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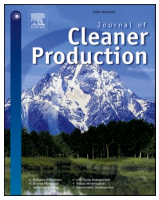

Sustainability assessment of plasma-based and electrolytic CO_2 conversion to CO

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ABSTRACT

Decarbonization technologies play a crucial role in addressing the global challenge of climate change by reducing the concentration of greenhouse gases, particularly carbon dioxide (CO_2), in the atmosphere. Electrolysis- and plasma-based technologies have emerged as alternatives to partial combustion of fossil fuels for carbon monoxide (CO) production. A holistic sustainability assessment is required for decision-making from an environmental perspective from the early design. In this paper, Green Chemistry and circularity metrics together with life cycle assessment are used to identify hotspots and opportunities for both plasma-based and electrolytic CO_2 conversion into CO, as compared with conventional procedures, such as incomplete fossil fuel combustion. In terms of environmental impacts, plasma- and electrolysis-based CO production exhibit reductions in 7 over 10 environmental impact categories when compared with the equivalent conventional process of partial combustion of fossil fuels, while electrolytic improvements are more modest. Particularly significant are the benefits in terms of acidification, freshwater ecotoxicity, and the use of fossil resources, with 86, 91, and 83 % impact reductions respectively for plasma, while 85, 87 and 77 % are the respective impact reductions for electrolysis. Sustainability metrics indicate a 40 % energy savings in plasma-based production compared to electrolysis. The essential recycling loop operation of unreacted CO_2 increases the process circularity to material circularity indicator (MCI) values above 0.8, with the plasma process exhibiting 10 % higher MCI than electrolysis, in contrast to the partial combustion of fossil fuels, which is linear and non-restorative. In terms of Green Chemistry metrics, plasma-based CO production outperforms globally the electrolysis metrics by around 10–30 %.

1. Introduction

The global imperative to address climate change has intensified the pursuit of innovative solutions to reduce carbon emissions and mitigate the impact of human activities on the environment. Carbon dioxide (CO_2) is a major contributor to global warming, mainly released into the atmosphere by human activities, such as burning fossil fuels and deforestation, contributing significantly to climate change, human health and global economy. Scientific organizations, including the Intergovernmental Panel on Climate Change (IPCC), consistently emphasize the link between human activities and the observed changes in the Earth's climate, leading to rising global temperatures and causing more frequent and severe heatwaves, changes in precipitation patterns, rising sea levels, and disruptions to ecosystems (IPCC, 2023). Given the net-zero target by 2050, it is required a global CO_2 uptake in the range of 52 Gt per year is required. One part of the potential CO_2-based products market is related to solid materials for construction, biochar, enhanced oil recovery and C_{2+} chemical products. The need for a real decarbonization opens the door for the development of innovative methods to capture and/or convert CO_2 into useful products, as effective CO_2 conversion can lead to the production of fuels, chemicals, and materials, offering both environmental and economic benefits.

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Emerging decarbonization technologies based on CO_2 capture, utilization and storage (CCUS) have become pivotal in reducing emissions. Technologies include (i) direct air capture, which involves capturing CO_2 directly from the air using specialized sorbents or solvents to absorb CO_2 and then releasing it for storage (IEA, 2022a); (ii) biological CO_2 conversion by using genetically engineered biological systems, such as bacteria or algae, to capture and convert CO_2 (Nisar et al., 2021); or (iii) chemical looping combustion encompassing the combustion of fossil fuels in a way that allows for the separate capture of CO_2 without the need for energy-intensive separation processes (Czakiert et al., 2022). All these technologies promote CO_2 capture and further storage, with the payback of secondary waste generation, insufficient productive capacities, questionable economic viability at high scales, and high energy demands. Regarding direct air capture, a main challenge is the high energy requirement for capturing CO_2 from the atmosphere due to its low concentration. This can reduce the economic competitiveness, of which the adverse effect, however, can be mildened by the use of renewable energy. The effect on the process itself is low efficiency, as large volumes of air are needed to be processed per ton of CO_2, which further drives up energy consumption. A second main challenge are the high costs of air capture technology, often ranging from $100 to $600 per ton of CO_2 captured, making large-scale operation economically unfeasible (IEA, 2022b). Infrastructure requirements are also very high, needing significant land and resources which can be a constraint in densely populated or ecologically sensitive areas. Biological CO_2 conversion has a main challenge regarding the commonly low efficiency of carbon fixation in natural organisms, which limits the conversion of CO_2 into biomass. Also, the metabolic pathways involved in CO_2 conversion are highly sensitive to environmental conditions, e.g. light intensity, temperature, and nutrient availability, hampering constant and reliable performance. Large-scale cultivation of microorganisms requires substantial land, water, and nutrient resources, which can compete with agricultural needs and raise sustainability concerns. Genetic engineering to enhance CO_2 conversion efficiency presents potential biosafety and ethical issues, as modified organisms may have unforeseen ecological impacts if released into the environment (Nisar et al., 2021). Finally, the economic viability of biological CO_2 conversion technologies is currently limited by high operational costs and the need for further advancements in bioprocessing techniques to increase yield and reduce production expenses. A main challenge of chemical looping combustion is the development and stability of oxygen carriers, which must maintain high reactivity and structural integrity over numerous cycles. The separation and handling of solid particles add complexity to the operation and maintenance of the system (Czakiert et al., 2022).

Other methodologies allow the consumption of CO_2 to produce e.g. carbon monoxide (CO) through endothermic processes (Chen et al., 2018; Kumaravel et al., 2020; Snoeckx and Bogaerts, 2017a). Conventionally, CO is obtained on industrial scale by incomplete combustion of hydrocarbons at temperatures in the range of 1500–1800 K and pressures of 3–8 MPa. Such process is highly dependent on the availability of fossil fuels, as well as highly energy demanding, which both make the process environmentally unsustainable, and unfeasible in a near future (Bierhals, 2001). The possibility to produce CO directly from CO_2, reducing the overall carbon footprint, as well as the dependence of fossil fuels, is enabled by technologies such as electrolysis (Küngas, 2020; Zheng et al., 2017) or more recently plasma (Snoeckx and Bogaerts, 2017a), combined with the use of renewable energy sources. The additional syngas (a mixture of CO and hydrogen) produced in electrolysis, or in plasma *via* dry reforming of methane (Cleiren et al., 2017; Wanten et al., 2022), might be used in fuel production *via* the Fischer-Tropsch process (van de Loosdrecht et al., 2013). Renewable energy sources offer significant advantages for CO_2 conversion technologies, especially in improving water quality while reducing toxicity. On the flip side, potential contamination from the materials used in renewable energy systems can create pollution, e.g. heavy metals from solar panels and batteries, leaching into water supplies (Choubey et al., 2012). As an example, the manufacturing of electronic devices such as inverters and regulators used in photovoltaic and wind generators, as well as those in electric networks, can lead to the release of heavy metals, including copper, into the environment (Dobaradaran et al., 2010). These heavy metals can leach into water bodies, causing significant toxicity to aquatic ecosystems.

The use of renewable energy sources such as solar or wind power for high energy demanding processes such as CO_2 conversion, significantly reduces the emission of harmful pollutants, including nitrogen oxides (NO_x) and sulfur oxides (SO_x), which are common by-products of fossil fuel-based energy production. These pollutants are known to contribute to acid rain, which can severely degrade water quality in rivers, lakes, and oceans (Chen et al., 2023). Additionally, renewable energy-driven CO_2 conversion technologies produce fewer toxic by-products, minimizing the risk of contaminating water sources with hazardous chemicals (Hu and Liu, 2010). The absence of heavy metals and other toxic compounds in the effluents of renewable energy processes further ensures the safety and health of aquatic ecosystems (Siekierka et al., 2023). Moreover, the reduced reliance on fossil fuels diminishes the likelihood of oil spills and other related disasters, which have devastating effects on water quality and marine life (Zhai et al., 2021).

