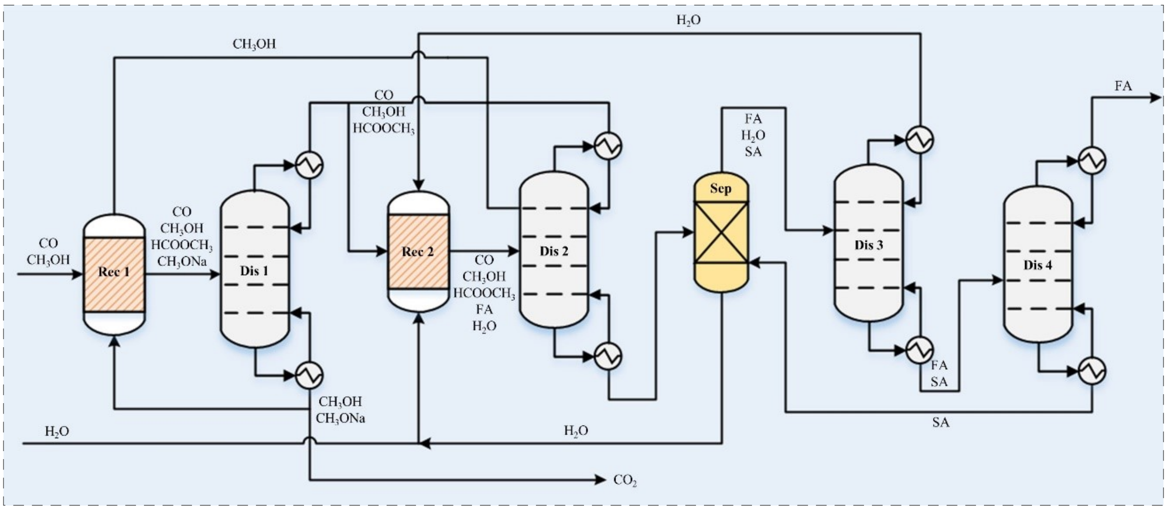

Fig. S1. System boundary of conventional FA production strategy; $HCOOCH_3$ (Methyl formate), CH_3ONa (Sodium methoxide), SA (Secondary amide).

S.1.2 Catalytic CO_2-based FA (cCtF) production strategy

The cCtF process requires triethylamine (NEt_3), 1-n-butylimidazole (BIZ), H_2 and CO_2 to produce FA using the AUROlite (Au/TiO_2) catalyst [3, 4]. The net reaction equation is to produce FA through hydrogenation of CO_2 (Eq. 4).

$$CO_2 + H_2 \leftrightarrow HCOOH \qquad \text{(Eq. 4)}$$

The FA adduct ($HCOOH\text{-}NEt_3$) can be obtained by NEt_3 that reacts with FA at 40 ℃ and 180 bar (Eq. 5).

$$CO_2 + H_2 + NEt_3 \leftrightarrow HCOOH\text{-}NEt_3 \qquad \text{(Eq. 5)}$$

In next reaction step, the amine and FA are separated by an amine-shift reaction in which BIZ is added to the amine FA adduct (Eq. 6).

$$HCOOH\text{-}NEt_3 + BIZ \leftrightarrow NEt_3 + HCOOH\text{-}BIZ \qquad \text{(Eq. 6)}$$

The BIZ and FA are separated by distillation, and 1-n-butylimidazole is reused to remove NEt_3, and the FA is produced (Eq. 7).

