CO$_2$ electroreduction: Sustainability analysis of the renewable synthetic natural gas

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A B S T R A C T

Capture and utilization of industrial CO$_2$ emissions into low-carbon fuels is a promising alternative to store renewable electricity into chemical vectors while decarbonizing the economy. This work evaluates the viability pathways of producing synthetic natural gas (SNG) by direct CO$_2$ electroreduction (ER) in Power-To-Synthetic Natural Gas electrolyzers (PtSNG). We perform an ex-ante techno-economic (TEA) and life cycle analysis (LCA) for a 2030 framework in Europe. ER performance is varied in defined scenarios and assessed using a built-in process model of the PtSNG system, revealing uncharted limitations and benchmarks to achieve. Results show that substitution of fossil natural gas with renewable SNG could avoid more than 1 kg CO$_{2e}$/kg SNG under moderate ER conditions when using low-carbon electricity (< 60 kg CO$_{2e}$/MWh). SNG profitability for 2030 would rely on: i) higher CH$_4$ current densities (800–1000 mA/cm^2), ii) improvements in energy efficiency (higher than 60%), and iii) valorization of the anodic product or additional carbon incentives. Our study proves that if market and technology evolve appropriately in the coming years, the SNG by CO$_2$ ER may be a mid-term climate change mitigation technology, among others.

1. Introduction

Carbon capture and utilization technologies (CCU) are a promising alternative for the decarbonization of specific industrial sectors. This is essential for achieving a net-zero carbon dioxide (CO$_2$) emissions horizon and meet the Paris Agreement's goal of a climate-neutral society by 2050 (United Nations Framework Convention on Climate Change (UNFCCC), 2016). The current penetration of intermittent renewable energy leads to an increasing number of hours where generation exceeds demand, known as surplus power. This can be effectively managed by using energy storage systems (Sternberg and Bardow, 2015). Hence, CCU would be a CO$_2$ sink that would serve as a storage of electricity from renewable sources in the form of a variety of chemical compounds such as hydrocarbons or alcohols called Power-to-X (Uusitalo et al., 2017). This work is focused on the so-called Power-to-Synthetic Natural Gas technology (PtSNG), in which synthetic methane (CH$_4$) is produced by the electrochemical reduction (ER) of CO$_2$ and later injected into the natural gas grid. The common production route of Synthetic Natural Gas (SNG) production involves a two-step process known as methanation, a thermochemical pathway based on the Sabatier's reaction: it produces

CH$_4$ from CO$_2$ and H$_2$. However, this work explores the one-step ER of CO$_2$, which has gained increasing interest as it would be able to reduce CO$_2$ into CH$_4$ at ambient temperature and pressure directly, without H$_2$ as a reactant (Irabien et al., 2018).

One of the critical problems to tackle when facing the CO$_2$ ER systems is the low technology maturity, which is currently associated with low Technology Readiness Levels (TRL) between 2 and 3 (Roh et al., 2020). Many efforts have been made to develop the electrochemical conversion of CO$_2$ at very different lab-scale conditions, mostly obtaining C$_1$ and C$_2$ compounds as CH$_4$ (Manthiram et al., 2014; Merino-Garcia et al., 2017; Qiu et al., 2017; Wang et al., 2020), carbon monoxide (Ma et al., 2014), methanol (Albo et al., 2015), formic acid (Fan et al., 2020), or ethylene (Dinh et al., 2018) depending on the electrocatalytic material, the associated morphology or the cell design. Even though some outstanding results have been obtained in terms of current density and selectivity (García de Arquer et al., 2020; Grigioni et al., 2021; Ma et al., 2016; Sedighian Rasouli et al., 2020), the technology's maturity stands still at the previously low TRL's, and large-scale systems have been investigated to a lesser extent (Li and Oloman, 2007). As uncertainty remains in the future development of ER
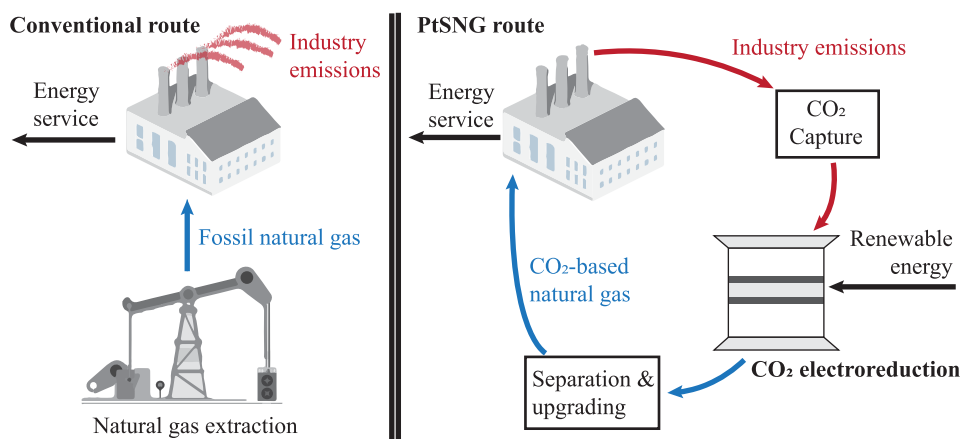
Fig. 1. Comparison of the fossil-based (conventional) and the CO_2-based (PtSNG) natural gas routes considered in this work.

technology and the conditions needed to reach a sustainable technology, an ex-ante analysis could help in identifying the key benchmarks to become viable at a higher scale (Cucurachi et al., 2018).

Three keystones must be achieved to ensure the sustainability of the technology before its implementation: to be economically competitive and profitable, to serve as a net CO_2 sink avoiding CO_2 emissions, and to have a social acceptance. The social perspective could be expected to be positive due to the direct and indirect job creation and the low risk associated with electrochemical technologies, in which no dangerous solvents or intermediates are generated. Furthermore, the latest acceptance research has indicated that despite the low base of awareness, there is a high initial acceptance of CO_2 utilization technologies (Perdan et al., 2017).

The environmental perspective has been typically explored by life cycle assessment (LCA) studies for evaluating the potential environmental impacts of CO_2 ER systems. This includes CO_2 conversion products (Aldaco et al., 2019; Chen and Lin, 2018; Li et al., 2016; Rumayor et al., 2019a; Thonemann and Pizzol, 2019; Thonemann and Schulte, 2019), such as CH_4 (Dominguez-Ramos and Irabien, 2019), concluding the critical role of the source of the supplying energy (electricity and heat) with low carbon intensity but not providing a high level of detail in other considerations. Regarding the economic perspective, some ER conversion products' profitability has been studied (De Luna et al., 2019; Jouny et al., 2018; Kibria et al., 2019; Orella et al., 2020; Spurgeon and Kumar, 2018), and CH_4 has been usually considered a non-profitable route for CO_2 utilization (Verma et al., 2016). However, SNG is likely to be, from an environmental and market point-of-view, the most attractive product due to its large global consumption and straightforward integration in the already existing T&D infrastructure all around the globe (NG grid).