Such direct decarbonization technologies require holistic sustainability tools for decision-making, for a quantitative perspective (Hessel et al., 2021). A holistic sustainability assessment of a process encompasses Green Chemistry metrics, circularity assessment, and life cycle assessment (LCA) (Hessel et al., 2021). While Green Chemistry metrics strongly emphasize on design and process development (gate-to-gate), providing efficiency performance indicators and valuable insights into the environmental and resource efficiency of a chemical process, circularity assessment focuses on the promotion of resource efficiency through raw materials recycling and waste reduction (cradle-to-cradle). In between, LCA evaluates the environmental impacts of products and processes throughout their entire life cycle, from raw material extraction to end-of-life disposal (cradle-to-grave). These tools allow the identification of environmental hotspots, including challenges and opportunities, defining implementation pathways. Whilst environmental studies on this topic are limited to midpoint metrics, such as carbon footprint, holistic sustainability implications have been relatively unexplored. Their integration within a holistic sustainability assessment framework provides a more comprehensive understanding of complex interactions. The sustainability of CO production is additionally a critical consideration, due to the significant environmental and health impacts associated with this gas, as well as the decarbonization potential derived from CO_2 consumption. In this paper, sustainability is addressed holistically through quantification metrics for both plasma-based and electrolytic CO_2 conversion into CO, using (i) Green Chemistry metrics (improving the existing linear production), (ii) circularity metrics (quantifying the recycling and reuse of mass flows of each compound) and (iii) LCA (as a quantification of environmental impacts). Benchmarking against conventional partial combustion of fossil fuels for CO production serves as a valuable learning tool, providing insights that can guide the development and implementation of new processes, to ensure their success and competitiveness in the market (Osorio-Tejada et al., 2024). Therefore, we analyse the future of CO production via plasma- and electrolysis-based technologies toward industrial implementation through sustainability assessments as alternative to partial combustion of fossil fuels.

Only a few environmental assessments are reported for gas conversion applications in plasma. Specific for plasma-based CO production (Pou et al., 2022), compared the compensated CO_2 emissions and found that photovoltaic panels are much more beneficial than conventional electricity from the Spanish grid. While switching from fossil fuels to electricity can reduce greenhouse gas emissions of the process, these limited analyses can omit other negative environmental impacts that can arise from the use of electricity. Impacts could increase on water quality when electricity is mainly generated from coal or lignite, or on

terrestrial or human toxicity when solar photovoltaic systems are used due to copper, silver, and other metal particles released during the equipment manufacturing (Osorio-Tejada et al., 2022b). Other applications, such as ammonia production with a decentralized plasma process, have been investigated, obtaining significant CO_2 reductions thanks to the avoided transport impact, and the best performance was obtained with a non-thermal plasma reactor using solar energy (Osorio-Tejada et al., 2022b, 2022c; King et al., 2021) studied H_2 production with a dielectric barrier discharge plasma steam reforming reactor. They found moderate environmental benefits, but only when using green electricity produced from wind (Delikonstantis et al., 2020). investigated various process models for ethylene production with plasma and optimised the process for the lowest carbon footprint. For the treatment of exhaust gas (*i.e.*, removing NO_x, SO_x, and volatile organic compounds (VOCs)) (Stasiulaitiene et al., 2016), found that the relatively high electricity demand is detrimental, but plasma technology is still more environment-friendly than conventional treatments thanks to lower process waste. Another application is plasma gasification for energy-from-waste recovery, where plasma technology has clear environmental benefits compared to landfilling and incineration (Ramos and Rouboa, 2022; Sanjaya and Abbas, 2023). These various applications demonstrate the potential of plasma technology as a sustainable alternative to conventional processes.

Whilst CO_2 electrolysers to produce CO have been widely studied, LCA studies of electrochemical CO_2 conversion are scarce and usually focussed on the production of specific compounds, such as fuels (Kibria-Nabil et al., 2021). In other cases, the studies are limited to the CO_2 conversion process only, rather than including the subsequent separation process. Systematic studies comparing electrochemical routes to new technologies such as plasma to assess advantages and disadvantages of each technology are, to the best of our knowledge, unprecedent. The present study aims to bridge this knowledge gap by performing a systematic and comparative assessment of these two CO_2 conversion routes, with great potential for electrification of process industry, to circumvent unsustainable and highly fossil-fuel dependent technologies such as the traditional partial combustion of fossil fuels.

For the reasons stated, it becomes essential to comprehensively address the complexity of varying specific parameters in CO_2 conversion. This requires understanding of how changes in one parameter can affect the others. Moreover, the values defined for the base derive from literature studies which report metrics for all required parameters. Relying on such studies helps avoid assumptions that could compromise the reliability of the results. In essence, our study aims to perform an exhaustive sustainability assessment for both plasma- and electrolysis-based CO production, utilising actual own data and individual studies developed under given experimental conditions. This approach sets itself apart from existing literature, which often relies on mixed data sets and overlooks the mutual relationship between the various operating parameters of the evaluated technologies.

2. Methods

2.1. Process definition

For the definition of the process parameters, we have analysed the various studies on plasma- and electrolysis-based CO production that report all the necessary parameters to conduct a comprehensive LCA, and we summarise them in Table 1. We present in this table only the parameter values for experiments using pure CO_2 feed, *i.e.*, not mixed with N_2, and operating under atmospheric pressure conditions.

Despite research on CO_2 conversion in plasma reactors and electrolysers has gained attention over the last decade (Snoeckx and Bogaerts, 2017a; Somoza-Tornos et al., 2021; Vertongen and Bogaerts, 2023), much of this research has focused on reactor improvements, catalyst development and reaction kinetics, with less emphasis on process design (De Mot et al., 2019). For both plasma- and electrolysis-based CO_2

Table 1
Operating parameters for various plasma and electrolysis types for CO_2 conversion.

Plasma-based CO production						
Authors	Type of plasma reactor	CO_2 feed rate (L/min)	CO_2 conversion (% CO_2)	Plasma power (W)	Energy efficiency (%)	Specific energy input (kJ/L)
Vertongen and Bogaerts (2023)	Gliding arc plasma	10	9.65	835	29	3.85
Girard-Sahun et al. (2022)	Gliding arc plasma	10	7.6	530	27.9	3.2
(Girard-Sahun et al., 2022)[a]	Gliding arc plasma + C-bed	10	12.6	530	45.4	3.2
Ramakers et al. (2017)	Gliding arc plasma	10	8.6	600	30	3.6
Uytdenhouwen et al. (2019)	μ- dielectric barrier discharge	0.0015	70	30	0.74	1200
Ozkan et al. (2017)	Dielectric barrier discharge	0.2	26	50	20	15
Mitsingas et al. (2016)	Microwave plasma	4	6	150	50	2.25
Electrolysis-based CO production						
Authors	Type of electrolyser	CO_2 feed rate (L/min)	CO_2 conversion (% CO_2)	Cell voltage (V)	Current density (mA/cm^2)	Faradaic efficiency (%)
(Endrődi et al., 2019)[b]	Zero gap	1.000	25	3.0	250	85
Jeanty et al. (2018)	Three compartment[e]	0.200	23	6.0	150	53
(Endrődi et al., 2021)[c]	Zero gap	0.100	23	3.2	420	90
Lee et al. (2021)	Membrane electrode assembly	0.075	64	2.2	223	93
(Endrődi et al., 2020)[d]	Zero gap	0.025	29	3.4	700	90
Bhargava et al. (2020)	Flow cell	0.017	36	3.0	866	98
Kim et al. (2015)	Flow cell	0.007	5	3.0	51	83

Notes: (a) Results after embedding a carbon bed; (b) Zero-gap type electrolyser with a multi-stack configuration with 3 cells in series; (c) To obtain these results using pure water as anolyte, the cathode needs to be activated by periodically infusing the cathode with different alkali cation-containing solutions; (d) The current density starts near 1000 mA/cm^2, but it stabilises around 700 mA/cm^2 after 2 h of operation; (e) Three compartment gas diffusion electrode (GDE).

production, pilot-scale plants with long-term runs have not yet been reported to provide reliable estimates on material durability necessary for commercial-scale implementation (Nouri and M, 2024a; 2024b). Therefore, we do not consider the impact of materials used for the equipment manufacturing and maintenance or stack replacement.

Additionally, the reported power in CO_2 conversion typically relates only to the energy required for the plasma or the electrolysis cell—not to the total energy drawn from the electric plug, accounting for the energy efficiency of the power supply unit, which should in fact also be taken into account (Tsonev et al., 2023). We assume this plug-to-power efficiency to be around 80 % as typically considered for power units. Another parameter that is hardly reported in electrolysis-based CO production is CO_2 conversion. In electrolysis, energy consumption is calculated based on cell voltage and current density, the latter being defined by the quantity of CO produced per hour and the Faradaic efficiency. For this reason, despite the numerous publications on electrolysis-based CO production, only a few (reporting CO_2 conversion) could be included in Table 1.

The processes are scaled to a production capacity of 100 tonnes CO d^{-1}, as this is the typical demand evaluated in previous analysis for alternative CO production (De Luna et al., 2019; Jouny et al., 2019).

2.1.1. Plasma-based CO production

The reaction parameters for the plasma-based CO production process are adopted from previous results obtained in our group (Vertongen and Bogaerts, 2023), detailed in the first row of Table 1, and outlined in Fig. 1. The reverse vortex flow enhances CO_2 conversion by mixing the hot plasma core and surrounding cooler gas, and the latter also limits the heat losses to the walls.