$$HCOOH\text{-}BIZ \leftrightarrow HCOOH + BIZ \quad \text{(Eq. 7)}$$

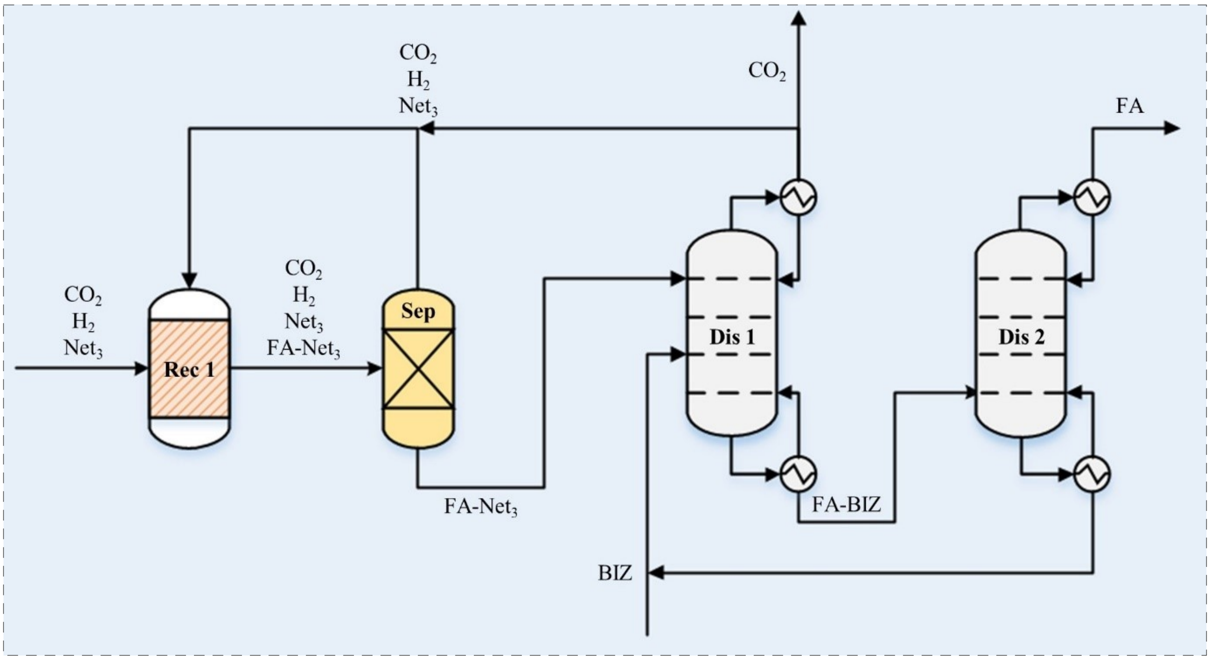

Fig. S2. System boundary of catalytic CO_2-based FA (cCtF) production strategy; Net_3 (Triethylamine), BIZ (1-Butylimidazole).

S.1.3 Electrocatalytic CO_2-based FA (eCtF) production strategy

The eCtF process is based on reactor design by three compartments cell (TCC), including a recirculation regime [5]. The characteristic of this study is that the no other chemicals are required as additional electrolytes. CO_2 reacts with water at the cathode compartment and is reduced formate ($HCOO^-$) and hydroxide (OH^-) (Eq. 8).

$$CO_2 + H_2O + 2e^- \leftrightarrow HCOO^- + OH^- \quad \text{(Eq. 8)}$$

Simultaneously, oxygen gas (O_2) and protons (H^+) are formed by oxidation of water at the anode compartment (Eq. 9).

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad \text{(Eq. 9)}$$

Both the formate and hydroxide ions meet at the center flow compartment of the protons produced at the anode compartment to product formic acid and water (Eqs. 10 and 11).

