Supplementary Information (SI) for Energy & Environmental Science.

Supporting Information

Closing the Carbon Cycle: Challenges and Opportunities of CO_2 Electrolyser Designs in Light of Cross-Industrial CO_2 Source-Sink Matching in the European Landscape

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I. Search Term strategy

Table S1 Search terms used for the employed SciFinder investigation in this work.

Level	**1**	**2**	**3**
Terms	**Scope**	**Process**	***Products***
Alternatives	CO2 Carbon Dioxide	Electroreduction Electrochemical reduction Electrolysis Electrocatalytic reduction Power to X P2X Electrocatalysis Electrochemical conversion	*Formate* *formic acid* *HCOO** *CO* *Carbon monoxide* *Syngas* *Synthesis gas* *Ethanol* C_2H_5OH *Ethylene* C_2H4 *Methane* CH_4 *Ethane* C_2H_6 *Formaldehyde* CH_2O *Methanal* CH_2O *Methanol* CH_3OH

II. References Analysis

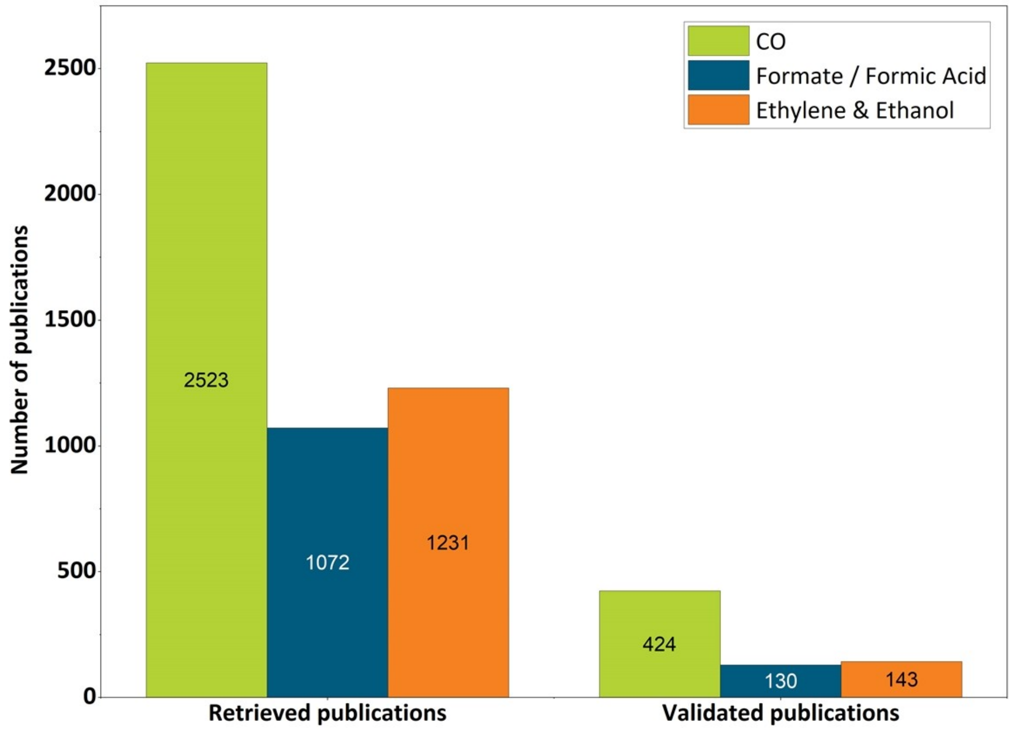

Fig. S1 : Comparison between the numbers of retrieved publications through the search term analysis and the final number of publications containing all the targeted KPIs