While the initial gas flow rate is set to 10 L min^{-1}, scaling-up to higher flow rates can be achieved by numbering-up, as demonstrated already for this gliding arc plasmatron (O'Modhrain et al., 2024). Although upscaling plasma reactors must meet technical challenges, such as the same mixing (mass transfer) and heat transfer (Escribà-Gelonch et al., 2019), internal numbering up suits better, as small-sized reactors are required to obtain high CO_2 conversion, like flow chemistry accesses unusual, highly productive process regions, coined 'novel process windows (NPW)' (Hessel, 2009; Hessel et al., 2013).

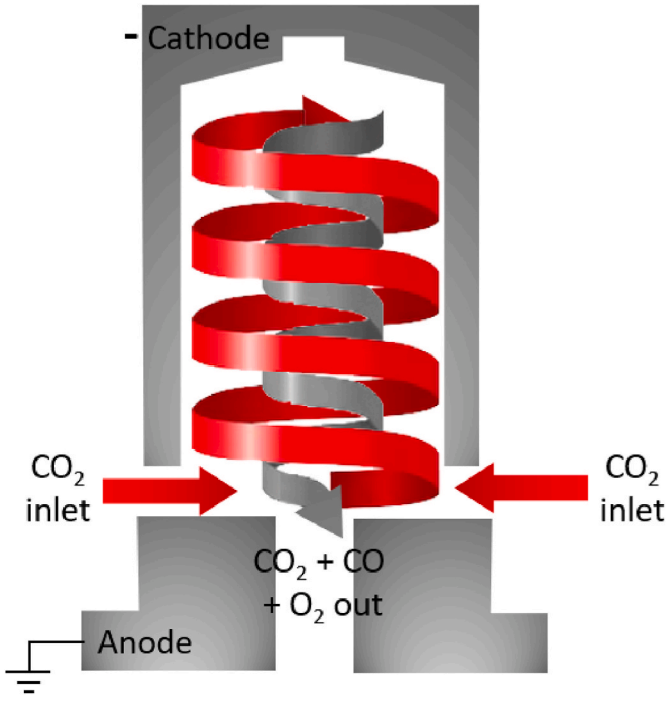

Fig. 1. Basic gliding arc plasmatron reactor. The red arrows indicate the gas flow inlet. The up- and downward vortex of the gas are in red and grey, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

As the reaction is uncomplete, the plasma reactor outlet stream leads to a mixture of unconverted CO_2, besides the produced CO and O_2, i.e., for our case (first row in Table 1): CO_2 (90.35 % wt), CO (6.14 % wt), and O_2 (3.51 % wt). The subsequent gas separation to obtain CO and recycle CO_2 is performed using a two-step process, see Fig. 2. First, oxygen is embedded by a carbon bed, which incorporates solid carbon, i.e. charcoal or biochar, at the stream outlet as proposed by (Girard-Sahun et al., 2022). Under these conditions, embedded oxygen atoms and molecules react with the carbon, generating additional CO following either $C + O \rightarrow CO$ or $2C + O_2 \rightarrow 2CO$ pathways, preventing the recombination of O/O_2 with CO, as concluded by the PLASMANT research group. Following this procedure, the CO_2 conversion increases by 66% and the CO concentration even triples (Girard-Sahun et al., 2022). Additionally, a portion of the CO_2 feed can also react with C to produce more CO via the reverse Boudouard reaction ($CO_2 + C \rightarrow 2CO$). In this stage we assume an additional 6.37 % of CO_2 converted by either the reverse Boudouard reaction, or (mainly) by preventing the O/O_2 recombination of CO back into CO_2, based on the 66 % enhancement reported earlier by PLASMANT for the same plasma reactor (Girard-Sahun et al., 2022) on top of the original 9.65 % conversion, leading to a total CO_2 conversion of 16.02 %wt.

Overall, the mass balance is fixed by assuming a CO_2 conversion of 16 %wt. This is obtained based on the initial stream (496 t d^{-1} CO_2) and the unconverted CO_2 in the outlet (416 t d^{-1} CO_2). The experimental gas proportions after the plasma reactor are ca. 90:6:3.5 wt% (CO_2:CO:O_2) (see previous paragraph), which become 80.5:19.5 wt% (CO_2:CO) after the oxygen elimination step. Indeed, in addition to the CO_2 decomposition inside the plasma (i.e., 47.8 t d^{-1} CO_2 converted to 30.4 t d^{-1} CO), also C oxidation (again 30.4 t d^{-1} CO, because of $2C + O_2 \rightarrow 2CO$) and the reverse Boudouard reaction (31.55 t d^{-1} CO_2 converted to 40.15 t d^{-1} CO, via $CO_2 + C \rightarrow 2CO$) take place, both due to charcoal, leading to a global production of 101 t d^{-1} CO in the outlet. By adding the charcoal operation, the CO_2 conversion is increased from 10 % in the plasma reactor, up to the overall 16 %, meaning an increase of 66 %.

In our case study, the plasma reactor is fed by two streams, i.e., a new (virgin) CO_2 source (83.5 t d^{-1}), and the CO_2 recycling stream coming from previous cycles (412 t d^{-1}), Fig. 2. Once reacted, the gas mixture crosses the carbon bed, leading to oxygen consumption, obtaining overall an approx. 4:1 CO_2:CO outlet mixture (see next paragraph), which is loaded to the separator. We assume 21.6 t d^{-1} charcoal to be used for this carbon bed, Fig. 2. Besides 100 tonnes CO productivity (target for our case study as defined above), 412 t d^{-1} CO_2 are recycled, assuming 1 % gas losses as stated in a similar study (Ramdin et al., 2021), Fig. 2.

The experimental parameters, such as the power required for these conversion steps, are defined accordingly. The equivalent plasma arc power demands are 3.75 kWh kg^{-1} CO, based on experimental results, scaling the power demands of 835 W when flowing 10 L min^{-1} CO_2 to 15,615 kW when flowing 187 m^3 min^{-1} CO_2 as required for the desired CO productivity (i.e., to produce 100 t d^{-1} CO, or 4167 kg h^{-1} CO). Furthermore, 80 % plug-to-power efficiency and no energy requirements for the carbon bed stage are assumed (Girard-Sahun et al., 2022), leading to 4.69 kWh kg^{-1} CO electricity demand for the synthesis stage, which corresponds to 469 MWh d^{-1} (cf. Fig. 2, and Table 2). The output streams in the carbon bed result in unconverted CO_2 (80.5 %wt) and CO (19.5 %wt), hence explaining the 4:1 CO_2:CO outlet mixture from previous paragraph. These numbers are derived from the previously described reactions in the carbon bed, which lead to a 66% increase in CO_2 conversion. This corresponds to 416 t CO_2 d-1 and 101 t CO d-1, Fig. 2. These streams proceed to the separation stage.

Pressure swing adsorption (PSA) units are very popular in similar industrial processes involving gas mixtures, especially in electrolysis-

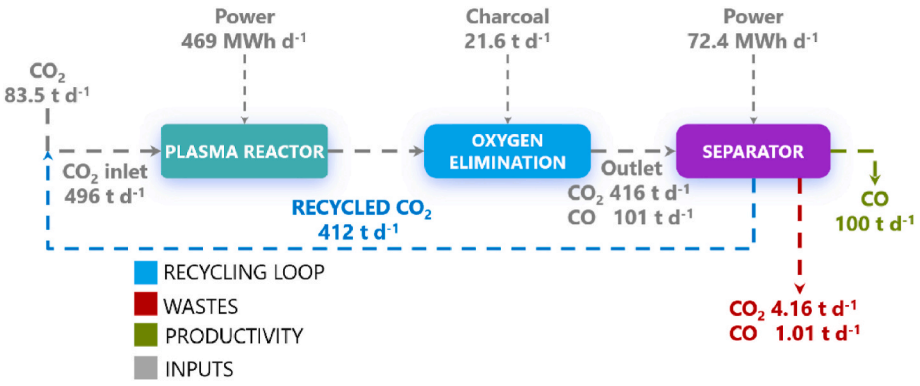

Fig. 2. Schematic flowchart for the plasma-based plant production of 100 tonnes CO per day.

Table 2
Life Cycle Inventory (LCI) for a plasma-based daily production of 100 tonnes CO, as shown in Fig. 2.The numbers are given in two different units, as both are needed for the calculations.

