

FEATURE ARTICLE

Reuse of CO₂ in energy intensive process industries[†]Siglinda Perathoner,^{*a} Kevin M. Van Geem,^b Guy B. Marin^b and Gabriele Centi^{a,c}Received 00th January 20xx,
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Closing the carbon cycle and enabling a carbon circular economy in energy intensive industries (iron and steel, cement, refineries, petrochemistry and fertilizers) are topics of increasing interest to meet the demanding target of defossilizing the production. The focus of this perspective contribution is on CO₂ reuse technologies in this context. While this is a topic with abundant literature, the analysis of applying CO₂ reuse technologies evidences the need to go beyond those receiving most of the attention today, such as conversion of CO₂ to methanol. Depending on the specific context, different scenarios are expected. Some examples illustrating the search for novel solutions are provided such as those starting from the efficient conversion of CO₂ to CO. Once CO is produced from CO₂ many bio-chemical and catalytic conversion routes open up next to direct uses of CO in the steel and chemical sector.

Introduction

“Energy-intensive industries” (EIs) are defined as the series of industries responsible for most CO₂ emissions, in total accounting for about 70% of the European ETS (EU emissions trading system), as shown in Figure 1. EIs represent five major industrial sectors: iron and steel, refineries, cement, petrochemicals, and fertilizer. All these industrial sectors should accelerate decarbonization of the production to meet targets of carbon neutrality (in Europe by 2050), but there is a variety of situations to consider, and different strategies are under evaluation. A system approach to define opportunities and current limitations, to identify priorities in the approaches, scientific and technological gaps, and potential overall impact is useful. An important role is played by EIs in the transformation towards a carbon-neutral economy, but this involves the high challenge of combining a significant (>50%) reduction of the carbon footprint, an acceleration of the transition to renewable energy (RE) and an improvement in the competitiveness. While multiple aspects will determine the possibility to achieve this challenge, we will focus our attention here on the scientific and technological issues and prospects allowing to reach these objectives, with focus on catalysis aspects.

Competitiveness in a decarbonised global economy will be impossible continuing to use the current technologies and maintaining the carbon linearity of the current approach based on fossil fuels (FFs). Changing from a linear model based on the extraction of fossils with emission of CO₂ as end-product (eventual capture and storage does not modify this linear

model), to a carbon circularity model will be a key necessary transformation largely affecting the current energy and chemistry system. We could identify a two-step sequence (Figure 2): a first transformation step to create the backbone elements for a carbon (C) circular industry, followed by a second, longer term transformation step enabling a full C circular society, e.g., a fossils independent society based on new (distributed) production models. The key element is the progressive substitution of fossils with renewable energy (RE) combined with alternative C sources and technologies to close the C cycle.

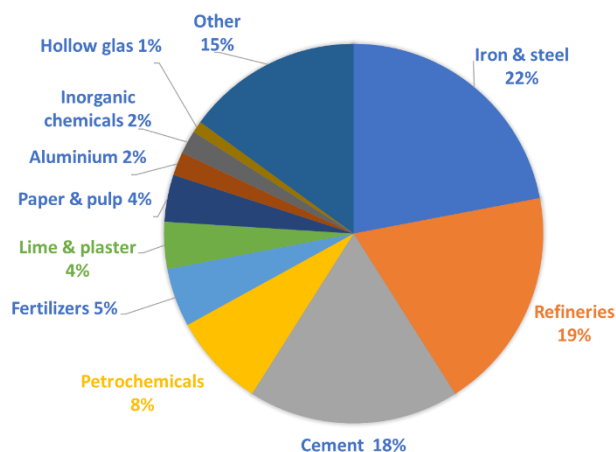


Figure 1 Share of CO₂ emissions in the total industrial CO₂ emissions in the EU ETS in 2018. Emissions of the iron and steel sector exclude emissions from burning waste gasses to generate electricity. Adapted from ref.^{1a}

Reutilization of CO₂ emissions to close the carbon cycle in EIs, using technologies based on RE as input energy source, is a key element in the first transformation to realize this C industry circularity. By analysing the current emissions of CO₂ in EIs (in total about 760 Mt CO₂-equivalent in Europe, year 2018), about

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50% is related to furnaces, i.e., combustion of FFs for high-temperature processes, 21% to process emissions, 20% to steam and hot water, and 9% for space heating.¹ There are different options to reduce these emissions:^{1,2}

- Improve energy efficiency: this was already largely done in the past decades with limited further large improvements expected.
- Electrification, using electricity from RE sources: depending on the application, rebuilding/redesigning furnaces and heating systems is required, with as main constraint the need of green electricity 24/7 (avoiding natural fluctuations) and in large amounts.
- Foster introduction of chemical energy vectors - CES (H₂, but not only): CES will facilitate transport, storage and distribution of RE (or of vectors such as H₂) from remote area, enabling a worldwide RE economy equivalent to that based today on FFs.
- Use of direct solar heating (concentrated solar power, CSP): this is an interesting option, but with severe constraints limiting larger applicability.
- Promote further the use of biobased fuels: they are a valuable, but transitional solution, for the limited carbon footprint reduction and many associated other environmental impacts.
- Introduce at a large-scale CCS (carbon storage, in the different forms) technologies: there is an increasing awareness that this solution will negatively impact the introduction of cleaner options, and increasing economic evidence remark of missing effective economic advantages, although still discarding idea are present on them; they will be not considered here.

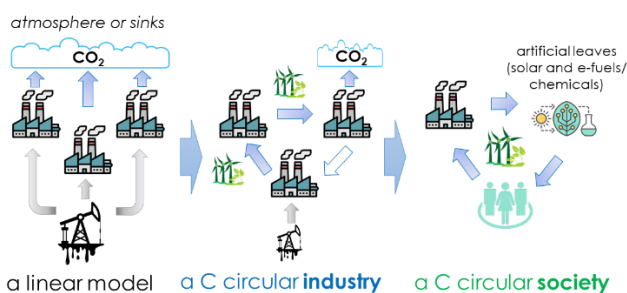


Figure 2 From a linear model for carbon (C) use to a carbon circular industry and in a longer-term perspective of a carbon circular society.

Electrification is thus one of the main challenges for EILs to realize intensive decarbonization and defossilization.² Current technologies already allow industrial companies to replace part (around 20%) of their FFs use with electricity. A technology gap, however, exist in higher temperature operations. For example, for medium-high process temperatures (above about 400°C, the most common case for EILs) technologies need to be still improved, in terms of energy efficiency, tailored design and cost-effectiveness. Average electrical price should be in the 5-20 \$/MWh range, thus higher than current values, to make them competitive.² Even by including CO₂ emissions cost reduction (for example, 100\$/ton of CO₂) the electrification remains often still not cost-competitive.² This scenario may vary, depending on whether more efficient electrification technologies will be developed and cost of production of renewable electrical energy will largely decrease. Limits anyway

will be the large amounts of RE necessary and the need of continuous (24/7) availability of RE. We consider that these gaps can be solved only by introduction of CES on a worldwide scale to transport RE from remote areas enabling their cost-effective distribution and implementation in EILs.

The cost and time for this transformation (electrification of the processes and creation of a worldwide based RE system and infrastructure) indicates the need to find complementary solutions, which can be introduced more effectively on a shorter term. Thus, intensive decarbonization of EILs requires to (i) develop technologies to close the carbon cycle, (ii) minimize the need of FFs, and (iii) find alternative solutions to introduce RE in the industrial value chain overcoming the issues related to direct electrification. These technologies to close the carbon cycle and introduce alternative RE in the process out of the direct electrification of furnaces are thus critical to implement the energy transition and industrial decarbonization.³

These technologies are often indicated as CCU (carbon capture and utilization) technologies, although this definition is conceptually limitative because it presents them as an alternative to CCS (carbon capture and storage) technologies, and hence implicitly assumes that they are part of the linear model (Figure 2), while they should be considered as an intermediate but essential step in the transformation from a linear to a C circular society.⁴

Indeed, in a longer-term perspective, carbon circularity could be based on a C circular society (Figure 2). The concept here, with respect to a C circular industry, is that it is extended to the whole society, not only industry, with thus a large role of distributed production technologies. Here, thus full circularity requires to use solutions which use CO₂ directly from the air in a distributed application model, i.e., the concept of artificial leaf as further step to enable a society based on solar and e-fuels/chemicals. Technologies to close the carbon cycle will thus reduce their role but will still likely remain as one of the backbone elements to realize a C circular industry and society.