The novelty of this work is to approach an integrated profitability and carbon footprint assessment of the PtSNG system with special detail to the CO_2 ER performance variables. We aim to provide insights into the endogenous (electrochemical technology-related) and exogenous (market, policies) conditions that would pave the way for the economic profitability and the favorable CO_2 emissions profile of a PtSNG system based on the CO_2 ER. The scope considers: 1) the set of additional processes that ER of CO_2 demands (capture, reaction, separation, and compression stages) to provide a high-purity SNG that can be directly injected into the grid; 2) life cycle considerations to provide a fair balance both in economic and carbon terms; 3) mass balances and a cost model for the assessment. This way, it would be possible to discuss not yet settled questions in the overall performance, such as what the effects of the operating conditions in the PtSNG system are, which must be the desired performance of the electrochemical reactor (ECR) to be reached in the next decade (2030), or what is the best combination of the set of electrochemical performance variables.

Table 1
Reactions occurring in the electrochemical reactor (basic environment).

Reaction	Stoichiometry	
CO2RR	$CO_2 + 6\,H_2O + 8e^- \rightarrow CH_4 + 8\,OH^-$	(Eq. 1)
HER	$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$	(Eq. 2)
OER	$4\,OH^- \rightarrow O_2 + 2\,H_2O + 4\,e^-$	(Eq. 3)
CO2RR + OER	$CO_2 + 2\,H_2O \rightarrow CH_4 + 2\,O_2$	(Eq. 4)
HER + OER	$2\,H_2O \rightarrow 2\,H_2 + O_2$	(Eq. 5)

2. Material and methods

2.1. Process description

A general comparison between the conventional and the PtSNG routes is shown in Fig. 1. The system boundaries of the PtSNG system include CO_2 capture, reaction, separation, and compression stages. A first separation unit may be needed for the CO_2 capture and purification from an industry-emitting source, such as the iron and steel manufacture or the cement production. This work assumes an initial 30% concentration of CO_2 coming from the cement industry (Bains et al., 2017). The CO_2 capture unit is based on mature technology using aqueous monoethanolamine (MEA) (Giordano et al., 2018) that captures CO_2 with an efficiency of ~90% (Fredric Bauer, Christian Hulteberg, Tobias Persson, 2013; Pourjazaieri et al., 2011).

The ER cell is divided into the cathode and anode compartments. In the cathode, the captured CO_2 reacts to produce CH_4 (CO2RR), while H_2 is also produced because of the H_2 evolution reaction (HER), a competing cathodic reaction. In the anode, O_2 may be formed due to the O_2 evolution reaction (OER). Mass balances are based on the global reactions of the ER system that are summarized in Table 1, covering Eq. 1 to 5. It should be considered that in an ideal ECR, a perfect electrode would lead to a value of 100% faradaic current efficiency (FE) to the desired product. This would correspond to the formation of pure CH_4 in the cathode and pure O_2 in the anode. But in real practice, a fraction of the applied current density is deviated to other parallel/parasitic reactions (Oloman and Li, 2008), reducing the FE of the CH_4 production. In this work, the HER is assumed as the only parallel reaction, and so a mix of CH_4, H_2 and unreacted CO_2 leave the cathode. It is considered that water is the chemical compound that is consumed regardless of the pH in the half-cell, being acid or basic (which means the exclusion of supporting electrolytes). The OER is the only reaction taking place in the anode. Electrolytes are continually being recirculated via external pumping, assuming that no pretreatment is needed. A typical set of performance variables are assumed for determining the ER operation, which are: i) total current density (CD); ii) total cell voltage (V_{cell}), iii) FE to CH_4 (FE_{CH4}); and iv) CO_2 single-pass conversion (X_{CO2}). Energy

Table 2

Cost model parameters used in this study.

Parameter	Value	Unit
Average production	86.0	ton/d
Design capacity	125.5	ton/d
Plant lifetime	20	yr
Capacity factor	0.68	–
Start-Up year	2030	–
Nominal interest rate	9.23	%
Inflation rate	1.9	%

consumption is only supplied with electricity, and it is determined by the number of electrons involved in the reaction, the FE, and the V_{cell}. The electrode area needed to produce the design capacity is calculated from CD and FE_{CH4}. More details are provided in the SI.

The ER can be defined, from a macroscopic point of view, by two leading indicators: i) the partial current density (CD_{CH4}), and ii) the ER energy efficiency (EE) to the desired CH_4 product. The CH_4 current density does reflect the reaction rate to CH_4 per unit of electrode area. The higher the partial current density, the lower the electrode area. It can be straightforwardly calculated as a function of the total current density (i) and the faradaic efficiency to CH_4 (FE_{CH4}) as follows in Eq. 6:

$$CD_{CH4} = CD \cdot FE_{CH4} \tag{6}$$

The EE accounts for the energy losses in the reactor for producing CH_4 concerning the minimal thermodynamic energy consumption. The thermodynamic minimum specific energy consumption (SEC_{min}) for producing CH_4 is 14.17 kWh/kg CH_4. EE depends on the cell overpotential (η) and the faradaic efficiency to CH_4 (FE_{CH4}) as indicated in Eq. 7:

$$EE = \frac{E^0 \, FE_{CH4}}{E^0 + \eta} \tag{7}$$

where E^0 is the standard cell potential for Eq. 4 (1.061 V). Unreacted CO_2 needs to be recovered and recycled back into the ECR to maximize the CO_2 conversion, while products need to be separated individually. Since all the catholyte products are in the gas phase (CH_4, CO_2, and H_2), a Pressure Swing Adsorption (PSA) cycle is proposed for performing this separation. We assume that a first PSA module would ideally recover H_2 and a second one CH_4 (Augelletti et al., 2016; Fredric Bauer, Christian Hulteberg, Tobias Persson, 2013). Finally, compression of products to the high-purity commercial standards is required for its market

valorization.

2.2. Cost model

The scenarios are evaluated under the cost model parameters described in Table 2. A spreadsheet calculates the discounted revenues and costs along the project lifetime with each operating year's cash flows following the H2A model framework (Colella et al., 2014). Each year's total taxable income is calculated as the sum of the revenues from selling the products (SNG, and H_2/O_2 under proper valorization) minus the operation cost and the depreciation charge. Depreciation is calculated by using a 10-year modified accelerated cost recovery system (MARCS). A total effective tax rate of 25% is considered. CO_2 carbon taxes from avoiding CO_2 emissions to the industrial carbon source are considered a tax incentive (e.g., within applying the EU emissions trading system (EU ETS)). A salvage value of 10% of the total capital investment and a working capital value of 15% are used. A construction period of 1 year is considered. These cost model parameters are similar to the ones used for H_2 production in water electrolysis systems (Colella et al., 2014) and analogous to techno-economic assessments for CO_2 ER systems to other products (Adnan and Kibria, 2020; Jouny et al., 2018; Rumayor et al., 2019b; Spurgeon and Kumar, 2018).

