

# What shall we do with steel mill off-gas: Polygeneration systems minimizing greenhouse gas emissions

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## Abstract

Both the global steel and the chemical industry contribute largely to industrial greenhouse gas (GHG) emissions. For both industries, GHG emissions are strongly related to the consumption of fossil resources. While the chemical industry often emits GHG emissions as direct process emissions, steel mills globally produce 1.78 Gt of off-gasses each year, which are currently used in subsequent heat and electricity generation. However, these steel mill off-gases consist of high valuable compounds, which also can be utilized as feedstock for chemical production, and thereby reduce fossil resource consumption and thus GHG emissions. In the present work, we determine

climate-optimal utilization pathways for steel mill off-gases. We combine a non-linear, disjunctive model of the steel mill off-gas separation system with a large-scale linear model of the chemical industry to perform environmental optimization. The results show that the climate-optimal utilization of steel mill off-gases depends on electricity’s carbon footprint: For the current electricity grid mix, methane, hydrogen and synthesis gas are recovered as feedstocks for conventional chemical production and enable a methanol-based chemical industry. For low electricity footprints in the future, the separation of steel mill off-gases supports CO<sub>2</sub>-based production processes in the chemical industry, supplying up to 30% of the required CO<sub>2</sub>. By coupling the global steel and chemical industry, industrial GHG emissions can be reduced by up to 79 Mt CO<sub>2</sub>-equivalents per year.

## Keywords

Life Cycle Assessment, carbon capture and utilization, industrial symbiosis, Carbon2Chem®

## Synopsis

This paper investigates the industrial symbiosis of the steel and chemical industry, utilizing steel mill off-gases as feedstock for the chemical industry. Thereby, less fossil resources are consumed, reducing greenhouse gas emissions.

## Introduction

The steel industry is globally responsible for 2.1 Gt direct CO<sub>2</sub> emissions per year<sup>1</sup>. In 2019, 87% of the steel-related greenhouse gas (GHG) emissions came from so-called integrated steel mills<sup>2</sup>, where several manufacturing steps are carried out at one site, e.g., iron making, steel making, and casting<sup>3</sup>. These GHG emissions are mainly caused by the waste streams of the

coke-oven (coke oven gas, COG), the blast furnace (blast furnace gas, BFG) and the basic oxygen furnace (basic oxygen furnace gas, BOFG), which are also called steel mill off-gases.

The steel mill off-gases contain significant amounts of combustible compounds (e.g.,  $H_2$ , CO,  $CH_4$ ) and thus, are currently used for on-site heat and electricity generation<sup>4,5</sup> to supply the steel mill; excess electricity is fed into the grid.

To reduce GHG emissions of steel mills, two approaches can be considered: direct and indirect mitigation. Direct mitigation eliminates the cause of GHG emissions by adopting alternative process routes. Currently, direct mitigation is mainly achieved by substituting coke as a reducing agent, e.g., by biomass<sup>6,7</sup>, electricity<sup>8</sup> or hydrogen<sup>9,10</sup>. However, the viability of direct reduction processes highly depends on the availability of low-emission electricity at low cost or, conversely, higher prices for carbon emissions<sup>9</sup>. Thus, direct reduction requires significant structural changes and, thereby, capital expenditure<sup>11</sup> since the blast furnaces have to be modified and the power grid has to be expanded.

Indirect mitigation can be achieved by utilizing steel mill off-gases as feedstock, substituting other emission-intensive processes. These utilization alternatives can be classified into three categories: thermal utilization, fractionation and production of high-value products<sup>4</sup>. Thermal utilization includes the combustion of steel mill off-gases in on-site power plants, as well as heat recovery and Top Gas Recycling<sup>12</sup>, where the steel mill off-gases are sent back to the coke oven as a reducing agent. Fractionation separates valuable compounds from the steel mill off-gases, which are then be sold as feedstock, e.g., for the chemical industry<sup>13</sup>. Alternatively, the steel mill off-gases' valuable compounds can be used directly on-site to produce high-value products, e.g., carbon dioxide-based methanol<sup>14</sup>.

Since steel mill off-gases consist of a mixture of compounds, a combination of utilization alternatives could potentially further reduce greenhouse gas emissions by exploiting the diversity of components in the off-gases. Therefore, polygeneration seems promising to mitigate GHG emissions by utilizing steel mill off-gases<sup>15</sup>. ~~The term polygeneration originally refers to the co-production of electricity and/or heat and chemicals~~<sup>16</sup>. However, in this

~~work, the definition is expanded such that the co-production of several chemicals from the steel mill off-gases is also referred to as polygeneration, although no energy for external markets is produced on-site.~~ The joint production of steel and chemical goods is sometimes also referred to as industrial symbiosis<sup>17</sup>.

Several polygeneration systems combining steel production and steel mill off-gas utilization have already been proposed in the literature. Lundgren et al.<sup>18</sup> investigated the polygeneration of steel, thermal utilization of the steel mill off-gases and methanol and assessed the co-production economically. The authors show that integrating methanol production may improve energy efficiency and is economically viable. Lee et al.<sup>19</sup> expanded this technological economic assessment by including methanol-to-olefin processes as a subsequent process step. However, the production of ethanol and longer-chain hydrocarbons was not economical.

The polygeneration of steel and methanol was evaluated regarding environmental impacts in further work using the method of Life Cycle Assessment<sup>20-24</sup>. Deng and Adams<sup>20</sup> review in detail the literature assessing methanol produced from steel mill off-gases environmentally. Thonemann and Maga<sup>22</sup> show that the climate benefits of polygeneration strongly depend on the electricity carbon footprint and the steel mill off-gas used. Assuming the ESDP 2030 electricity grid mix as electricity supply, the integrated production of methanol and steel increases global warming impact by up to 47% compared to the stand-alone production. In contrast, assuming wind power as electricity supply, the polygeneration becomes environmentally favorable with an impact reduction of up to 42% compared to the stand-alone production. The break-even point of the electricity supply's impact, at which mill off-gas based methanol becomes favorable, is calculated to 0.22-0.23 kg CO<sub>2</sub>-eq./kWh. However, methanol is not the only product from carbon capture and utilization (CCU) technologies, and thus, assessments of further CCU alternatives seem promising.

Several utilization alternatives have been qualitatively compared regarding economic and environmental benefits by Uribe-Soto et al.<sup>4</sup>. The authors summarize several pathways to utilize steel mill off-gases, which use different steel mill off-gas compounds and thus can

exploit a large share of the steel mill off-gas.