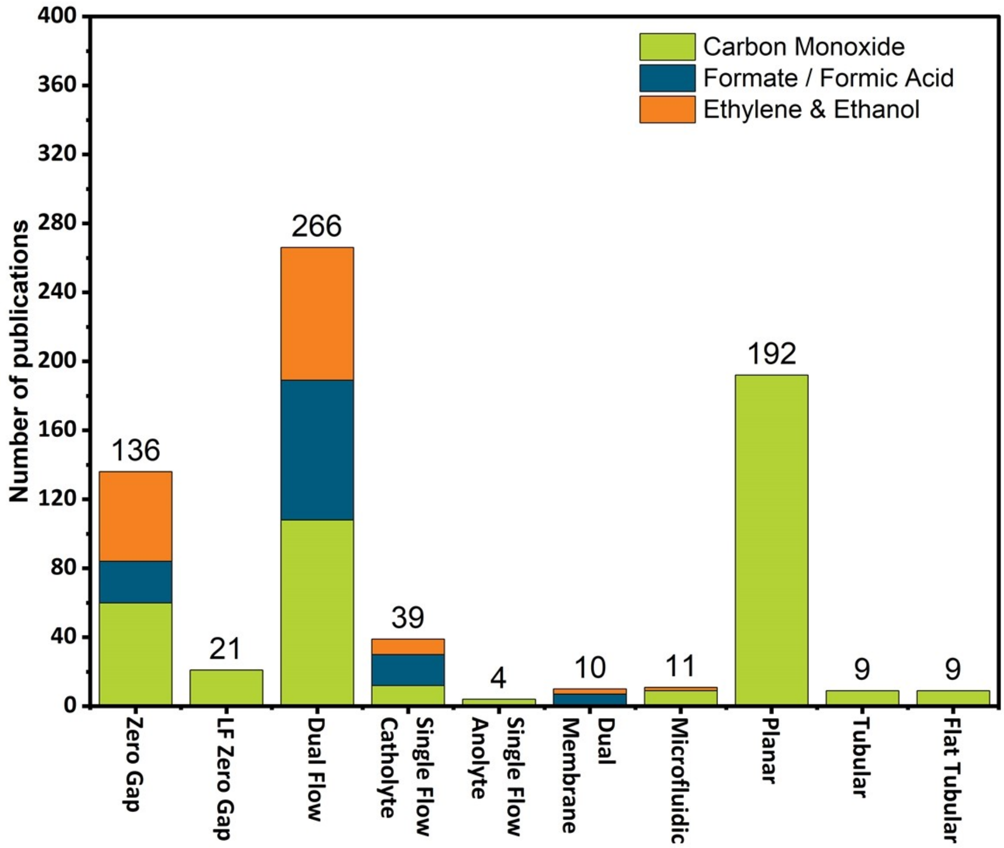

Fig. S2 Segmented analysis of the number of publications featuring an investigated reactor type (both for the low and high temperature CO_2 electrolysis) for the different CO_2R products

III. Source and CO2 emissions analysis

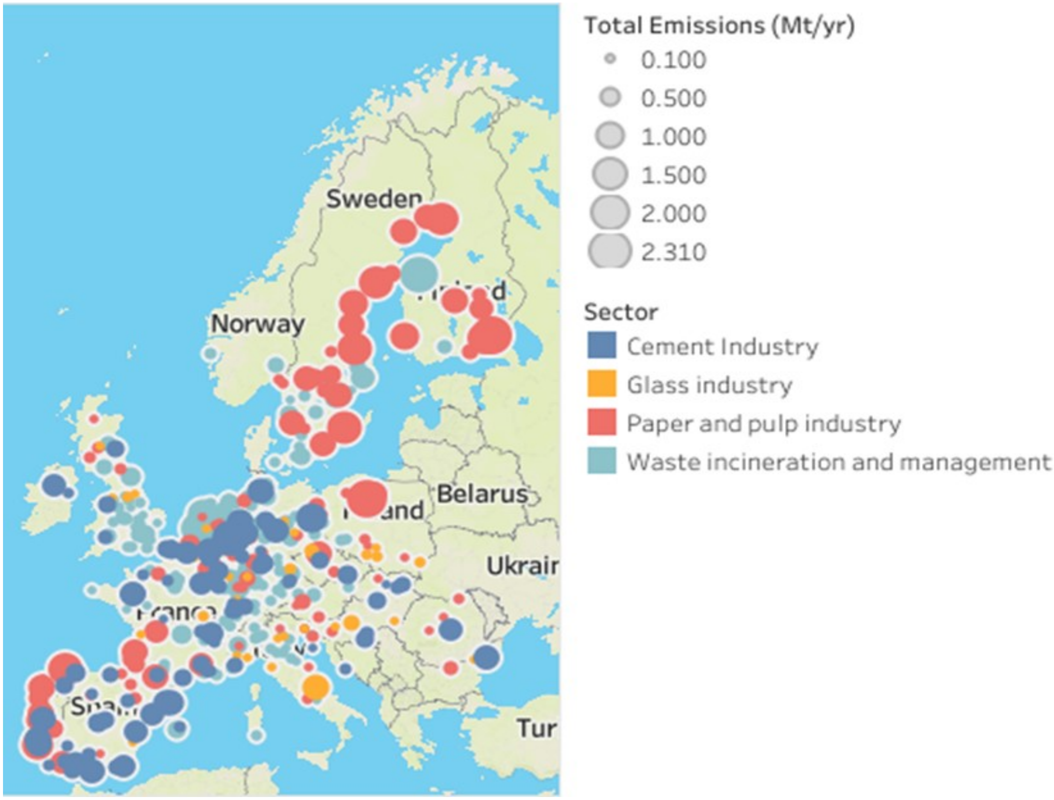

Fig. S3 Source and CO_2 emission analysis in Europe from the four different industries that were analysed in this work. Data from: European Pollutant Release and Transfer Register (EPRTR) – Dataset 2017 Data from: European Pollutant Release and Transfer Register (EPRTR) – Dataset 2017

