Carbon capture and utilization in the steel industry: challenges and opportunities for chemical engineering

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Abstract

The availability of green electricity, changes to the Emission Trading Scheme (ETS) system and technological breakthroughs will determine how the steel industry will evolve in the coming decades. The blast furnace (BF) technology will continue to dominate steel production in the coming decade and the only way to substantially reduce the associated CO_2 emissions is to combine it with Carbon Capture and Utilization (CCU) and/or Carbon Capture and Storage (CCS). CCU options that do not require a lot of hydrogen and with high added value are logical step stones towards production of bulk chemicals and even fuels such as oxymethylene ethers. BF waste gas recycling and conversion will require a multisectoral approach creating new dependencies between the steel, energy, and chemical sectors. Energy efficient, cheap and CO_2 free hydrogen production using green electricity is the ultimate solution to drive this transition. This hydrogen could on the long term also open the door to replace blast furnaces by hydrogen-based steel making. However, today it makes economically more sense to use thermally produced hydrogen by (bio)methane pyrolysis or steam reforming, potentially electrified and intensified, rather than from water electrolysis. Having novel and existing elements from the chemical engineers' toolbox such as artificial intelligence, catalysis and reaction engineering, process intensification principles and multiscale modeling and design, should bring these emerging technologies within reach by the end of the next decade.

Keywords: Steel Production, CCU, CCS, Blast Furnace, CO_2 conversion, CO valorization

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1. A sustainable future for steel production

The steelmaking industry stays on the verge of a major technological evolution required to deal with the significant amounts of greenhouse gases (GHG) emitted during steel production, in order to meet the GHG emission targets of the Paris climate agreement [1]. The total emission of carbon dioxide reached an all-time high of 37.1 billion metric tons in 2018 and the amount is still expected to increase the coming years [2]. According to the World Steel association, 7 to 9 % of these total CO_2 emissions originate from the steelmaking industry [3]. In 2017, on average 1.8 tons of CO_2 were emitted per ton of steel produced [4]. There are two main production routes: the blast furnace basic oxygen furnace (BF-BOF) route and the electric arc furnace (EAF) route. Variations and combinations of production routes also exist. The BF-BOF route produces steel starting from raw materials such as iron ore, coal, limestone and steel scrap. About 75% of steel is produced using the BF-BOF route. First, the iron ores are reduced in the BF to metallic iron with carbon monoxide as main reducing agent. CO is formed by reaction between cokes and oxygen in the furnace. The effluent gas leaving the blast furnace consists of ~22 mol% CO, ~22 mol% CO_2, ~5 mol% H_2 and ~51 mol% N_2 [5]. Per ton of steel 2.5 to 3.5 tons of blast furnace gas is formed. The blast furnace gas still contains caloric value, due to the presence of CO and hydrogen, which is recovered by combustion for energy generation resulting in even higher CO_2 emissions. Then the iron from the BF, also called hot metal or pig iron, is converted to steel in the BOF. After casting and rolling and/or coating, the steel can be delivered as strips, plates, sections or bars. The remaining 25% of steel is produced via the EAF route. Steel made in an EAF uses electricity to melt steel scrap. Depending on the plant configuration and availability of steel scrap, other sources of metallic iron such as direct-reduced iron (DRI) or pig iron can be used. Additives may be needed to adjust the steel to the desired chemical composition with associated properties. Electrical energy can be supplemented by injection of oxygen into the EAF. The EAF route results in reduced carbon emissions, i.e. only 0.6 ton CO_2 per ton steel. Downstream process stages, such as casting, reheating and rolling, are similar to those found in the BF-BOF route.

Several legislations and taxes, e.g. the emission trading scheme (ETS) enforced in the European Union to meet the long-term goal of GHG reduction with 95% by 2050 compared to 1995, force steelmaking companies to revisit their production chain. At a carbon price of around 60 euros per ton of CO_2, some of the routes for steel mill off-gas recycling already become profitable, even with high costs for renewable energy and green hydrogen [6]. Keeping the steel industry viable and meeting the long-term greenhouse gas emission objectives requires drastic technological solutions which will deal with the large amounts of carbon dioxide emitted during steel production.