A first quantitative comparison of direct and indirect GHG mitigation possibilities for steel mills is presented by Ghanbari et al.<sup>25–27</sup>. The authors presented an economic superstructure optimization of improvements in a steel mill, including direct GHG mitigation, e.g., blast furnace top gas recycling and alternative reducing agents, but also the separation of the steel mill off-gases and the subsequent conversion into methanol as representative for CCU. GHG emissions are considered indirectly by taking CO<sub>2</sub> prices into account in the economic objective function. This work was further developed for transient optimization<sup>28</sup>, considering the fluctuating availability of steel mill off-gases. Both works estimate the GHG mitigation potential of polygeneration by assessing the change of direct gate-to-gate GHG emissions at the steel mill with and without methanol production. The polygeneration system’s GHG mitigation potential again depends on the electricity supply’s impact. However, these assessments might be misleading due to inconsistent system boundaries for the stand-alone productions and the polygeneration system<sup>29</sup>.

All presented studies assessed one representative steel mill and methanol as an exemplary CCU technology. Although this polygeneration is already shown to be potentially environmentally favorable, scaling up this GHG mitigation strategy on the global steel industry would exceed methanol’s global market capacity. Additionally, complimentary utilization alternatives might better exploit the steel mill off-gas components, increasing the GHG savings. Thus, in this paper, we provide an environmental optimization of polygeneration systems on a global scale [to answer the research question: To which extent is it useful to go for a CCU-symbiosis of the steel and chemical industry beyond methanol to mitigate GHG emissions? For this purpose, our](#) optimization includes power and heat supply as well as carbon monoxide (CO)- and carbon dioxide (CO<sub>2</sub>)-based routes for chemicals besides methanol. We include the products given in<sup>4</sup> and additional products that are the focus of the *Carbon2Chem* project<sup>30</sup>. Furthermore, methanol-to-X processes as proposed in Kätelhön et al.<sup>31</sup> and all CO-based processes provided in IHS Markit<sup>32</sup> for the region Germany are included.

As a result, all currently published CO- and CO<sub>2</sub>-based chemicals, as well as ammonia and urea are considered in the model.

For the optimization, we combine two models of different scale: (1) a large-scale, linear model of the CO- and CO<sub>2</sub>-based chemical industry, which includes 195 processes to provide the global demand of the considered chemicals and to allow for utilization of the global amount of steel mill off-gases from integrated steel mills; and (2) a more detailed, non-linear model for the separation of the steel mill off-gases according to Ghanbari et al.<sup>25</sup>.

## Goal and scope definition

The goal of this study is to answer the question: "What shall we do with steel mill off-gases to minimize climate impacts?". For this purpose, a polygeneration system combining the global steel and chemical industry is optimized regarding their GHG emissions. The GHG emissions are characterized using the Recipe (H) v1.1 Midpoint characterization method<sup>33</sup>. The system boundaries for our optimization are given in Figure 1. We apply the system expansion approach and compare a benchmark system representing the stand-alone steel and chemical industries with a polygeneration system, wherein a separation unit allows for fractionating the steel mill off-gases and, thus, enables their subsequent utilization as feedstock in the chemical industry. In both systems, we exclude the steel mill from the comparison since no technological changes of the steel mill are considered. To ensure a constant supply of energy to the steel mill, the steel mill's internal power plant is within the system boundaries. To ensure a sound comparison between benchmark and polygeneration system, both systems' outputs have to be equal. Therefore, we also include fossil-based processes, which conventionally produce the CO<sub>2</sub>-based products obtained in the polygeneration system in the benchmark systems. In summary, the functional unit, which serves as the basis for comparing benchmark and polygeneration systems, contains three elements: (1) the global demand of all regarded chemicals must be produced (Table S1 in the Supporting Information

(SI)). (2) The global amount of steel mill off-gases must be used. (3) The heat and electricity produced conventionally globally by the combustion of the steel mill off-gases must be provided.

## Scenarios

In total, we assess four production scenarios: two benchmark scenarios and two polygenerations. The first benchmark scenario describes the current fossil-based chemical industry (*business-as-usual* scenario), producing the global demand for carbon-based chemicals and combusting steel mill off-gases in the power plant to meet the energy demand in the steel mill. In this scenario, the chemical industry does not use CCU or methanol-to-X processes.

In the second benchmark scenario (*optimized chemical industry* scenario), the chemical industry can implement CCU and methanol-to-X technologies if they are climate beneficial. Additional CO<sub>2</sub> can be obtained from point-sources, e.g., ammonia plants, and via direct air capture<sup>34</sup>. Ammonia plants are included as exemplary point sources providing up to 220 Mt CO<sub>2</sub><sup>35</sup>. However, the steel mill off-gases cannot be used and are thus still combusted in the power plant in this scenario.

Both polygeneration scenarios allow for the industrial symbiosis of the steel and chemical industry. Steel mill off-gases can be separated and used as feedstock in the chemical industry. We further distinguish between a polygeneration scenario, including additional point sources and a polygeneration scenario with steel mill off-gases only. In the *polygeneration scenario, including additional point sources*, additional CO<sub>2</sub> can be obtained as feedstock for CCU technologies from ammonia plants and direct air capture as in the optimized chemical industry scenario. In contrast, in the *polygeneration scenario with steel mill off-gases only*, CO<sub>2</sub> can only be obtained as a raw material by separating steel mill off-gases. The polygeneration systems can use all globally available steel mill off-gases (1.78 Gt). However, the energy demand of the steel mill has to be met and thus, the used steel mill off-gases need

to be replaced by fuels or energy supply from the chemical industry (cf. Figure 1). ~~To meet the steel mill's energy demand, energy supply processes can substitute the power plant in the steel mill in both polygeneration scenarios.~~ The energy supply varies depending on the energy scenario chosen.

In addition to the four production scenarios, we consider two energy scenarios: a *today* and a *future* electricity scenario. In the *today* electricity scenario, electricity is supplied by the current EU grid mix 2020. As a result, additional hydrogen is supplied by steam methane reforming since water electrolysis would lead to higher GHG emissions. Thermal energy is provided by natural gas combustion. In the *future* electricity scenario, electricity is supplied by wind power with an impact of 9.57 g CO<sub>2</sub>-eq./kWh. As a result, additional hydrogen supply by electrolysis becomes climate beneficial. The electrolysis is modelled according to Artz et al.<sup>36</sup> with an electricity demand of 180 MJ/kg H<sub>2</sub>, and direct emissions are adopted from the process *GLO: Electrolysis with wind, 50 (kW h)/ kg of H2 ts* from Gabi database<sup>37</sup>. Due to the low GHG emissions of electricity, heat is supplied by power2heat with an assumed efficiency of 95%.

The scenarios presented for benchmark, polygeneration system and energy supply result in numerous possible combinations for discussion. Therefore, we defined three combinations as Case 1 to 3 in the Results section, which are discussed in detail.

