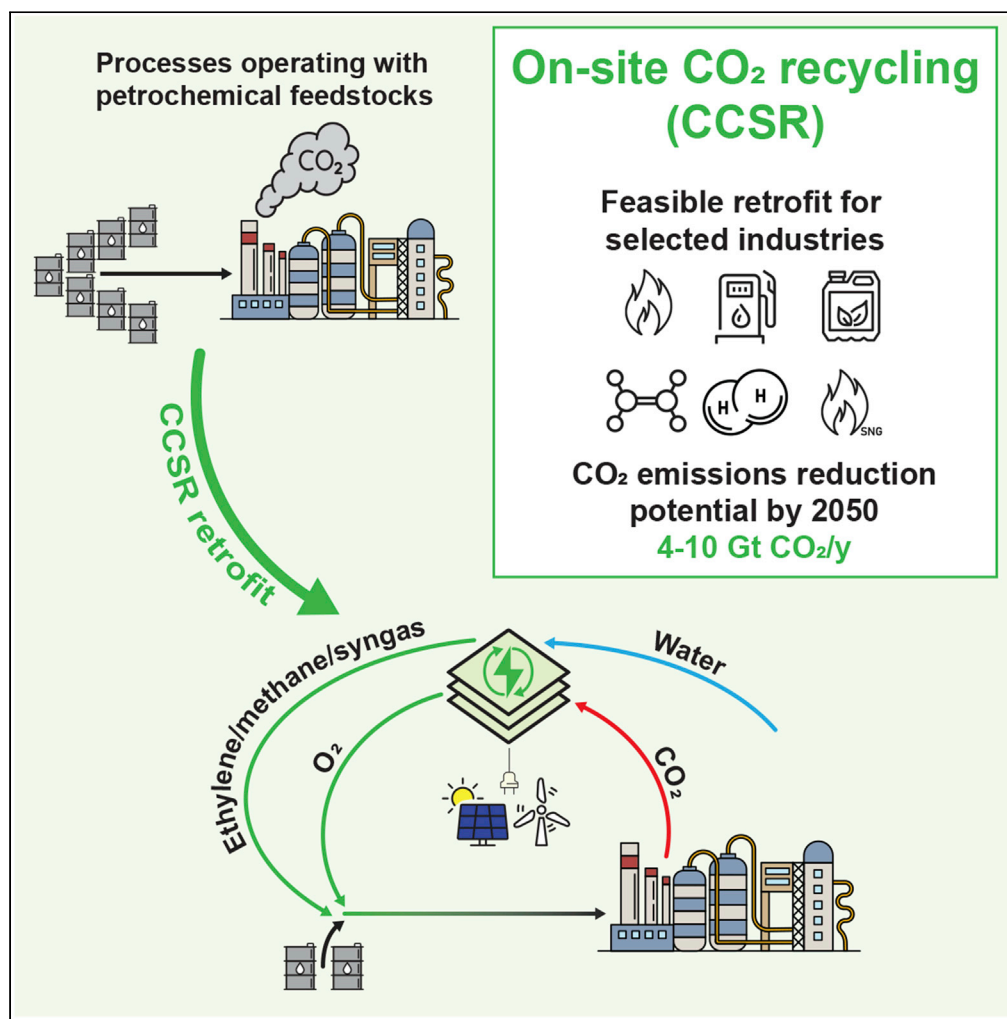


Article

Carbon neutral manufacturing via on-site CO₂ recycling

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Highlights

CO₂ electroconversion is a feasible retrofit for petrochemical plants

On-site recycling removes several barriers against large-scale CO₂ processing

CO₂ recycling concept is economically viable in the current market

On-site recycling has potential to remove 4–10 Gt of CO₂ emissions annually by 2050

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Article

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SUMMARY

The chemical industry needs to significantly decrease carbon dioxide (CO₂) emissions in order to meet the 2050 carbon neutrality goal. Utilization of CO₂ as a chemical feedstock for bulk products is a promising way to mitigate industrial emissions; however, CO₂-based manufacturing is currently not competitive with the established petrochemical methods and its deployment requires creation of a new value chain. Here, we show that an alternative approach, using CO₂ conversion as an add-on to existing manufactures, can disrupt the global carbon cycle while minimally perturbing the operation of chemical plants. Proposed closed-loop on-site CO₂ recycling processes are economically viable in the current market and have the potential for rapid introduction in the industries. Retrofit-based CO₂ recycling can reduce annually between 4 and 10 Gt CO₂ by 2050 and contribute to achieving up to 50% of the industrial carbon neutrality goal.

INTRODUCTION

Immediate changes of the established manufacturing methods are required to achieve the 2050 carbon neutrality goal defined by the Intergovernmental Panel on Climate Change (Masson-Delmotte et al., 2018). Carbon dioxide (CO₂) conversion to chemicals enables re-using of CO₂ instead of its underground storage and reduces the need for extraction of petrochemical feedstocks. Most proposed methods for CO₂ conversion deploy thermochemical hydrogenation of CO₂ feedstock with carbon-neutral hydrogen, obtained using renewable energy. CO₂ technologies that use renewable energy to drive CO₂ conversion and which do not require hydrogen source are of special interest for the transition to more sustainable production methods and a carbon neutral future.

Among emerging techniques proposed for CO₂ to chemicals such as, e.g., photocatalysis (Ulmer et al., 2019; Albero et al., 2020) and biohybrid processes (Cestellos-Blanco et al., 2019), the electroconversion (CO₂R) is projected to be the first to reach the necessary technological readiness level (Bushuyev et al., 2018), as exemplified by several small-scale industrial projects summarized in a recent review (Garg et al., 2020). Looking forward toward large-scale implementation of this technology requires a holistic view of the whole CO₂-based value chain.

Currently investigated CO₂R systems use typically a concentrated CO₂ feed, which implies a significant energetic and economic expense necessary for CO₂ capture (detailed techno-economic analysis suggest optimistic prices of 40 \$/t [Jouny et al., 2018a]). Furthermore, the electrochemical utilization processes still do not demonstrate requisite selectivity at industrially relevant CO₂ conversion rates (>50%), and thus, a CO₂-based plant necessitates also a multistep separation chain, again adding to both investment and operational expenses (Greenblatt et al., 2018). From a carbon abatement perspective, CO₂ conversion must be powered by renewable energy to reduce life cycle emissions (Artz et al., 2018); therefore, CO₂R-based manufacturing needs flexible operating frameworks enabling to store surplus intermittent energy in bulk chemicals.

These aspects have been scrutinized in numerous techno-economic and life cycle assessment studies (Quadrelli et al., 2011; Verma et al., 2016; Bushuyev et al., 2018; Jouny et al., 2018a; Spurgeon and Kumar, 2018; Kibria et al., 2019; Luna et al., 2019; Centi et al., 2020) that investigate a concept of CO₂R as a method to deliver chemical products by means of electrocatalytic conversion instead of petrochemical methods. While CO₂ electroreduction is considered a promising technology, stand-alone CO₂R plants are not yet competitive with the well-established manufacturing processes. Furthermore, deployment of CO₂R on

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the scale necessary to meet the raising demand for bulk chemicals would require a vast investment into commissioning of completely new plants and energy systems, which is not likely to happen by 2050 (Deutch, 2020).