Inputs					Ecoinvent inputs
CO_2	0.835	kg kg^{-1} CO	83.5	T d^{-1}	CO_2 production, liquid
Power reactor	4.69	kWh kg^{-1} CO	469.0	MWh d^{-1}	Electricity production, wind, <1 MW turbine, onshore in the Netherlands
Separation	0.724	kWh kg^{-1} CO	72.4	MWh d^{-1}	
Charcoal	0.216	kg kg^{-1} CO	21.6	T d^{-1}	Charcoal [allocatable product]
CO_2 recycled flow stream	17163	kg h^{-1}	412	T d^{-1}	
Product intermediates					
CO_2	17337	kg h^{-1}	416	T d^{-1}	
CO	4209	kg h^{-1}	101	T d^{-1}	
Wastes/Released gases					
CO_2	0.0416	kg kg^{-1} CO	4.16	T d^{-1}	
CO	0.0101	kg kg^{-1} CO	1.01	T d^{-1}	

based CO_2 conversion systems, due to their high efficiency and cost-effectiveness (Ardolino et al., 2021; Greenblatt et al., 2018; Jin et al., 2021; Jouny et al., 2018; Kibria et al., 2019; Kibria-Nabil et al., 2021; Yue et al., 2022). This procedure was used in both the electrolysis and plasma process, to keep the downstream process the same and strictly compare the effect of the CO_2 conversion process. According to (Paturska et al., 2015), the energy consumption for this step was estimated to be 0.23 kWh m^{-3}, as also described in other processes where PSA systems were involved (Jouny et al., 2018, 2019; Kibria et al., 2019; Kibria-Nabil et al., 2021; Yue et al., 2022), which corresponds to 72.4 MWh d-1 (cf. Fig. 2) when considering an inlet flow rate of 517 t d-1 (or 13,114 m^3 h-1) at PSA (considering 1.84 and 1.14 kg m-3 as CO_2 and CO densities, respectively). As a key point in terms of sustainability, once separated, the CO_2 is recycled back into the reactor feed, reducing the gas emissions and consequently the carbon footprint, as only 1 % of all products are lost during the separation according to a similar study (Ramdin et al., 2021); see red numbers (wastes) in Fig. 2.

2.1.2. *Electrolysis-based CO production*

Regarding the electrolysis-based process, the closest values to plasma process operating conditions were selected, *i.e.* intrinsic parameters obtained in the study performed at 1 L min^{-1} by (Endrődi et al., 2019), in order to make a 1-on-1 comparison with the plasma process, and because this is one of the few papers in literature providing proper data for performing the essential calculations for this assessment. The capacity of electrolytic CO production is also scaled to 100 tonnes CO d^{-1} to allow fully comparable dimensions, by numbering up the electrolysers, Fig. 3. The process requires accordingly a feed of 6813 kg CO_2 h^{-1}, which corresponds to 634.5 t d^{-1}, of which 163.5 t d^{-1} is the new (virgin) CO_2 source, and 471 t d^{-1} is recycled, Fig. 3. The CO_2 conversion is not affected by the higher scale, hence, we assume a single-pass conversion (SPC) of CO_2 of 25 % (cf. Table 1), leading to 476 t d^{-1} CO_2 after the electrolyser, as well as 101 d^{-1} CO, 1.27 t d^{-1} H_2 and 40 t d^{-1} O_2; cf. Fig. 3. The amount of water needed for this conversion is 45.4 m^3 d^{-1}. Energy demands in electrolytic cells are around 6.82 kWh kg^{-1} of CO, which leads to a total requirement of 8.53 kWh kg^{-1} of CO (or 676 MWh d^{-1}; cf. Fig. 3), considering again 80 % plug-to-power efficiency.

The reacted gas mixture comes to the separator, leading to three streams, including the produced CO (defined as 100 t d^{-1}), the recycled CO_2 (471 t d^{-1}), releasing the remaining 1% to the environment, for proper comparison with the plasma process, see Fig. 3. The energy required for the separator is 83.4 MWh d^{-1}; cf. Fig. 3. This is somewhat higher than in the plasma process, given the higher gas flow stream needed to achieve the same CO productivity (cf. Figs. 2 and 3). Indeed, the electrolysis efficiency is lower, because of the generation of secondary gases, such as H_2. We consider no CO_2 losses due to carbonate formation and CO_2 crossover to the anode channel, allowing the unused remaining 75 % of CO_2 to flow through the cathode gas output and consequently be recycled back after gas separation. We indeed set the gas losses to 1 % of all products in the separation process, as stated in previous studies (Ramdin et al., 2021). Both oxygen and hydrogen are directly released to the atmosphere because investing in equipment and energy for purification and storage would not be profitable, so hydrogen is not considered in this study. Whilst impacts regarding potassium hydroxide (KOH) electrolyte are not considered because of insignificant consumption or degradation, the deionised water consumption rises to a rate of 0.458 L kg^{-1} CO, which corresponds to an expense of 45.4 m^3 d^{-1}, Fig. 3.

2.2. *Sustainability assessment design*

We consider the mass flows described in Figs. 2 and 3 for the plasma and electrolytic process, respectively. General assumptions include 1 % CO_2 losses in the recycling process, based on literature (Ramdin et al., 2021), and the direct use of the recycled flow stream without further changes. The utility factor (commonly used in circular metrics calculation methodology) is considered neutral, since both processes (plasma

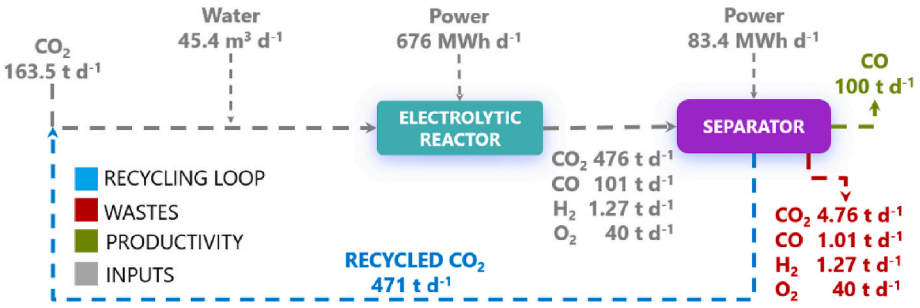

Fig. 3. Schematic flowchart for the electrolyser-based plant production of 100 tonnes CO per day.

and electrolysis) are designed for the same productivity (same intensity factor) and the final compound (CO) has the same lifetime in both methodologies (Escribà-Gelonch et al., 2021). Charcoal is used as oxygen adsorbent, because other alternatives reported higher environmental impacts, as disclosed in section 3.1.

2.2.1. *Life cycle assessment*

The LCA for the plasma-based CO production was performed to evaluate the environmental sustainability of a plasma-based daily production of 100 tonnes of CO as functional unit. The evaluation is subsequently compared with electrolysis and partial combustion of fossil fuels. The reactor inlet flow stream includes the input CO_2, as well as the CO_2 recycled fraction, in both electrolytic and plasma-based processes. As a cradle-to-gate LCA is performed, the upstream CO_2 production prior to the plasma-based reaction is also considered, including environmental impacts of other steps of the gas value chain, such as gas extraction and transportation, properly calculated using data retrieved from the Ecoinvent 3.9.1 database. Further byproduct processing that may be required (i.e. compression and liquification) is outside of the system boundaries. Electricity from wind energy located in the Netherlands is considered as case study. Indeed, the location of the energy must be defined in the methodology, because impacts and energy sources are highly influenced by the location where they are obtained. Charcoal decomposes when absorbing oxygen. The impacts assessment was performed using Sphera LCA for Experts software, version 10.7.0.183. The environmental impacts for the partial combustion of fossil fuels are directly extracted and scaled from the Ecoinvent 3.9.1 database.

Given the high recycling flow in the plasma-based process, the recycling loop is considered as tight when the process stops, so the CO_2 contained might be reused when production would start again. Impacts related to a very first loop (where no recycling is possible) production are accounted as negligible as compared with the overall lifetime of the production plant. The life cycle inventory (LCI) for the plasma-based plant is presented in Table 2.