## Optimization problem formulation

The polygeneration system is formulated similarly to the work by Ghanbari et al.<sup>25</sup> as a generalized disjunctive program (GDP)<sup>38</sup>:



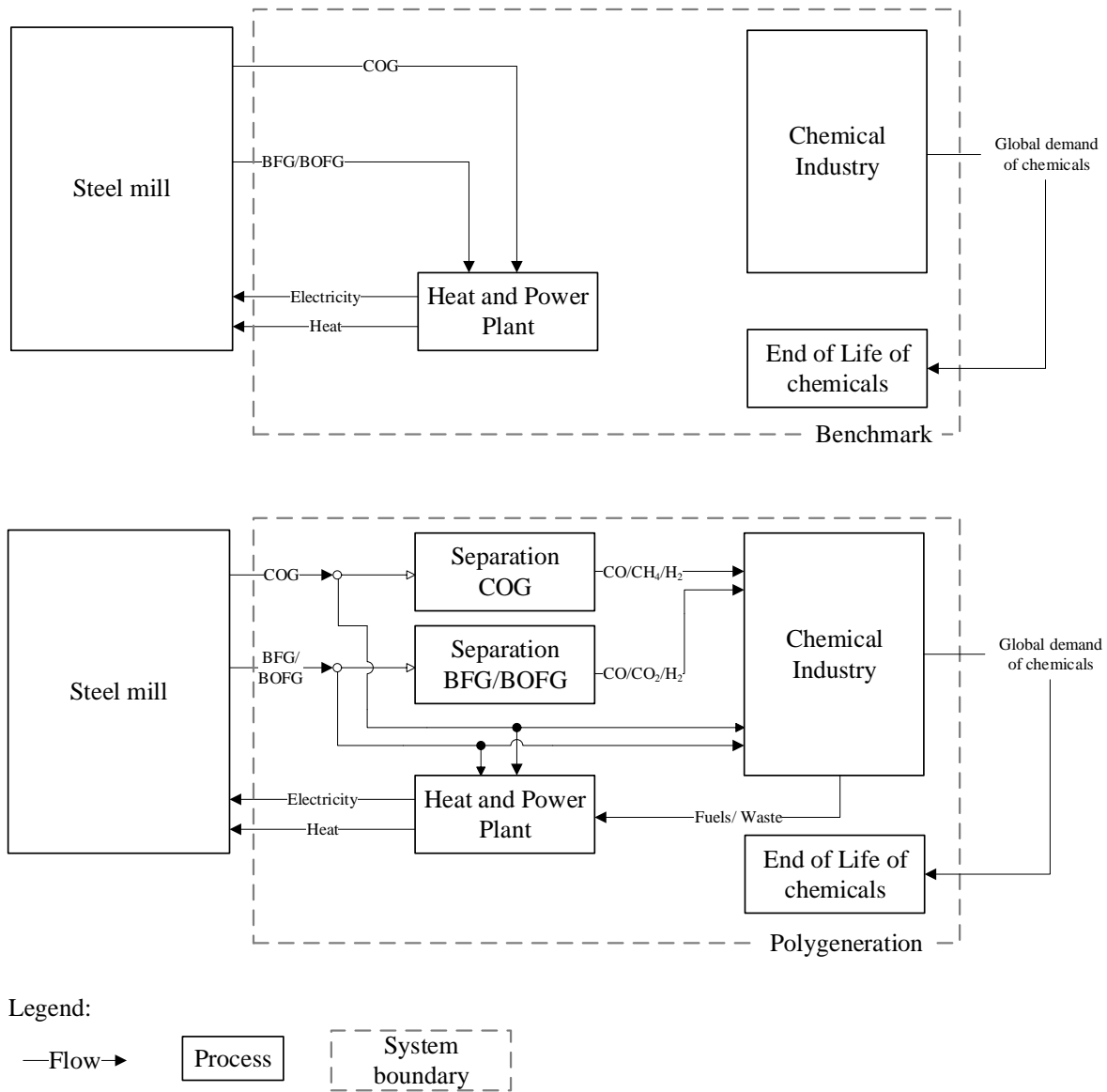


Figure 1: System boundaries. To ensure a sound comparison between the polygeneration system, and the benchmark system, both systems' products must be equal. Thus, the system boundaries of the benchmark system are expanded to include the conventional production of chemicals, which are produced additionally in the polygeneration system. H<sub>2</sub> and CO<sub>2</sub> supply are assumed as part of the chemical industry and are thus not given explicitly. The functional unit, which serves as the basis for comparing benchmark and polygeneration systems, contains three elements: (1) The global demand of all regarded chemicals must be produced. A list of all considered chemicals is given in Table S1 in the SI. (2) The global amount of coke oven gas (COG), blast furnace gas (BFG) and basic oxygen furnace gas (BOFG) must be used. (3) The heat and electricity usually produced by the combustion of the steel mill off-gases must be provided.

$$\min_{s, Y_{k,i}, x} z(s) \quad (1a)$$

$$\text{s.t.} \quad g(s) \leq 0 \quad (1b)$$

$$\forall_{i \in D_k} \begin{bmatrix} Y_{ki} \\ r_{ki}(x) \leq 0 \end{bmatrix} \quad k \in K \quad (1c)$$

$$\forall_{i \in D_k} Y_{ki} \quad Y_{ik} \in \{True, False\} \quad (1d)$$

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The objective (Equation 1a) is to minimize the cradle-to-grave GHG emissions  $z$  generated during the functional unit's provision, including the combustion of all produced chemicals as their end of life. The degrees of freedom for the optimization are the scaling vector  $s$ , the binary design variables  $Y_{k,i}$  choosing unit operations in the separation superstructure, and the operating variables  $x$  of the separation system, e.g., pressure and temperature of a unit operation. The global constraints (Equation 1b) contain the linear subproblem describing the chemical industry and overall mass and energy balances of the polygeneration system. These mass balances link the chemical industry with the separation system. Equation (1c)-(1d) describe the non-linear unit alternatives of the separation superstructure according to Ghanbari et al.<sup>25</sup> (cf. Section 5 in the SI). The global constraints  $g(s)$  contain the detailed formulation of the chemical industry as Technology Choice Model<sup>39</sup>:

$$A^f s = f \quad (2a)$$

$$A^p s \geq p \quad (2b)$$

$$A s \geq 0 \quad (2c)$$

$$s \geq 0 \quad (2d)$$

$$(2e)$$

Herein,  $A$ ,  $A^f$  and  $A^p$  describe technology matrices. Each column represents one process of the chemical industry, and each row describes one technical flow exchanged between these processes. In  $A$  and  $A^f$ , inputs of a process are negative entries, and outputs are denoted by positive entries. In contrast,  $A^p$  only includes positive entries, i.e., the outputs of each process.  $A^f$  and  $A^p$  both contains only subgroups of flows, while  $A$  includes all 122 technical flows exchanged within the model of the chemical industry.