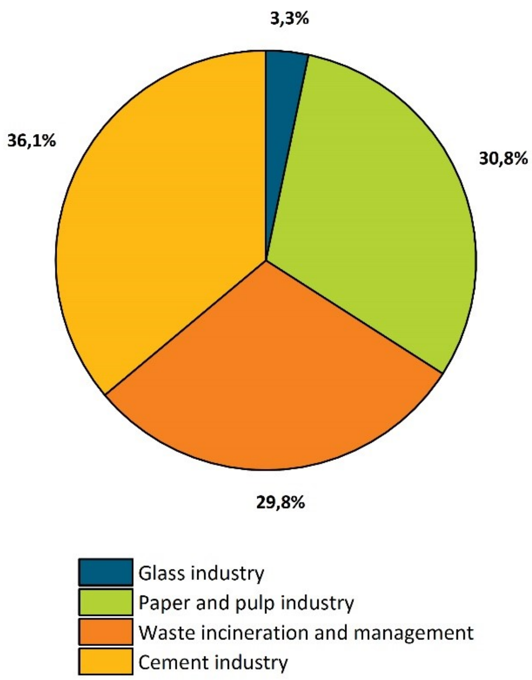

Fig. S4 Distribution of unavoidable CO_2 emissions of the four industrial sectors investigated in this work