A schematic overview of steel production via blast furnaces and the associated solutions for greenhouse gas emission reduction are depicted in Figure 1. A first part of the solution can come from Carbon Capture and Storage (CCS). CCS is necessary for decarbonization of the industry, representing a cost-effective and realistic way to avoid post-combustion and process emissions. It is a crucial technology to safeguard the existing industrial activity, jobs and growth while decarbonizing economic activity to meet the Paris Agreement objectives. Although CCS is considered a promising solution for emission reduction based on the present state of the art, it contributes to reducing the overall efficiency of a steel plant due to the high energy consumption for solvent regeneration during capture processes and therefore innovations are still highly needed [7]. An even better option would be CO_2 utilization: CCU options that do not require a lot of hydrogen and with high added value are logical step stones towards production of bulk chemicals and even fuels such as oxymethylene ethers. CO_2 to fuels and chemicals could potentially lead to profits, while CCS is only a waste mitigation technology. CCU has therefore obtained major interest from a chemical engineering point of view to mitigate greenhouse gas emissions, climate change and aiming for a carbon-neutral society [8, 9]. Another part of the solution will encompass valorization of carbon monoxide (CO) present in steel mill off-gases rather than burning it. A wide range of catalytic and enzymatic processes are available to turn CO into valuable chemical bulk products by reaction with hydrogen gas, so-called syngas. The large amount of hydrogen gas required shifts the problem to the need for efficient and sustainable hydrogen gas production. On the other hand if CO_2 can be converted into more reactive carbon monoxide via for example (super) dry reforming [10, 11], the CO can be re-used in the BF route [7]. In addition, a transition is expected in which production of steel via the electric arc furnace (EAF) route will become more dominant. Steel via the EAF route will become more sustainable compared to the BF-BOF route if green electricity is available. Recently, hydrogen, plastic waste and biomass-based steelmaking have also gained attention by steel producers [12, 13] which offer very attractive perspectives, while raising lots of major challenges. Nevertheless, this still requires much research and development before they can be proven and implemented at a commercial level. In addition to technological advancements in the production process, evolving towards a circular economy where recycling of steel is key, will definitely be part of the solution.

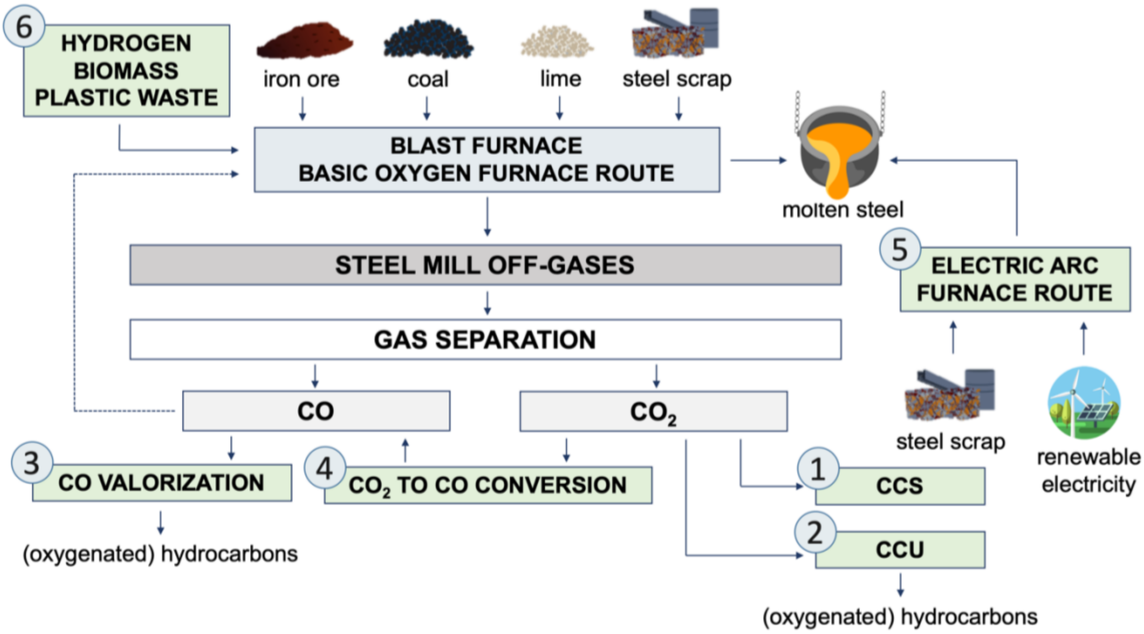

Figure 1: Schematic overview of steel production and associated solutions to reduce CO_2 emissions. 1: CCS, 2: CCU, 3: valorization of CO, 4: conversion of CO_2 to CO by (super) dry reforming, 5: transition from the BF-BOF route to the EAF route, 6: using hydrogen, biomass or plastic waste as reducing agent instead of coal.