All technology matrices include 357 processes in total, describing the considered chemical industry. For the production of high-value chemicals, all CCU technologies with high and low Technology Readiness Level (TRL) and methanol-to-X processes as published in Kätelhön et al.<sup>31</sup> and Artz et al.<sup>36</sup> are included. The processes are extended by the production of urea<sup>40</sup>. To produce all chemicals in the benchmark scenarios serving the functional unit, and to allow for the separation of valuable compounds and their subsequent utilization as feedstock for conventional processes, the conventional processes are obtained from IHS<sup>32</sup> and included additionally (cf. Table S1 in the SI). As thermal usage of the steel mill off-gases, the combustion of BFG, BOFG, COG and waste gases from the separation in a combined heat and power plant is considered (cf. Table 5 in the SI). For most processes, unit processes are used to allow for a sound analysis of changing background systems. However, to limit the size of the model, we used aggregated processes for auxiliary materials (e.g., calcium oxide, sulfur trioxide) as well as utilities (e.g., cooling water, steam from natural gas) and natural resources (e.g., natural gas, gasoline, lime). Furthermore, we include aggregated processes to satisfy the system expansion approach when no unit processes were available for the required products (e.g., xylene) (cf. Table S1 in the SI). The IHS data is translated from economic into environmental data following the procedure from Meys et al.<sup>41</sup>.

The scaling vector  $s$  is a degree of freedom in the presented optimization problem. The scaling vector quantifies how often the processes are executed to produce the final demand  $f$  or to cover the production volume  $p$ . The final demand vector  $f$  ensures that the functional unit is served as the system’s output. Specifically,  $f$  contains the global amount of steel mill

off-gases, which must be utilized or combusted inside the system boundary (cf. Section 4 in the SI). Additionally,  $f$  contains the global demand for heat and electricity in steel mills, which would usually be obtained by steel mill off-gas combustion and thus, has to be supplied by combustion or any alternative supply inside the system boundaries. The inclusion of the global chemical demand is more difficult since data is not available for all chemicals.

When a market capacity for the regarded chemical  $i$  was available, this market capacity is also included in the final demand and the referring flow is considered in  $A^f$ . In contrast, if only a production volume for chemical  $i$  was found in literature, this production volume is denoted in the production vector  $p$  and the flow is considered in  $A^p$ . Thus, (2a) ensures that the functional unit is met, while Equation (2b) constrains the production of the chemicals to ensure that at least the production volume is met. Both market and production capacities are gathered for 2030 when available; otherwise, estimations or current capacities were used (cf. Table 2 and 3 in the SI). Equation (2c) connects the subsystems of Equation (2a) and (2b) and thereby ensures that the mass balances for each process are met. Finally, Equation (2d) ensures that production processes can only run in the specified direction.

This linear subproblem is linked by Equation (1b) to the non-linear subproblem of the separation superstructure, described by Equation (1c) and (1d). The superstructure is set up as proposed by Ghanbari et al.<sup>25</sup>. The superstructure contains unit operations to separate hydrogen and methane from the COG; and to separate hydrogen, carbon monoxide, and carbon dioxide, respectively, from the BFG and BOFG. Since BFG and BOFG’s compositions are similar, the individual separation of these gas streams is [not worth the extra complexity for the optimization model](#)<sup>25</sup>. Thus, both gases are mixed and taken into account as one gas stream for the separation. The CO separated from the BFG/BOFG stream can be converted to  $H_2$  and  $CO_2$  in a water-gas-shift reactor. The resulting  $H_2/CO_2$  stream can be merged with the CO separation by-product stream for subsequent separation steps.

Additionally, methane reforming reactions are included to produce synthesis gas in various compositions from the by-product stream of the COG hydrogen separation. However,

the superstructure also allows for using methane as feedstock itself. All valuable compounds can be used as feedstocks in the chemical industry afterwards. Details on the gas compositions and unit operations, as well as a visualization of the superstructure, can be found in the SI.

In the separation system, the degrees of freedom are the operating variables  $x$  of each unit operation and the binary design variables  $Y_{k,i}$ , selecting so-called disjuncts to be integrated in the optimal separation flowsheet. Each disjunct  $i$  represents one unit alternative for a separation [process](#) (Equation 1c), e.g., pressure swing adsorption (PSA) for  $H_2$  separation from COG. A list of all considered unit operations and the corresponding separation tasks are given in the SI (cf. Section 5). Each disjunct consists of the indicator (design) variable  $Y_{k,i}$  and unit constraints  $r_{k,i}(x) \leq 0$ . The unit constraints incorporate shortcut equations and operation limits. If a disjunct is selected,  $Y_{k,i} = True$  and  $r_{k,i}(x) \leq 0$  is fulfilled. Equation (1d) ensures that in a set of disjuncts having the same separation task, i.e., a so-called disjunction  $k$ , exactly one disjunct is selected, according to one unit being selected for the final flowsheet. For example, for the  $H_2$  sequestration from COG, either a PSA or membrane unit must be selected and not both or neither of the unit operations.

All required inputs and generated outputs of the separation superstructure are passed to the linear subproblem as additional flows in the technology matrix  $A$  and are thus integrated into the objective function.

The optimization problem is set up in Pyomo Version 5.6.8<sup>42</sup> using the Pyomo.GDP extension<sup>43</sup> and Python Version 3.6. We selected the GDPopt solver with a logic-based outer approximations strategy<sup>44</sup>, using GLPK as (MI)LP and IPOPT as NLP subsolver<sup>45</sup>.

## Results

In the following, we discuss the optimization results with the scenarios presented in Section *Scenarios*: First, we calculate the maximum achievable GHG savings of the polygeneration,

comparing the *business-as-usual* benchmark with the *polygeneration scenario with steel mill off-gases only* for the *today* electricity scenario (Case 1). Low-TRL technologies (cf. Table 1 in the SI) are excluded from this comparison to establish a base case that could be implemented today. The results of this first comparison indicate that significant GHG reductions can be achieved using high-TRL CCU technologies compared to the current chemical industry in the *business-as-usual* benchmark scenario.

To determine the specific contribution of the steel mill off-gas utilization to this reduction, the *polygeneration scenario, including additional point sources*, is then compared to the *optimized chemical industry* scenario using also the *today* electricity scenario (Case 2). Finally, since the polygeneration structure of the chemical industry and thus, the GHG savings strongly depend on the electricity impact, *polygeneration scenario, including additional point sources* is compared to the *optimized chemical industry* scenario using the *future* electricity scenario (Case 3).