$$H^+ + OH^- \leftrightarrow H_2O \quad \text{(Eq. 10)}$$

$$H^+ + HCOO^- \leftrightarrow HCOOH \quad \text{(Eq. 11)}$$

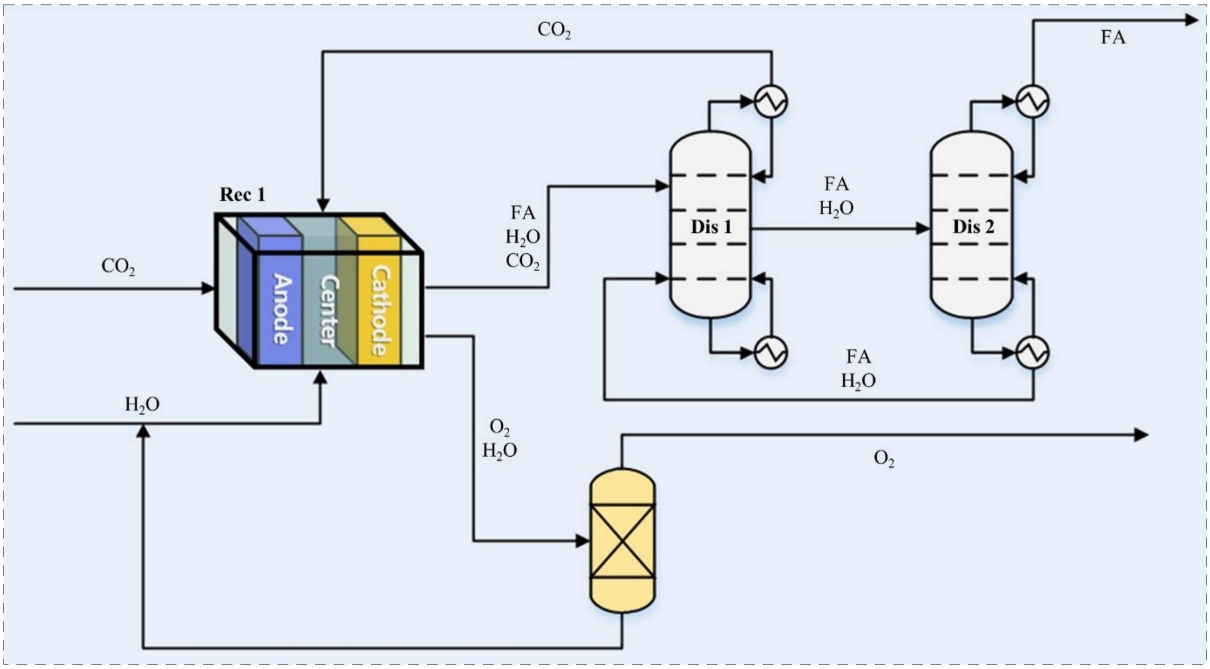

Fig. S3. System boundary of electrocatalytic CO_2-based FA (eCtF) production strategy.

Table S1. Details of three-compartment cell for eCtF strategy.

Cathode	CO_2 flow rate: 20 mL/min
Anode	Anolyte: Deionized water
Center flow compartment	DI water input flow rate: 0.03 mL/min Faradaic efficiency: 32% FA concentration: 19.5~20.4%
Anion membrane	Dioxide Materials Sustainion™ X37 imidazolium-based anion membrane
Cation membrane	DuPont Nafion® 212
Cell active membrane geometric area	5cm^2
Cell operating temperature	Ambient, 20-25 ℃
Cell current density	140 mA cm^{-2}

S.2 FA production simulation

S.2.1 cCtF production strategy

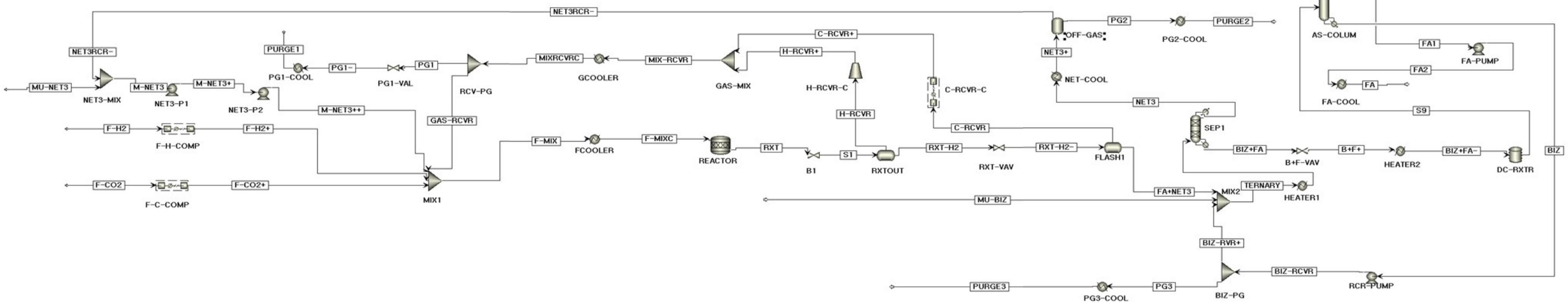

Fig. S4. Process flow diagram of eCtF production strategy.

Table S2. Detailed stream data of eCtF production strategy (part 1).

Unit	F-H2	F-H2+	F-CO2	F-CO2+	MU-NET3	M-NET3	M-NET3+	M-NET3++	GAS-RCVR	F-MIX	F-MIXC	RXT	S1	RXT-H2	RXT-H2-	FA+NET3	MU-BIZ	BIZ-RVR+	PG3
Mass Flow (kg/hr)	201.6	201.6	4401.0	4401.0	41.0	4286.4	4286.4	4286.4	2277.9	11166.8	11166.8	11166.8	11166.8	9890.3	9890.3	8865.9	25.0	26287.1	26.3
FA									44.9	44.9	44.9	4548.9	4548.9	4538.7	4538.7	4503.6		1343.5	1.3
BIZ																	25.0	24943.6	25.0
NET3					41.0	4257.1	4257.1	4257.1	118.0	4375.0	4375.0	4375.0	4375.0	4349.6	4349.6	4255.9			
CO2			4401.0	4401.0		29.3	29.3	29.3	1692.5	6122.7	6122.7	1816.0	1816.0	991.1	991.1	106.5			
H2	201.6	201.6							422.5	624.1	624.1	426.8	426.8	10.9	10.9				

Table S3. Detailed stream data of eCtF production strategy (part 2).