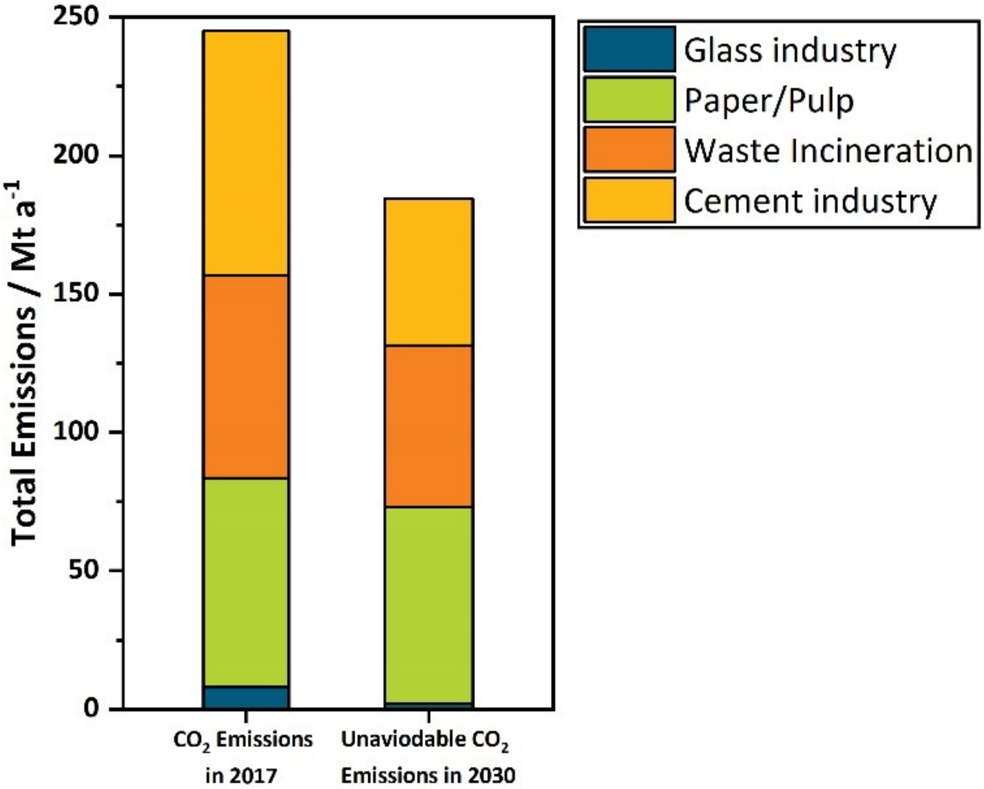

Fig. S5 Distribution of CO_2 emissions in 2017 and 2030 per industrial sector

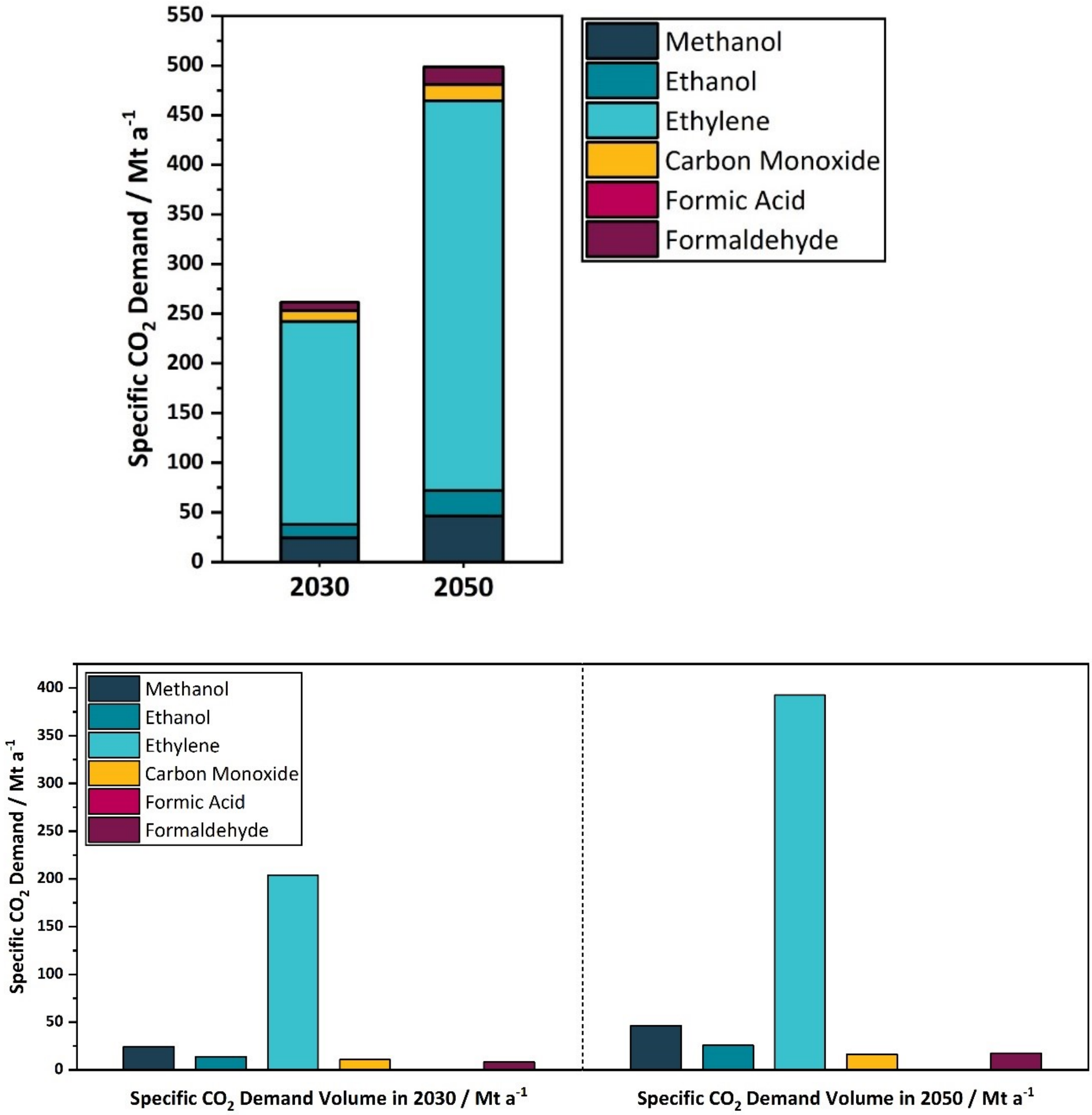

Fig. S6 Cumulative and specified CO2 demand for different carbon products in 2030 and 2050.