We sought instead to develop an alternative strategy to bring CO₂ electroconversion technology to large-scale operation in such a way as to avoid direct competition with the established manufacturing methods and take the advantage of the already existing infrastructure and value chain. Instead of focusing on CO₂R as a method to deliver chemical products on its own, we propose to use CO₂R to retrofit selected current chemical manufacturing processes and drastically reduce their carbon footprint, enabling the chemical industry to continue using the entrenched methods while reducing their environmental impact.

By realization of on-site closed-loop recycling, we mitigate several economic and technical barriers against CO₂R deployment as well as create an energy usage model facilitating the penetration of renewables into the energy system. Here, we assess the feasibility of such an approach as a decarbonization solution on a larger scale. In our forward-looking analysis, we discuss how to implement CO₂ on-site recycling in an economically viable way and present possible pathways to achieving up to 50% of the industrial 2050 carbon neutrality goal.

RESULTS AND DISCUSSION

Carbon capture on-site recycling concept

Exploring first the most simplified scenarios for the integration of CO₂ electroconversion units into the manufacturing plants, we focused on the processes that currently emit concentrated CO₂ waste streams. These streams do not only offer a high driving force for conversion of waste CO₂ into useful molecules but also typically contain impurities that could potentially poison the electrocatalysts (e.g. O₂, NO_x, H₂S; see Section [Limitations of the study](#)). Hence, these streams are potentially applicable for direct use in the valorization process as CO₂ feed is available at no additional expense. We propose integration concepts for a number of petrochemical processes which allow matching the multicomponent CO₂ electroreduction product mixture to the specification of the main or co-process feed streams and thus maximize the utilization of both cathode and anode outputs (the general concept is demonstrated in [Figure 1A](#)). As a result, our approach does not require downstream and upstream processing expenses and maximizes the use of the existing infrastructure. By realizing CO₂ valorization on the same site, there are virtually no additional logistical costs, and the need for the technologies underpinning CO₂ value chains is drastically limited, which addresses a key limitation in carbon utilization identified previously (Yuan et al., 2016; Jarvis and Samsatli, 2018). Importantly, the proposed CO₂ recycling operates as an add-on process and has the potential to be activated only upon availability of renewable energy. We define the integrated approach, carbon capture on-site recycling (CCSR), as a specific type of utilization being performed on the CO₂ emitting site which acts as retrofit for current manufactures and limits their carbon footprint. Although CCSR is a retrofit-based technology, it has in the long term the potential to address the gigatonne-scale problem of CO₂ emissions.

Potential markets for CCSR deployment

To identify the plants where CCSR can be directly embedded into the manufacturing processes, we first shortlisted the production processes where on-site recycling is technically feasible. Three criteria that must be met are as follows: (i) availability of waste CO₂ streams of required purity at the plant, (ii) demand for molecules that can be produced instead by CO₂R, and (iii) capability of the currently available CO₂ electroconversion systems to deliver these molecules. We will demonstrate that there is a large market of chemical manufactures for which these three criteria can be met. In further steps, we will scrutinize which of shortlisted plants are most promising for CCSR from an economic and environmental perspective.

As the availability of mature electrocatalysts is the limiting factor, we sought first to identify the catalysts suitable for our application. We anticipated that the CO₂R deployment for the on-site recycling purposes should be more straightforward and, hence, we screened experimental reports using a slightly less restrictive metrics as previously considered (Jouny et al., 2018a; Spurgeon and Kumar, 2018), setting the minimum requirement on catalyst selectivity (Faradaic efficiency) at 70% instead of 90%. We focused on current density >100 mA/cm² as minimally required for systems operating on large scales (Burdyny and Smith, 2019) and low full cell voltage (<3–4 V), translating into an acceptable energy conversion efficiency. Further, we selected systems which were tested in at least one report for a stable long-term performance

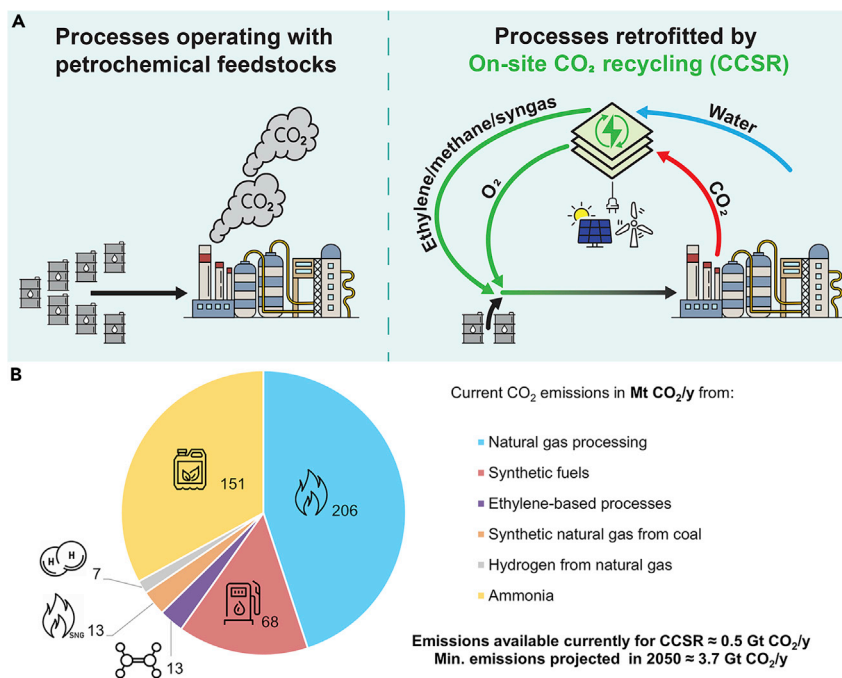


Figure 1. Carbon capture on-site recycling (CCSR)

(A) Scheme of the on-site CO₂ recycling as an add-on for processes operating with petrochemical feedstocks and emitting concentrated CO₂ as a waste stream; see Figure S1 for technical flowsheets.

(B) Plants identified as present opportunities for CO₂ electrorecycling deployment and estimated annual CO₂ emissions (globally) from these plants. CO₂ emissions currently valorized in e.g. urea production are discounted. Complete data for all processes, raw materials, intermediate products, emission densities, and plant capacities are available in Table S1.

(>150 hr on stream). Deployment of selected catalytic systems (Table 1) will still necessitate effort for the process scale-up and addressing stability during at least several months of operation (Lee et al., 2020) and engineering of large-scale units. However, further improvement of, e.g., selectivity is not necessary, significantly shortening the pathway to large-scale applications.

Out of C1 products only formic acid (Yang et al., 2017) and carbon monoxide (Kutz et al., 2017; Haas et al., 2018) production fulfill the above criteria at present. Although requisite long-term selectivity to carbon monoxide is rarely reported, there are numerous demonstrations of less selective, though stable systems which yield a syngas, a mixture of carbon monoxide, hydrogen, methane (produced upon higher temperature and pressure [Bernadet et al., 2017]), and unreacted CO₂. The specific component ratio can be controlled via process operational parameters, and hence, CO₂ reduction can very selectively yield syngas mixtures tailored for different applications (Ebbesen et al., 2009). Out of the wide variety of systems proposed for electrocatalytic syngas production, solid oxide high temperature electrolysis is at present the most energy efficient and stable and is thus recommended for large-scale deployment (Hauch et al., 2006, 2020; Ebbesen et al., 2011; Graves et al., 2011; Kungas, 2020).