Unit	TERNARY	TERNARY+	BIZ+FA	NET3	NET3+	PG2	PURGE2	NET3 RCR-	B+F+	BIZ+FA-	S9	BIZ	BIZ-RCVR	PG3	PURGE3	FA1	FA2	FA
Mass Flow (kg/hr)	35178.0	35178.0	30815.6	4362.4	4362.4	117.1	117.1	4245.4	30815.6	30815.6	30815.6	26313.4	26313.4	26.3	26.3	4502.2	4502.2	4502.2
FA	5847.1	5847.1	5847.1						5847.1	5847.1	5847.1	1344.8	1344.8	1.3	1.3	4502.2	4502.2	4502.2
BIZ	24968.6	24968.6	24968.6						24968.6	24968.6	24968.6	24968.6	24968.6	25.0	25.0			
NET3	4255.9	4255.9		4255.9	4255.9	39.9	39.9	4216.1										
CO2	106.5	106.5		106.5	106.5	77.2	77.2	29.3										
H2																		

S.2.2 eCtF production strategy

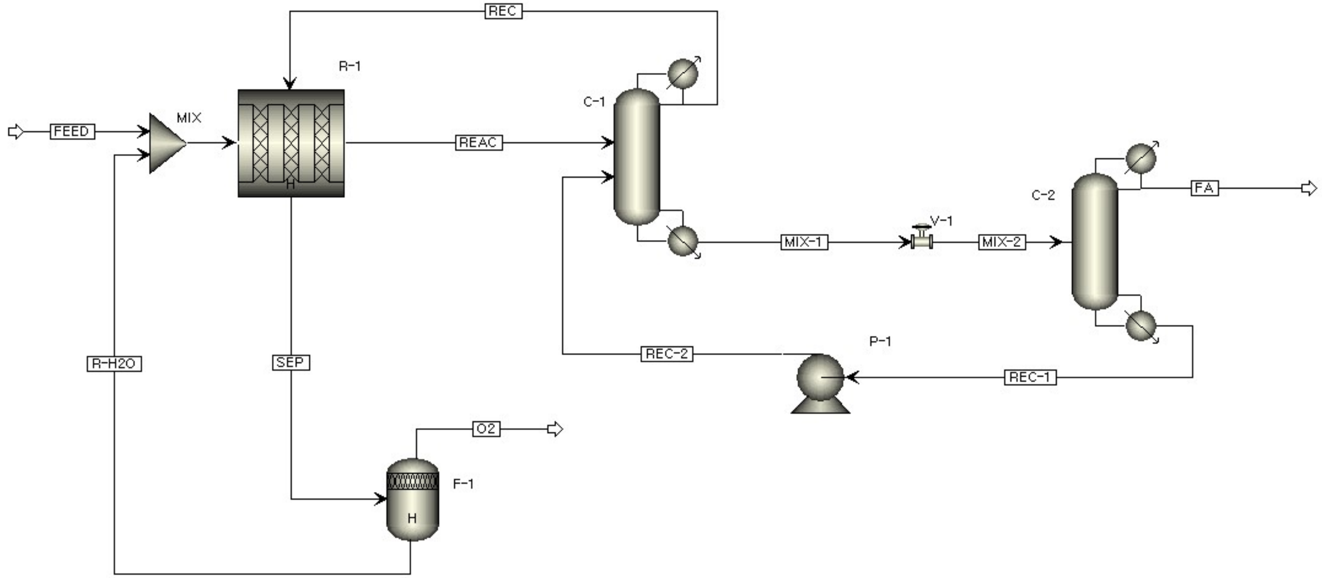

Fig. S5. Process flow diagram of eCtF production strategy.

Table S4. Detailed stream data of eCtF production strategy.

Unit	FEED	R-H2O	SEP	O2	REAC	MIX-1	MIX-2	REC	REC-1	REC-2	FA
Mass Flow (kg/hr)	13492.6	1093.2	1762.4	669.2	13457.1	4571.2	4571.2	11532.1	2646.1	2646.1	1925.1
FA	1937.9				2040.0	3718.8	3718.8	403.8	2082.5	2082.5	1636.3
H2O	8000.0	1093.2	1093.2		7960.0	852.4	852.4	7671.2	563.6	563.6	288.8
CO2	3554.7				3457.1			3457.1			
O2			669.2	669.2							

S.3 Life cycle inventory (LCI)

Table S2 shows the details of life cycle inventory database for LCA. Each component indicates Name (Characteristic) / [Country] / Production method / Allocation. This study assumed that the input CO_2 was originate from a natural gas power plant source employing an amine-based CO_2 capture process, and details of inventory data for CO_2 capture is shown in Table S3.