## Case 1: Polygeneration system with steel mill off-gases only

In Figure 2, the *polygeneration scenario with steel mill off-gases only* ~~structure of the optimal polygeneration system with minimum GHG emissions using steel mill off-gases as the unique point source of CO<sub>2</sub>~~ is compared to the *business-as-usual* benchmark using the *today* electricity scenario. ~~The polygeneration system can use all globally available steel mill off-gases (1.78 Gt).~~

The steel mill off-gases COG (grey input flow) and BFG/BOFG (black input flow) are separated into carbon monoxide, carbon dioxide, methane and hydrogen. In the separation system, COG is separated into 4.8 Mt hydrogen and 16 Mt methane via PSA. From the BFG/BOFG, first, 20 Mt carbon monoxide are separated via temperature swing adsorption (TSA). Afterwards, 29 Mt carbon dioxide are separated using chemical absorption (CCA). Finally, 27 kt hydrogen are separated using PSA. The separation configuration is in agreement with the findings of Ghanbari et al.<sup>25</sup>. However, the subsequent utilization of the gases differ:

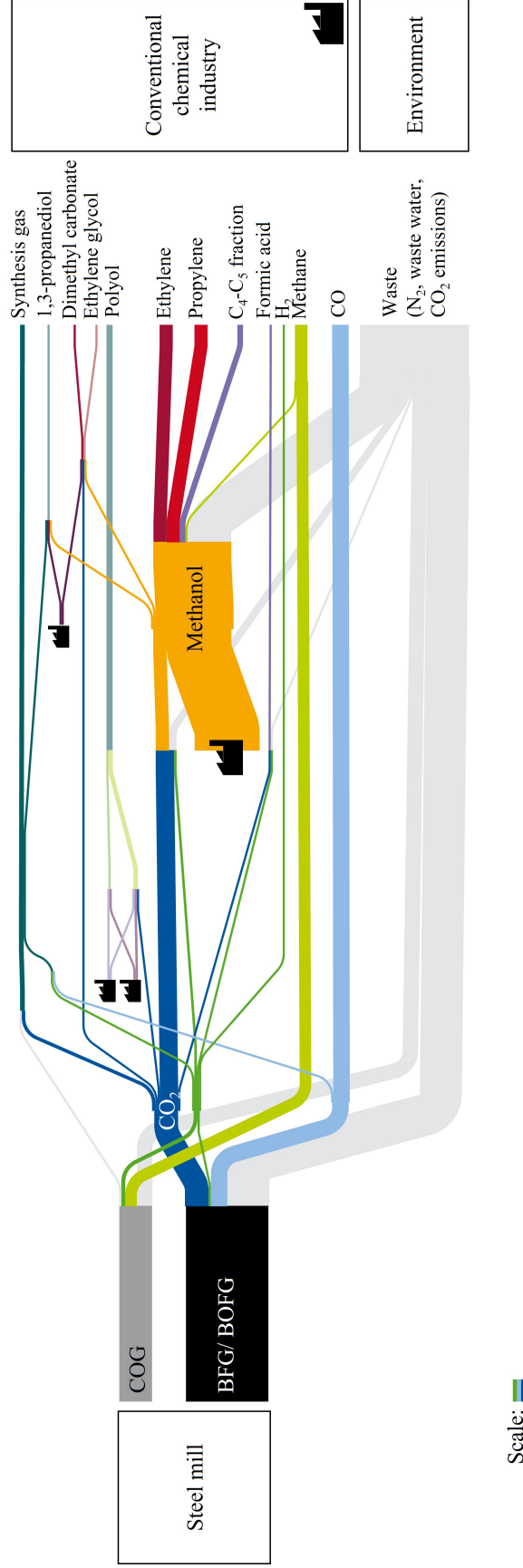


Figure 2: Sankey diagram of mass flows in polygeneration for Case 1: The polygeneration system with steel mill off-gases only is compared to the business-as-usual benchmark for the *today* electricity scenario. For reasons of clarity, only flows that are added or increased compared to the benchmark without steel mill off-gas utilization are shown. A reference flow, consisting of 3 x 5 Mt, is given at the bottom left as a scale. Raw material flows starting at the factory symbol are supplied by the conventional chemical industry.

In Ghanbari et al.<sup>25</sup>, CO<sub>2</sub>-based methanol and dimethyl ether are produced, while in the optimization presented in this work, fuels are not included in the optimization and thus, no dimethyl ether is produced. In contrast, all obtained gases (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, syngas) are used as feedstocks for the conventional, fossil-based chemical industry. 36% of the obtained hydrogen is used to substitute all hydrogen from steam methane reforming; the remaining hydrogen is used as feedstock to produce CO<sub>2</sub>-based methanol and formic acid. The carbon monoxide substitutes the conventional CO supply via steam methane reforming from natural gas. 1.5 Mt methane from the COG is converted using 4.2 Mt carbon dioxide captured from BFG to produce 5.7 Mt synthesis gas (1:1). The obtained syngas is used as feedstock for the conventional chemical industry. Several compositions of syngas are provided for the chemical industry, but for clarity, these streams are summarized into one syngas stream in Figure 2. The remaining 89% of methane is utilized as a substitute for fossil methane from natural gas. The carbon dioxide is used as feedstock for methanol, formic acid, polyol and dimethyl carbonate. CO<sub>2</sub>-based methanol substitutes fossil-based methanol. Methanol is used as feedstock in a methanol-to-olefin process to produce ethylene and propylene, as well as for CO<sub>2</sub>-based production of dimethyl carbonate and 1,3-propanediol production.

In total, the polygeneration system avoids 107 Mt GHG emissions, [which equals a reduction of 2% when compared to the 5.52 Gt GHG emissions of the business-as-usual steel and chemical industry](#). However, no distinction is possible whether the savings are due to the use of steel mill off-gases or the chemical industry's optimization towards CCU technologies. Thus, the comparison of the polygeneration to an optimized chemical industry without steel mill off-gas utilization is studied in Case 2.

## Case 2: Polygeneration including additional CO<sub>2</sub> point sources

In Figure 3, the mass flows of the *polygeneration scenario, including additional point sources*, is compared to the *optimized chemical industry scenario* using the *today* electricity scenario. ~~The polygeneration system can still utilize the globally available steel mill off-gases (1.78 Gt)~~



~~as feedstocks. However, to satisfy the functional unit, steel mill off-gases not used chemically must be combusted. Additional CO<sub>2</sub> can be obtained from ammonia plants and via direct air capture.~~ Details including Sankey diagrams of the optimized chemical industry are given in the SI.