Regarding methane production, numerous low-temperature electrocatalysts were reported both in the context of CO₂ utilization (Zhang et al., 2019; Pan and Barile, 2020) and space exploration (Sheehan, 2021). However, currently available systems are still not reaching the selectivity and stability desired for CCSR applications; therefore, we integrated in our analysis an approach based on coupling of electrocatalytic syngas production with catalytic conversion to methane (Koschany et al., 2016).

Among the C2 products, only electrosynthesis of ethylene (Dinh et al., 2018; Vennekoetter et al., 2019; García de Arquer et al., 2020; Ma et al., 2020) is reaching the defined performance benchmarks, and development of tandem systems with two-step electrolysis (CO₂ to CO, CO to C2 products) is likely to further improve the overall process selectivity (Jouny et al., 2018b; Overa et al., 2021).

Table 1. Summary of selected CO₂ electroreduction systems demonstrated with metrics yielding industrially relevant processes

CO ₂ electrolysis product	Catalyst	Faradaic efficiency	Current density range tested (mA/cm ²)	Full cell voltage (V)	Hours on stream	Ref.
CO	Ag	>90%	200	3	4380	(Kutz et al., 2017)
Syngas	Ag	100%	150–300	3–5	1200	(Haas et al., 2018)
	Ag	100%	250	1.025	1100	(Ebbesen et al., 2009)
	Ag	100%	200	0.95–1.95	850	(Ebbesen et al., 2011)
CH ₄ (via electrolysis and chemical conversion)						
	Ni/YSZ-supported SOCs high pressure	100%	250–500	0.9–1.3	1000	(Graves et al., 2011; Koschany et al., 2016)
HCOOH	Sn	94%	100–200	3.5 (@140 mA/cm ²)	550	(Yang et al., 2017)
C ₂ H ₄	NPs/Cu/PTFE	70%	100–750	2.4 (@100 mA/cm ²)	150*	(Dinh et al., 2018)
	Cu	94%	100–300	<2.0 (@100 mA/cm ²)	0.7	(Vennekoetter et al., 2019)
	Cu-CIBH	67.5%	200–1500	3.9 (@1000 mA/cm ²)	60	(García de Arquer et al., 2020)
	F-Cu	65%	up to 1600	2.8 (@ 225 mA/cm ²)	40	(Ma et al., 2020)

Faradaic efficiency is defined as the products of the number of electrons transferred, amount of product and Faraday constant, divided by the charge passed.

Having identified the compounds that can be produced via CO₂R with feasible metrics, we further analyzed which processes utilize these chemicals as raw materials, based on reports from Independent Commodity Intelligence Services for European, Asian, and American markets (Independent Commodity Intelligence Services, 2019). The portfolio of manufacturing processes was screened to identify the processes emitting concentrated streams of waste CO₂. We shortlisted eleven production processes (Table S1, Figure 1B) which are suitable for integration of CO₂ recycling. For these processes, the demand for the electrolysis reactor feed (CO₂) and products (e.g. CO) is met at the same time and in the same plant. Though the total size of CO₂ emissions market applicable for CCSR is currently reaching half gigatonne, it is forecasted to increase several times by 2050 (International Energy Agency, 2011).

We finally compared our results to literature reports on CO₂ sources for carbon capture storage (CCS) (Zakkour and Cook, 2010; International Energy Agency, 2011; Bains et al., 2017), emissions from the chemical industry (Eggleston et al., 2006; Buendia et al., 2019), and CO₂ utilization chains (Pieri et al., 2018). We found that our analysis identified more processes emitting CO₂ than listed in the cited reports, due to different scale focus. While CCS/CO₂ value chains are deployable only for large-scale CO₂ sources, justifiable for creation of the necessary logistical network, the CCSR approach is not scale restricted and can bring economic benefit to plants across different capacities.

Largest opportunities for CCSR: Natural gas extraction plants

Focusing first on the largest market for CCSR, we scrutinized the possibilities of retrofitting natural gas production by means of CO₂ recycling. Natural gas requires processing prior to export to the markets, including removal of CO₂ (present in concentrations between 2 and 70%), and the high purity waste CO₂ stream is usually vented to the atmosphere (only <5% of CO₂ emissions from gas exploration are utilized in the industry [Zakkour and Cook, 2010]); hence, large streams of CO₂ are available for conversion.

We propose to recycle on-site-related CO₂ emissions by catalytic carbon dioxide methanation coupled to high temperature and pressure co-electrolysis of water and CO₂ in solid oxide cells (SOECs), which enhances the energy efficiency (Parigi et al., 2019) and reduces processing costs (Figure 2A). The reduction of the electrical energy input is possible at an expense of higher thermal energy requirement, which is fulfilled by thermal integration with exothermic methane production. Co-electrolysis of water and waste CO₂ enables to obtain a syngas mixture, which is further converted to pure methane in a cascade of state-of-the-art methanation reactors (Topsøe, 2009), applicable for direct injection in the gas grid (Figure S1). To model the recycling section (Table S2), we used here the process performance metrics derived from an integrated SOEC and methanation process model (Giglio et al., 2015b), built up on the experimental data and accounting for scale-up effects such as e.g. dynamics in the electrolyzer operation and resulting need for

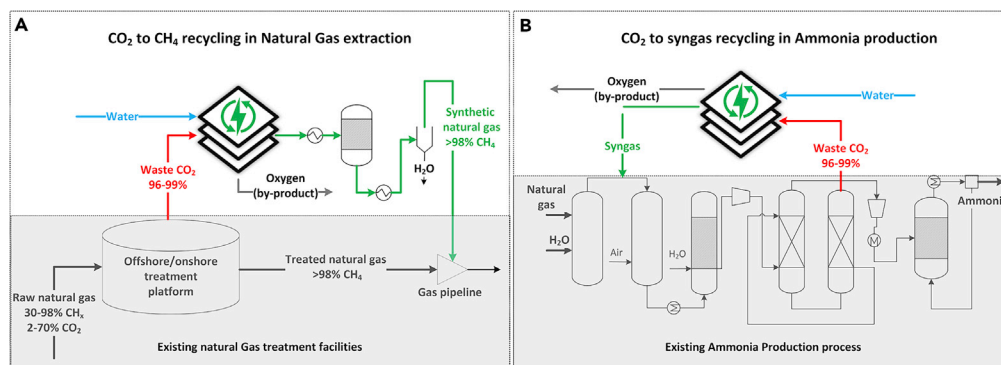


Figure 2. Carbon capture on-site recycling (CCSR) for exemplary manufacturing processes (A and B) (A) natural gas extraction, (B) ammonia production.

an additional stack. The proposed integration concept allows for conversion of complete or a part of CO₂ stream and flexible operation by running electrolysis upon the availability of low-cost electricity.

CCSR for decarbonized ammonia production

Ammonia (NH₃) production plants are another excellent large-scale target for CCSR, and their capacities are likely to be extended due to the emerging market for ammonia as a green fuel. Currently, ammonia is mainly produced from natural gas (being source of hydrogen) and air (source of nitrogen). The process starts with two-step reforming of natural gas: (i) syngas production in the primary reformer and (ii) reaction of syngas in the secondary reformer with the oxygen supplied with the air. Consequently, carbon monoxide from syngas reacts to CO₂, which is removed in the CO₂ scrubbing section. Importantly, such division of the reforming into two reactors enables to use air instead of (costly) pure nitrogen: removal of oxygen from the air happens via oxidation reaction. Therefore, it is not straightforward to replace natural gas as the source of hydrogen in the currently operating plants, as there is a need to generate syngas in a first place. If natural gas were replaced by, e.g., pure hydrogen from water electrolysis, the whole plant would require re-design. Hence, sustainable ammonia production necessitates either vast carbon storage solutions in place (so-called “blue ammonia”) or recommissioning of the whole manufacturing plant to use hydrogen obtained from water electrolysis (“green ammonia”) (MacFarlane et al., 2020).