Note that we use here the terms of C circularity and defossilization, rather than the most used decarbonization term. In fact, avoid the use of carbon-based fuels/chemicals is almost impossible to realize. Our live system is based on carbon, what necessary are solutions enabling the full circularity of carbon, as occurs in the nature, but with a faster rate of circularity. The terms defossilization and C circularity are two strict interconnected terms and the elements to create a pathway for new sustainable EILs.

Reuse of CO₂ in EILs is thus an important element towards this vision and implementation of a sustainable society. The large actual effort towards a hydrogen economy is a positive element towards decarbonization, but without implementing effective solutions to close the C cycle, starting from EILs, it will address only partially the challenge of realizing defossilization and C circularity of production.

Iron and steel

Among EILs, this is the industrial sector with the largest impact in terms of CO₂ emissions (Figure 1), and one of the core pillars

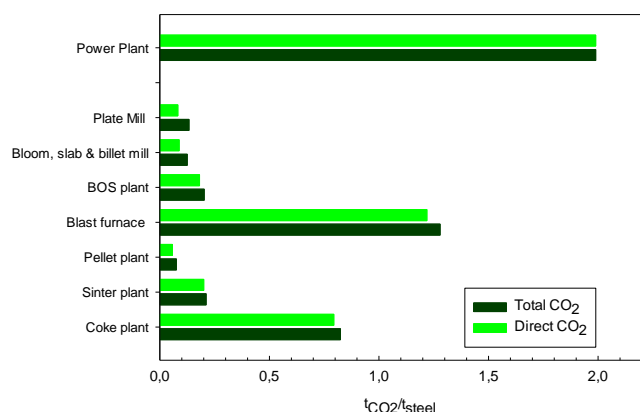


Figure 3 Total and direct CO₂ emissions per ton steel in various operations to produce steel through the blast furnace route (plate mills). Elaborated from data in ref.^{5b}

of society, steel being the most important engineering and construction material, and iron a necessary intermediate. Global crude steel production reached about 1.9 Bt for the year 2020. Steel recycling is a valid low-carbon solution (using scrap iron as the main iron-bearing raw material in electric arc furnaces – EAF), but this accounts for a fraction (around 40% presently) of the global steel need. Thus, the production of iron from iron ore will remain an important issue also in the future. Steel manufacture occurs using a combination of technologies, typically coke ovens, sinter plants, Blast Furnaces (BF) and Basic Oxygen Furnace (BOF) converters. Coal is used as a reductant in the integrated BF/BOF process. Alternatively, direct reduced iron (DRI) as main raw material could be used in EAF, but the pyrophoric character of the reduced iron, and the costs related to use of non-carbon-based reducing agents indicates that the integrated BF/BOF process will remain the main routes in the coming decades, although progressively substituted by DRI. Every ton of crude steel cast produced in 2019 emitted CO₂ on average 1.83 tons (an energy intensity of 19.84 GJ/ton crude steel cast) corresponding to about 8 percent of global carbon dioxide emissions.⁵

Several possibilities to decrease the CO₂ emissions are currently investigated, from improving the BF/BOF efficiency of operations, to waste or H₂ cofeeding, use of DRI or of Hot Briquetted Iron (HBI), and carbon capture and sequestration (CCS) technologies. All them show advantages and limits, particularly in terms of cost-benefits to proceed towards a full decarbonization, including H₂ utilization often considered a silver bullet.^{5b} CCS is often considered a ready solution to apply to existing plants (thus avoiding the large investments required for other solutions, particularly in an uncertain future), but the increasing evidences of high costs and societal opposition questioned the use of this technology^{4,6} that, in addition, does not allow to proceed towards a carbon circularity, as mentioned before. CO₂ recycling to produce fuels or chemicals to be used in symbiosis by other industrial sectors is the alternative solution of growing interest, although largely underestimated in the past for incorrect ways of accounting the potential impact.⁶

The actual main integrated steel manufacture occurs through the blast furnace route where the iron ore is first

converted to obtain pellets, then charged together with coke and coal into a blast furnace to produce a hot metal and pig iron further treated in a BOS (Basic Oxygen Steelmaking) plant to remove the residual carbon. The liquid steel obtained is casted into semis and further processed in mills. Boilers and a power plant are also necessary to generate the steam and electricity used in these operations. A breakdown of the total CO₂ emissions per ton of steel is given in Figure 3.^{5b} Total CO₂ emissions are those directly related to the specific operation plus those related to the upstream emissions (emitted by suppliers).

The blast furnace (BF) represents the main source of CO₂ together with the coke plant, while the other process steps have lower, although not negligible contributions to the overall emissions. Typically, BFs operate in close conjunction with coke ovens, creating opportunities for joint use of byproducts.

The operations in steel manufacture also require an energy input in terms of steam and electrical energy, provided by an integrated power plant which is an energy-intensive element for the overall carbon footprint. Electrification of boilers and providing directly renewable electrical energy would thus decrease CO₂ emissions associated to the integrated power plant. However, the reduction by over 50% of the carbon footprint in steel manufacture implies to address CO₂ emissions from BF.⁷

The steel mill produces three main sources of gases: (i) Coke Oven Gas (COG), rich in methane and H₂ and containing limited amounts of CO, CO₂, N₂ plus other gaseous components, (ii) Blast Furnace Gas (BFG), containing typically around 22% CO and 22% CO₂ together with few percentages of H₂ (and other gases) in N₂ (up to about 50%), and (iii) Basic Oxygen Steel Gas (BOFG), containing mainly CO (up to 40-50%), with about 15% CO₂, few percentages H₂ and other gases. To recover some of the energy from these gases while converting CO to CO₂, steel mill gases are typically burned to generate heat and electricity. CO₂ emissions generated from the steel mill and power plant may be eventually send to a pressure-swing adsorption (PSA) unit to produce a concentrated CO₂ stream which can be sequestered or preferably used as carbon source in producing fuels and chemicals. Figure 4 reports the simplified scheme of a steel mill manufacture and CO₂ recovery, remarking the utilization of CO₂ as key aspect to close the carbon cycle.

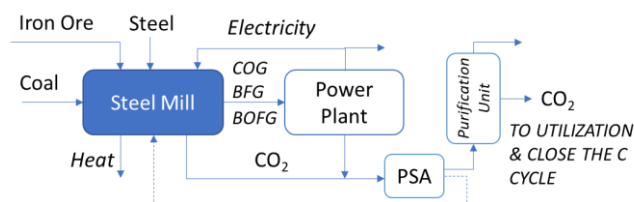


Figure 4 Simplified scheme of steel mill manufacture and CO₂ recovery.

Flores-Granobles and Saeys,^{7b} by analysing different options to minimizing CO₂ emissions in steel manufacture, evidenced that scenarios including conversion of captured CO₂ to chemicals or fuels would result preferable in terms of overall economics and impact with respect to CO₂ storage or H₂-based steel mills. De Ras et al.⁸ also remarked the need of valorisation of CO₂ streams

by their conversion to valuable products. However, still the question remains what the optimal solution for the downstream operations for converting CO₂ streams could be. This question will be further analysed below.

Industrial demo approaches for CO₂ utilization to close the carbon cycle in steel manufacturing.