According to the inventory, environmental impacts are calculated using European environmental footprint (EF) 3.1 methodology, including 10 midpoint impact categories. The selection of impact categories is designed not only to reflect the major motivation for CO_2-based processes but also to address pressing environmental concerns articulated through various laws, policies, and international agreements, as proposed in previous studies. (Maranghi and Brondi, 2020; Morales-Gonzalez et al., 2019; Osorio-Tejada et al., 2022a). Beyond freshwater ecotoxicity (FET), the study incorporated categories such as acidification (AP), global warming potential (GWP), eutrophication (both freshwater – EPw – and terrestrial – Ept –), human toxicity (cancer – HTc – and non-cancer – HTnc –), photochemical ozone formation (Ph), and resource use (fossils – CEDf – and minerals/metals – CEDm –). Mitigating EPw reduces the release of potential nitrogen oxides (NOx), which contribute to eutrophication in terrestrial ecosystems. Plasma reactors that operate at lower temperatures might reduce these emissions (Shah et al., 2023), while in electrolytic cells the nitrogen sources can be controlled by employing membranes that prevent nitrogen crossover to minimize nitrogen leakage (Kim et al., 2018). The use of renewable energy sources to power these new technologies might also reduce the overall environmental impact, as well as GWP, aligned with the commitments within climate change. By selecting these impact categories, the study ensures a comprehensive assessment that aligns with both sector-specific characteristics and broader environmental protection goals (Guinée et al., 2011). The EF methodology, aligned with European policies and regulatory frameworks, is used for impact quantification due to its robust, comprehensive and standardized approach to assessing environmental impacts across multiple categories, enhancing accuracy and comparability of results, enabling the identification of environmental hotspots, aiding in the development of more sustainable products and processes. Following the same procedure, an LCA for the electrolytic CO production was performed using the process described in Fig. 3, which leads to the corresponding LCI in Table 3. Material sources were kept constant to allow benchmarking.

Table 3
Life Cycle Inventory (LCI) for an electrolytic daily production of 100 tonnes CO, as shown in Fig. 3.

Inputs					Ecoinvent inputs
CO_2	1.635	kg kg^{-1} CO	163.5	T d^{-1}	Carbon dioxide production, liquid
Power reactor	6.76	kWh kg^{-1} CO	676	MWh d^{-1}	Electricity production, wind, <1 MW turbine, onshore in the Netherlands
Power separator	0.834	kWh kg^{-1} CO	83.4	MWh d^{-1}	
Deionised water	0.454	kg kg^{-1} CO	45.4	T d^{-1}	Water (deionised)
CO_2 recycled flow stream	19643	kg h^{-1}	471.4	T d^{-1}	
Product intermediates					
CO_2	19841	kg h^{-1}	476	T d^{-1}	
CO	4209	kg h^{-1}	101	T d^{-1}	
H_2	53.3	kg h^{-1}	1.27	T d^{-1}	
Wastes/Released gases					
CO_2	0.0476	kg kg^{-1} CO	4.76	T d^{-1}	
CO	0.0101	kg kg^{-1} CO	1.01	T d^{-1}	
O_2	0.4	kg kg^{-1} CO	40	T d^{-1}	
H_2	0.0127	kg kg^{-1} CO	1.27	T d^{-1}	

2.2.2. Circularity metrics

A circularity assessment using circular economy metrics aims at quantifying the performance of products, the degree of use and reuse of materials and resources up to exhaustion, as well as an evaluation of minimization of waste generation, to propose a sustainable and regenerative economic process (Escribà-Gelonch et al., 2023). By measuring factors such as material efficiency, product life extension, and waste minimization, circularity metrics enable innovation by-design, identifying opportunities for resource optimization and waste reduction throughout the product life cycle. The integration of circularity metrics facilitates the development of circular economy strategies that emphasize closed-loop systems and the reduction of environmental impacts associated with resource extraction and consumption, as aligned with global sustainability agendas, such as the United Nations Sustainable Development Goals (UN, 2020). For this purpose, the methodology developed by the Ellen MacArthur Foundation (EMAF) is commonly accepted (Ellen MacArthur Foundation, 2012). The indices included in the calculation procedure converge on a main indicator, the material circularity indicator (MCI), measuring how restorative and regenerative the material flows are in a scale from 0 (fully linear process) to 1 (fully circular). Plasma-based and electrolytic CO production processes were assessed using this pattern.

2.2.3. Green chemistry metrics

Green Chemistry metrics are used for assessing the adequation of a process to Green Chemistry postulates, to quantitatively evaluate the efficiency and environmental benignity of a chemical process. These metrics help prioritize the reduction of hazardous substances and waste generation, encouraging the development of innovative technologies which minimize resource consumption and energy requirements. These metrics enhance transparency newly designed processes, supporting informed decision-making and policy development aimed at environmental protection. These metrics are quantified in a gate-to-gate fashion, as they quantify the adequation and performance of chemical processes to Green Chemistry postulates. Plasma-based and electrolytic production of CO processes were benchmarked in terms of chemical yield, atom economy, environmental impact factor (E-factor), mass intensity, process mass intensity, mass productivity, reaction mass efficiency and wastewater intensity, as compiled by (Hessel et al., 2021; Pho et al., 2021; Roschangar et al., 2015).

Green chemistry and circularity metrics are essential to boost practically the transition towards circular economy. The first provide quantifiable measures of the environmental impact of chemical processes, promoting more sustainable and less wasteful production methods (Sheldon, 2007), encouraging the design of processes that minimize hazardous substances and energy consumption, aligning with the principles of a circular economy where resource efficiency is paramount (Trost, 1995). The second (circularity metrics) evaluate the lifecycle of products and materials, ensuring that they remain in use for as long as possible through strategies like recycling, remanufacturing, and reuse (Ellen MacArthur Foundation, 2015). Upon integration of these metrics, process hotspots can be identified, reducing their environmental footprint, and contributing to the development of closed-loop systems that are essential for sustainable economic growth (Stahel, 2016). Furthermore, these metrics provide a standardized framework for comparing the sustainability performance of different processes and products, facilitating better decision-making and policy development (Kirchherr et al., 2017).

3. Results and discussion

3.1. Life cycle assessment

3.1.1. Plasma-based CO production

LCA is a prominent tool for the implementation of new cleaner, energy-efficient and sustainable technologies. Process emission impacts are distributed in categories informing about environmental and human health risks (HTnc) (see abbreviations explained in section 2.2.1). Besides the atmospheric effects regarding greenhouse gases (GWP) and their effects on soil and water (AP), categories are focussed on biosphere impacts either concerning ecosystem's nutrient over enrichment (acquatic -EPw- or terrestrial -EPt-) or potential freshwater contaminations (FET), and on depletion of natural resources (fossil -CEDf- or non-fossil -CEDm-).

The environmental impacts of plasma-based CO production for the defined midpoint impact categories are summarized in Table 4 and presented in Fig. 4. The main contribution to environmental impacts is assigned to the raw material CO_2 production, globally followed by electric demands, while charcoal demands remain behind in most of categories, Fig. 4a. The impacts regarding waste emissions and gas separation are low. If only the plasma process is considered (gate-to-gate), the main contributions are the electricity source and the charcoal, Fig. 4b. The contribution of CO_2 input scores between 60 and 80 % in 8 over 10 impact categories, including AP, GWP, FET, EPw, EPt, HTnc, CEDf, and CEDm. The main reason is that the industrial CO_2 production is based on its capture as by-product from primary manufacturing processes, such as ammonia, alcohol and fertilizer production. The subsequent purification, compression, and liquefaction of CO_2, together with the storage and transportation at low temperature, produce significant environmental footprint. As a result, the raw material production (CO_2) generates higher environmental impacts than the conversion into CO mediated by plasma, including energy demands. To assess better the process itself (gate-to-gate), the impacts caused for the raw material production were subtracted in Fig. 4b, showing the prominent contribution of energy, but also a significant contribution of charcoal, especially regarding GWP and Ph.

A comparative assessment was performed regarding three alternatives to oxygen absorbents: charcoal, activated carbon (granular from hard coal) and ferrite, Table 5. Charcoal and ferrite production environmental impacts are compared with activated carbon production in the last two columns, noting as positive ratio an increase and as negative value a decrease of environmental impacts with respect to activated carbon, respectively. Overall, charcoal exhibits better performance than ferrite and activated carbon in most of the 10 categories under assessment. Yet, the environmental impacts for the production of all absorbents under assessment are high when compared with the CO plasma production process; compare Tables 5 and 6th column of Table 4. Even taking charcoal as absorbent as the most environmentally favourable, the absorbent contribution to the overall process remains significant, especially regarding GWP and Ph categories.

3.1.2. Electrolysis-based CO production

Following the same procedure, we performed an LCA for the electrolytic CO production. Material sources were kept constant to allow benchmarking. Impact categories were calculated using the same methodology (EF 3.1) including 10 midpoint impacts, Table 6. As also noted in plasma-based CO production, all impact categories are highly influenced by the CO_2 raw material.

3.1.3. Benchmarking plasma-, electrolysis-based CO production and partial combustion of fossil fuels

Electrolysis and partial combustion of fossil fuels were used as a reference for benchmarking the plasma-based CO production. Fig. 5 shows the environmental impacts variation observed when comparing impact categories from Tables 4 and 6, normalized with those from the conventional process, and centered to zero. With this approach, positive values denote higher environmental impacts with respect of the conventional partial combustion of fossil fuels, leading to worse environmental scenarios, while negative values denote the opposite, with the corresponding environmental benefits. Overall, plasma-based CO production exhibits a reduction of environmental impacts in 7 over 10 categories when compared with conventional fossil fuel combustion,

Table 4
Life Cycle Assessment impacts derived for the plasma-based production of 100 tonnes CO. (E = energy; Emissions = impacts caused by released gases).