To enable a retrofit of the current design of ammonia plants, we propose to embed an SOEC co-electrolysis unit, which converts waste CO₂ to a syngas mixture of a same composition as the one leaving primary reformer and feeds it to the secondary reformer (Figure 2B). As a significant amount of thermal energy is required to run co-electrolysis in high temperature, we analyzed the thermal balance of the retrofitted process. Our modeling shows that the amount of heat necessary to supply to the primary reformer equals the heat demand of SOECs (Table S3). Therefore, the overall plant heat balance remains unaffected and the only additional expense is the electrical energy supplied to run the SOEC. Interestingly, CO₂ on-site recycling offers a unique opportunity to reduce the carbon footprint of the existing plant without a need to redesign a whole manufacture; thus, the existing ammonia plants could be used to produce green ammonia in a simplified manner.

CCSR in other manufactures

Beyond natural gas extraction and ammonia plants, CCSR can be deployed by means of CO₂ to syngas recycling in synthetic fuel, hydrogen, and synthetic natural gas from coal production plants. Despite of the policies supporting carbon phaseout, we note an interest in carbon-to-methane processes, with the planned capacities up to 200 billion cubic meters annually (Qin et al., 2017). The proposed CO₂ recycling on-site integration can be used to reduce the CO₂ footprint of this process. Detailed technical considerations of CO₂R integration are given in the STAR Methods section.

Further, we have identified several plants suitable for embedding CO₂ to ethylene recycling. In our previous work, we scrutinized the technical and economic aspects behind the use of electrochemical methods to supply the ethylene-rich feed for ethylene oxide production process (Barecka et al., 2021). Based on the

market analysis presented here, we propose the deployment of a similar method among several ethylene-based industries. The integration concepts, process flowsheets, models, and the data for underlying the economic analysis for all other plants listed in [Figure 1B](#) are given in the [Tables S2–S4](#) and in [STAR methods](#) section.

Techno-economic analysis

To quantify the economic benefit of CCSR use in all shortlisted manufactures, we modeled the cost of CO₂ conversion and the savings achieved through both recycling of CO₂R outputs and avoidance of CO₂ taxes ([Table S5](#)). We assumed that a CO₂R-based retrofit can be considered as economically viable only if it allows reducing the overall manufacturing costs at the given plant. Hence, we sought to explore the limiting price of the renewable energy, which can yield a profitable recycling process and the potential for final product cost reduction by means of recycling-based retrofit.

Uncertainty on electricity prices is usually the main limitation of techno-economic studies focusing on deployment of processes powered by green energy; hence, we used a broad set of systematically collected data on the levelized cost of renewable electricity (LCOE) reported by the International Energy Agency 2020 (IEA) ([International Energy Agency, 2020](#)) to determine a range of power prices to consider. The current LCOE with no CO₂ taxes in place starts at ca. 0.01 USD/kWh (hydropower plants in Norway). About 70% of industrial scale (>1 MW) low-carbon projects reported worldwide by IEA show a low range of LCOE <0.05 USD/kWh, corresponding typically to the operational cost of a power plant with no battery storage. We anticipated that as CCSR technology operates only with a waste CO₂ stream, there will be no disruption to the main production processes in case if CCSR is on shut down and recycling can operate only upon the availability of renewable energy. Thus, we focused on the range of electricity prices that may not include energy storage solutions and evaluated cost reduction under different electricity prices between 0.01 and 0.05 USD/kWh and also in various CO₂ taxation environments (from zero up to the highest taxes recently considered ([The World Bank, 2020](#)), ca. 0.13 \$/kg CO₂, [Figures 3A–3F](#)). In case of high CO₂ taxes being adopted, we assumed the worst-case scenario that the chemical prices will rise accordingly to cover the emerging emission cost.

In a CO₂ tax-free environment, savings through CCSR will reduce operational production costs when electricity is available for less than ca. 0.020 \$/kWh for different syngas-based processes ([Figures 3A–3C](#), [3E](#), and [3F](#)) and less than 0.045 \$/kWh for ethylene-based processes ([Figure 3D](#)). The identified prices correspond to low-end benchmark electricity costs cited by IEA and also to recent bids for new projects (ca. 0.013 \$/kWh [[Bellini, 2020a](#); [2020b](#)]), making recycling viable on the current market even without CO₂ taxation in place. Our techno-economic analysis (TEA) results are based on an assumption that the cited low-cost renewable energy sources are available within a reasonable proximity of a chemical plant. While at least some natural sources of energy (e.g. wind, sun) are widely available, pursuing new renewable energy projects is frequently limited by the lack of potential end user of the intermittent energy. The renewable power price has a potential to be drastically reduced in a consumption model without a grid connection, where the electricity is directly consumed on site ([Swider et al., 2008](#)). Creating links between intermittent energy and chemical production has been identified as an important driver for the penetration of renewables into the market and enables to reduce renewables curtailment ([Haegel et al., 2017](#); [Arbabzadeh et al., 2019](#)), and thus, CCSR provides a needed synergy.

Potential for final product cost reduction is related mainly to the density of CO₂ emissions per product unit ([Figure S1](#)), which translates into the amount of feedstock available for the electrolysis section. Accordingly, production of synthetic natural gas, hydrogen, and ammonia has potential for largest price reductions (up ca. 40% without considering CO₂ tax benefit). Interestingly, there have been several large investments aimed at finding scalable ways to mitigate CO₂ emissions by means of green ammonia projects. However, these approaches yield ammonia at a significantly higher cost (ca. \$510 per tonne [[Tullo, 2020](#)]) as compared to the established petrochemical-based methods (around \$150–\$200 per tonne [[Ewing, 2019](#); [Tullo, 2020](#)]). In contrast, CCSR will reduce CO₂ emissions from ammonia processing while maintaining the economic advantages of the existing technology.

In processes with lower CO₂ emission density such as, e.g., natural gas extraction, CCSR can reduce costs to 11%. In ethylene oxide (EO) production, being an example of an ethylene-based process, recycling does not have a significant margin for final cost reduction (up to 10%), though considering high throughput of EO plants and EO price, annual savings are in order of M\$.