IV. High Temperature CO_2 Electrolysis to CO

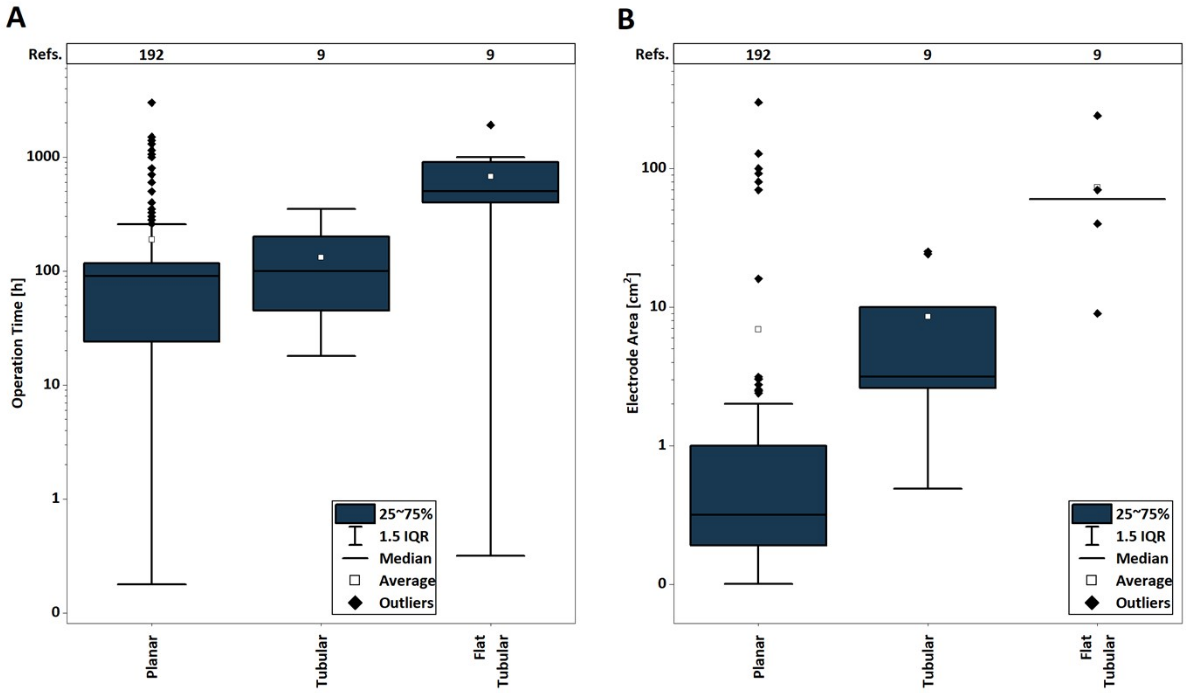

Fig. S7 Electrolysis experiment durations (A) and electrode active area (B) of high temperature CO_2 electrolysis to CO through various reactor technologies, reported by 210 references.

V. Low Temperature CO_2 Electrolysis to CO

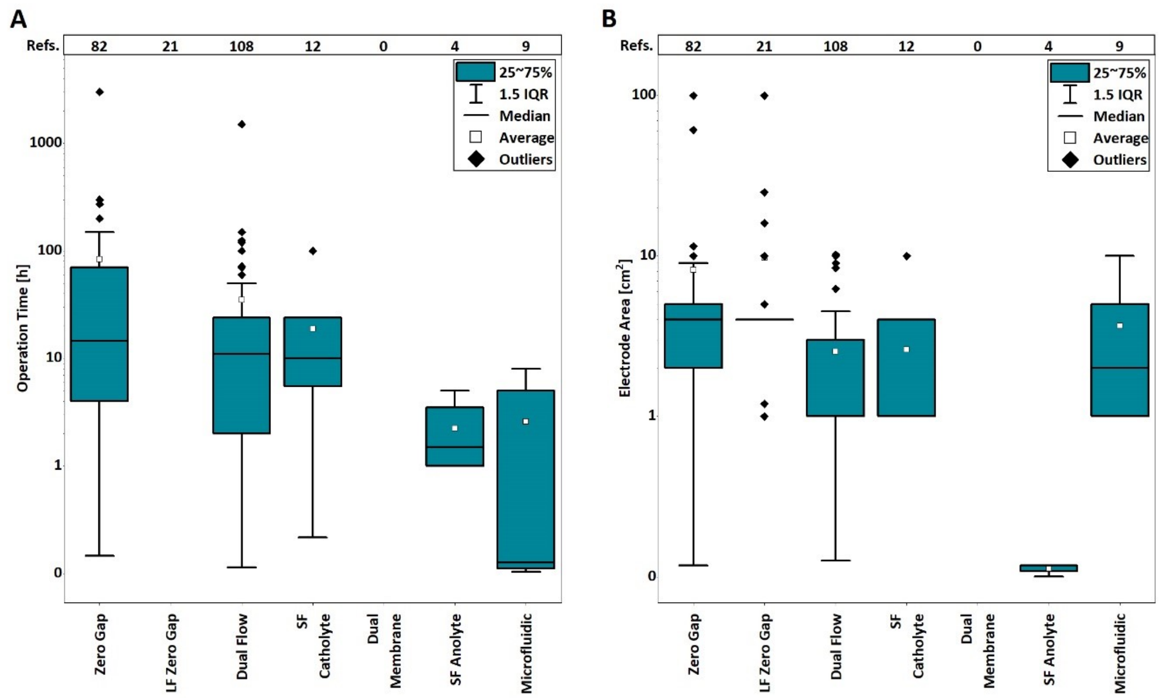

Fig. S8 Electrolysis experiment durations (A) and electrode active area (B) of low temperature CO_2 electrolysis to CO through various reactor technologies, reported by 249 references.