Impact category	Units	Abbreviation	Total	CO_2 input	E-Plasma	Emissions	E-Separator	Charcoal
Acidification	Mole of H^+ eq.	AP	1.30E+02	8.93E+01	1.77E+01	0.00E+00	2.72E+00	2.01E+01
Global warming potential	kg CO_2 eq.	GWP	1.17E+05	7.32E+04	6.80E+03	4.16E+03	1.05E+03	3.17E+04
Ecotoxicity, freshwater	CTUe	FET	2.89E+05	1.96E+05	4.46E+04	2.31E+01	6.89E+03	4.15E+04
Eutrophication, freshwater	kg P eq.	EPw	2.33E+01	1.77E+01	3.16E+00	0.00E+00	4.88E-01	1.96E+00
Eutrophication, terrestrial	Mole of N eq.	EPt	6.39E+02	4.53E+02	7.65E+01	0.00E+00	1.18E+01	9.79E+01
Human toxicity, cancer	CTUh	HTc	1.14E-04	4.41E-05	5.34E-05	0.00E+00	8.25E-06	8.76E-06
Human toxicity, non-cancer	CTUh	HTnc	2.43E-03	1.84E-03	2.83E-04	0.00E+00	4.37E-05	2.71E-04
Photochemical ozone formation	kg NMVOC eq.	Ph	4.00E+02	1.55E+02	3.01E+01	4.61E+01	4.65E+00	1.64E+02
Resource use, fossils	MJ	CEDf	8.46E+05	6.75E+05	8.88E+04	0.00E+00	1.37E+04	6.82E+04
Resource use, mineral and metals	kg Sb eq.	CEDm	9.44E-01	6.97E-01	2.05E-01	0.00E+00	3.16E-02	1.05E-02

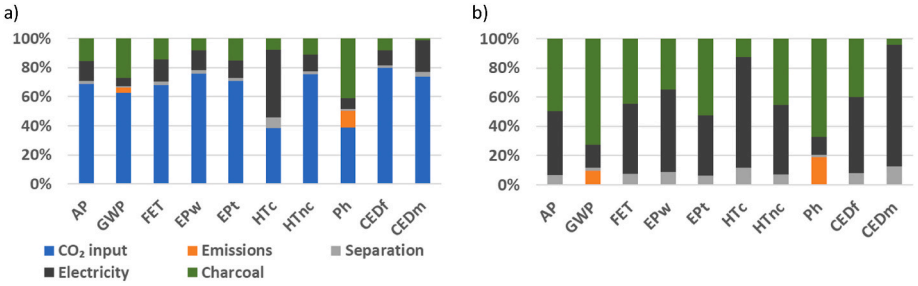

Fig. 4. Impact categories contribution for plasma-based production of 100 tonnes CO. a) Global quantification; b) subtracting CO_2 raw material impacts.

Table 5
Alternatives assessment for oxygen absorbents in terms of environmental impacts, scaled to 100 tonnes CO production.

Impact category	Units	Abbreviation	Charcoal	Ferrite	Activated carbon	Charcoal vs Activated carbon	Ferrite vs Activated carbon
Acidification	Mole of H^+ eq.	AP	2.01E+01	1.45E+02	3.64E+02	−0.94	−0.60
Global warming potential	kg CO_2 eq.	GWP	3.17E+04	4.38E+04	1.68E+05	−0.81	−0.74
Ecotoxicity, freshwater	CTUe	FET	4.15E+04	5.08E+05	3.88E+05	−0.89	0.31
Eutrophication, freshwater	kg P eq.	EPw	1.96E+00	1.82E+01	9.76E+01	−0.98	−0.81
Eutrophication, terrestrial	Mole of N eq.	EPt	9.79E+01	7.45E+02	1.89E+03	−0.95	−0.61
Human toxicity, cancer	CTUh	HTc	8.76E-06	1.98E-03	4.33E-05	−0.80	44.82
Human toxicity, non-cancer	CTUh	HTnc	2.71E-04	6.18E-04	1.97E-03	−0.86	−0.69
Photochemical ozone formation	kg NMVOC eq.	Ph	1.64E+02	2.34E+02	5.56E+02	−0.70	−0.58
Resource use, fossils	MJ	CEDf	6.82E+04	5.23E+05	2.93E+06	−0.98	−0.82
Resource use, mineral and metals	kg Sb eq.	CEDm	1.05E-02	1.34E-01	6.16E-02	−0.83	1.17

Table 6
Life Cycle Assessment impacts derived for the electrolytic production of 100 tonnes CO. (E = energy; Emissions = impacts caused by released gases).

Impact category	Units	Abbr.	Total	CO_2 input	Water	E-Electrolysis	Emissions	E-Separator
Acidification	Mole of H+ eq.	AP	1.38E+02	1.09E+02	1.34E-01	2.54E+01	0.00E+00	3.14E+00
Global warming potential	kg CO2 eq.	GWP	1.36E+05	1.20E+05	1.97E+01	9.80E+03	4.76E+03	1.21E+03
Ecotoxicity, freshwater	CTUe	FET	4.00E+05	3.25E+05	2.30E+03	6.43E+04	2.31E+01	7.94E+03
Eutrophication, freshwater	kg P eq.	EPw	3.99E+01	3.47E+01	7.06E-03	4.56E+00	0.00E+00	5.62E-01
Eutrophication, terrestrial	Mole of N eq.	EPt	6.50E+02	5.26E+02	1.83E-01	1.10E+02	0.00E+00	1.36E+01
Human toxicity, cancer	CTUh	HTc	1.68E-04	8.17E-05	2.27E-08	7.70E-05	0.00E+00	9.50E-06
Human toxicity, non-cancer	CTUh	HTnc	3.83E-03	3.37E-03	4.10E-07	4.08E-04	0.00E+00	5.03E-05
Photochemical ozone formation, human health	kg NMVOC eq.	Ph	3.00E+02	2.05E+02	6.77E-02	4.35E+01	4.61E+01	5.36E+00
Resource use, fossils	MJ	CEDf	1.17E+06	1.03E+06	2.40E+02	1.28E+05	0.00E+00	1.58E+04
Resource use, mineral and metals	kg Sb eq.	CEDm	1.70E+00	1.37E+00	2.40E-04	2.96E-01	0.00E+00	3.65E-02

Fig. 5a. Exceptions are both human toxicities (cancer and non-cancer), mainly caused by the application of charcoal. Significant impact reductions are in acidification (AP – 86 %), freshwater ecotoxicity (FET – 91 %), and fossils resource use (CEDf – 83 %), while cancer human toxicity is doubled as a counterpart. Differences between plasma and electrolysis are generally small, but plasma performs better in all cases except for Ph, where plasma scores 4 times more than electrolysis, although the absolute impact is limited, compared to the other categories, Fig. 5a. Significant improvements of plasma compared to electrolysis are observed in CEDm and freshwater eutrophication EPw, scoring 3 times lower impacts and 25 % reduction, respectively. Finally, whilst plasma-based CO production improves the conventional fossil-based combustion in terms of GWP by 7 %, electrolysis generates 8 % higher impacts when compared with the conventional method; consequently, when comparing plasma and electrolysis, the difference becomes 15 %; cf. Fig. 5a.