2. Challenges and opportunities for carbon-neutral steel production

Advancements in gas separation techniques make that it is nowadays possible to separate both CO and CO_2 from steel mill off-gases into pure streams suitable for CCU [14]. The state of the art in industry is respectively via pressure swing adsorption and absorption via chemical absorbers such as alkanolamines, though this separation step is energy-intensive. Associated, several promising processes are proposed which reuse the CO and CO_2 by catalytic or enzymatic conversion into valuable chemicals, i.e. (oxygenated) hydrocarbons. Transformation of all carbon emitted during steel production, which can amount to millions of tons for a single production facility, will lead to the introduction of new large-scale producers on the chemical market which limits the production possibilities to bulk chemicals such as fuel additives.

To evolve towards a sustainable future, the large amount of hydrogen required for syngas has to originate from a source without extra CO_2 emissions. Figure 2 schematically depicts the possibilities to produce sustainable hydrogen and the applications in the context of steel production. One option is consuming hydrogen formed as byproduct in other processes, e.g. coke oven gas can be used more optimally as hydrogen source and oil refineries produce hydrogen by catalytic reforming of naphtha. Additionally, hydrogen can be produced by high temperature methane pyrolysis in bubble columns where solid carbon is produced [15] and steam reforming can be electrified [16, 17]. In order to be completely renewable, biomethane should be used as feedstock for steam reforming [18]. Alternatively, production of hydrogen via steam reforming could be replaced by electrolysis of water with renewable electricity. ThyssenKrupp plans to phase out CO_2-intensive coke-based steel production and replace it with a hydrogen-based process by 2050 [13]. Alkaline water electrolysis (AWE) is a mature technology and the basis for industrial plants with capacities of the order 100 MW [19, 20]. Because of the technology's maturity, efforts to improve AWE are primarily focused on total plant optimization. Proton exchange membrane water electrolysis (PEMWE) provides advantages over AWE by reducing Ohmic resistance and allowing for pressurized operation [21]. Currently, the largest industrial system has a capacity reaching up to 15 MW via the PEMWE route [22]. A significant obstacle to further scale-up is the scarcity of iridium, which is used in the electrocatalyst at the anode [23]. Alternative materials that are both catalytically active and stable in an acidic environment remain elusive despite significant research efforts; hence the remaining options are to significantly reduce iridium loadings or develop and introduce anion-conducting membranes to obviate the need for stability under acidic conditions [24]. High temperature solid oxide electrolysis cell (SOEC) based systems form a third electrolysis technology which have smaller sizes, but with efficiencies reaching up to 90% [25]. Because of the small stack size and modularity of SOEC systems, there are particular needs for automated production technologies and better multiscale modeling tools at the cell and stack level to determine the optimal design for industrial-scale plants. Thus, SOEC is still under development with only prototypes being built [26].