VI. CO_2 Electrolysis to Formic Acid / Formate

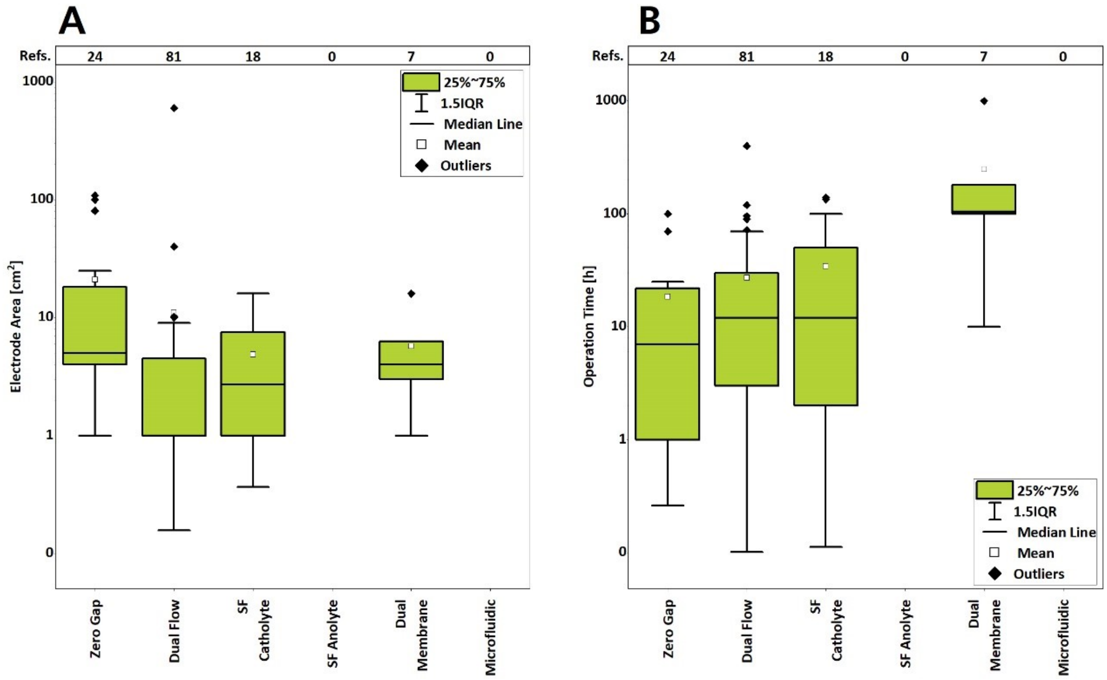

Fig. S9 Electrolysis experiment durations (A) and electrode active area (B) of low temperature CO_2 electrolysis to formate/formic acid through various reactor technologies, reported by 130 references.