The economic metrics accounted for in the cost model are: i) the levelized costs and revenues; ii) the Net Present Value (NPV); and iii) the Minimum Selling Price (MSP). The levelized costs and revenues indicate the gains and the costs allocated to produce 1 kg of product. These are calculated by dividing their discounted values by the total production of SNG. The NPV is a well-known metric to estimate the present value of an investment. It can be calculated using the net cash flows (NCF) of each operating year and the nominal interest rate (NIR), as the Eq. (8) indicates. The MSP is the product selling price (€/SNG) that would make the NPV equal to zero. A MSP lower than the market price is related to profitable investments.

$$NPV = \sum_i \left(\frac{NCF_i}{(1 + NIR)^i} \right) \tag{8}$$

2.3. Cost assumptions

The following section explains the assumptions made for the cost model of the PtSNG system. The uninstalled capital cost C_i^{2020} estimation of an individual equipment/item/unit follows a common expression as
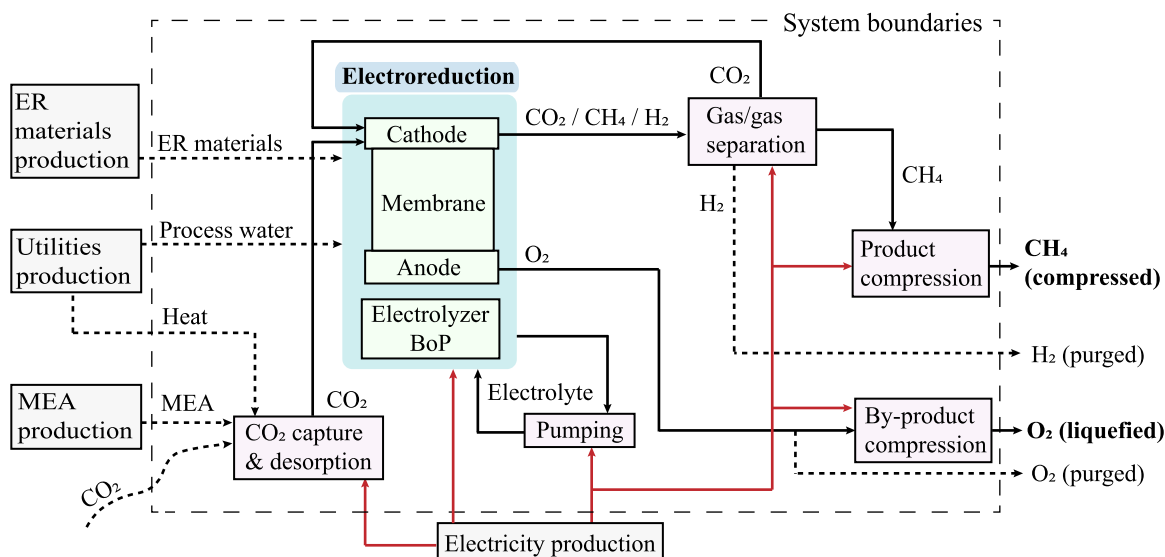

Fig. 2. Flowsheet of the cradle-to-gate PtSNG system by ER of CO_2.

shown in Eq. 9:

$$C_i^{2020} = C_i^{ref} \left(\frac{\text{CEPCI}^{2020}}{\text{CEPCI}^{ref}} \right) \cdot \left(\frac{S}{S_0} \right)^{\alpha} \tag{9}$$

Where it is used a reference cost at a particular year currency (C_i^{ref}), an updating factor using the chemical plant cost index (CEPCI), a capacity reference (S_0), the actual design capacity (S), and a scaling factor (α). Inside battery limits plant costs (ISBL) are calculated by multiplying the base costs with Lang factors (Eq. (10)), so including the installation and additional utilities or instrumentation costs. Off-site, contingency and engineering costs are also considered to determine the total fixed capital cost (TFCC), as expressed in Eq. 11:

$$\text{ISBL} = \sum_i \left(C_i^{2020} \cdot LF_i \right) \tag{10}$$

$$\text{TFCC} = \text{ISBL} \left(1 + f_{\text{Off-site}} \right) \left(1 + f_{\text{contigency}} + f_{\text{engineering}} \right) \tag{11}$$

An off-site factor of 0.17, a contingency factor of 0.1, and an engineering factor of 0.15 are assumed for all the units (Colella et al., 2014). The TFCC is updated with the inflation rate to the star-up year and depreciated using the MARCS method. A 0.5% of TFCC as unplanned yearly replacement cost is also assumed. Additional information on the cost methodology followed for each unit and the fixed capital costs are detailed in the SI.

2.4. Carbon footprint assessment

According to the system boundary displayed in the previous section, the carbon footprint (CF) of the SNG production is calculated by performing an attributional LCA in a cradle-to-gate system. Fig. 2 shows the system boundaries considered for the assessment. Detailed process flowsheet for a given scenario is shown in Appendix A. LCA is a well-established tool to assess the associated environmental impacts of a product, process, or service. In this study, the environmental Global Warming Potential indicator (GWP) was evaluated as the basis for the corresponding CF, identifying critical ER technology areas to make improvements. The functional unit is 1 kg of SNG compressed. LCA is carried out using the mid-point method CML 2001, which restricts quantitative modeling to early stages in the cause-effect chain to limit uncertainties (Guinée, 2001). This method allows the assessment grouped in midpoint categories according to common mechanisms (e.g., climate change, abiotic depletion, etc.) or commonly accepted groupings (e.g., ecotoxicity). This study is strictly focused on the CF category, which is the intended benefit from the ER technology. Of course, other impact categories should be analyzed in the future in a techno-economic positive scenario.

In this context, GWP contribution of ER materials (electrodes, membrane, BoP construction), utilities (e.g., electricity, steam, and water), auxiliary chemicals (MEA), and emissions involved in each stage are considered. CO_2 feedstock is accounted as a negative net emission minus the impacts from its capture (Müller et al., 2020a). Secondary products (H_2 and O_2) are considered wastes with no avoided burdens when they are not valorized. O_2 is valorized in some scenarios as liquefied O_2, applying the system boundaries expansion approach and using its conventional production from cryogenic air separation as reference for the negative impact (Swiss Centre for Life Cycle Inventories, 2020). The net GWP of the system is defined as the difference in the CF of the CCU product (SNG) and the conventional fossil-based one (NG) (Müller et al., 2020b). The mean CF of NG in Europe is estimated as 0.593 kg CO_{2e}/kg NG and varies from a representative range depending on the country and source within 0.166 to 0.917 kg CO_{2e}/kg SNG (Swiss Centre for Life Cycle Inventories, 2020). The electricity emission factor greatly fluctuates depending on its source, and its value is changed depending on the scenarios described in the following section. Other emission factors used in the LCA are listed in Table S4.

Table 3
Model parameters used for 2030-scenarios. The currency exchange rate is €$_{2020}$.