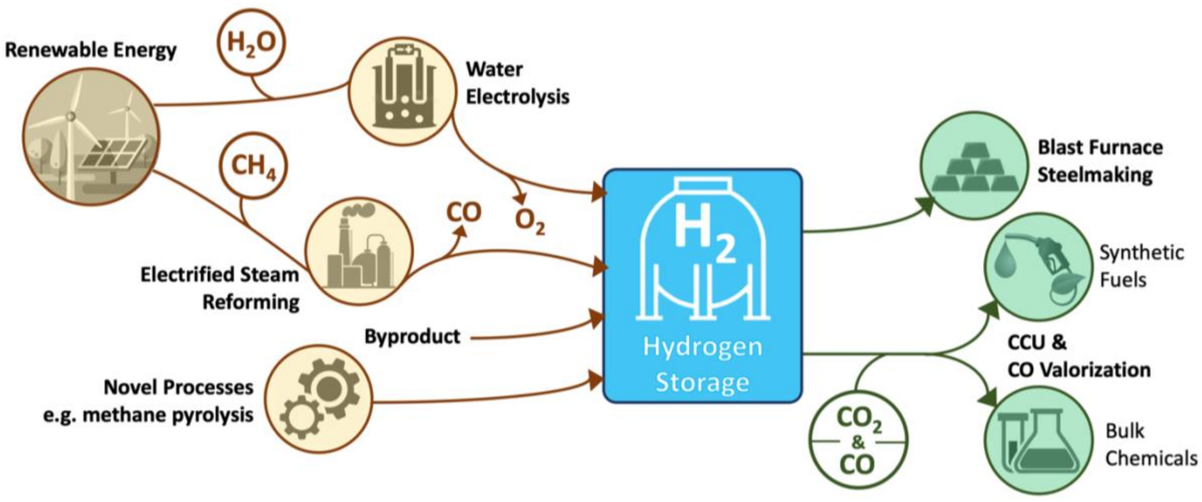

Figure 2: Hydrogen production forms one of the missing links for CO_2 emission mitigation in the steelmaking industry, next to the availability of renewable energy. Most important production routes for a sustainable future and applications are schematically depicted.

Production of hydrogen via water electrolysis will increase the energy consumption drastically, which has to originate from renewable sources to be an improvement. As an additional benefit, a pure oxygen stream is formed as byproduct during electrolysis of water which can be used directly for injection in both the blast furnace and the basic oxygen furnace. Currently, the high cost of water electrolysis, originating from the capital cost of the electrolyzers and renewable electricity, is the major challenge for commercial feasibility. For electrolytic produced hydrogen 60 to 70% of the cost is from electricity [27]. The most mature and cheapest technology is production via alkaline electrolytes in combination with metal catalysts with efficiencies reaching 60% associated with a production cost of ~ 5.50 US dollar per kg H_2 (assuming 0.07 US dollar per kWh). In contrast to fuel markets, the electricity market is less flexible due to the lack of large, long-term and efficient storage options. The production of fuels from CO_2 and renewable electricity represents therein an ideal opportunity for balancing the electricity grid in addition to evolving towards a transportation system with carbon-neutral fuels.

A recent example of the ongoing efforts is provided by the Carbon2Chem project [28] which has succeeded in synthesis of methanol on pilot scale starting from mixed blast furnace gas and basic oxygen furnace gas with a $Cu/ZnO/Al_2O_3$ catalyst. Further research is still ongoing in fine-tuning the catalyst to optimally convert both CO_2 and CO [29]. The future objectives of the project aim to produce all hydrogen by water electrolysis and to convert the nitrogen rich byproduct from gas separation into fertilizers [30].

2.1 Syngas conversion

A wide range of products is possible by reaction of carbon monoxide with hydrogen in the presence of a catalyst, e.g. hydrocarbons via Fischer-Tropsch synthesis, methanol and dimethyl ether. However, the intensive pre-treatment of steel mill off-gases in order to obtain pure CO forms the current challenge. For example, desulphurization by a ZnO bed is necessary to avoid poisoning of catalysts by minor components [29, 31]. Current research focuses on selection of optimal catalysts and regeneration, in addition to optimization of the energy intensive gas separation.

Lanzatech developed an industrial process for conversion of industrial waste gases enzymatically with anaerobic acetogens [32, 33]. CO from the steel mill off-gases can be captured and reacted with hydrogen in the presence of microorganisms, often referred to as gas fermentation, with formation of renewable low carbon liquid fuels and chemicals [34]. In theory both CO and CO_2 can be converted via fermentation, but in practice it is limited to a CO rich feed since the CO_2 conversion is minor. In contrast to conventional catalyzed processes, e.g. Fischer-Tropsch, the enzymes can withstand a higher sulfur concentration and operate at milder operation conditions [35]. Though, a challenge is present in providing the large amounts of sustainable produced hydrogen, in addition to scale-up in particular of the reactors. The promising future of syngas fermentation is indicated by the construction of the largest industrial facility in the Steelanol project for the production of 64 million ton of bio-ethanol per year from steel mill off-gases [36].