In the polygeneration system, 4.9 Mt hydrogen is separated via PSA from the COG. The remaining stream mainly consist of CH<sub>4</sub>. Thus, 15.6 Mt CH<sub>4</sub> are obtained, from which 2.58 Mt are converted together with 7.2 Mt CO<sub>2</sub> captured from an ammonia plant to 9.8 Mt syngas (1:1). Syngas is used mainly to substitute fossil-based syngas supplying the same processes as in the optimized chemical industry. 2% syngas is used as feedstock for a different fossil-based acetic acid production route, and 35% syngas is used to produce a different fossil-based n-butyraldehyde route than in the optimized chemical industry without steel mill off-gas utilization. The remaining methane substitutes fossil methane from natural gas.

Of the separated hydrogen, 54% is used to meet the demand for hydrogen in conventional chemistry and replace the supply with hydrogen from steam methane reforming. The remaining hydrogen is used as feedstock to produce CO<sub>2</sub>-based methanol, which becomes environmentally beneficial due to the excess of hydrogen from steel mill off-gases. 98.2% of the CO<sub>2</sub>-based methanol substitutes syngas-based methanol and saturates the methanol market capacity. The 0.8% excess methanol is used in a methanol-to-olefin process to produce ethylene and propylene. In total, the polygeneration system can achieve GHG savings of 35 Mt CO<sub>2</sub>-eq. compared to the ~~stand-alone steel and~~ optimized chemical industry. ~~In percentage terms, the reduction potential equals 0.6% considering the savings in relation to the 5.52 Gt GHG emissions of the stand-alone steel and optimized chemical industry.~~

The optimization results for mass flows in the polygeneration system are in good agreement with results found by Man et al.<sup>46</sup>. The authors assessed a COG-assisted coal-to-olefins process, producing syngas-based methanol. The syngas was obtained from coal and COG, separated via PSA into hydrogen and methane. The methane is shifted together with CO<sub>2</sub>

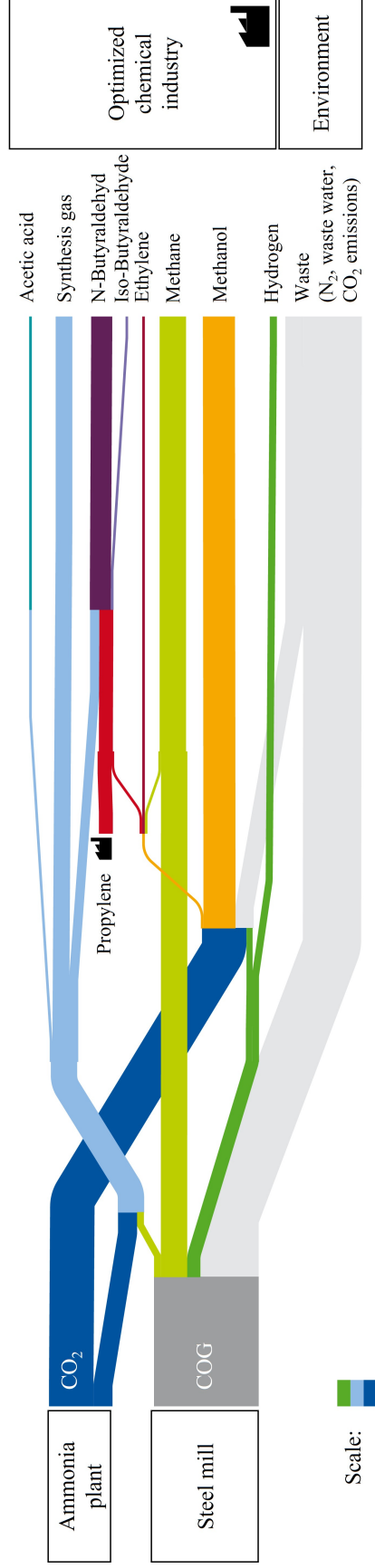


Figure 3: Sankey diagram of mass flows in polygeneration for the *today* electricity scenario compared to an optimized chemical industry. For reasons of clarity, only flows that are added or increased in comparison to the optimized chemical industry without steel mill off-gas utilization are shown. A reference flow, consisting of 3 x 5 Mt, is given at the bottom left as a scale. Raw material flows starting at the factory symbol are supplied by the optimized chemical industry. The BFG/BOFG mixture is combusted in the power plant in both systems and is thus, not shown in the figure.

obtained from coal gasification to produce syngas. This syngas is enriched with the hydrogen from the COG and is then used as feedstock for methanol. These process steps also resulted from the presented optimization of this work. Man et al.<sup>46</sup> stated a GHG saving potential of their process, which can be confirmed by the optimization presented in this work. However, in this work, the CO<sub>2</sub> for the water-gas-shift reaction is separated from the ammonia plant and not produced using coal gasification.

In contrast, Thonemann and Maga<sup>22</sup> found that the integrated production of methanol and steel increases global warming impact by up to 47% compared to the stand-alone production when using using ESDP 2030 electricity mix. The difference to the presented results in this work results from the fact that in Thonemann and Maga<sup>22</sup>, the hydrogen demand cannot be met by the steel mill off-gases due to limited availability of COG. Instead, additional hydrogen is provided by electrolysis, which is the main contributor to the high GHG emissions.

In conclusion, the CO<sub>2</sub>-based production of methanol using steel mill off-gases can reduce GHG emissions compared to the fossil-based or the stand-alone CO<sub>2</sub>-based methanol production. However, the reduction strongly depends on the availability of hydrogen with low carbon footprint. Therefore, the GHG savings are discussed in the following depending on the COG availability and thus the hydrogen availability.

## **GHG savings depending on steel mill off-gas availability**

Since the availability of COG was identified as limiting factor, a reduction efficiency is defined as the specific GHG savings per kg COG available (Figure 4).

The resulting merit order curve for COG utilization consists of three steps: For the first step, the reduction efficiency is constant at 1.025 kg CO<sub>2</sub>-eq./kg utilized COG up to 25 Mt COG available. Savings are achieved by separating the COG into hydrogen and methane which substitutes fossil-based feedstocks. The hydrogen substitutes fossil-based hydrogen from steam methane reforming. 37% of the separated methane is shifted together with CO<sub>2</sub>

captured from ammonia plant to syngas. The syngas and the remaining methane substitute feedstocks based on natural gas.