Parameter	Unit	Base	RD/RD-Co
Total current density	mA/cm2	300	1000
Cell voltage	V	3.0	1.8
CH_4 faradaic efficiency	%	70	90
H2 faradaic efficiency	%	30	10
CO_2 single-pass conversion	%	25	50
Cathode lifetime	years	2	5
Anode lifetime	years	10	10
Membrane lifetime	years	5	7
Stack uninstalled cost	€/m^2	6000	1500
SNG selling price	€/kg	0.252	0.252
O_2 selling price	€/kg	Not sold	Not sold/0.060
H_2 selling price	€/kg	Not sold	Not sold
Average carbon tax[1]	€/ton CO_2	70	120
Electricity cost	€/MWh	50	10
Separation cost multiplier	–	1	0.75
Electricity emission factor	kg CO_{2e}/MWh	85	35

[1] Average for the period 2030–2050.

2.5. Market & technology assumptions

Two main scenarios are defined regarding the technology (endogenous) and market (exogenous) situation for a 2030 future-based perspective:

- **Base scenario**, which assumes modest technology improvements from the current status-quo and pessimistic market conditions. ER performance is similar to present electrolyzers (Sánchez et al., 2019), with high energy losses and low current density, selectivity, and conversion. The cathode lifetime is one of the main issues in current CO_2 electrolyzers (Singh et al., 2017), and it gets improved to an average 2-year operation. Anode and membrane durability is similar to present conditions (Schmidt et al., 2017). Tailored on-purpose renewable power plants exclusively dedicated to the ER are not installed, so the grid mix electricity is partially needed to operate. Carbon taxes evolve from today's rate, reaching 50 €/ton CO_2 by 2030 (Schjolset, 2014).
- **Rapid-development (RD) scenario** assumes important advances in CO_2 electrolyzers, renewable energy, and carbon policies. ER conditions get closer to H_2 electrolyzers performance in terms of current density, energy efficiency, and durability (Küngas, 2020; Schmidt et al., 2017). Ideally, tailored on-purpose renewable power plants exclusively dedicated to the CO_2 ER are available, which is equivalent to a deep penetration of renewable energy in the grid. This makes it possible for the ER to be supplied most of the time by low-carbon power. Active policies in carbon taxation increase the emission allowances to 100 €/ton CO_2 by 2030. Separation costs for the chemical absorption and PSA are improved. A sub-alternative scenario called RD-Co is defined when the O_2 produced is valorized (liquified and sold).

The full list of parameters is summarized next in Table 3. SNG market price is considered at 16 €/MWh in both scenarios based on European market fluctuations around 12 €/MWh and 15 €/MWh (MIBGAS, 2017) and the World Bank forecast of increasing in 2030 up to 17 €/MWh (World Bank, 2016). O_2 selling prices fall around 60 €/ton O_2 (Dorris et al., 2016). Carbon taxes are assumed to increase linearly 2 € per year. The levelized cost of electricity (LCOE) is used in this study for predicting the price at which future electricity could be purchased. This assumption must be taken carefully since LCOE only reflects the cost of a project to break even, while the market price of electricity is truly variable over time and other factors. The LCOE in 2030 could be ranging from 25 to 40 €/MWh for PV (Kost et al., 2018) and 30–50 €/MWh for wind (IRENA, 2019). Estimations provide LCOE values of 20 €/MWh by 2050 when using PV technology (Vartiainen et al., 2015). A very low

Table 4

Life cycle inventory and technology metrics for the 2030-scenarios calculated with the process model for 1 kg of SNG.

Component	Unit	Base	RD/RD-Co
Material inputs			
CO_2	kg	3.446	3.203
Cooling water	kg	12.0	11.2
Process water	kg	6.48	5.04
MEA make-up	g	4.96	4.61
Stack area[1]	cm^2	0.54	0.12
Cathode area[2]	cm^2	5.36	0.50
Anode area[2]	cm^2	1.07	0.25
Membrane area[2]	cm^2	2.14	0.36
Material outputs			
SNG	kg	1	1
O_2	kg	5.76	4.48
H_2	kg	0.21	0.06
CO_2	kg	0.67	0.43
Energy inputs			
Electricity	kWh	62.5	29.69/31.97
Heat	MJ	12.1	11.2
Technology metrics			
ER energy efficiency	%	24.5%	52.1%
Total energy efficiency[3]	%	21.1%	42.3%
Net CO_2 conversion[4]	%	89.4%	96.2%

[1] Calculated assuming the same lifetime as the plant.
[2] Calculated from the total area and their specific lifetimes.
[3] Ratio of LHV for CH_4 and total energy (heat+electricity) consumption.
[4] Ratio of converted CO_2 and industrial CO_2 inlet flow.

value of 10 €/MWh is used as an ideal scenario. Electricity carbon intensity is based on the current mix of wind/solar energy for RD scenarios (wind: 10.5 kg CO_{2e}/MWh (Sphera, 2020); solar: 70.2 kg CO_{2e}/MWh (Sphera, 2020)), and an estimation of the European Environment Agency of a grid mix carbon intensity around 75.5–96.8 kg CO_{2e}/MWh in 2030 (European Environment Agency (EEA), 2020). The production of conventional liquefied O_2 has a CF of 0.121 kg CO_{2e}/kg O_2 assuming electricity from the 2030 European grid mix (85 kg CO_{2e}/MWh). Further discussion is provided in the SI.

2.6. Sensibility procedure

The uncertainties concerning this system can drastically change the results due to the sensitivity in some performance variables. For this reason, a deep sensibility analysis is done to provide a wide-ranging reference of what endogenous (ER performance) and exogenous (market/policies) conditions could be needed in the future for producing sustainable renewable SNG. The energy variables are critical in the LCA because of the process's intrinsic high energy demand, so ER energy efficiency and electricity carbon intensity are the variables accounted

for. Regarding the TEA, it is varied the CH_4 current density and the ER energy efficiency, as these variables are strongly bonded to the intrinsic material and energy needs. CH_4 current density and ER energy efficiency are altered by changing total current density and the cell voltage in the model process, as Eq. (6) and Eq. (7) indicate, respectively. All the remaining variables are fixed to the values stated in Table 3.

3. Environmental benefits of SNG by CO_2 ER

Table 4 shows the process modeling results for the proposed scenarios based on the mass balances per 1 kg of SNG. The RD and RD-Co scenarios provide almost the same inventory results as they have the same operating conditions differing whether produced O_2 is liquefied and valorized (needing 0.51 kWh of electricity per kg of O_2) or not.