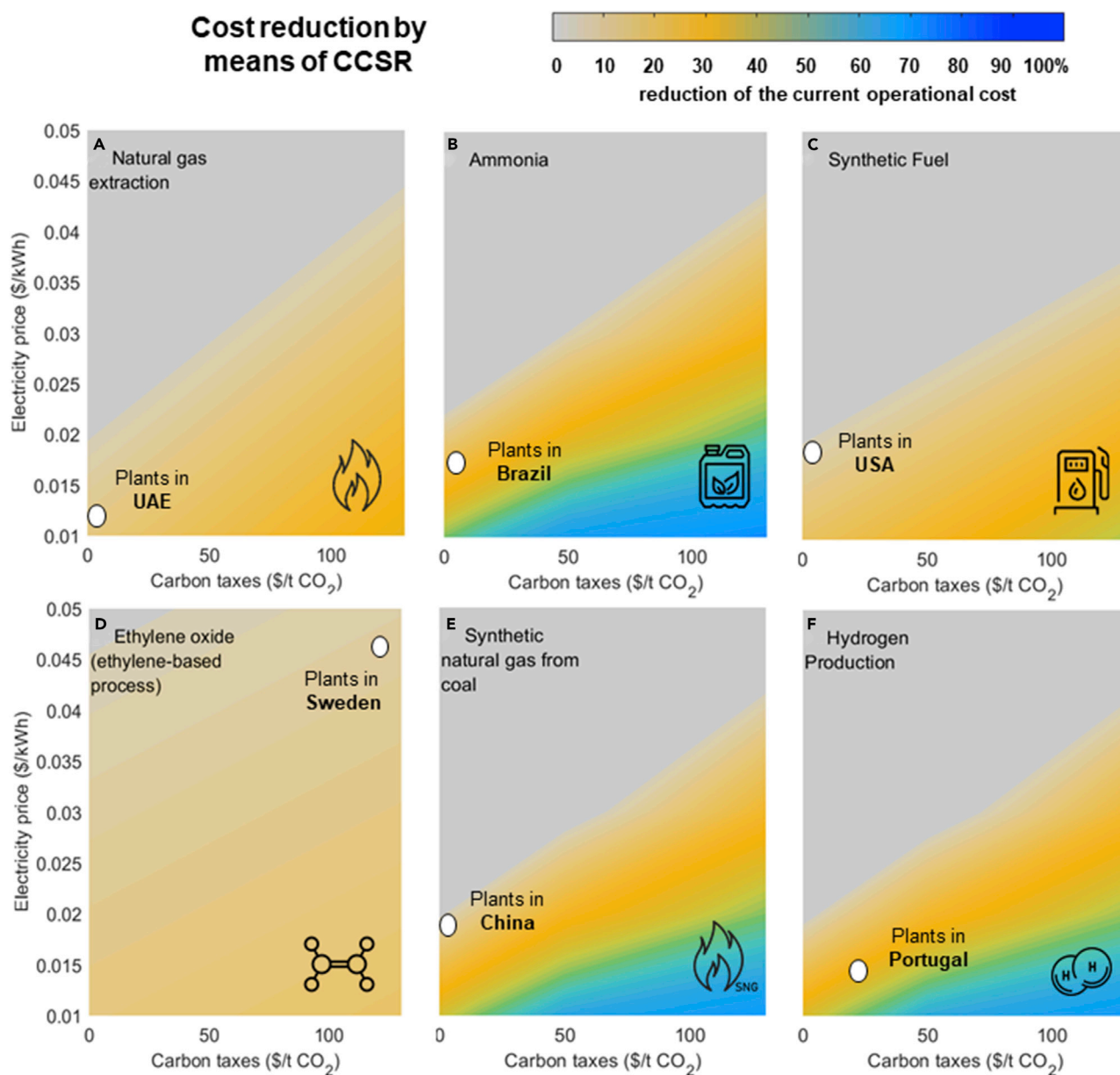


Figure 3. Techno-economic analysis for representative CCSR examples

Potential for final product processing cost reduction by deployment of CO₂ recycling in (A) natural gas extraction (40% CO₂ concentration in raw natural gas), (B) ammonia, (C) synthetic fuel, (D) ethylene oxide, (E) synthetic natural gas from coal, (F) hydrogen production. For all processes, continuous recycling operation is assumed. White dots refer to existing plants and depict current renewable energy bid prices and CO₂ taxes in exemplary countries where analyzed chemicals are produced. Economic data and plant references are provided in Table S5.

In the CO₂ tax-restricted economies, the recycling process has a more pronounced savings potential for all processes (up to 60%) and becomes viable already under higher electricity prices. Importantly, deployment of CCSR reduces the final product prices to the pre-taxation level and allows for economically viable manufacturing for all analyzed processes even in case of extreme CO₂ levies.

To further benchmark our findings, we exemplified achievable savings in different countries where the case study chemicals are produced (white dots in Figures 3A–3F), accounting for the most recent renewable energy bids and accepted CO₂ taxation environment. Operational cost reduction is currently possible in all cited cases. Furthermore, we identified some economies where the benefit of CCSR is intensified due

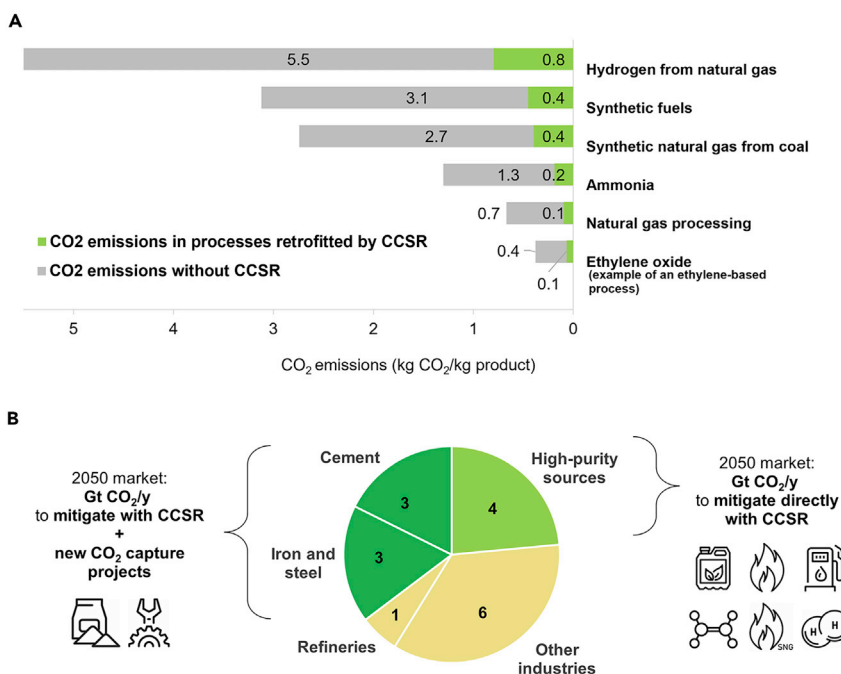


Figure 4. Global potential for CO₂ emissions reduction by means of CCSR

(A) Current direct CO₂ emissions from selected processes without (gray) and with CCSR (green), accounting for the additional life cycle CO₂ emissions arising from electricity generation (hydropower energy considered; reference data in Table S1)

(B) Projected industrial CO₂ emissions in 2050 (International Energy Agency, 2011) and the share of CO₂ emissions market that can be utilized by means of CCSR (green slices). High-purity sources (light green) include only ammonia, natural gas extraction, synthetic natural gas, and synthetic fuel production.

to CO₂ tax implementation (e.g. Sweden and Portugal). Savings are projected to drastically increase with further reductions in the price of renewable sourced power or with wider adoption of CO₂ taxes and other policies supporting decarbonization (Schmidt, 2021), which will encourage investment in CO₂R retrofit projects.

Life cycle CO₂ emission reduction by CCSR

Scrutinizing the decarbonization potential of CCSR, we quantified the additional life cycle CO₂ emissions arising from generation of energy required to power the process and considered this additional input in the overall carbon balance (Figure 4A). In case of renewable energy integration (e.g. hydropower), the additional impact of the electricity used for recycling is minor as opposed to the achieved direct CO₂ emission reduction. Moreover, CO₂ recycling reduces the need for petrochemical feedstocks, not quantified here, as the related emissions are due to significant geographical variation.