Carbon2Chem[®], started in 2016 with a first phase ended in 2020 (60 M€) and a second phase of further 75 M€ up to 2024, is one of the most relevant demo industrial projects to show the feasibility and advantages of converting CO₂ in top gas emissions from steel manufacture (specifically in Thyssenkrupp plants) to chemicals. The project addresses both the methanol synthesis by catalytic reaction of CO₂ with H₂ (produced by water electrolysis) and the downstream production of other chemicals (higher alcohols, oxymethylene ether, isocyanates and polymers, urea). One goal of the project, funded in the 1st phase by the German Federal Ministry of Education and Research (BMBF), is to exploit the synergies (symbiosis) between steel industry, energy industry, and chemical industry, with the goal to demonstrate a flexible production of chemicals. The methanol prototype plant in the first phase has a capacity of methanol production of 50 kg/day (around 15-16 t/y) fed by H₂ produced with a 2-MW alkaline water electrolyzer (Uhde Chlorine Engineers). In the second phase of the project, long-term stability, and demonstration that the Carbon2Chem[®] technology can be upscaled will be the main targets. In addition, the focus will be on transferability to other industries besides steel production, particularly cement and lime producers, as well waste incineration plants.

Three main challenges are addressed in the Carbon2Chem[®] project: i) the dynamic nature of the overall system resulting from the coupling of several large production units with RE, ii) the production of marketable chemicals from the steel mill gases; this requires a large amount of H₂, which can be provided only in a limited extent from the steel mill gases themselves and iii) realize an efficient process retrofitting and optimization of existing production processes into the new production scheme.

Coupling the previously independent sectors by reuse of CO₂ is an aspect specifically addressed in the project and which results have been published by Stiebel et al.⁹ Technical, economic, and public acceptance aspects were considered, using a weighted multicriteria analysis. Some interesting aspects emerge from this analysis:

- The crucial issue of green H₂ production is cost, and thus minimizing these costs is the crucial factor in comparing different routes [to methanol, to urea, to polymers (TDI - toluene diisocyanate, and DPC - diphenyl carbonate) and higher alcohols (ethanol, propanol and butanol)]; those which have the lower consumption of H₂ as to TDI and DPC (based on the full process) achieve thus the best results.
- The existence of established large-volume markets and technologies is an important factor for the choice of the preferable route; methanol and urea are preferential from this perspective.
- It is necessary to include the dynamics of the supply of CO₂ and H₂ in the evaluation, and thus also storage units to

minimize their fluctuations. In addition, it is crucial to include a) alternative supplies of H₂ which are independent on the fluctuations of REs; for example, by methane pyrolysis, and b) detailed estimations related to the fraction of RE sources present in the (future) power generation mix (see below).

- There are high CAPEX (capital expenditure) costs: approximately 40% are related to electrolysis and methane pyrolysis and 20% to methanol synthesis; they should be minimized with novel engineering approaches.
- Operating expenditure (OPEX) have a high dependence on RE % in the energy mix; if this is up to 50%, there are high equivalent operating hours of the electrolyzer at high power prices, while when higher renewables share (86%) is present, OPEX reduces and up to 50% of the production costs are related to CAPEX. By including methane pyrolysis, the production costs are leveled.

A significant economically competitive reduction of CO₂ emissions in steel works requires an additional source of H₂ besides grid-fed electrolysis, as long as the power generation mix is not far above what is expected for year 2030 (< 50%).

The cost of production of methanol is a crucial aspect. There are still large discrepancies in estimating the actual and projected costs, the latter strongly dependent on the scenario assumed and of carbon taxes considered. A comparison of these costs, with respect to the current methanol price and cost (but not projected to future costs, and not including carbon taxes) was recently made by IRENA,¹⁰ and summarized in Figure 5. Bio-methanol is obtained from biomass (including waste), while e-methanol indicates that obtained from CO₂ (either capture from industrial sources or directly captured from air) and green H₂. There is a large variety of cost estimations for methanol (see also later), but we consider IRENA estimations among the most reliable data.

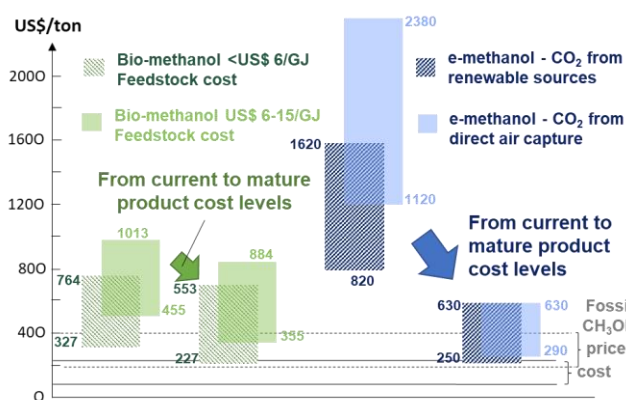


Figure 5 Current and projected production costs of bio- and e-methanol. Elaborated from IRENA.¹⁰

Note that in Figure 5 a carbon credit of US\$ 50/t CO₂ reduces the production cost of methanol by about US\$ 80/t MeOH. According to these IRENA estimations, current costs of e-methanol are two-three times higher than those for bio-methanol, but a large improvement is possible in passing to

mature technologies, which become competitive over prices of methanol from fossil fuels, if carbon taxes are considered.

Bailera et al.¹¹ reported costs for methanol production in the 760–1540 €/t_{MeOH} range, thus like those of IRENA, but not considering the possible costs reduction. They thus concluded that CO₂ avoidance cost (352 €/tCO₂) for iron and steel production is unacceptable. They also evaluated a range of alternative Power-to-X options, particularly H₂ and CH₄.

Many technology providers have existing, or planned, e-methanol facilities, as summarized by IRENA,¹⁰ although not specifically referring to the iron and steel production section, except the pilot unit (1 t/d capacity) developed in Sweden as part of the FreSMe EU project.¹²

Thonemann and Maga¹³ have carried out a LCA (Life Cycle Assessment) study on the methanol production based on steel mill gas. This so-called Carbon2Chem[®] process (framed in Fig. 2) uses COG and BFG from the steel mill and converts it in methanol. An integrated power plant feed by methane is included in the process boundary next to a water PEM electrolysis unit to produce H₂. Electricity for the whole process is provided either by an energy mix relying on the German Energy System Development Plan (ESDP) 2030 or by wind power. It is partly produced also by an integrated power plant. The German ESDP 2030 electricity mix relies on 47 % renewable and 53 % conventional sources. Nuclear power is phased out in Germany. The results of the process simulation are summarized in Figure 6 in terms of global warming impact (GWI) for the reference case (stand-alone production of methanol and steel) considering as functional unit (FU) the production of 4.4 Mt methanol and 8.4 Mt steel (steel mill in Duisburg by ThyssenKrupp), and the integrated simulated process (indicated by Thonemann and Maga¹³ as process-technology model).

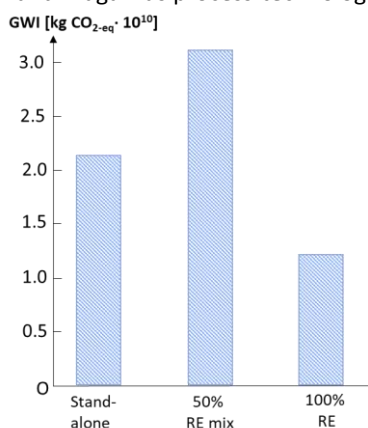


Figure 6 Global warming impact (GWI) of stand-alone production of steel and methanol with respect to the integrated production of steel and methanol (by using ESDP 2030 energy mix, i.e. about 50% renewable energy - RE, and 100% RE by wind). Elaborated from Thonemann and Maga¹³ referring to Carbon2Chem[®] project.

The stand-alone (separate units) steel and methanol productions contribute 82 % and 18 %, respectively to the overall GWI. This is approximately the same when 100% RE (by wind) is considered. The overall GWI decreases from $2.13 \cdot 10^{10}$ kgCO₂-eq to $1.23 \cdot 10^{10}$ kgCO₂-eq (thus about 42%) while increases to $3.13 \cdot 10^{10}$ kgCO₂-eq (thus about 46% increase) when considering the about 50% renewable energy (RE) mix expected

in Germany by year 2030. This is largely due to the great impact on GWI given from electricity to produce H₂. The contribution to the GWI of the electricity provision for electrolysis ranges between 59 % and 62 %.