When 25 Mt COG utilized is reached, the global demand for hydrogen in the optimized chemical industry is saturated. Thus, no further GHG savings are possible from the substitution of fossil-based hydrogen are possible. However, the global demand for syngas is not saturated and can be further substituted. As a result, additional COG up to 39 Mt is still separated to provide methane for the shift to syngas, forming the second step with a constant reduction efficiency of 0.66 kg CO<sub>2</sub>-eq./kg utilized COG. The excess hydrogen that is a side-product of the separation process but not required for the substitution of fossil-based hydrogen replaces the conventionally used n-butyraldehyde process with a more hydrogen-intensive but energetically more advantageous process. Similarly, the production of CO<sub>2</sub>-based methanol becomes environmentally favorable due to the availability of hydrogen with low carbon footprint.

At 39 Mt COG available, n-butyraldehyde's market capacity is saturated by the hydrogen-intensive technology. As a result, the reduction efficiency decreases to 0.485 kg CO<sub>2</sub>-eq./kg utilized COG. Further GHG savings are only achieved by substituting fossil-based syngas and increasingly substituting methanol from syngas by CO<sub>2</sub>-based methanol using the excess hydrogen. This third step is limited by the global amount of 39.7 Mt COG available.

The discussion of the reduction potential reveals that the GHG savings are achieved by substituting fossil-based processes. The reduction potential of the steel mill off-gas utilization strongly depends on the feedstock demands in the chemical industry. However, the chemical industry might move from fossil-based to CO<sub>2</sub>-based processes, with decreasing carbon footprints for the electricity supply. Thus, the changes in the chemical industry and their impact on the polygeneration depending on the electricity impact are evaluated in the next section.

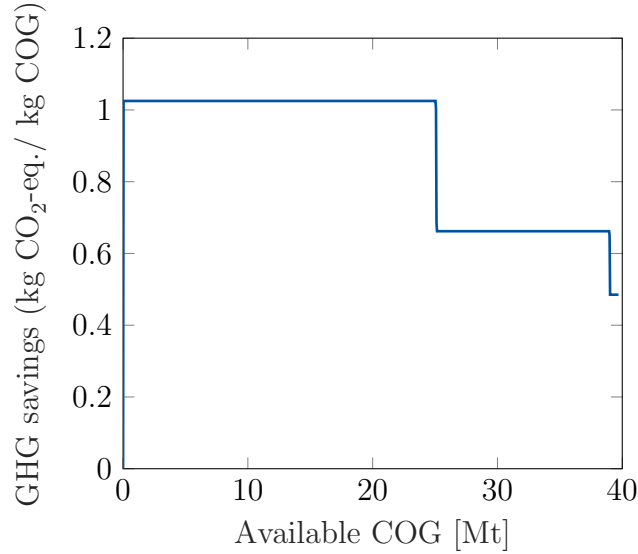


Figure 4: Environmental merit-order curve of the GHG savings due to the utilization of COG as feedstock for the chemical industry.

### GHG savings depending on electricity impact

Figure 5a visualizes the cradle-to-grave GHG savings due to the utilization of steel mill off-gases depending on the impact of electricity supply. The GHG savings increases for the *polygeneration scenario, including additional point sources*, compared to the *business-as-usual* benchmark scenario from 115 Mt CO<sub>2</sub>-eq. in the *today* electricity scenario up to 3.6 Gt CO<sub>2</sub>-eq. for the *future* electricity scenario. With decreasing GHG emissions of electricity supply, the chemical industry changes from syngas-based to CO<sub>2</sub>-based production in the polygeneration system as discussed in Kätelhön et al.<sup>31</sup>. Therefore, the savings are not only due to the use of steel mill off-gases. **Even more, most of the GHG savings are achieved outside the steel industry:** Comparing the *business-as-usual* benchmark scenario to the *optimized chemical industry* reveals that 80 Mt CO<sub>2</sub>-eq. of the 115 Mt CO<sub>2</sub>-eq. savings are due to the optimization of the chemical industry in the *today* electricity scenario. Similarly, 3.521 Gt CO<sub>2</sub>-eq. of the 3.6 Gt CO<sub>2</sub>-eq. savings are due to the optimization of the chemical industry in the *future* electricity scenario. Thus, the GHG savings of the polygeneration are mainly achieved by optimizing the chemical industry and not by utilizing steel mill off-gases.

The total GHG savings obtained by the optimization of the chemical industry are comparable to the savings calculated by Kätelhön et al.<sup>31</sup>. The authors state GHG savings of 3.5 Mt CO<sub>2</sub>-eq. for the 20 largest-volume chemicals resulting in 0.7 Gt CO<sub>2</sub>-eq. residual annual emissions of the chemical industry. In contrast, the optimization presented in our work results in 1.9 Gt CO<sub>2</sub>-eq. residual GHG emissions for the steel and chemical industry. The large offset of 1.2 Gt CO<sub>2</sub>-eq. total GHG emissions compared to the 0.7 Gt CO<sub>2</sub>-eq. residual emissions presented by Kätelhön et al.<sup>31</sup> is due to the fossil-based input into the steel mill, resulting in fossil-based carbon in the steel mill off-gases. As a result, the steel and chemical industry cannot become carbon-neutral. Overall, the utilization of steel mill off-gases can contribute to a changing chemical industry by providing an additional point source of CO<sub>2</sub>.

The changing demand for feedstocks in the chemical industry can be seen in the electricity impact-dependent change of the separation system (Figure 5b (COG) and 5c (BFG)): In the *today* electricity scenario, the separation system provides H<sub>2</sub>, CH<sub>4</sub> and syngas from COG while BFG is combusted. With decreasing GHG emissions of electricity supply, COG is only separated into H<sub>2</sub> and CH<sub>4</sub>, and the methane is no longer converted into syngas. This change is caused by the changing feedstock demands of the chemical industry, moving from syngas to CO<sub>2</sub>-based processes. Additionally, at a grid mix of 180 g CO<sub>2</sub>-eq./kWh, the separation of BFG becomes climate-favorable since the CO<sub>2</sub> demand of the chemical industry exceeds the maximum capacity of CO<sub>2</sub> from ammonia plants (Figure 6). Finally, at an electricity impact of 120 CO<sub>2</sub>-eq., the CO<sub>2</sub> from steel mill off-gases is completely exhausted as feedstock. With further decreasing electricity impact, the additional CO<sub>2</sub> demand of the chemical industry is supplied by direct air capture as the ultimate CO<sub>2</sub> source. However, the reader should note that only two exemplary point sources were considered in this optimization. If other point sources were available in the optimization, they would be used before direct air capture.