Importantly, the upper limit on both economic savings and emission reduction is derived from a scenario where CO₂ recycling is operating continuously, which can be challenging for some carbon-free energy sources. In case of, e.g., intermittent photovoltaic energy powering the conversion process, small-scale CO₂ storage tanks would be necessary to store CO₂ emitted while the electrolysis units are on shut down. Illustrating with the ammonia production case study, a typical middle-sized plant of 200 kt annual capacity emits ca 0.03 kt of CO₂/h (Table S1); the foreseeable two-day storage would require therefore temporal storage tanks for 1.4 kt of CO₂. Storage on such scale is not unknown to the processing industry, as ammonia plants where CO₂ utilization to e.g. urea or food beverages is deployed (discounted from the global CCSR potential), accommodate CO₂ storage tanks with capacities up to 3 kt (Haugen et al., 2017). While adding further complexity is not desired for early-stage process applications, storage tank integration might be feasible once the technology is better explored and be used for complete emission abatement in a longer term.

CO₂ emission reduction potential by 2050

Based on TEA, we identified that for each of the processes, on-site recycling can be economically viable when energy is available in the range of prices between 0.02 and 0.45 USD/kWh, which corresponds to the price with no battery storage in many economies. Hence, CCSR could provide a necessary economic incentive to realize CO₂ utilization projects, and consequently, the emissions from identified manufactures have potential to be mitigated with CCSR. Based on estimated market sizes, the cumulative market of CO₂ emissions for CCSR is currently around 0.5 Gt of CO₂ annually (Table S1). We questioned therefore how this market can evolve in the upcoming decades. International Energy Agency (2011) has presented a detailed projection of industrial CO₂ emissions by 2050 that accounts for the growing population and the increase of the demand for chemical products. The emissions from the high-purity sector defined by IEA are foreseen to raise to ca. 4 Gt annually by 2050 and have potential to be recycled by CCSR.

Furthermore, throughout large-scale deployment of CCSR, process improvements may further increase the benefit, making CO₂ recycling attractive enough to extend it to other processes that currently do not emit concentrated CO₂ streams. With investment in new CO₂ capture projects, which are foreseen to become much more affordable by 2030 (Singh et al., 2019), CO₂-intensive industries such as cement and steel production could also integrate on-site recycling of CO₂ to methane (energy carrier) or syngas, following the similar, economically viable concepts presented for natural gas processing and syngas-based industries (see STAR methods). In case of the complete capture of CO₂ from these industries, CCSR could be used to treat 5.6 Gt predicted to be emitted annually in 2050 by these manufactures. Overall, CCSR can potentially mitigate up to ca. 10 Gt/year of CO₂ and, thus, contributes on its own to achievement of around a half of the chemical industry 2050 carbon neutrality goal (Figure 4B).

Notably, deployment of new technologies across different industries might affect the projected CO₂ emissions in 2050. For instance, reduction of the emissions from e.g. electricity sector through drastic increase of energy efficiency is feasible and favored within forward-looking technology roadmaps (International Energy Agency, 2011). Nevertheless, the direct CO₂ emissions analyzed here that originate from petrochemical feedstock extraction, unselective chemical conversion reactions, or from natural gas use cannot be significantly reduced just by use of more efficient processing technology, and the only solution considered on the gigatonne scale is carbon sequestration. The amount of CO₂ emitted from the considered industries is consequently likely to be close to the predicted values, and hence, it is meaningful to benchmark our findings against cited here 2050 emissions scenario.

Scale-up considerations

Realizing the promising CO₂ emission reduction by means of CCSR will require not only effort in the scale-up of electrolyzers but also a vast investment into new renewable energy production needed to power the process. We questioned therefore how much energy would be globally needed to recycle all CO₂ emissions projected by 2050. As the majority of processes proposed here are based on syngas-based recycling, we extracted from used models the energy requirement to convert 1 kg of CO₂ (6.3 kWh/kg CO₂). Scaling-up the energy requirement to gigatonnes-sized goals for CCSR, 1 Gt emission abatement would require 2.3×10^4 PJ of energy annually, which corresponds to ca. 15% of the renewable energy available in 2050 as predicted by the International Renewable Energy Agency (2018a), 2018b. Recycling all of these emissions requires consequently larger expansion of the renewable grid that is currently being considered. CCSR is in position to provide the necessary stimulus for further renewables growth.

New renewable energy projects would also need to fit within the footprint of the chemical plants, and we used ammonia production as a case study to discuss if this is feasible. We selected a typical, middle-sized plant of 200 kta capacity located in Oklahoma, USA. Based on models developed here, such manufacture would require ca. 200 MW of energy input to recycle direct CO₂ emissions. Using the local energy calculator PVWatts published by the National Renewable Energy Laboratory, we estimated the average solar radiation at 5.48 kWh/m²/day, yielding roughly 1 km² of the panels required to power the process. Given the size of large, integrated plants, estimated footprint shall not be impossible to integrate.

Finally, recycling CO₂ to hydrocarbons necessitates a significant input of water as the source of hydrogen. The most hydrogen-intensive recycling scenario, production of methane, necessitates 2 moles of water per 1 mole of recycled CO₂, yielding 0.046 kg of water input per MJ of energy output. In comparison, a coal-fired plant requires 25 kg/MJ (Magneschi et al., 2017). While our TEA incorporates a relatively high cost

benchmark for water (Jouny et al., 2018a), both price and availability of water is due to significant geographical variations and will need to be carefully assessed for CCSR projects.

Lastly, presented TEA and carbon balances are derived from currently demonstrated electrocatalytic process metrics and reflect real-scale process deployment, including critical product separation steps. However, our analysis does not reflect the anticipated benefits of the learning curve and scale-up and therefore does not foresee the performance of a mature and optimized technology.

Comparison to other carbon abatement methods

Given that CCSR could potentially be used to recycle gigatonnes of CO₂ emissions, it is meaningful to compare this technology to other abatement methods that can be deployed at large scale, such as carbon sequestration or using the intermittent renewable energy for battery storage/heat generation instead of powering the electrolyzers. CCSR will still necessitate effort for process scale-up and demonstration of long-term stability, as is not as mature as underground or battery storage. However, it offers an advantage of reducing both CO₂ emissions and fossil fuels extraction. As CCSR enables to gather experience in large-scale electroreduction, it accelerates future adoption of other CO₂ valorization routes. This experience is also projected to be a breakthrough in the development of less mature electrocatalytic systems for, e.g., propylene oxide (Leow et al., 2020), bypassing multi-step petrochemical-based processes by direct conversion of CO₂ to more complex products. Ultimately, when the existing manufactures will entirely transition to sustainable production methods, CCSR electrolyzers can accommodate new electrocatalysts for direct production of commodity chemicals.

CONCLUSIONS

We found that the deployment of CO₂ electroreduction as an on-site recycling enables to simultaneously reduce CO₂ emissions from manufacture and the cost of chemical production in a wide range of markets. Significant savings achieved through exploring the synergies between mature and novel processes make the on-site recycling the most economical and de-risked platform for large-scale CO₂ electroreduction. In a forward-looking scenario, CCSR can be deployed to recycle between 4 and 10 Gta of the projected CO₂ emissions by 2050. Large-scale CCSR would require a drastic increase of renewable energy generation; thus, we propose an on-site consumption model enabling the use of intermittent energy and supporting the growth of the renewables market.