When considering the environmental impacts of chemicals, the use of electrolysis and plasma are advantageous in 6 out of 10 categories, Fig. 5b. Plasma remains ahead of electrolysis in all categories. Since the feedstock highly influences the overall impact quantification, it is not

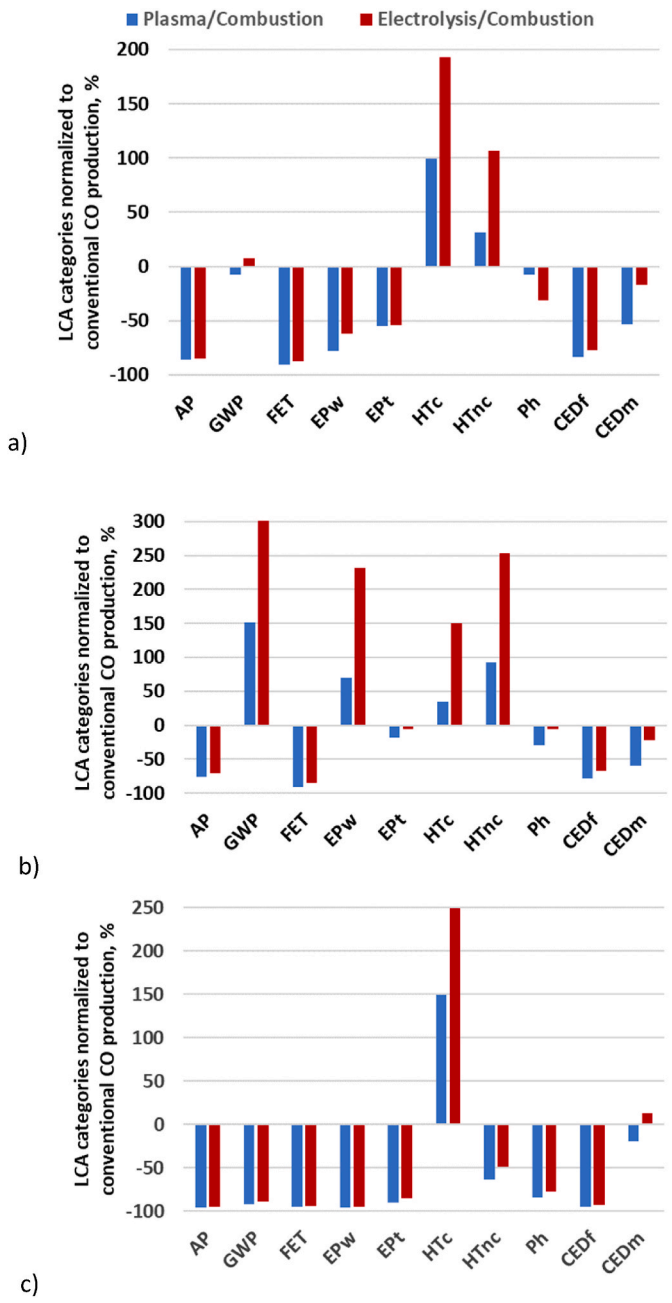

Fig. 5. Impact categories variation when considering plasma-based and electrolytic CO production normalized to the results of partial combustion of fossil fuels. a) Global quantification; b) Influence of chemical feedstocks, and c) Influence of energy requirements.

strange that the highest reductions include AP (76 %), FET (90 %), and CEDf (78 %), denoting that most of the overall reductions are attributed to chemicals. Yet, the use of reactants penalizes both plasma and electrolysis in 4 over 10 categories when compared with the conventional combustion method. Especially relevant is the increase in GWP, where electrolysis triples the conventional process emissions, while plasma increases it by a factor of 1.5. EPw emissions are also significantly higher than the conventional process, increasing the impact by a factor of 230 % and 70 % for electrolysis and plasma, respectively. As expected, the use of metals (in electrolysers) and charcoal (in plasma) also significantly increases human toxicities in electrolysis and plasma-based CO production, respectively, Fig. 5b.

Energy consumption, including electricity and heat, is a central parameter in the process design, for both economic and environmental reasons. Both plasma and electrolysis lead to significant electricity savings when compared with the conventional fossil fuel combustion, with plasma exhibiting additionally 40 % of energy savings compared to electrolysis, when comparing Tables 2 and 3 Indeed, 9 of the 10 environmental categories benefit from the use of plasma technology as alternative to the conventional process, achieving in 6 of them impact reductions above 90 %. On top, AP (96 %, from 534 to 20.4 mol H^+ eq.), FET (95 %, from 1.11E+06 to 5.15E+04 CTUe), EPw (96 %, from 94.5 to 3.65 kg P eq.) and CEDf (95 %, from 1.99E+06 to 1.03E+05 MJ) exhibit the highest impact reductions of plasma *versus* the conventional combustion. The same applies for electrolysis, although with more modest benefits. Yet, the counterpart is the human toxicity impact derived from electricity use. In this case, plasma and electrolysis increase the cancer human toxicity by a factor of 1.5 and 2.5, respectively. Plasma has lower impact than partial fuel combustion concerning the use of minerals and metals, reporting 20 % benefits, whereas electrolysis has a higher impact, with a 13 % increase of emissions compared to fuel combustion, Fig. 5c.

3.2. Circularity metrics

Calculations were based on the description of material flows extracted from the respective life cycle inventories (Tables 2 and 3), summarized in Table 7. Assumptions include (i) 1 % losses while recycling unreacted CO_2, (ii) an equal utility factor (see section 2.2), since any of the processes increase the lifetime of the final CO and both are equally dimensioned, and (iii) charcoal is decomposed not generating waste. As also considered in the LCA, the production plant shutdowns would not generate additional gas releases, as the looping flow tubing is considered as tight and closed once the plant is stopped. Sankey diagrams for the mass flow streams in the plasma- and electrolysis-based CO production are presented in Figs. 6 and 7, showing that for the same CO productivity, electrolysis demands more inputs and generates more mass losses. Plasma technology requires lower mass flows to achieve the same productivity, denoting a higher process efficiency and simplicity. Charcoal decomposition when absorbing oxygen reduces the waste production in plasma processing, while the water consumption penalizes the electrolytic pathway in terms of waste generation.

The calculation of circular indices encompasses the mass of a product in the inlet (*M*), which includes a fraction coming from the recycling loop with a ratio denoted as F_R. The virgin material (coming from new raw materials) is calculated consequently (*V*). The recycling fraction is corrected (C_U) according to the recycling efficiency (E_C). Mass wastes are calculated using the EMAF methodology, leading to a linear flow index (*LFI*), from which the material circularity indicator (MCI) is directly obtained, as the utility factor remains univariable, see Table 8. MCI denotes the circularity of the process with a value between 0 (linear) and 1 (circular), as a function of a linear flow index *(LFI)*, normalized by the utility factor *F(X)*, equations (1) and (2).

$$MCI_P = 1 - (LFI - F(X)) \quad \text{(eq.1)}$$

$$a)\ LFI = \frac{V+W}{2M + \frac{W_F}{2}} \;;\; b)\ F(X) = \frac{0.9}{\left(\frac{L}{L_0}\right)\cdot\left(\frac{U}{U_0}\right)} \quad \text{(eq. 2)}$$

Table 7
Overall material flows used for the circularity assessment based on Figs. 2 and 3). Note that for "inputs", the global process loadings are considered, including the new (virgin) input, the recycled flow stream and the charcoal or water (for plasma and electrolysis, respectively).

	Plasma	Electrolysis	Units
INPUTS	517.0	680.3	t d^{-1}
RECYCLED	412.0	471.4	t d^{-1}
LOSSES	5.17	47.04	t d^{-1}

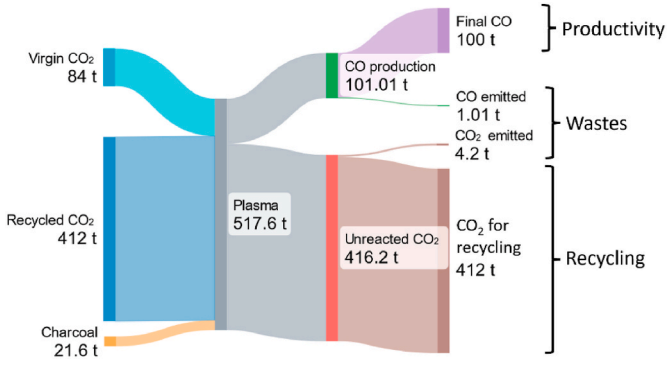

Fig. 6. Sankey diagram for mass flow streams in plasma-based CO production.

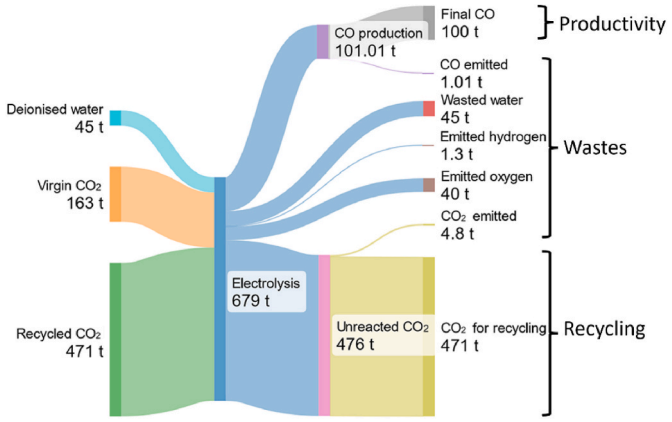

Fig. 7. Sankey diagram for mass flow streams in electrolysis-based CO production.

Table 8
Circularity metrics, benchmarking plasma and electrolytic CO production.