2.2 CO_2 utilization & storage

Direct conversion of CO_2 is more difficult compared to CO since the molecule is more stable, though some processes are available for production of methanol and oxymethylene ethers starting from CO_2 [37]. Electrochemical CO_2 reduction has potential on long-term to supply the transport sector with sustainable fuels considering that renewable electricity and green hydrogen is available at cost-competitive prices [38].

Multiple conversion processes are investigated to reduce CO_2 to CO. A first possibility is reduction in homogeneous catalytic (copper, silver or gold) environments for which optimal catalyst selection is the main challenge [39]. Similarly heterogeneous catalyzed processes are investigated which can be combined with other processes such as the water gas shift reaction in order to allow production of multiple valuable products [40]. Electro catalytic reduction has been the major breakthrough but still requires optimization of the stability of the catalyst and overcome mass transport limitations to active sites [41]. In addition plasma and photo catalytic [42, 43] conversion processes are investigated but are still far from commercial applications. A step whereby CO_2 is converted into CO via (super) dry reforming seems more promising [10, 44]. It is especially super dry reforming, for which the carbon dioxide to methane ratio amounts to 3, in combination with methane originating from a renewable source, e.g. biomethane [45, 46], that can form a breakthrough for valorization of CO_2 via chemical looping in the steel industry. The strength of chemical looping indeed lies in its flexibility, which results from the fact that a single reaction is separated into two sub-reactions coupled through the oxygen carrier material. Formed CO can be recycled to the BF or used in the aforementioned syngas conversion processes.

In case the steel industry sticks to using steel mill off-gases as fuel for energy generation, the only feasible solution for drastic CO_2 emission reduction is carbon capture and storage (CCS). However, great breakthrough of CCS in steelmaking companies is not expected since valorization of CO and CCU of CO_2 show much more potential. After capture, a highly concentrated CO_2 stream can be transported and injected to one of the storage options, i.e. geological storage, deep ocean storage or mineral carbonation. Valorization of this is difficult except when CO_2 can be sold for enhanced oil recovery. Essential for the future of CCS is a reduction of the large investment costs (CAPEX) and an optimization of the energy-intensive separation and compressions steps. Current research focuses on development of new capture technologies. A first aspect looked at aims for intensification of the heat and mass transfer by reactor selection, e.g. vortex reactors [47] or aerosol reactors [48] and optimal adsorbent screening [49], which could lead to smaller sized units and higher efficiencies. A second aspect covers electrification of CO_2 capturing by studying alternative heating sources, e.g. inductive [50] and microwave heating [51]. A final aspect considers integration of capturing technology into the conversion processes. For industrial applicability, capital costs and costs related to energy for gas separation and compression will have to decrease in order to become economically interesting [52].

Dry reforming of plastic waste allows to combine two of the biggest challenges that the world is currently facing, being the increasing CO_2 emissions and plastic waste. A solution is converting plastic waste to synthesis gas. However, it must be clear that this combination is not obvious and that substantial engineering is needed to overcome all the challenges to produce a clean synthesis gas. Therefore novel structured catalysts need to be developed and these need to be implemented in robust and compact reactors to reduce the CAPEX. The resulting synthesis gas needs to be treated to make it ready for further use and unconverted CO_2 needs to be separated in an energy efficient way [53].

3. Final remarks

Public acceptance of CCU and CCS will play a major role in the steel industry's future. Synergies need to be maximized between the steel, chemical and energy sector by working together on solutions to re-use the CO and CO_2 produced in the blast furnaces during steel production. Logistically this comes also with challenges. Essential is the efficient conversion of CO_2 to CO. Once large amounts of CO are produced, existing, novel or intensified processes can create an enormous variety of chemicals and fuels under the condition that hydrogen is available as well. Hence, the ball is put into the court of cheap and sustainable hydrogen production and therefore both thermal and electrolytic options need to be developed that result in substantially less CO_2 emissions compared to the current state of the art. An increase in renewable electricity production is therefore essential to evolve towards a sustainable and carbon-neutral steelmaking future. Nevertheless, for all these new options, speeding up scale-up for industrial applicability is essential as time is not on our side. Therefore extracting information from experimental databases via machine learning [54], process intensification, multiscale modelling on high performance computer infrastructure, 3D printing of equipment and materials, etc. should allow to go substantially faster than the classically 20 years to go from lab scale to industrial scale.

Declarations of interest: none.

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