Gigatonne-scale CO₂ abatement potential and promising economic performance of the on-site CO₂ recycling concept justifies taking immediate steps to scale-up the electroreduction technology, which previously has not been widely perceived as competitive enough to penetrate the established chemical market. As CCSR deployment does not require investment into construction of new chemical plants nor creation of new value chains, it addresses key barriers toward achievement of net zero emissions (Deutch, 2020) and has a potential to be deployed on large scales within the limited time available to achieve 2050 neutrality goal and support in a long term the transition to fully sustainable manufacturing methods.

Limitations of the study

The process integration concepts presented here are derived from currently available data on both electrocatalytic systems and industrially deployed chemical production processes. Large-scale CCSR will necessitate experimental insights into the integration concepts, necessary in the context of, e.g., verification of the possible impact of minor impurities in CO₂ gas streams. We focused first on industrial processes that typically emit CO₂ emissions without potential impurities (Bains et al., 2017) (e.g. O₂/NO_x) to the particular catalysts considered in this study (Ag, Ni, Cu), see (Bains et al., 2017) and Table S1. In forward-looking scenarios, such as cement and steel production, sulfur-based impurities (H₂S) are identified (Bains et al., 2017). The solid oxide (SO) electrolysis community is addressing this problem, and we anticipate that the developments from the SO fuel cells on Ni electrodes resistant to H₂S contamination can be extrapolated to CO₂ conversion (Aguilar et al., 2004; Zhang et al., 2010). On the contrary, CO₂ sources in petroleum refineries and ethylene production contain much more impurities and are therefore not included in the projected CCSR market by 2050.

Flexible integration of CO₂ on-site recycling into the manufacturing will necessitate as well further research on efficient electrolyzer startup and shut-down procedures. The typical warm start-up for the SOEC

electrolysis is around 15 min (Keçebaş et al. (2019), whereas the shut-down of SOECs is reported as immediate after the power cut (La Vadum Cour, 2021). Overall, start-up times in the range of minutes seem to be acceptable for the integration with the renewable energy sources, e.g. photovoltaics, where the data collected over a long term shows that the peaks of electricity generation are observed typically over hours (National Renewable Energy Laboratory, 2006; Jahid et al., 2019). Though SOEC electrolyzers were selected here to illustrate the CO₂ to syngas recycling method, applicable to the largest share of CO₂ emissions, the concept of CCSR is not restricted to high-temperature electrolysis and will benefit greatly from advances across all electrocatalysis fields.

SUPPORTING CITATIONS

The following references appear in the supplemental information: Al-Mayman et al., 2018; Barecka et al., 2017; BP, 2020; Brown, 2019; Business Insider, 2020; Chandel and Williams, 2009; Cheung et al., 2003; Cucchiniella et al., 2017; Eckert et al., 2003; Eurostat, 2019; Fu et al., 2010; Garside, 2018, 2020; Guilera et al., 2020; Hiller et al., 2003; International Energy Agency, 2019; International Renewable Energy Agency, 2019; Luyben and Tyréus, 1998; Metz et al., 2005; Montebelli et al., 2015; Nexant, 2018; Peschel, 2012; Rebsdatt and Mayer, 2003; Shell South Africa, 2020; Wang et al., 2013; Wisner and Bolinger, 2019.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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 - CO₂ to ethylene
 - Electroreduction reactors sizing and TEA

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2021.102514>.

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AUTHOR CONTRIBUTIONS

M.H.B. devised the concept of on-site CO₂ recycling, developed the methodology, visualized the data, and wrote the original manuscript; M.H.B and J.W.A conceptualized the paper; J.W.A and A.A.L acquired funding for the project, administered the project, supervised the project, reviewed, and edited the manuscript.

DECLARATION OF INTERESTS

The authors filed patent applications US 62/987,369 and US 63/036,477 for CO₂ recycling in ethylene-based plants. There are no other conflicts of interest to declare.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Deposited Data		
Dataset on CO2 emissions market	This paper (supplemental information, Table 1)	

RESOURCE AVAILABILITY

Lead contact

Further information should be directed to and will be fulfilled by the lead contact, Magda H. Barecka (mb2363@cam.ac.uk).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The attached [supplemental information](#) file includes all datasets generated or analyzed during this study.

METHOD DETAILS

Recycling processes modeling: CO₂ to methane

Simulation of the integrated solid oxide electrolysis cell (SOEC) and methanation employs a detailed electrocatalytic model ([Giglio et al., 2015b](#)), which accounts for heat exchange optimization yielding the most energy efficient process and considers several scale-up effects such as stack deactivation, possible carbon formation etc. Following assumptions were considered during the model implementation: (i) SOEC feed composition (vol %): 65% H₂O, 25% CO₂ and 10% H₂, with the H₂ ratio provided by the outlet gas recycling; (ii) SOEC product distribution is derived from experimental studies ([Bernadet et al., 2017](#)), with similar results and trends reported in several experimental and experiment-guided modeling works ([Ebbesen et al., 2009](#); [Stoots et al., 2009](#); [Sun et al., 2012](#)); (iii) long-term operation at 850°C experimentally demonstrated in several reports ([Hauch et al., 2006](#); [Ebbesen et al., 2011](#); [Graves et al., 2011](#)); (iv) feed conversion rate is set as 70%, as demonstrated feasible by [O'Brien et al. \(2009\)](#); (v) on the anode side, oxygen is produced as a pure gas; though operation in concentrated oxygen conditions implies additional safety concerns, those were reported to be already solved by Idaho National Lab ([O'Brien et al., 2009](#)); (vi) cost-wise, the worst-case scenario of the cell voltage and current density was extracted from the modeling results; (vii) the methanation part uses the Haldor-Topsøe TREMPTM technology; (ix) in previously reported model ([Giglio et al., 2015a](#)), nitrogen blending takes places as the last treatment step before the grid injection of the synthetic natural gas; in our model we do not consider costs of nitrogen blending, as the synthetic natural gas produced by recycling is a co-feed to the extracted natural gas, containing already different dilution gases and the raw natural gas can be used for blending purposes. [Table S2](#) summarizes key modeling parameters and process streams. Apart from natural gas extraction, CO₂ to methane on-site recycling can be also deployed in biogas production, following the same processing concept or other CO₂ intensive industries where methane can be used as an energy carrier (e.g. cement industry).

CO₂ to syngas in ammonia production

CO₂ recycling in ammonia uses the same SOEC stack as described in CO₂ to methane process, coupled with an evaporation unit where an additional amount of water is being evaporated to meet the specifications of the second reformed feed stream (minor impurities N₂ and Ar in the industrial stream are not listed), plus correction of the CO₂ concentration by addition of a small part of pure CO₂ ([Table S3](#)). Importantly, concentration of the SOEC outlet stream can be further adjusted by selection of different operational pressure, feed composition or reactant utilization ([Sun et al., 2012](#)).

Heat balance for the primary reformer. Thermal expense required for operation of the primary reformer was evaluated based on industrial reports on the primary reformer feed composition and energy balance (Singh and Saraf, 1981; AL-Dhfeery and Jassem, 2012). We estimated the thermal heat necessary to heat-up and vaporize water and natural gas to the reformer operational temperature, and the heat necessary to maintain the reactions happening in the first reformer. The overall heat input is $1.11 \cdot 10^4$ kJ/kg of syngas produced.