Fig. 3 shows the PtSNG carbon footprints calculated by the LCA procedure for the three scenarios referred to 1 kg of SNG as the functional unit. The Base scenario would mean to produce SNG emitting 4.35 kg CO_{2e}/kg SNG, which is around one order of magnitude higher than the conventional NG CF (0.166–0.917 kg CO_{2e}/kg NG). The net GWP assuming a mean NG CF of 0.596 kg CO_{2e}/kg NG would be 3.76 kg CO_{2e}/kg SNG. Most of the impacts would come from the electricity, which is assumed to come from the future European grid mix and have a mean emission factor of 85 kg CO_{2e}/MWh, which combined with the high energy needs in the process (62.5 kWh/kg SNG) makes useless this conversion of CO_2 for avoiding emissions. A competitive process CF around −0.68 kg CO_{2e}/kg SNG and −1.16 kg/SNG is estimated in the RD and RD-Co scenarios, respectively, which would mean a negative net GWP of −1.28 kg CO_{2e}/kg SNG (RD) and −1.75 kg CO_{2e}/kg SNG (RD-Co). Improvements come mainly because of the use of renewable energy with lower carbon intensity (35 kg CO_{2e}/MWh) and the reduced energy demands thanks to the better ER performance (~30 kWh/kg SNG). RD-Co scenario gets lower CF because of the valorization of O_2, which is produced at a ratio of 4.48/1 with respect to SNG, and its allocated avoided emissions reduce the total CF significantly (−0.47 kg CO_{2e}/kg SNG) even though the total energy needs are slightly increased.

Fig. 4 shows the sensibility in the net GWP when the ER energy efficiency and the electricity carbon intensity are varied. The Base scenario would save emissions only if low-carbon electricity (< 30 kg CO_{2e}/MWh) and significant EE (> 50%) is achieved. Even when indirect electricity emissions are very reduced, there is still a significant contribution of the heat emissions (0.993 kg CO_{2e}/kg SNG) and the electrolyzer-related materials (0.798 kg CO_{2e}/kg SNG). Higher current densities, electrification of the heat supply, and longer electrode durability would be necessary to improve the process's environmental performance under this situation. CO_2 savings around 1 kg CO_{2e}/kg SNG in the RD scenario are possible, especially under moderate ER energy efficiencies (~40%) and electricity carbon intensities of 60 kg CO_{2e}/MWh
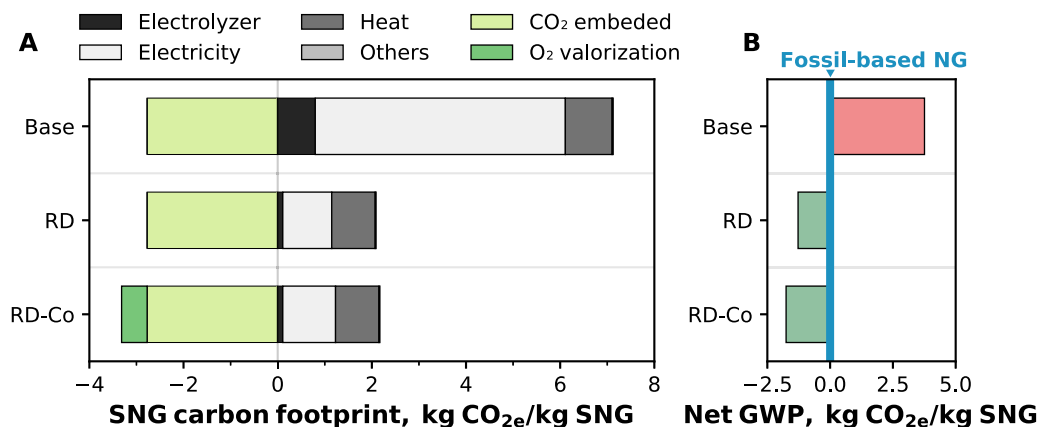

Fig. 3. (A) Carbon footprint of SNG production for the Base, RD, and RD-Co scenarios. (B) Net GWP of the SNG (CF_{SNG}-CF_{NG}). A carbon footprint of fossil NG of 0.596 kg CO_{2e}/kg NG is used.
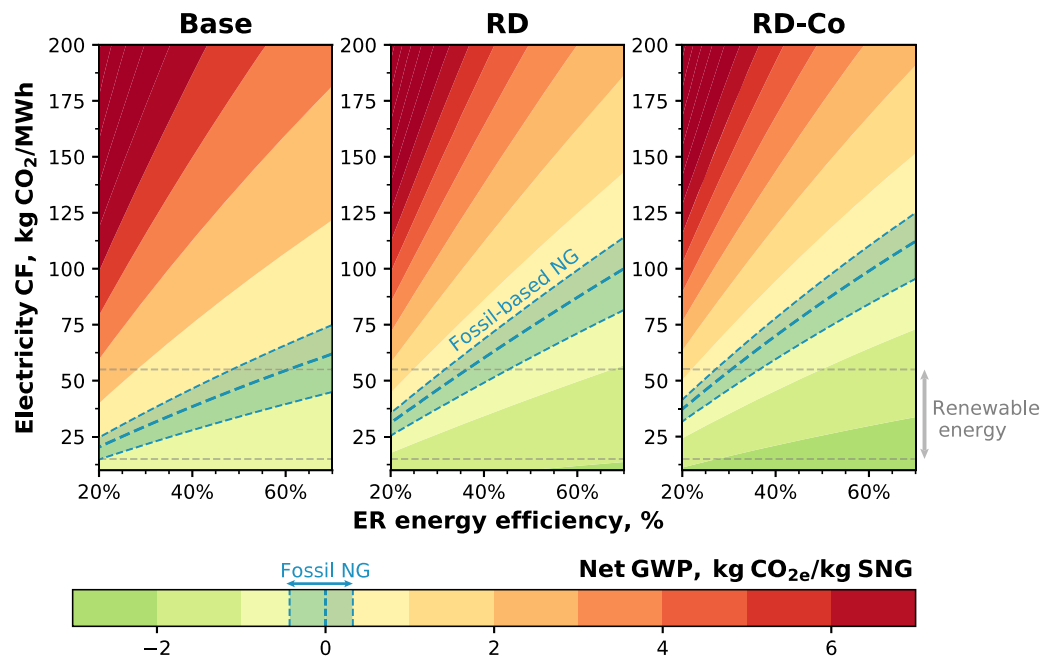
Fig. 4. Net GWP ($CF_{SNG} - CF_{NG}$) as a function of ER energy efficiency and electricity carbon intensity for the Base, the Rapid-development (RD), and the Rapid-development with O_2 valorization (RD-Co) scenarios. Renewable energy range: 15–55 kg CO_{2e}/MWh is given as a representative reference for PV/Wind technologies.
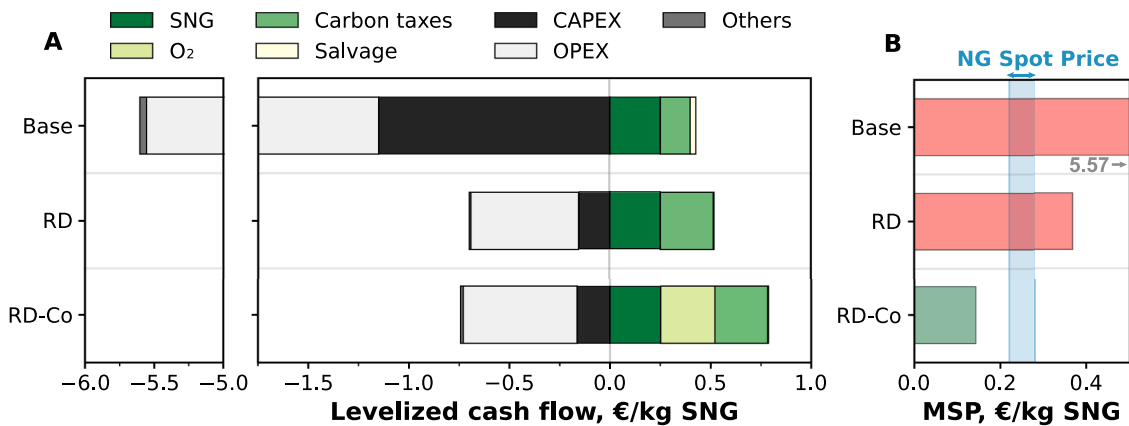