Various studies on the LCA impact of CO₂-based methanol production have been reported in literature, for example in ref.¹⁴⁻²² While quite different indications have been reported, being largely depending on boundary conditions and the specific cases analyzed, we consider that the study by Thonemann and Maga¹³ represents the most correct and preferable study in evaluating the CO₂ impact on producing methanol from steel off gases. The clear indications of this study, well summarized in Figure 6, are that only when the energy mix will have about over 70% of RE share, the methanol production by using CO₂ in steel manufacture will cause a decrease of the carbon footprint. This is largely related to the impact of the production of green H₂.

Although the further conversion of methanol can lead to applications where part of the H₂ used in methanol manufacture could be released and recirculated thus reducing the carbon footprint and generating higher added value products, with benefits in terms of economics and GWI, the above analysis of the Carbon2Chem[®] process indicates a basic issue in the route of producing methanol (and related value chain products) from CO₂ of steel mill.

It is thus necessary to analyse alternative solutions. The Steelanol[®] project, supported by a 75 M€ EU contribution (a total 165 M€ investment) is developing an industrial-scale demonstration plant at ArcelorMittal Ghent, Belgium, in collaboration with LanzaTech, with whom ArcelorMittal has entered a long-term partnership, together with other companies (Primetals and E4tech). The Steelanol[®] route produces ethanol via the Lanzatech proprietary gas fermentation process by using exhaust gases emitted from the BF (or BOF) units. The route is coupled to another innovative process, called Torero, of torrefaction of waste wood to feed the BF rather than fossil coal. This is a first-of-its-kind industrial size demonstration plant to produce ethanol with such a process. The demo unit is under construction and the start of operations is expected in 2022. It will produce 80 million litres of sustainable ethanol a year, with a potential to be extended to other ArcelorMittal plants in EU, for a potential of 294 kt ethanol per year,²³ equivalent to over 2.2 Mt/y CO₂ reduction as direct emissions and about 5 Mt/y CO₂-eq. reduction by considering the full impact of the technology.

Based on preliminary Life Cycle Assessment (LCA) studies by E4tech the process realizes GHG savings > 60%. The BFG or BOFG are sent before to a PSA unit to remove CO₂ and then to the gas fermentation (GF) unit. The feed to GF contains a mixture of CO, CO₂ (the part not removed by PSA) and some H₂. In the case of CarboChem[®] process CO₂ pure feed was instead considered, because BFG/BOFG gas streams were sent to a power plant to produce electricity and steam for the process. This difference in the raw gas stream must be accounted in comparing the two process options and related impact. Eliminating the power plant unit, the electricity and heat (generated by the integrated power plant) should be provided

otherwise, and their related impacts accounted for. LCA preliminary estimations indicate for the ethanol produced in the Steelanol® process a reduction by 87% of the GHG impact ($\text{gCO}_{2\text{eq}}/\text{MJ}$) with respect to a fuel (gasoline) produced starting from fossil sources, although not including the impact related to elimination of the power unit.²³ Bioethanol from cellulosic biomass has an equivalent reduction in the GHG impact (86%), while the reduction in the case of bioethanol from corn ranges from 19% to 52% (thus significantly lower) depending on technology.²³

The microbes in the gas fermentation unit convert the CO , CO_2 , and H_2 into ethanol and chemicals which can be recovered from the fermentation broth. While both CO/CO_2 and H_2 are utilized in the process by the proprietary (Lanzatech) microbes, they can also consume H_2 -free CO -only gas streams, due to a highly efficient biological water gas shift (WGS) reaction that occurs within the microbes. The simplified scheme of the Steelanol® process is outlined in Figure 7. Although the Steelanol® process is perhaps one of the largest demo plants of the Lanzatech gas fermentation technology, it has been demonstrated on industrial scale (for steel manufacture case) in other cases, although at a smaller scale: i) the pilot-scale unit since 2008 using waste flue gas streams from the BlueScope Steel mill in Glenbrook (NZ), ii) the precommercial facility with leading steel producer Baosteel in Shanghai, China since 2012, and iii) the pre-commercial facility using steel mill waste gases near Beijing (China) with Capital Steel.

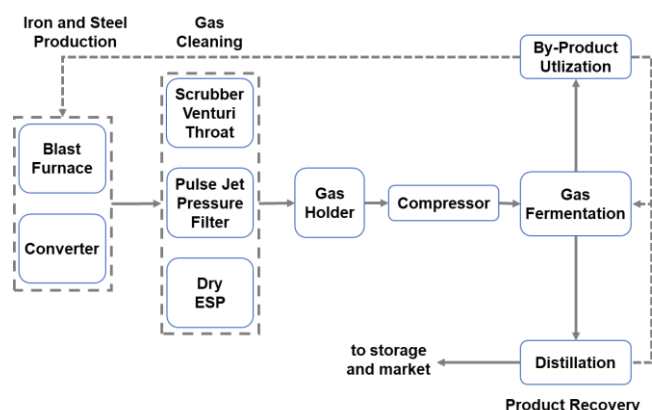


Figure 7 Simplified flow sheet of Steelanol® process.

Data on the process economics are not made public for the Steelanol® case, but indications are of an ethanol production cost comparable to that of bioethanol from biomass. Thus, even if data available in literature on Steelanol® are lacking, general indications suggest a cost- and carbon footprint advantage of this route, that should be sustained from more precise comparison data.

In terms of impact of these two routes, an important element of evaluation is the possible use of the chemicals/fuels produced. Both methanol and ethanol have a double function as chemical and fuel, but the energy density of the latter is slightly higher and the toxicity is lower (15.8 MJ and 21.1 MJ per litre for methanol and ethanol, respectively; as reference, gasoline energy density is about 32.6 MJ/l). Both alcohols can

be transformed to a range of other products. Crucial is the possibility to produce from them the base chemicals to transform to a fossil-free chemical production. Due to the large volume of CO_2 emissions from iron and steel manufacture, it is important to address large volume chemicals which are the building blocks for the whole chemical industry.

However, the conversion of ethanol to ethylene is very straightforward (catalytic dehydration, highly selective and already implemented on a large scale),²⁴ while methanol transformation to olefins (MTO, methanol-to-olefin) is more complex, costly and has a lower atom efficiency, even if implemented on a large scale.^{25,26} It forms a range of products (olefins, aromatics and some oxygenated), while ethanol to ethylene is very selective²⁴ and thus highly suitable for dedicated productions. Lanzatech is developing also modified microbes able to produce propanol (with acetone)^{27,28} and thus the Steelanol® process could be tailored to produce propanol and then propylene. Acetone as by product has also a variety of chemical applications. While also other chemicals could be produced from the microbes in the gas fermentation, the technology is not yet ready for a large-scale implementation.

In terms of the alcohols as fuels, both methanol and ethanol can be added to gasoline, but the latter has a wider miscibility range, better energy density and a larger worldwide experience in its use is available (bioethanol market was 34 billion US\$ in 2020). Both alcohols can be transformed to other quality fuels, such as aviation fuels, but the process is more straightforward and less costly for ethanol compared to the methanol case (for example, alcohol-to-jet - ATJ route by a first step of ethanol dehydration/oligomerization to C8-C12 hydrocarbons then hydrogenated to bio-jet, while methanol conversion produces a broader range of products and is more complex).^{29,30} In addition, atom economy considerations are in favour of the ethanol versus methanol route.

Although not exhaustive, this comparison thus indicates a preference towards the higher alcohols which can be produced by gas fermentation. By modification of the catalysts, it is possible to produce higher alcohols also from $\text{CO}_2 + \text{H}_2$ by heterogeneous catalysis, but not selectively. CAPEX (Capital Expenditure) in microbial gas fermentation is higher than in methanol synthesis from CO_2 , even if the latter is highly depending on electrolyzer costs. OPEX (Operative Expenditure), due to the need of large amounts of green electricity for electrolysis, are instead higher for the methanol case. However, precise public indications on these aspects are largely unavailable.

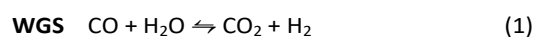
Improvements in the demo approaches for CO_2 utilization.

Besides the above critical analysis of the demo approaches to reuse of CO_2 emissions in steel manufacture to close the carbon cycle, it is useful to analyse also the possible further improvement of these demo technologies.