Heat balance for the SOEC stack. The heat requirement for SOEC based syngas production was evaluated in a similar way, accounting for heating up and evaporation of water and heating up of the CO₂ stream required to obtain the same product as from the primary reformer (based on reported data by Giglio et al., 2015a and necessary vapor content correction). There is no additional supply of thermal energy for the reaction itself, as the energy requirements are covered by the electrical energy. The overall heat input for SOEC is $1.04 \cdot 10^4$ kJ/kg of syngas produced. Estimated heat input has a potential for further minimization by means of thermal integration within the plant.

CO₂ to syngas in other processes

Other identified syngas-based processes are either related to the production of basic chemicals and energy carriers such as hydrogen, methane and synthetic fuels obtained from coal gasification. Though multiple designs for the syngas productions steps exist, in all cases the removed CO₂ can be converted on SOEC stack back to syngas with a specific composition adjusted by SOEC operational parameters (Sun et al., 2012). The SOEC cathode output can be recycled to the final product manufacturing section, and the anode output - oxygen stream is recycled to the reforming unit (Figure S1D). The main difference between the deployments for various processes is the quantity of CO₂ available for conversion (Table S1), what results in how much of the actual process feed will be replaced by the recycled syngas. Some hydrogen production plants are operated with air stream instead of oxygen, so the economic benefit of oxygen production is accordingly discounted in the following TEA. In a full-scale deployment scenario for hydrogen plants, complete need for syngas could be covered by CO₂ recycling, eliminating the need for reforming on any scale; in this case, oxygen also becomes a sellable side-product.

Stream composition from SOEC stack. Concentration of the SOEC outlet stream can be adjusted by selection of different operational pressure, feed composition or reactant utilization and meet the desired syngas ratio for any syngas-based processes (Sun et al., 2012). In coal to fuels or coal to liquid no vapor content correction is needed. In hydrogen production, minor correction is required (Table S4).

Hydrogen production process. The proposal to use CO₂ electroreduction to syngas in hydrogen production might seem surprising, as direct, one-step hydrogen production by water splitting is much more established and promising as an ultimate alternative to fossil fuels based production. However, the retrofit for the already existing hydrogen production plants is technically much easier with CO₂ electroreduction than water splitting units. The reason behind this is twofold. First, a smaller electrolyzer area will be necessary to meet the plant design capacity. Production of syngas in the first place enables to produce only a part of hydrogen by an electrochemical reaction, whereas the rest is produced by the established steam reforming. On the contrary, while using water splitting, all hydrogen is produced electrocatalytically, requiring larger capital-cost intensive units. Second, maintaining the product delivery route based on syngas enables to the continuous production independently of the availability of the renewable energy. Thus, a plant deploying CO₂ based recycling can meet its production capacity anytime.

Heat balance. As SOEC operation is thermal energy intensive, possibilities for of heat integration within the plant should be identified. Similar as for the ammonia case study, we verified how much thermal energy is currently used for reforming purposes and assumed that this energy can be delivered instead to the SOEC stack.

The particular conditions for syngas production in different processes where recycling can be embedded are usually optimized with respect to the operational requirements of the main reaction sections and might differ in terms of the operational temperature and pressure. However, the overall heat input is mainly governed by the activation energy of the reforming reaction which is similar among different processes (usual reported range is between 95-114 kJ/mol (Biesheuvel and Kramer, 2003), with carbon feedstock

105-130 kJ/mol (Álvarez et al., 1995)). Therefore, our estimation of the energy input for syngas production in the ammonia process (based on low activation energy value of 100 kJ/mol) can be used to benchmark also other reforming processes. Similar energy input (ca. $1.31 \cdot 10^4$ kJ/kg) can be estimated specifically for synthetic fuels from coal production based on plant design reported (Sudiro and Bertucco, 2009). Furthermore, this reference shows also that a carbon based syngas production yields a significant amount of ashes and impurities which require removal prior to subsequent fuels production and additional energy-intensive separation steps. SOEC based syngas production does not yield such impurities and consequently enables further reduction of the thermal energy inputs. The energy input estimated for SOEC syngas production ($1.04 \cdot 10^4$ kJ/kg of syngas produced) has a potential to be lower by up to 50% in case of e.g. hydrogen production, where the syngas composition required by the state-of-the-art industrial process (Carrara et al., 2010) may not require vapor content correction. Given the further potential of heat integration, we assume that the heat flow to the classical reforming units is in the worst-case scenario roughly equal to the heat flow to the SOEC stack.

CO₂ to ethylene

All ethylene-based processes identified incorporate oxidation of the ethylene feedstock to different bulk chemicals. In these processes, ethylene can either react to the desired product, either undergoes a total oxidation to CO₂.

Due to operational similarities emerging from common underlying chemistry, the CO₂ conversion can be integrated following same concept depicted in Figure S1E. Following operational parameters were considered for recycling modeling: (i) cell voltage: 2V; (ii) Faradaic efficiencies: C₂H₄ 88.7%, CO 3.8%, H₂ 7.5% (Venekoetter et al., 2019).

As CO₂ is already partially fed to the main reactors in the identified ethylene-based processes, there is no need for full CO₂ conversion to make CO₂ recycling viable to integrate within the chemical plant. Consequently, the stack can operate with CO₂ conversions rates between 50-100%. Further technical details about the integration of CO₂ recycling specifically into ethylene oxide plants are given in separate report (Barecka et al., 2021) and the same concept can be deployed across all ethylene-based industries identified here.

Electroreduction reactors sizing and TEA

The reactors sizing is based on the available CO₂ feed, target conversion and experimentally demonstrated conversion per unit area:

$$\text{electroreduction reactor area (m}^2\text{)} = \frac{\text{available CO}_2 \left(\frac{\text{mol}}{\text{s}}\right) \cdot \text{CO}_2 \text{ conversion}}{\text{CO}_2 \text{ converted during reaction} \left(\frac{\text{mol}}{\text{s} \cdot \text{m}^2}\right)} \quad (\text{Equation 1})$$

Where available CO₂ is defined by the process emissions (see Table S1), CO₂ conversion is set as given in the recycling processes descriptions, CO₂ converted during reaction is calculated from the product flow (based on reaction stoichiometry).

The power needed for operation is a function of the cell voltage and total current:

$$\text{power (W)} = \frac{\text{product flow} \left(\frac{\text{mol}}{\text{s}}\right) \cdot \text{nb of electrons needed} \cdot \text{Faraday constant} \left(\frac{\text{C}}{\text{mol}}\right)}{\text{Faradaic efficiency}} \cdot \text{cell voltage (V)} \quad (\text{Equation 2})$$

Where the product flow, Faradaic efficiency and cell voltage is derived from the experimental reports cited above and the number of electrons is reported in various literature sources (e.g. (Jouny et al., 2018a))

Final reduction of the final product price (e.g. ammonia) was evaluated as following:

$$\begin{aligned}
 \text{Final product cost reduction} = & \left(-\frac{\text{recycling operational costs}}{\text{kg of CO}_2 \text{ recycled}} + \frac{\text{value of the recycling stream}}{\text{kg of CO}_2 \text{ recycled}} \right. \\
 & \left. + \text{CO}_2 \text{ taxes} \right) * \text{CO}_2 \text{ emissions density} \Big/ \left(\text{final product price} \right)
 \end{aligned}$$

(Equation 3)

Where the recycling costs are evaluated from the energy requirement (see [Equation 2](#)), value of the recycling stream is based on the product flow and bulk chemicals prices ([Table S5](#)) and the emissions density is given in [Table S1](#). CO₂ taxes are scrutinized during the sensitivity analysis and vary between 0-130 \$/t.