Fig. 5. (a) Levelized costs and revenues on the Base, RD, and RD-Co scenarios ($€_{2020}$). (b) The minimum selling price of SNG in proposed 2030-scenarios ($€_{2020}$) when compared with the expected NG spot price range of 0.221–0.284 €/kg.

or lower. This is a suitable range considering the expected carbon intensities from wind (~15 kg CO_{2e}/MWh) and solar (10–55 kg CO_{2e}/MWh) technologies in the near future (Hertwich et al., 2016). When O_2 is valorized and its emissions are allocated (RD-Co), net CO_2 savings over 1–2 kg CO_{2e}/kg SNG could be obtained for a wide range of ER energy efficiency. Overall, switching from fossil-based NG to CO_2-based SNG may be a significant mitigation measure if similar conditions to the proposed RD/RD-Co scenarios are achieved.

4. Economic competitivity of SNG

4.1. Cost and revenues break-down

The discounted levelized costs and revenues of the PtSNG technology for the 2030-scenarios are shown in Fig. 5.a. A levelized net benefit of 0.046 €/kg SNG for the RD-Co scenario led to a positive NPV of 16.1 M€ for the whole project lifetime and a MSP of 0.143 €/kg SNG (Fig. 5.b). In contrast, when O_2 is not valorized (Base and RD scenario), the profitability of the PtSNG is not feasible. The Base scenario was far from

showing positive profitability, with negative net levelized benefits of −5.17 €/SNG and MSP of 5.57 €/kg SNG. The RD scenario assumed favorable developments in both the ER performance and market/technology state, meaning a vast decrease in either the capital (~88%) and the operating costs (~89%) for a future PtSNG facility. So, the total levelized cost for the RD scenario was reduced from 5.60 €/kg SNG to 0.702 €/kg SNG, but still, a negative benefit of −0.18 €/kg SNG and an uncompetitive MSP of 0.37 €/kg SNG are obtained. Operating costs are the main contribution of the three scenarios (~77%).

Revenues distribution shows that SNG only would represent between 58.7% (Base) and 49.0% (RD) of the total revenues when the O_2 is not sold, and 32.2% when it does (RD-Co), which reflects the low profitability of the SNG by itself. As a reference, it was calculated that the minimum levelized cost under ideal ER conditions would be 0.420 €/kg SNG (Table S5). Considering that SNG European market prices could be ranging in the best case around 16–19 €/MWh (0.25–0.30 €/kg SNG), the only market valorization of SNG is not expectable to be feasible even in future and optimistic scenarios, and complementary revenues (secondary products, carbon credits) could be expected to be of foremost
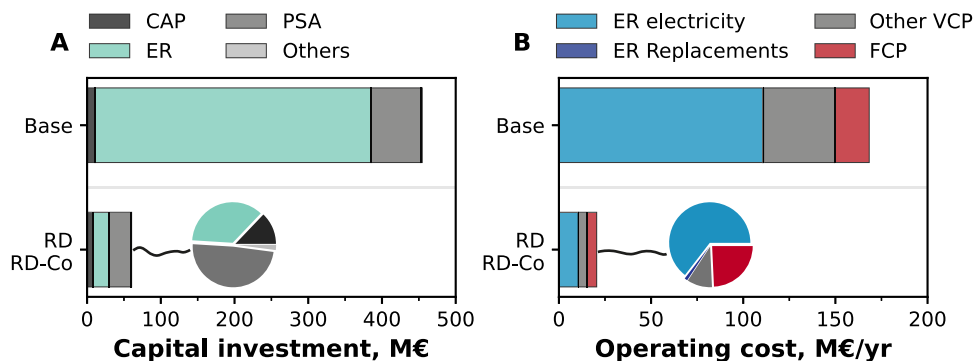
Fig. 6. (a) Capital investment and (b) operating costs distribution for the Base, RD, and RD-Co scenarios in €_{2020}.

importance in its economic viability. This clearly means that the process is not viable from an economic perspective using the current ER performance conditions, which is why it is typically excluded from TEAs of CO_2 utilization. The very tight bound of the revenues to the selling of O_2 really handicaps the overall economic performance of the PtSNG process. The O_2 market is miles from the global market of SNG, thus matching the future of the PtSNG to the commercialization of O_2 at the same scale can be described at least as myopic from a market perspective.

More in-detail cost distribution of the capital investment and the operating cost is shown in Fig. 6. RD-Co scenario is grouped for its similarity in costs with the RD scenario. For the investment, the ER electrolyzer is the primary capital cost in the Base scenario, while it is getting surpassed by the PSA separation train in the RD/RD-Co scenarios. CO_2 capture would be a minor cost, while compression and pumping investment is almost negligible. A very significant reduction in the ECR investment is caused by the lower electrode area needed (an increase in the current density with better electrocatalysts from 300 mA/cm^2 to 1000 mA/cm^2) and the lower uninstalled stack cost, from 6000 $\text{€}/m^2$ to 1500 $\text{€}/m^2$, which strongly depends on the materials used on the ECR, the production scale, and the market evolution. Electricity is

the dominant operating cost in both scenarios, and its reduction in the RD scenario mostly relies on purchasing electricity at a lower cost (from 50 €/MWh to 10 €/MWh) and operating at lower cell overpotentials (1.2 V lower). Most of the electricity is consumed in the ER (~95% in both scenarios), so improving the ER energy efficiency and operating when cheap electricity is available is critical for reducing the associated electricity costs.