In methanol production, the critical issues are the cost (and availability) of renewable electricity for the electrolyzer (which results in a high H_2 cost) and its high CAPEX. Improvements in catalyst productivity (productivity is lower with respect the syngas case, when CO with maximum 3% CO_2 is fed together

with H₂) are necessary, but interesting developments are under way.³¹ Methanol reactor design has to be optimized for coupling with the electrolyzer unit to produce H₂ (in terms of heat integration, dynamics of operation), solutions to overcome equilibrium limitations in the process from CO₂ (due to WGS reaction, equilibrium conversions are low and require larger recirculation rates with respect to the syngas case), and reduction of poisoning sensitivity of the methanol catalyst (particularly, when alkaline electrolyzers are used) are further aspects to be improved. However, it is expected that these improvements would have an impact of less than 10-20% in cost reduction and carbon footprint. They are thus relevant, but not crucial aspects for the success of the technology. The major development element is related to the electrolyzer. There is a large worldwide, and especially in EU, R&D push in hydrogen production and its use to decarbonize the energy and production system.³² The intense worldwide effort will impact on the H₂ production costs. However, the electrolyzers and the technologies to produce RE already largely optimized, it is difficult to expect a cost reduction by 100-200% as would be necessary. In addition, a very large range of applications of green H₂, from mobility to heating and chemicals are pushed, creating thus a competitive market, with a huge demand of RE and thus a tendency to increase the costs. Although the possibility to substitute the existing production with electrolysis powered by RE is generally considered positive,³³ a large debate whether this could be effectively realized is ongoing. It is also unlikely that the share of RE in the energy mix will be largely above 50% by the year 2030. This will significantly affect the effective decarbonization impact of the methanol route (Figure 6). Thus, the methanol route suffers from the large dependence on green H₂ and its impact in terms of costs and carbon footprint. The success of this route is associated to the possibility to increase above about 70% the share of RE in the energy mix.

The absence of a dedicated production of green H₂ (water electrolyzer) in the ethanol (gas fermentation) route avoids the above issues, but introduces new requirements: i) to treat directly BFG/BOFG rather than to send them to a power plant (to produce heat/electricity) and then use the CO₂ emitted from the power plant (with thus a lower global impact in terms of CO₂ reduction and the need to supply otherwise the heat/electricity produced in the power plant), and ii) to produce in the gas fermentation unit the H₂ necessary (missing from the BFG/BOFG feed with respect to that needed to produce ethanol or propanol); this will occur through a microbial WGS reaction:



which, however, decreases the overall rate of reaction and further the fraction of carbon utilization. The overall carbon utilization in gas fermentation depends on the feed composition, but in steel off gas is typically in the range between 50-60%, which further decreases by considering that without sending the BFG/BOFG stream to the power plant (Figure 4), additional fuel should be fed to the power plant and its CO₂ emissions are not treated.

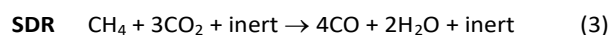
One solution is to introduce an additional step to convert the CO₂ to CO not via WGS, but for example by a direct catalytic process. Introducing this step will allow to send the BFG/BOFG stream to the power plant and then treat directly the CO₂ recovered from the power plant (as outlined in Figure 4, and like in the Carbon2Chem® case). The consequence is to increase the overall carbon utilization and thus decrease the carbon footprint. If some green H₂ is cofed to the gas fermentation unit, the carbon utilization can further increase as well as the overall reaction rate. With respect to the Carbon2Chem® case the need to produce green H₂ by electrolysis is largely decreased, at least to half. This makes the difference with respect to the case of methanol, allowing to decrease costs and effectiveness in decarbonization. However, there are still no dedicated studies which analyse these aspects to determine the optimal situation and amount of cofed H₂, to estimate costs and the carbon footprint. The above considerations, however, outline the interest in moving in this direction.

In terms of technology for the catalytic conversion of CO₂ to CO, there are different possible options, such as solar thermal processes, plasma reforming and photo- or electrocatalytic processes, the latter either at near ambient temperature or at high temperature in solid oxide electrolyzers.³⁴⁻⁴² However, only the catalytic route is currently ready for relevant industrial application.

There are two main options to convert catalytically CO₂ to CO: (i) reverse water gas shift, i.e., the reverse of WGS stated in eq. (1), which is limited by equilibrium and requires to cofeed green H₂, and (ii) the dry reforming. The dry reforming is endothermic and use CH₄ as the source of hydrogen to reduce CO₂, thus conventionally indicated as dry reforming of methane (DRM). As it is more endothermic than the reverse WGS it requires higher temperatures. A biomethane source to avoid the use of fossil methane is also needed. It produces two molecules of CO for each molecule CO₂ converted:



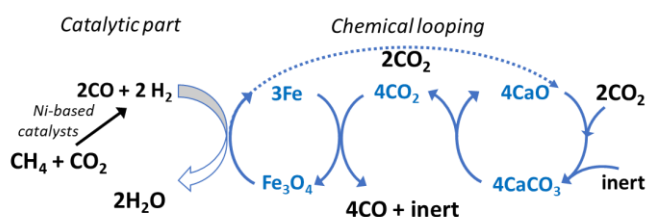
Rather than co-producing hydrogen, the so-called super dry reforming (SDR) maximizes the reduction of CO₂⁴³



In SDR three molecules of CO₂ are converted per molecule of biomethane, limiting thus the requirement of biomethane. The trick of the process, however, is to avoid the WGS which otherwise would not allow to maximize CO production. It is thus a process well-suited for converting CO₂ (recovered from PSA of steel mill emissions, see Figure 4) to CO, boosting the downstream gas fermentation process.

The SDR process can be considered a combination of dry reforming and chemical looping.⁴³ The general scheme of the process is presented in Figure 8. Chemical looping acts through a solid mediator which can be reduced and regenerated cyclically and transfer part of the feed/products to a different reactor zone. The chemical looping system used with the SDR technology consists in an oxygen carrier (Fe₂O₃/MgAl₂O₄) and a CO₂ sorbent (CaO/Al₂O₃).^{44,45} This system circumvents the equilibrium mixture of CO₂, CO, H₂O and H₂ by avoiding the WGS

reaction. It also allows to combine the exothermic formation of CaCO_3 from CaO and CO_2 with two endothermic processes, i.e., methane reforming and Fe_3O_4 reduction, leading to a high energy efficiency. The required heat can be supplied via auto-



thermal operation of the reactor when air rather than an inert, see Figure 8, is used.⁴⁶⁻⁴⁸

Figure 8 Reaction scheme for the super dry reforming process (SDR). Elaborated from the scheme presented in ref.⁴³

The preliminary carbon footprint calculation⁴⁹ for introducing this SDR in the Steelanol[®] process scheme, and some other complementary technologies such as electrical heated reactors and biomethane production from plastic waste, indicates that in front to an average carbon footprint for fossil fuels of around $90 \text{ g}_{\text{CO}_2\text{-eq}}/\text{MJ}$ (gasoline, for example) and around $70 \text{ g}_{\text{CO}_2\text{-eq}}/\text{MJ}$ for biofuels (bioethanol, for example), the Steelanol[®] process can allow to produce ethanol with a carbon footprint around $30\text{--}35 \text{ g}_{\text{CO}_2\text{-eq}}/\text{MJ}$ (thus half that of bioethanol), and $60\text{--}70\%$ reduction with respect to fossil-based fuels). By introducing the SDR and other mentioned technologies it is estimated that the ethanol carbon footprint can be below $20 \text{ g}_{\text{CO}_2\text{-eq}}/\text{MJ}$, thus a further lowering of the carbon footprint with respect to the already significant achievements realized by the Steelanol[®] process. Also the carbon footprint reduction for the produced olefins (by dehydration of the alcohols produced by gas fermentation) is positive. The conventional technology - naphtha steam cracking results in a carbon footprint of about $2.4 \text{ kg}_{\text{CO}_2\text{eq}}/\text{kg}_{\text{ethylene}}$ results in the highest emissions, followed by bio-based ethylene ($2.0 \text{ kg}_{\text{CO}_2\text{eq}}/\text{kg}_{\text{ethylene}}$). The advanced Steelanol[®] process described before yields the most sustainable ethylene production at only $0.8\text{--}1.0 \text{ kg}_{\text{CO}_2\text{eq}}/\text{kg}_{\text{ethylene}}$.⁴⁹ Indirect CO_2 -based ethylene production (i.e., CO_2 -to- CH_3OH and CH_3OH -to-olefins) has a high energy footprint and results in a carbon footprint almost three times higher than the advanced Steelanol[®] process.