VII. CO_2 Electrolysis to Ethylene & Alcohols

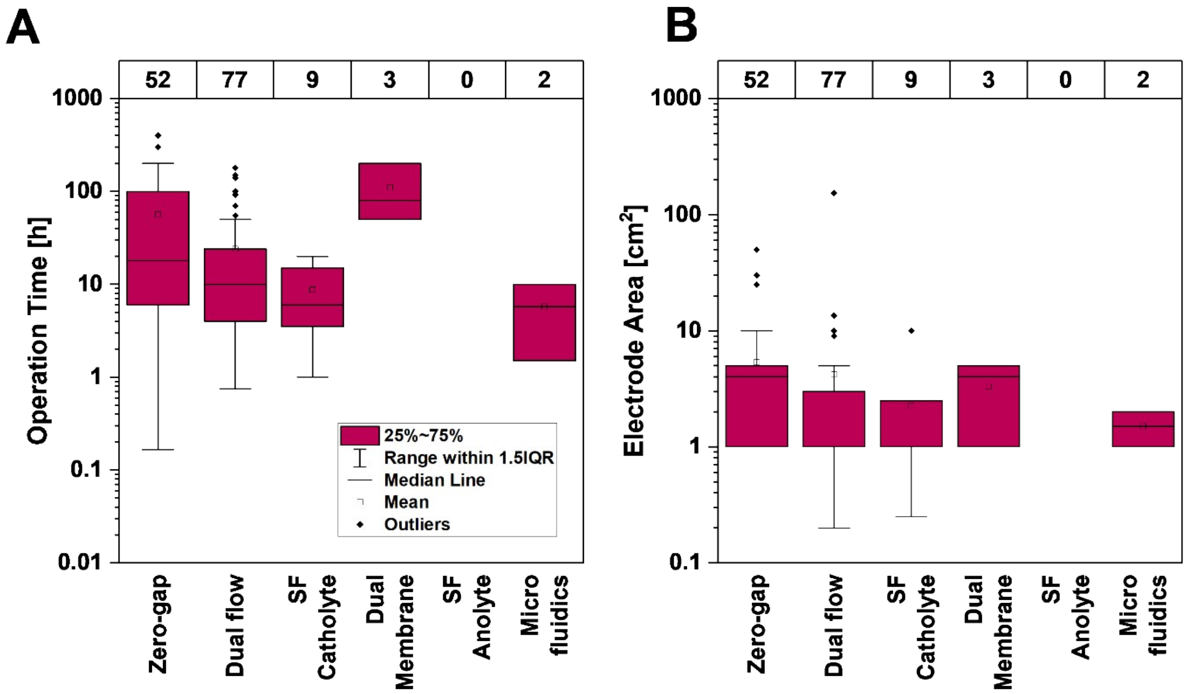

Fig. S10 Statistics of experiment durations (A) and electrode active areas (B) of low temperature electrolysis of CO_2 to ethylene and ethanol using different reactor technologies, reported by 143 references.

VIII. CO_2 to CO technologies (Supplementary Note 1)

Table S2 Summarizing table of the strong and weak point of each technology (HT and LT) for the conversion of CO_2

Aspect	**High-Temperature (HT) CO_2 Electrolyzers**	**Low-Temperature (LT) CO_2 Electrolyzers**
Operating Temperature	500–1000°C	Room temperature to ~80°C
Performance	- High reaction kinetics and faster CO_2 conversion rates. - High efficiency for CO and syngas production.	- High selectivity for liquid products like alcohols. - Moderate reaction rates.
Materials	- Requires ceramic-based materials (e.g., solid oxide cells) that can withstand high temperatures. - Material degradation due to thermal cycling is a concern.	- Use of polymer or aqueous electrolytes. - Corrosion-resistant metals and cost-effective catalysts can be employed.
Catalyst Requirements	- Ni-based catalysts for CO2 splitting are robust but require high stability under thermal stress.	- Ag,Cu-based and molecular catalysts for gaseous and liquid products. - Catalyst poisoning (e.g., by impurities, oxygen) can be an issue. -Ir is currently necessary in the

		anode.
Energy Efficiency	- High thermodynamic efficiency due to thermal energy integration with electrical energy. - Less overpotential required for reactions.	- Lower energy efficiency due to higher overpotentials and ohmic losses. - Energy cost increases with product concentration.
Product Spectrum	- Primarily CO and syngas ($CO+H_2$), which are precursors for fuels and chemicals.	- Flexible product range including CO, hydrocarbons and alcohols. - High selectivity possible for specific products.
Durability	- Ceramic components are stable over long-term operation, but sensitive to thermal cycling and redox cycling.	- Membrane durability is moderate but can degrade over time, especially in highly acidic or alkaline conditions.
Scalability	- Limited by high-temperature reactor designs and thermal management requirements. - Suitable for centralized, large-scale facilities.	- Highly scalable for distributed and modular systems. - Easier to integrate with renewable energy sources.
Startup/Shutdown	- Long startup and cooldown times. - Not suitable for intermittent operation.	- Rapid startup and shutdown. - Well-suited for intermittent operation with renewables.
CO_2 Utilization Efficiency	- High conversion rates, but product diversity limited to CO and Syngas	- Moderate conversion rates with potential for diverse and value-added products.
Cost	- High capital cost due to materials, reactor design, and thermal energy requirements. - Maintenance costs related to thermal stress.	- Lower capital cost compared to SOEC. - Necessary time to exchange stacks currently unclear.
Industrial Applications	- Well-suited for CO_2 conversion in industrial syngas applications (e.g., Fischer-Tropsch synthesis).	- More ideal for producing alcohols and other organics for decentralized applications.
Challenges	- Thermal management and material durability under extreme conditions. - Integration with renewable energy sources is complex.	- Catalyst development for high selectivity and durability. - Mitigating mass transport limitations in zero-gap designs.