4.2. Towards profitability in the ER technology

A tornado analysis is performed in the Base and RD-Co scenarios to analyze the influence of the system variables on economic profitability (Figure S1). It shows the change in the MSP when internal (ER conditions) and external (market) variables are altered from their value in the Base and RD-Co scenarios. Under the Base scenario assumptions, the MSP shows higher priority to electrode-related variables (current density and stack price) as the system costs are co-dominated by the energy and electrode needs. When the electrode costs are lower because of the ER technology improvements (RD/RD-Co scenarios), energy-related variables (electricity cost and cell voltage) show critical importance as the system is highly energy-intensive. Most of the variables show linear
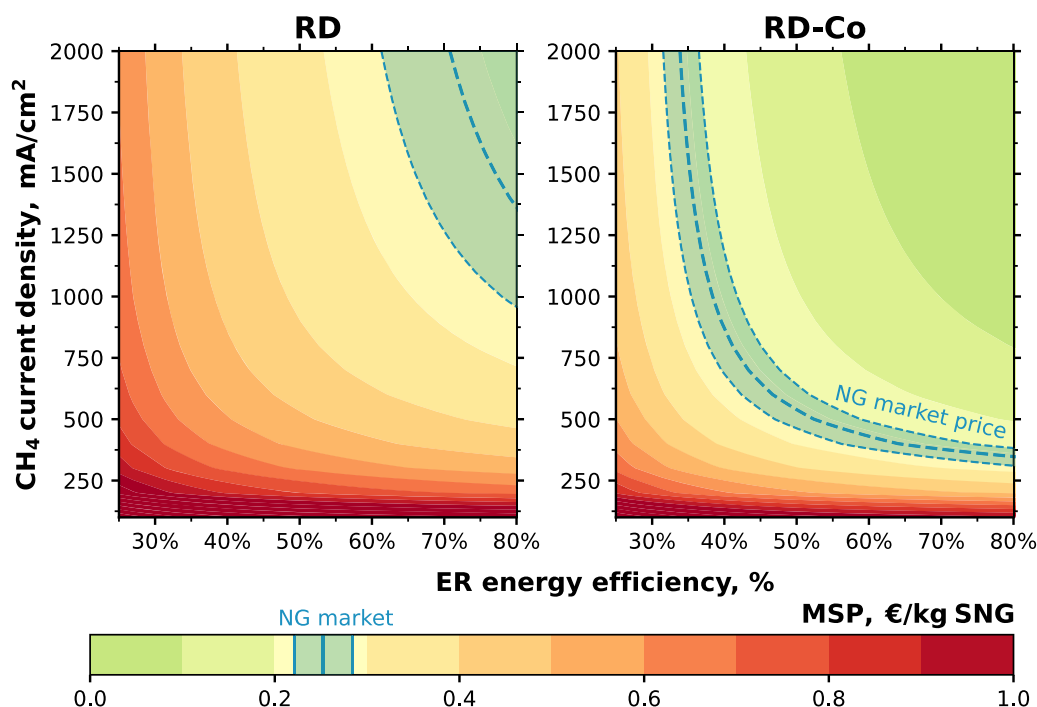

Fig. 7. Minimum selling price (MSP) as a function of ER energy efficiency (%) and CH_4 current density (mA/cm^2) for the Rapid-development (RD) scenario and Rapid-development scenario with co-production of O_2 (RD-Co). The blue area represents the range of NG spot prices in the market.

relationships (e.g., carbon taxes, cell voltage, or electricity cost), while some others show a non-linearity impact on the MSP. Current density is a clear example, as the needed electrode area is inversely proportional to it. Combining relatively high current densities with lower stack costs would be especially important to reduce the capital investment cost initially, and it would lose weight when the electricity starts dominating the cost contribution. Other important non-linear variables are the average production rate and the capacity factor. The capital costs' contribution is strongly affected by both of them, so lower-scale and very intermittent PtSNG systems may need higher current densities to compensate for this situation.

It must also be underlined the relevance of two ER parameters: the electrode/stack stability and the CO_2 single-pass conversion. Regarding the electrode stability, long-lasting cathodes (2 and 5 years) were considered assuming that similar behavior to water electrolyzers could be achieved in the 2030-scenarios. It was calculated (Figure S2) that the cathode replacement would contribute to the total levelized costs a 10% or lower if lifetimes surpass the 6000 h operation in the RD scenario. Cathode lifetime has received much lower attention than the other components, but new studies in this regard are in the literature (Popović et al., 2020). Operating with intermediate capacity factors (3000–6000 h per year) could also reduce the stability problems (Rakousky et al., 2017). Concerning CO_2 single-pass conversion, it is not considered in most of the electrochemical studies, where excess CO_2 is added to minimize mass transport limitations. However, controlling the CO_2 consumption would be essential to reducing its later recovery in the PSA system. When compared to an ideal 100% conversion process, a single-pass conversion of 59% (RD scenario) could be enough to minimize the levelized cost contribution of the CO_2 recovery to 10% (Figure S3).

Fig. 7 shows the MSP as a function of the ER CH_4 current density and electrolyzer EE at considered scenarios. The Base scenario is not included for being unprofitable in all the range of the variables considered, even with current densities close to the ones obtained in PEM electrolyzers and highly energy-efficient reactors. This means that other variables as the electricity price, carbon taxes, or electrode cost also need to evolve favorably in coming years from the current situation to achieve a competitive technology.

If the most favorable market and technology conditions are met with O_2 valorization (RD-Co scenario), CH_4 current densities over 800 mA/cm^2 and energy efficiencies around 60% could be adequate for producing SNG at a positive NPV and a competitive MSP. Current densities in this order of magnitude are already being obtained to other ER products within a similar energy efficiency range (Fan et al., 2020; García de Arquer et al., 2020; Verma et al., 2018), so it could be possible to achieve similar conditions in a CO_2 electrolyzer to CH_4 in the forthcoming years. The RD scenario with no O_2 valorization reflects the situation in which it is impossible to find a potential customer for all the O_2 produced. This is the expected scenario, as it was mentioned previously, as the market for O_2 is orders of magnitude lower than the global NG one. When considering this situation, even with optimistic market and technology assumptions, the viability ranges get considerably narrower than when the O_2 was sold, needing very efficient and highly reactive electrolyzers. An upcoming alternative to the O_2 formation is to substitute the OER reaction with different anodic processes. This enables the production of commercially attractive compounds like alcohols, acids, or aldehydes (Vass et al., 2021). Some techno-economic studies have assessed coupling the CO_2 reduction to a wide variety of anodic products (Na et al., 2019), and economic profitability is substantially improved depending on the product obtained. This trend could be a great complement to the inherent low value of the SNG, but the oxidized product must be such that it can match the market volumes of NG. Fig. 7 manifests that a very stringent set of technical conditions must be met just to touch the historical NG spot prices in the RD scenario, leaving almost no room for mild performance when no anodic product is valorized. Values of EE over 80% and current densities over 1500 mA/cm^2

must be reached to have a PtSNG that rivals the global NG production system.

Both RD and RD-Co scenarios assumed a very optimistic electricity price of 10 €/MWh. Even with a very high penetration of renewable energy, it is not possible to neglect that it is unlikely to be able to operate as much as 6000 h per year at that mean price. Considering a more realistic price within the range of 30–40 €/MWh, the MSP of both scenarios goes over 1 €/kg SNG, and only carbon incentives as high as 200–300 €/ton CO_2 may balance the high operating cost (Figure S4). An example of carbon incentives in this order of magnitude has been recently proposed by Norway's government, which recently suggested increasing carbon taxes up to 200 €/ton CO_2 by 2030 (Government.no, 2021). However, it is quite clear that the profitability of SNG is bonded to a compromise of several ER performance exogenous variables such as anodic product valorization, electricity price, and carbon incentives. Only under very particular combinations, the NG production could be decarbonized by the PtSNG by CO_2 ER route.