Only preliminary estimations are also available for costs⁴⁹ and therefore they can be only indicative. However, these preliminary estimations indicate an ethanol production cost like the market price (effectively slightly lower), with about 75% of the costs related to OPEX. For isopropanol, the production cost is about 15% lower than the market value, with also about 75% of the costs related to OPEX.

The introduction of these novel technologies on the Steelanol[®] process can further improve economics, reduce the carbon footprint, and improve utilization of the emitted CO_2 , even if further studies are necessary. But the data presented here highlight the potential of these carbon-utilization

technologies to reduce the GHG emissions of iron and steel manufacture.

An additional important element to consider is that these technologies can be added downstream to a steel mill, and create positive symbiosis with other industrial sectors, particularly chemical production. The first aspect means these technologies do not require to modify the core of steel manufacture plant, thus can be easier retrofit in actual steel plants. The second element of symbiosis with other industrial sectors is also an important element to boost a common transformation of the whole industrial sector towards sustainability.

Cement production

The technologies discussed for iron and steel cases, being applied to downstream processing of recovered CO_2 from the emissions (in Carbon2Chem[®] and advanced Steelanol[®] processes) can be in principle applied to other EII's cases, although their integrability and other aspects (such as different contaminants in the emissions) should be analysed.

However, in reality the carbon cycle closing technologies have to be instead tailored to each specific EII case, being many additional factors determining the process cost-effectiveness, in addition to the level of contaminants present in the emissions. In cement production, CO_2 is released during the production of clinker, a component of cement, due to thermal decomposition of CaCO_3 to CaO in a rotary kiln. This occurs in the upper, cooler end of the kiln, or during precalcination at temperatures of $600\text{--}900^\circ\text{C}$. At higher temperatures in the lower end of the kiln, CaO reacts with other cement component (silica, aluminium, and iron-containing materials) to produce an intermediate product which after cooling, grinding and addition of other components (such as gypsum) form the cement. CO_2 emissions depend on the content of CaO (lime) in the cement. Typically, up to 0.95 t of CO_2 are released per t of cement produced, but the carbon footprint depends on several factors, among which i) the ratio of clinker to cement, ii) the manufacturing process (dry or wet method), iii) the level of heat recovery, iv) the fuel used, v) the moisture content of the raw materials, and vi) the capacity of the plant. There are two main sources of CO_2 emissions, i) one associated to the process itself (Ca-carbonate decomposition) and typically accounting 65% of total CO_2 emissions, and ii) the other associated to the production of the heat necessary for the thermal processes. A typical kiln-off gas composition is 30% CO_2 , 11% H_2O , 10% O_2 , and 0.01-0.04% SO_2 , NO , and CO . However, also metals such as Hg could be present in the emissions. According to IEA (International Energy Agency) in a scenario limiting to 2°C maximum the average temperature increase, the direct emissions of the cement sector should be reduced by about 25% by 2050, corresponding to a cut of about 7.7 Gt CO_2 .

As for the iron and steel case, a range of mitigation solutions are under investigation to reach this CO_2 emission reduction target, among which i) increase energy and materials efficiency, ii) use less carbon intensive fuels, iii) replacing part of the clinker with other components, iv) integration with REs, and v) carbon

capture use and storage (CCUS). We analyse here only the utilization case. IEA⁵⁰ estimated that around 25% of the global cumulative CO₂ emissions reductions by 2050 should be derived from CCUS.

CO₂ can be recovered by different technologies from cement plant emissions, either involving a significant modification of the plant itself (pre-combustion, oxyfuel combustion, direct CO₂ capture), or requiring minimal modifications of the existing cement manufacturing plants (these are indicated as post-combustion CO₂ capture technologies).⁵¹ Only the energy management strategies and the start-up and shut-down procedures would be affected, and thus retrofitting to the existing plants is easier and less costly. Constructing new plants, where thus new technologies could be introduced, will be limited for the next decades, and consequently post-combustion CO₂ capture technologies are receiving most attention.⁵²

Different post-combustion CO₂ capture technologies are available or under development, among which the main are i) chemical absorption, where amine scrubbing is the largest and oldest in use method; an alternative is the chilled ammonia process using an ammonium aqueous solution), ii) membrane separation, iii) sorption with solids, iv) calcium looping.⁵¹ Chemical absorption, although energy intensive, is the method mostly applied for large-scale projects. After this separation step, concentrated and nearly pure CO₂ would be available for chemical uses alternative to sequestration.

In terms of CO₂ utilization, cement industry is facing the same issues discussed for iron and steel production. When green H₂ is used to convert catalytically CO₂, where methanol production is the most common target, the cost and availability of green H₂ is the most critical issue. A broad range of estimations are available about costs and impact of producing methanol from CO₂. Several studies were compared by IRENA.¹⁰ The results considerably depend on the cost of electricity ranging from 1.7 to 16.2 US\$/kWh, making comparisons difficult. Cost of CO₂ also varied from 0 (in one case also -278) to 59 US\$/t. Even CAPEX largely varies, from 16 to 3890 US\$/t per year and OPEX from 2.6 to 755 US\$/t. With such a large variation in costs, the numbers for the methanol cost, ranging from 365 to 1610 US\$/t may be questionable. Note that such variation is largely above the normal variations in techno-economic estimations, typically not above ±30%. An analysis of some possible motivations in this large variation in cost estimations was attempted by Centi et al.⁵³ As summarized in Figure 5, IRENA¹⁰ conclusions in analysing these data was that the cost of e-methanol (produced from CO₂ and green H₂) is on the average 3-4 times higher than methanol from fossil sources. In future (year 2050), the estimated costs are predicted to decrease but remaining about two times higher than the current fossil methanol price. As discussed by Centi et al.⁵³, great care should be taken in trusting these indications, but the general indication is that without large carbon taxes or other legislative impositions, converting CO₂ to methanol also in cement production emissions will be a not economic solution, neither acceptable in terms of impact of CO₂ reduction, as long as the share of RE in the energy mix will not be above about

70%.

Although more precise and reliable studies would be necessary, given the large variability in estimations, and studies extending the evaluation to also other possible chemicals (but accounting to form large volume chemicals or fuels, otherwise the impact on cement industry will be minimal), there are no indications towards economic conversion of CO₂ in cement production to chemicals, even if technically feasible.⁵⁴

A recent study⁵⁵ supported by the European Cement Research Academy analysed using a multicriteria (technology status, energy performance, investment and operating costs, CO₂ utilization, sustainability social acceptance) different routes of CO₂ utilization (to chemical, fuels, durable materials, minerals and construction materials, algae growing and enzymatic conversion) the different routes of CO₂ utilization. The conclusion is that methanol formation (with CO₂ use for algae growing) is the preferable and feasible option. Several projects at demonstration scale are ongoing (cited in the paper). However, the crucial issue of costs, related to a large and continuous need of RE, and the carbon footprint dependence on the fraction of RE in the energy mix (see Figure 6) are not properly addressed by Chauvy and De Weireld.⁵⁵

Exploiting synergies in cement production.