IX. Methodology for the carbon source-sink matching (Supplementary Note 2)

A. General remarks

Unavoidable CO_2 Emissions

- CO_2 emitters have been selected based on processes, which cannot be eliminated due to an inherent CO_2 emission from the process chemistry (Cement, Glass) or lack of alternative technologies (Paper/Pulp, Waste incineration)
- Two scenarios are deduced from data:
  1. **Business as usual based on the current market size / emission data and expected market growth rates**
  2. **Progressive Scenario, where the CO_2 emissions per unit produced is reduced over time based on individual factors; market growth rates are similar**
- The CO_2 emissions in the manuscript are given with a capture (87 %) and utilization factor (70 %) as presented in [1][1]; Data in the following tables are quoting the total CO2 emissions excluding the capture and utilization factor

CO_2R Product Demand

- Product scope based on technical analysis
- Data for the products based on market reports with the scope Europe (only ethylene is scoped to EU due to data availability)
- The growth is according to market studies with a typical scope of ~ 5-10 yrs and extrapolated to 2050
- Two scenarios are deduced:
  1. **Data extrapolated as is → higher boundary**
  2. **Compensation of certain product value chains, which interfere with each other (i.e., MtO synthesis of ethylene) → Lower boundary**
- CO_2 Demands are calculated from the specific kg CO_2 need per kg of product and the product demand from market studies

B. Unavoidable CO_2 sources and sinks in Europe

Cement industry

- Cement production in 2021 from a market study for Europe and is extrapolated with a CAGR of 1.9% [2]
- CO2 emissions are estimated based on an IEA study (0.6 t_{CO2}/t_{Cement}) [3]
- Progressive scenario is based on a linear weighting factor for the prior "business as usual" and an ideal case assuming complete reduction any non-raw material (limestone) connected from cement production (60 % from current CO2 emissions are from raw materials) [4]

Glass Industry

- Base case for CO_2 emissions is from 2017 based on Europe [5]
- Growth rate based on European flat glass market study (CAGR: 3.0%) [6]
- Progressive scenario is based on a linear weighting factor for the prior "business as usual" and an ideal case assuming a total reduction of 75 % (25% remaining) from today's CO_2 emissions [7]

Paper/Pulp Industry

- Base case for CO_2 emissions is from 2017 based on Europe [8]
- Growth rate based on market history from CEPI (European Paper/Pulp Association) (CAGR: 0.8%) [9]
- Progressive scenario is based on a linear weighting factor for the prior "business as usual" and an ideal case assuming a total reduction of 63 % (37 % remaining) from today's CO_2 emissions [10]

Waste Incineration

- CO_2 emissions based on waste/capital [10], UN population development prediction [11] for Europe and the balance of Energy and CO_2 emissions per ton of waste [1]
- "Business as usual" scenario assumes a recycling factor of 48 %; an ideal 73% [12]
- Progressive scenario is based on a linear weighting factor for the prior "business as usual" and the ideal case

C. CO_2 source/sink matching-Chemical demand

Carbon monoxide

- Global market volume for in USD for 2022 and projected market growth of 4.4 % CAGR [13]
- Conversion into global CO tonnage demand with the market price of CO [14] (CO price (adj. by 1.5 % inflation/year) and Europe market share)
- Market share of Europe based on the market share of European chemical industry on the global market (20 %)

Formic Acid

- Global formic acid demand is known for 2021 from [15] along with the CAGR (4.45 %) for market development based on a forecast until 2035
- The European share of the formic acid market is reported to be 21% of the global market. [16]

Ethylene

- European Ethylene market demand and projected growth rates are relatively precisely projected until 2030 [17]
- For further projection, the CAGR was averaged for the data from 2023-2030 → -1.38 %
- Projection to 2050 based on the average CAGR

Methanol

- European market development in Mt/a is projected until 2030 [18]
- Methanol market includes the production of ethylene and formaldehyde based on [19]. 10.16-12.92 % of global methanol is used for ethylene production via MtO (28.79 %) and 24.01 % is used for formaldehyde production.
- The ratio for Ethylene from MtO was derived from [20] these were subtracted from the total market demand for Methanol

Ethanol

- EU Ethanol market demand and projected growth rates are relatively precisely projected until 2030 [21]
- CAGR data on Europe level was not available, but total market size & market prize (=ethanol demand) are known from [22]
- For further projection, the CAGR was averaged for the data (EU) from 2023-2030 → +1.35 %
- Projection to 2050 based on the average CAGR on the Europe demand

Formaldehyde

- Global formaldehyde demand is known for 2021 from [23] along with the CAGR (3.39%) for market development based on a forecast until 2035
- The European share of the formaldehyde market is reported to be 14% of the global market in 2020. [24]

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