5. Conclusions

This work has performed an ex-ante techno-economic and environmental analysis to explore the viability variables of the PtSNG by CO_2 ER for 2030-scenarios. A competitive minimum SNG selling price of 0.143 €/kg SNG and net CO_2 emissions of −1.75 kg CO_{2e}/kg SNG are obtained when very optimistic market and technology assumptions are made and the O_2 produced is valorized. In the short term, it was revealed that improving CH_4 current densities up to values of 500–800 mA/cm^2 would be the primordial keystone to minimize the ER capital investment costs and associated emissions. Once this is achieved, studies may focus on increasing the energy efficiencies by over 60% to reduce electricity consumption, which would be the critical contributor to the total expenses and carbon footprint in the mid-term. When O_2 is not valorized in the Rapid-development scenario, EE over 50% with carbon intensities below 60 kg CO_2/MWh could lead to neutral CO_2 systems. However, for profitability, the ER performance must be pushed to the limits of EE over 80% and simultaneous partial current densities for CH_4 over 1500 mA/cm^2 to match the NG MSP in the spot market. The availability of cheap electricity would be crucial for making laxer or stricter the ER parameters to achieve, and additional carbon incentives around 200 €/ton CO_2 or higher may be needed under most of the possible scenarios. Production scale and other uncertain market parameters as electrode costs or SNG market prices would also be relevant. Electrode stability should be improved to lifetimes of 6000 h for minimizing its economic and environmental contribution, while CO_2 single-pass conversions over 50–60% could be enough from an economic point of view. The only valorization of SNG is hardly profitable by itself because of its low market price, and anodic product valorization should be considered to boost economic competitiveness. Due to the low volume of the O_2 market compared to the NG market, it should be considered the replacement of the oxygen evolution reaction (OER) with a different anodic process to manufacture a second value-added product.

CRediT authorship contribution statement

Javier Fernández-González: Investigation, Software, Visualization, Writing – original draft. **Marta Rumayor:** Investigation, Software, Writing – review & editing. **Antonio Domínguez-Ramos:**
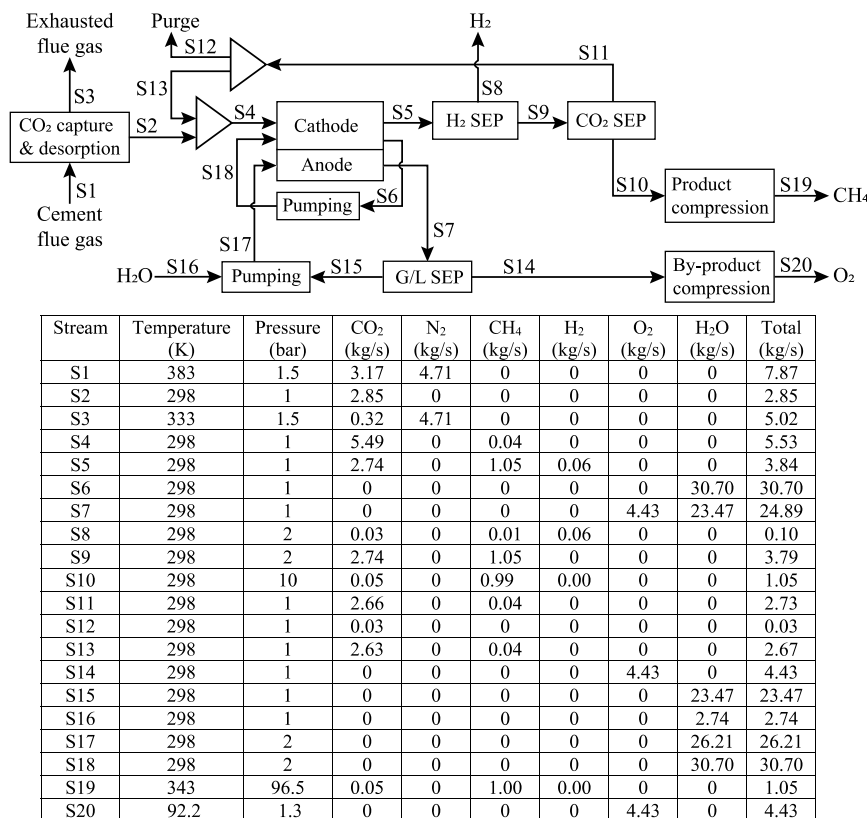
Fig. A1. Process flowsheet of the CO_2 ER plant for a SNG flow of 1 kg/s in the RD-Co scenario.

Stream	Temperature (K)	Pressure (bar)	CO_2 (kg/s)	N_2 (kg/s)	CH_4 (kg/s)	H_2 (kg/s)	O_2 (kg/s)	H_2O (kg/s)	Total (kg/s)
S1	383	1.5	3.17	4.71	0	0	0	0	7.87
S2	298	1	2.85	0	0	0	0	0	2.85
S3	333	1.5	0.32	4.71	0	0	0	0	5.02
S4	298	1	5.49	0	0.04	0	0	0	5.53
S5	298	1	2.74	0	1.05	0.06	0	0	3.84
S6	298	1	0	0	0	0	0	30.70	30.70
S7	298	1	0	0	0	0	4.43	23.47	24.89
S8	298	2	0.03	0	0.01	0.06	0	0	0.10
S9	298	2	2.74	0	1.05	0	0	0	3.79
S10	298	10	0.05	0	0.99	0.00	0	0	1.05
S11	298	1	2.66	0	0.04	0	0	0	2.73
S12	298	1	0.03	0	0	0	0	0	0.03
S13	298	1	2.63	0	0.04	0	0	0	2.67
S14	298	1	0	0	0	0	4.43	0	4.43
S15	298	1	0	0	0	0	0	23.47	23.47
S16	298	1	0	0	0	0	0	2.74	2.74
S17	298	2	0	0	0	0	0	26.21	26.21
S18	298	2	0	0	0	0	0	30.70	30.70
S19	343	96.5	0.05	0	1.00	0.00	0	0	1.05
S20	92.2	1.3	0	0	0	0	4.43	0	4.43

Conceptualization, Methodology, Writing – review & editing. **Ángel Irabien:** Conceptualization, Supervision, Writing – review & editing.

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.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2021.103549.

Appendix A

The mass and energy balances applied to the system boundaries shown in Fig. 2 are exemplified in Fig. A1. It is used the scenario RD-Co under conditions specified in Table 3. It should be noted that additional conditioning of the streams via heat or pressure exchangers may be needed. Gas/liquid separators, mixers, and minor units are neglected in the economic and environmental model. Catholyte and anolyte salts are excluded from the mass balance. Cement flue gas also contains a certain amount of water and oxygen, as well as other minor traces not considered in the model. PSA separation recoveries are oversimplified, assuming almost complete recovery for a certain product (98% H_2, 96% CH_4) and minor losses for the others (1% loss). Deeper considerations should be addressed on the process modeling when achieving higher TRL levels.

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