Previous section discussion remarked how differently from iron and steel case, there are issues in the case of cement production to use emitted CO₂ to produce chemical/fuels such as methanol. It is thus necessary to analyse whether the target products from CO₂ conversion could be internally used in the cement production, and especially in modifying the process for a less-intensive energy demand. This was the objective of the EU RECO₂DE (Recycling carbon dioxide in the cement industry to produce added-value additives: a step towards a CO₂ circular economy; ID 768583)⁵⁶ project, started in 2017 and still ongoing. Rather than produce chemicals/fuels such as methanol, RECO₂DE project aims to produce cement additives and concrete (nano)fillers (to be used internally in the cement production) from the CO₂ emitted from cement plants. Cement additives can be classified in two broad categories: i) those which improve the cement quality (cement additives, concrete (nano)fillers) and ii) those which reduce the energy intensity of cement production itself (grinding aids, accelerators, fillers). Using CO₂ emitted to produce these cement additives will have a multiple boosting effect on the reduction of the carbon footprint because in addition to the use of emitted CO₂, the products are used in the cement production itself to reduce the energy intensity of the process and the amount of the clinker used. In addition, also cement properties will improve.

Adding CaCO₃ nanoparticles (produced from the emitted CO₂) to cement leads to a significant strength enhancement for both bare cements and concretes (by filling their micro-voids) acting as accelerator of the cement hydration rate (by seeding effect, e.g., by breaking down the protective layer on C₃S - Tricalcium Silicate - grains during hydration, thus shortening the induction period and/or accelerating C-S-H nucleation). The net effect is to enhance concrete quality and reduce its embedded energy by enabling a reduction of its cement content.

Converting emitted CO₂ to formic acid (FA) and oxalic acid (OA) (for example, by an electrocatalytic process using RE) also gives rise to valuable cement additives. OA decreases the setting time of OPC (ordinary Portland cement) and increase early compressive strength. FA and its direct derivatives ammonium formate and Ca-formate, are additives used in the grinding process in the production of Portland cement, since they reduce the electrostatic charges of the cement particles, the grinding balls, and the mill walls, thus minimising cluster formation, improving the grinding efficiency and influencing positively the final characteristics of the concrete (the grinding process implies up to 40–45% of the energy employed in the plant). Such additives can be hosted in the cement for up to 10% of its weight to reduce up to 25% the grinding energy expenses.

The overall benefits of cement additives comprise: i) cost reduction (lower unit grinding energy; greater integration of Supplementary Cementitious Materials (SCM); fewer capital expenditures due to increased capacity), ii) production efficiency (higher mill throughput thanks to increased efficiency of grinding media and separators; decreased pack-set, easier material handling and storage due to better fluidity of cement; faster truck and ship loading; reduced plant downtime due to fewer shutdowns; longer intervals between scheduled maintenance), iii) product differentiation (higher early and late-age compressive strength; better rheological behaviour of cement in concrete; compensation for SCM drawbacks), and iv) sustainability (reduced electrical energy consumption; lower clinker factor and CO₂ emissions; preservation of natural resources by extension of quarry lifespan). Using grinding aids improves the mill efficiency and reduces the electric energy cost. Using accelerators is another relevant issue in cement manufacture. Many types of accelerating admixtures have been proposed for accelerating setting and hardening of concrete.

The concept outlined here (which is not limited to the specific products indicated) is that when the products deriving from CO₂ utilization could be used internally to boost the production itself (in terms of quality and reduction of the carbon footprint) an enhanced effect not limited to just the utilization of CO₂ to make chemicals is present. This concept was not enough explored in EIs but can be crucial for CCU implementation.

Refineries

In refineries several units emit CO₂, including steam methane reformers (used to produce the hydrogen used in many units), catalytic crackers, power plants and furnaces (to provide the energy and heat for the different operations). The emissions of an individual refinery depend on several factors, especially the refinery configuration, fuel used, and type of crudes processed. Figure 9 illustrates the CO₂ emission breakdown by process (% m/m) for a simple refinery scheme (“hydroskimming”) and for a complex 150 kbbl/d (1000 barrels per day) refinery. The simple refinery scheme is dominated by the crude distiller while the FCC and hydrogen plant are the largest contributors in the complex refinery scheme.⁵⁷

Refinery CO₂ emissions are dominated by those deriving from process furnaces and utilities, i.e., heat and power plants within the refinery are the largest single sources, but a moderately complex refinery may have 20 to 30 separate process heaters spread over a large area, thus combining them all in a single stream to treat is complex and costly to retrofit.

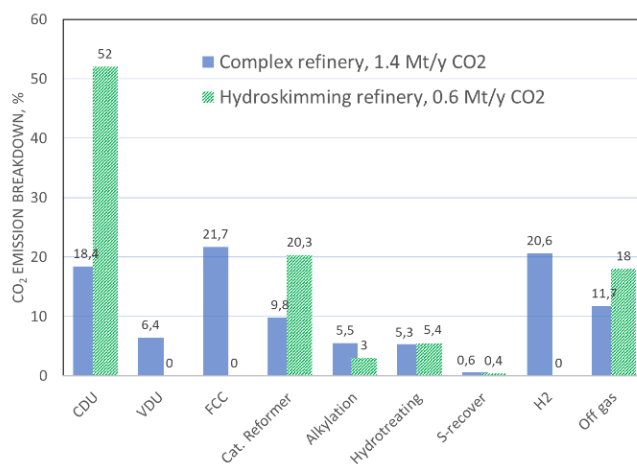


Figure 9 Refinery CO₂ emissions breakdown by process (% m/m) for a simple (hydroskimming) and a complex refinery scheme. Data are based on total energy requirement including allocation of utilities. Note: CDU Crude Distillation Unit, VDU Crude Distillation Unit, FCC Fluid Catalytic cracking. Elaborated from ref. ⁵⁷

Except for some cases, CO₂ is emitted in flue gases and off gases with low CO₂ concentrations, in the order of 3 – 12 %v/v CO₂. Utilities (electric power and process steam generation) generally are emitting CO₂ from a single stack albeit as part of the flue gases i.e., in diluted form (typically 4-15% v/v depending on the fuel used). They are usually among the largest single point sources in refineries. Process heaters all together are the largest emitters, with a power ranging from 2 to 250 MW, but spread over the entire refinery area, making often hard and costly to realize in existing refineries their collection to recover CO₂. In carbon rejection processes (such as FCC and thermal coking units) CO₂ is mainly associated to burning of the coke produced. The CO₂ concentration in these emissions is typically about 20% v/v but contains also high levels of SO₂ (originating from sulphur in the feed) and other contaminants. In H₂ production, CO₂ derives from both process energy requirements and the rejection of the carbon of the hydrocarbon (typically methane) used as hydrogen source. The total CO₂ produced in proportion to hydrogen is a function of the feed. For steam reforming the average is about 10 t_{CO₂}/t_{H₂}, roughly half deriving from the carbon rejection and half from the fuel required to supply heat. Depending on the hydrogen production scheme, and the way of CO₂ separation (most used is PSA, Pressure swing adsorption or absorption), quite pure CO₂ streams, up to over 99%, could be obtained.

On average, 40-50% of the total CO₂ emissions are associated to process furnaces, 30-35% to utilities, up to 15-20% to H₂ and/or FCC. Thus, an amount up to 20% of CO₂ emissions in refinery is represented from already concentrated CO₂ emissions which can be sent, after eventual further purification,

to a CO₂ conversion unit, an amount up to 30% represented by diluted CO₂ emissions and often requiring significant purification processes, and an amount up to about half of the emissions represented by those hard to be recovered and further treated. Therefore, together with changes in the furnaces and utilities units to intrinsically reduce their emissions (but requiring large investments in an uncertain future for refineries), the most obvious solution is to transform the concentrated CO₂ emissions to "solar" e-fuels (with adding RE) to be used in all furnaces and utilities where direct "electrification" is impossible. Note that often there is a misconception that producing a fuel such as methanol from CO₂ and then use it in a furnace has a minimal impact on carbon footprint, because CO₂ is "stored" for a short time. This error derives from the application of the model of value that only sequestration of CO₂ is relevant. In CO₂ utilization, as emerges also from the discussion above, the value is related to the service that CO₂ conversion is providing,^{4,6} for example the amount of FF which are saved and substituted from RE. Thus, the value in converting CO₂ emitted from refinery streams to produce fuels which are internally used in refinery is related to the carbon footprint reduction associated to the shift from FF to RE.