SYMBOL	DEFINITION	Plasma-based	Electrolysis	Units
M	Mass of raw materials	517	680	t
F_R	Fraction of mass from recycled sources	0.80	0.69	
V	Materials not from reuse	105	209	t
C_U	Fraction of mass going into reuse	0.79	0.69	
E_C	Efficiency of the recycling process	0.99	0.99	
W	Mass of unrecoverable waste	7.8	73.17	t
W_O	Mass of unrecoverable waste through emissions	5.2	47.04	t
W_F	Mass of unrecoverable waste generated when producing recycled feedstock	5.3	52.25	t
LFI	Linear Flow Index (material flowing in a linear fashion)	0.11	0.20	
F(X)	Utility factor built as a function of the utility X of a product	0.9	0.9	
X	Utility of a product	1	1	
MCI	Material Circularity Indicator	**0.902**	**0.817**	

The *LFI* (Eq. (2a)) is a function of the unrecoverable mass fraction *(W)*, the waste generated when recycling (W_F), the incoming mass *(M)* and the amount of virgin material *(V)*. Equation (2b) shows how *F(X)* is defined as a function of utility (use) *(U)* and lifetime *(L)*. Yet, in this study this value is kept constant *and equal to* 0.9 according to EMAF methodology, as this parameter is used in Eq. (1).

While both CO production processes have a high degree of circularity, pushed by the significant recycling loop for unreacted CO_2, the plasma process exhibits a 10 % higher MCI than electrolysis (0.902 vs. 0.817). Recycling is essential in processes with low conversions and yields, especially for those which use potentially contaminant raw materials, such as CO_2 (Pho et al., 2021). However, since the recycling potential of plasma (F_R) is 11 % higher than for electrolysis because of less amount of waste losses, the virgin material required for the same productivity in the plasma process is consequently around half the value needed for electrolysis (i.e., 105 vs 209 t; cf. Table 8). Waste production is also 90 % reduced in plasma production with respect of electrolysis (i.e., 7.8 vs 73.17 t; cf. Table 8), which is caused by the combination of two effects. First, the decomposition of biochar happens without waste generation and the gas recycling is efficient without significant losses. Second, electrolysis involves a significant oxygen release, which is considered as waste of the process here, increasing the mass losses. In contrast, the oxygen generated in the plasma process is used to oxidize biochar to produce CO, reducing the waste generation, enhancing the productivity, and reducing the input needs. These metrics justify the use of biochar as oxygen absorbent, despite the environmental impacts derived from its production in the LCA.

3.3. Green chemistry metrics

Green Chemistry metrics are used to assess sustainable and environmentally friendly practices in chemical processes, seeking to design and develop products and processes that minimize the use and generation of hazardous substances. Green Chemistry metrics are calculated for plasma and electrolysis considering both virgin and recycled CO_2 flow streams as raw materials, while charcoal and water were added as global input materials for plasma and electrolytic CO production respectively, Table 9.

As seen in Table 9, the process mass efficiency (PME) is 31 % improved when using plasma production as compared with electrolysis. This is caused by the higher needs of CO_2 loadings in the electrolytic process, as well as by the 28 % chemical yield (CY) improvement when using the plasma process. The environmental impact factor (E-factor), correlated with waste production, and the reaction mass efficiency (RME), pushed by the required CO_2 inputs, are also improved by 28 %. The mass intensity (MI), mass productivity (MP) and process mass intensity (PMI) yield lower improvements by 19, 23 and 24 %, respectively. The atom economy remains constant as the reaction is the same in both methodologies, while the waste water intensity is only relevant in electrolysis, as plasma processing does not use water. In summary, whilst both plasma-based CO production and electrolysis offer distinct approaches to generating CO, the difference between both methods in a Green Chemistry perspective relies on factors such as energy and mass efficiency, the use of water and the subsequent waste generation, and the chemical yield. Overall, plasma-based CO production outperforms the electrolysis metrics by around 10–30 %.

4. Conclusions

Plasma- and electrolysis-based CO production are efficient alternatives for CO_2 consumption, as compared to the conventional partial

Table 9
Green Chemistry metrics, benchmarking plasma and electrolytic CO production.

Green Chemistry Metric	Abbr.	Plasma	Electrolysis	Units
Chemical yield	CY	32	25	%
Atom economy	AE	64	64	%
Environmental impact factor	E-factor	4.17	5.80	$kg.kg^{-1}$
Mass intensity	MI	5.17	6.35	$kg.kg^{-1}$
Process mass intensity	PMI	5.17	6.80	$kg.kg^{-1}$
Process mass efficiency	PME	19.3	14.7	%
Mass productivity	MP	19.3	15.7	%
Reaction mass efficiency	RME	20.2	15.7	%
Waste water intensity	WWI	0.0	0.454	$kg.kg^{-1}$

combustion of fossil fuels. We used holistic sustainability assessment tools to quantify the benefits of emerging decarbonization technologies, in order to build comparable frameworks with the conventional partial combustion process. The sustainability assessment is addressed according to the principles of green and circular economy metrics, as well as life cycle assessment by means of an environmental footprint. The practical application of such holistic sustainability study in industrial contexts derives in an enhancement of environmental and economic performance, namely: (i) green chemistry metrics lead to safer, cost-effective manufacturing processes, (ii) LCA evaluates the environmental impact of products from cradle-to-grave regarding both emissions and consumptions, (iii) circularity metrics assess how well the described processing closed-loops promote the reuse, recycle, or repurpose of the well-used materials up to exhaustion. In an industrial perspective, this study can support decision-making processes, guiding the selection of raw materials, design of manufacturing processes, and development of end-of-life strategies to ensure sustainability, achieving significant reductions in environmental footprints while maintaining profitability and competitiveness in the market (Hessel et al., 2024).

When compared with electrolytic CO production, plasma-based CO production exhibits a reduction of environmental impacts in 7 over 10 categories when normalized to partial combustion of fossil fuels. The main environmental impact reductions are found regarding freshwater ecotoxicity and acidification, with around 80 and 90 % reductions. These reductions are driven by the reduction in water and materials consumption of plasma-based CO conversion when compared with electrolysis. These are the key factors which make the main differences between both technologies. The use of charcoal to convert O/O_2 to CO exhibits the best environmental indicator among other alternatives such as ferrite and activated carbon. Yet, it doubles the impact on the human toxicity category as a counterpart. The reduction of GWP impact category for plasma when compared with electrolysis is 7 %. When compared with the conventional combustion process, the benefits of using plasma are even more pronounced, since plasma technology improves 9 over 10 environmental categories, with significant impact reductions above 90 %, especially for AP (96 %), FET (95 %), EPw (96 %) and CEDf (95 %).

The circularity indicators are also favourable for plasma production, but only improving 10 % as compared with electrolysis, attributed to waste reduction and avoiding the use of water. In both technologies, recycling streams play a very important role to keep a high material circularity indicator in the range of 0.8–0.9 for electrolysis and plasma, respectively. The root causes of the difference are the higher material demands of electrolysis to achieve the same productivity, and the reduction of waste generation due to charcoal consumption in plasma-mediated CO production. Under circularity perspective, water consumption penalizes electrolysis since it is considered here as waste. The Green Chemistry metrics are 10–30 % better in plasma-based production compared to electrolysis. Especially relevant are the plasma improvements in terms of process mass efficiency (31 %) and E-factor (28 %) in comparison with electrolysis. Sustainability metrics lead to 40 % energy savings when comparing plasma-based production with electrolysis. Overall plasma-based CO production exhibits better metrics than electrolysis and other conventional technologies, offering a promising alternative for decarbonization strategies. When this process leverages renewable electricity sources, it ensures a sustainable production pathway, of which the scalability contributes to reducing greenhouse gas emissions (Llera et al., 2018). Whilst plasma-based CO_2 conversion has shown high reaction rates and high conversion efficiencies, as reported in this paper, challenges such as high energy requirements and reactor design complexity must be addressed for industrial-scale applications (Snoeckx and Bogaerts, 2017b). Future research is expected to focus on integrating these plasma-based processes with renewable energy sources to achieve a net-negative carbon footprint (Stauss et al., 2015).

On the other hand, mature electrolytic CO_2 conversion offers a scalability path, but with the payback of higher environmental footprint (Jhong et al., 2013). Comprehensive policy frameworks should contribute to shorten the transference of plasma-based CO_2 know-how to industry by the promotion of public-private partnerships. Examples could include the implementation of carbon pricing mechanisms to incentive safe and efficient CO_2 conversion technologies, highlighting the environmental benefits, making these technologies economically viable fostering public acceptance through transparent risk communication and stakeholder engagement.

CRediT authorship contribution statement

Marc Escribà-Gelonch: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jose Osorio-Tejada:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation. **Rani Vertongen:** Methodology, Investigation. **Annemie Bogaerts:** Writing – review & editing, Validation, Supervision, Funding acquisition, Data curation, Conceptualization. **Volker Hessel:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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