Table S5. Life cycle inventory details for FA production: RoW (Rest-of-World), KR (Korea)

	Input / material				**Input / utility**		**Output**			
Process	**H_2**	**CO_2**	**CO**	**H_2O**	**Electricity**	**Heat**	**CO_2** emission	**H_2O**	**O_2** byproduct	**FA** (kg)
Conventional	-	-	Carbon monoxide / [RoW] / production APOS, U	-	Electricity, high voltage / [KR] / electricity production, natural gas, conventional power plant | APOS, S	Heat, district or industrial, natural gas / [KR] / heat and power co-generation, natural gas, combined cycle power plant, 400MW electrical | APOS, S	Carbon dioxide	-	-	1
cCtF	Hydrogen, liquid / [RoW] / chlor-alkali electrolysis, membrane cell | APOS, S	CO2 capture	-	-			Carbon dioxide	-	-	1
eCtF	-	CO2 capture	-	Water, deionised, from tap water, at user / [RoW] / production | APOS, U			-	Water	Oxygen	1

Table S6. Life cycle inventory data of amine-based CO_2 capture process

/CO_2 1kg	**Input**	**Output**
Electricity (kWh)	0.15	-
Heat (kWh)	0.97	-
CO_2 (kg)	-	-1.00

Table S7. Details of utility sources for case study

	Sources									
Utility	**Natural gas**	**BFG**	**Biogas**	**Hard coal**	**Oil**	**Wood chips**	**Photovoltaics**	**Nuclear**	**Wind power**	**Hydro power**
Electricity	Electricity, high voltage / [KR] / electricity production, natural gas, conventional power plant | APOS, S	Electricity, high voltage / [KR] / treatment of blast furnace gas, in power plant | APOS, S	Electricity, high voltage / [KR] / heat and power co-generation, biogas, gas engine | APOS, S	Electricity, high voltage / [KR] / electricity production, hard coal | APOS, S	Electricity, high voltage / [KR] / electricity production, oil | APOS, S	Electricity, high voltage / [KR] / heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | APOS, S	Electricity, low voltage / [KR] / electricity production, photovoltaic, 570kWp open ground installation, multi-Si | APOS, S	Electricity, high voltage / [KR] / electricity production, nuclear, pressure water reactor | APOS, S	Electricity, high voltage / [KR] / electricity production, wind, >3MW turbine, onshore | APOS, S	Electricity, high voltage / [KR] / electricity production, hydro, run-of-river | APOS, S
Heat	Heat, district or industrial, natural gas / [KR] / heat and power co-generation, natural gas, combined cycle power plant, 400MW electrical | APOS, S	Heat, district or industrial, other than natural gas / [KR] / treatment of blast furnace gas, in power plant | APOS, S	Heat, central or small-scale, other than natural gas / [KR] / heat and power co-generation, biogas, gas engine | APOS, S	Heat, district or industrial, other than natural gas / [KR] / heat and power co-generation, hard coal | APOS, S	Heat, district or industrial, other than natural gas / [KR] / heat and power co-generation, oil | APOS, S	Heat, district or industrial, other than natural gas / [KR] / heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | APOS, S	-	-	-	-

Table S8. Comparison of CC and FD impacts by varying utility sources (Cases 2 and 3)

	Case 2 (Heat)						Case 3 (Electricity)					
	CC			FD			CC			FD		
	Conventional	cCtF	eCtF	Conventional	cCtF	eCtF	Conventional	cCtF	eCtF	Conventional	cCtF	eCtF
natural gas	2.05	0.27	2.00	1.05	0.35	0.98	2.05	0.27	2.00	1.05	0.35	0.98
BFG	2.43	0.33	2.28	1.01	0.34	0.95	2.07	0.30	2.58	1.04	0.32	0.63
biogas	1.72	0.21	1.76	0.89	0.32	0.87	1.98	0.16	0.40	1.02	0.30	0.26
hard coal	3.14	0.45	2.80	1.26	0.38	1.13	2.11	0.36	3.39	1.06	0.35	1.05
oil	2.98	0.42	2.68	1.38	0.40	1.22	2.10	0.34	3.14	1.07	0.37	1.28
wood chips	1.60	0.19	1.67	0.88	0.32	0.85	1.96	0.13	-0.01	1.02	0.30	0.21
photovoltaics							1.97	0.14	0.13	1.02	0.30	0.24
nuclear							1.96	0.13	-0.12	1.02	0.30	0.18
wind power							1.96	0.13	-0.11	1.02	0.30	0.18
hydro power							1.96	0.12	-0.14	1.02	0.29	0.17

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