As commented in the introduction, directly using renewable electrical energy (or other renewable energy sources) is often not feasible in many relevant cases, thus the reuse of CO₂ to form solar e-fuels is the way to "mediate" the use of RE for all these units where their direct use is impossible or requires high investments. Converting CO₂ to solar e-fuels is thus a way to accelerate decarbonization of a refinery but limiting the investment costs for the transformation. Given the already uncertain future of refineries facing many issues (shifting end markets, oil and product market volatility, declining fuel demand, energy transition and sustainability, international trade barriers)⁵⁸ solutions to decarbonize refineries have as a mandatory target the minimization of investment costs.

Thus, in contrast to CCS technologies (representing an additional cost, except for the reduction of eventual carbon taxes), the CO₂ utilization in refinery in the terms outlined above represents the preferable strategy to complement the direct use of RE, minimizing simultaneously the investment costs in retrofitting current refineries.

Availability and cost of non-grey H₂ is the main issue for CO₂ utilization as for the other commented cases. Less critical is the integrability of the products inside the refinery itself, although it represents an aspect to also consider. For example, at equivalent costs, producing ethanol is preferred in comparison to methanol, due to the higher energy density and wider use as additive in the fuel pools. Both methanol and ethanol productions are established from CO₂, but integrability of the first in the process schemes is better. But there is a specific increasing demand of low-carbon liquid fuels such as dimethoxymethane.^{59,60} Producing them from CO₂ refinery streams appear as the preferable solution, even if still often only CCS was the option considered for refineries.

A case-to-case evaluation is typically necessary, accounting also for the eventual valorisation of side streams containing H₂, which are present in some refineries schemes and that cannot

be directly used in the other refinery units. Integration of these sources with other non-grey H₂ sources is mandatory. Among these alternative H₂ sources, producing H₂ from waste⁶¹ or from biomethane (by catalytic decomposition)⁶² appears the most promising solution, and in part starts to be applied in some refineries. Eni in its bio-refinery near Venice (Italy), for example, is introducing a new process to produce H₂ from a mixture of municipal waste and plastmix (mix of non-recyclable plastics), with application of the technology also in another refinery in the south of Italy (Taranto).⁶³ Several refineries have on-going projects to produce/use green H₂ to produce low-carbon fuels.⁵⁹ The global refining carbon intensity are in the 13.9–62.1 kg of CO₂-equivalent (CO₂e) per barrel depending on country, with an estimated potential of reduction 56–79 GtCO₂e to 2100 by targeting primary emission sources.⁶⁴ This ambitious target cannot be reached without considering CO₂ utilization routes.

Petrochemicals and Fertilizers

The fertilizer industry covers many different products, but synthetic N-fertilizers (mainly urea and ammonium nitrate, accounting for ~75% of world's straight N-fertilizer consumption) are the key components. CO₂ emissions are mainly associated to the production of the H₂ needed for the common up-stream step of ammonia synthesis and will depend on the fuel used for the manufacture process. Emission factors (kg CO₂e/kg of N) range from 1.3 to 4 for urea and 6.2 to 10.3 for ammonium nitrate.⁶⁵ For P-fertilizer production (ammonium phosphates, single and triple superphosphate) the first has emissions in the range 1.3 to 8.9 (kg CO₂e/kg of P₂O₅), while being lower (0.4–1.6 range) for the superphosphate. Reducing the carbon footprint involves a better use of fertilizers, and introduce ways to enhance energy efficiency in fertilizer manufacture, with a potential to cut emissions in the 20–30% range.⁶⁶ A large impact, as necessary to meet the general targets in CO₂ reduction (at least 55% by 2030 in EU) require a technological shift. The effective step forward derives from the change of the technology to produce ammonia, passing to the so-called green ammonia which uses green H₂ as feed.⁶⁷ A drastic cut of CO₂ emissions is possible by this solution, limiting thus the interest in solutions for CO₂ utilization. By considering that CO₂ is a feed component for urea (NH₂CONH₂), if green ammonia is used as the other feed component, urea process may become a carbon negative technology.

In the petrochemical industry, a variety of processes generate CO₂, with the largest part of them, however, associated to combustion for thermal processes and to produce the power needed. Steam cracking is by far the most important source of CO₂ emissions and several electrification routes are currently being investigated.⁶⁸ Other sources of CO₂ derive from the side reaction of total combustion in selective oxidation processes or to produce the H₂ needed in hydrogenation processes. Another source of CO₂ is related to the various processes of waste disposal and incineration. The CO₂ emissions associated to provide the heating, facilities and electrical energy for the processes can be reduced by the so-called electrification

of operations and reactors.⁶⁸⁻⁷⁰ There is thus limited interest also in this case to use CO₂ emissions to make chemicals by its hydrogenation, for example to produce methanol, although this is often indicated as a need in reviews on CO₂ utilization.⁷¹⁻⁷³

An interesting analysis of carbon dioxide as raw material to close the carbon cycle for chemical and polymer industries, although focused to the German case, was given by Kaiser and Bringezu.⁷⁴ They analysed the carbon flow indicating that it is current dominated by fossil sources and highly linear, with a secondary input rate (the percentage of secondary material within the total material input) of only 6%. Also 12% (2 Mt/a) of the primary carbon input is lost due to dissipation. By introducing CO₂ utilization technologies would allow reaching a secondary input rate of 65% for the chemical industry, thus being a key towards implementing Circular Economy politics. However, this rate requires that between 80% to over 100% of the total net supply for renewable electricity in Germany in 2030 would be utilized, despite the need for many other industrial sectors. The most demanding scenario must produce methanol, while lower amounts of renewable energy (but still too high) would be necessary to produce other chemicals. Thus, alternative technologies to those based on the utilization of green H₂ to convert CO₂ (those considered in the paper by Kaiser and Bringezu⁷⁴) will be necessary. As discussed for iron and steel manufacture, there are less green H₂ demanding solutions, and solutions which direct capture solar energy to produce chemicals (the so-called artificial leaf)⁷⁵ are in fast development and could be ready for market introduction before 2030,^{26,76} while still often they are considered solutions not before 2050. For example, technologies to produce olefins from CO₂,⁷⁷ thus recycling CO₂ directly to a base chemical to give rise to a low-carbon chemistry could become relevant, if green H₂ production costs are significantly reduced. For example, by avoiding the loss of hydrogen in producing H₂O as the result of oxygen elimination from carbon dioxide. While there are possible solutions, although challenging (for example, the direct catalytic decomposition of CO₂ to C + O₂), research in this direction is lacking, while many researchers instead work on established areas such as CO₂ hydrogenation. Oxygen rejection alternative to water formation in CO₂ conversion is an important area to consider for the future of technologies to close the carbon cycle.

Thus, the scenario for introducing CO₂ utilization technologies in the petrochemical industry is depending on the creativity of researchers to find out of the box solutions.

Conclusions

The thematic of decarbonization of energy intense industries in relation to close the carbon cycle and carbon circular economy is a topic of recent large interest. Reuse of CO₂ is a part of this broader context, which often represents a crucial element to meet the target set at the political level. Starting from a thorough analysis of the five major EII sectors (iron and steel, cement production, refineries, petrochemistry and fertilizers) the major hurdles, opportunities and threads are identified. And although they appear to be different, there is some common

ground.

The low technology readiness emerges as one of the hurdles stands for the breakthrough of novel CO₂ reutilization technologies. While large research effort focused on the production on low value methanol, we commented here that often different solutions must be instead explored. A system approach is necessary to evaluate them, and we provided here some elements for this analysis. For example, in many of the alternative scenarios to methanol the transformation of CO₂ to CO (out of WGS reaction) plays a key role. Once CO is produced from CO₂ many bio-chemical and catalytic conversion routes open up next to direct uses of CO in the steel and chemical sector.

Discussion related to the possible different approaches in closing the carbon cycle by utilization of CO₂ in the different EIIs sector analysed evidence also the need to have broader impact in relation to the specific sector of application. It is necessary also to analyse alternative solutions to those most investigated. The analysis presented here provides thus food of thought to reanalyse priorities and necessities in closing the C cycle in energy intensive industries.

Author Contributions

All the authors equally contribute to the definition of the concepts presented here and to prepare the manuscript.

Conflicts of interest

There are no conflicts to declare.

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