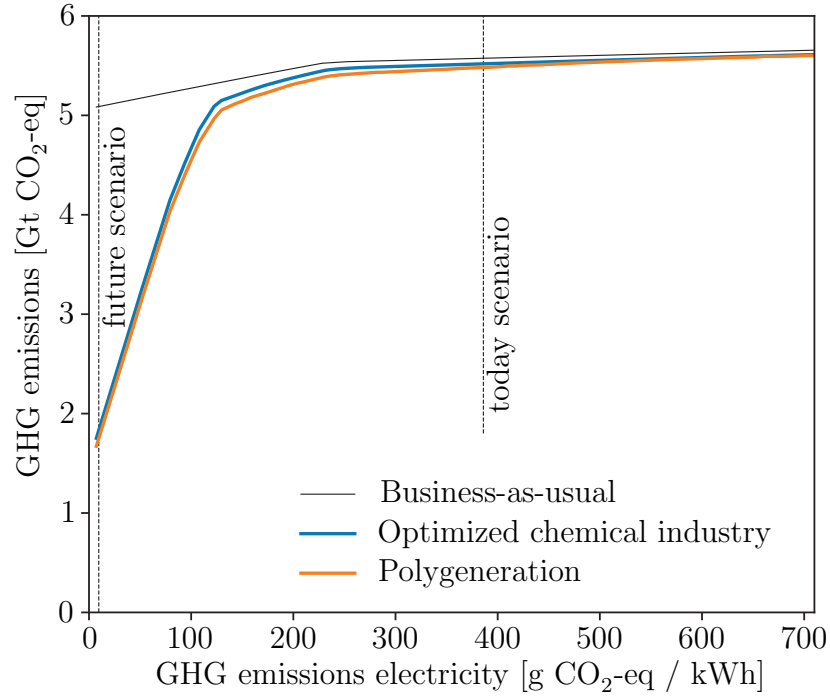


Figure 5 (a): Comparison of the global greenhouse gas emissions of the polygeneration scenario, including additional point sources to the *business-as-usual* benchmark scenario and the *optimized chemical industry* benchmark scenario

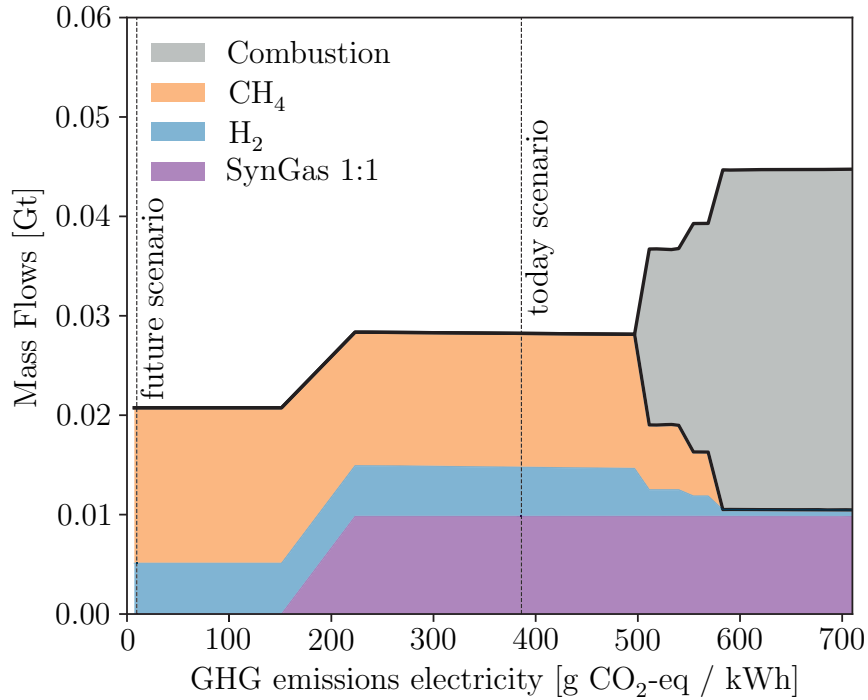


Figure 5 (b): Mass flows in the separation system for coke oven gas depending on the GHG emissions of the electricity supply

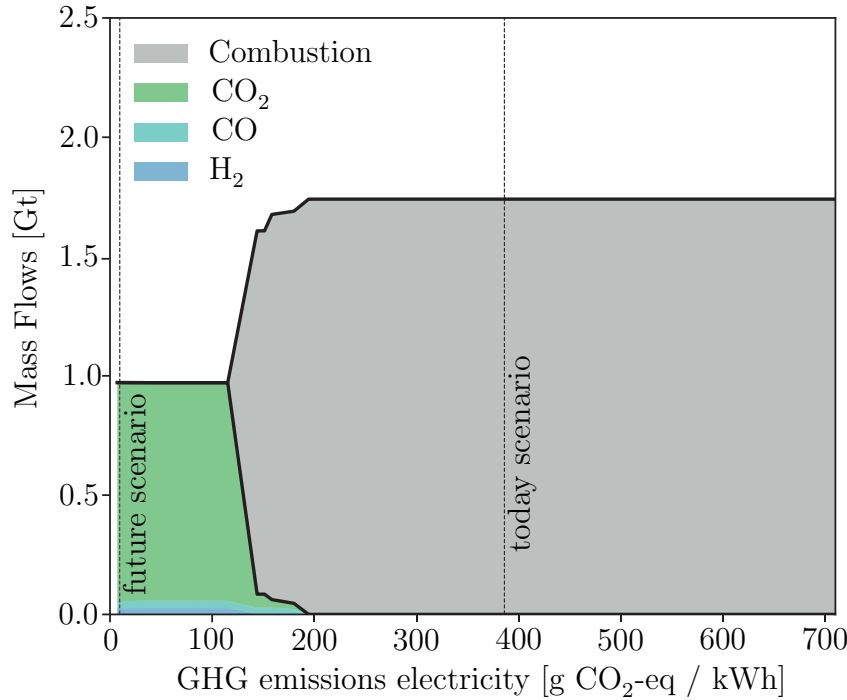


Figure 5 (c): Mass flows in the separation system for blast furnace gas depending on the GHG emissions of the electricity supply

Figure 5: Influence of the greenhouse gas emissions of electricity supply on the polygeneration system

### Case 3: Polygeneration in the future electricity scenario

Owing to the decreasing electricity impacts (Figure 5a) and a resulting change of the chemical industry to CCU processes, the mass flows in the overall polygeneration system change significantly. To consider the influence of the electricity impact on the polygeneration system, a second electricity scenario, the *future* electricity scenario, is analysed to compare of the *polygeneration scenario, including additional point sources*, to the *optimized chemical industry* scenario (Figure 7). ~~As in Case 2, the globally available amount of steel mill off-gases of 1.78 Gt can be utilized, and additional CO<sub>2</sub> can be obtained from ammonia plants or via direct air capture.~~

Owing to the change of the chemical industry from syngas-based to CO<sub>2</sub>-based processes and the resulting increased demand of CO<sub>2</sub>, the BFG/BOFG is now separated, in contrast to



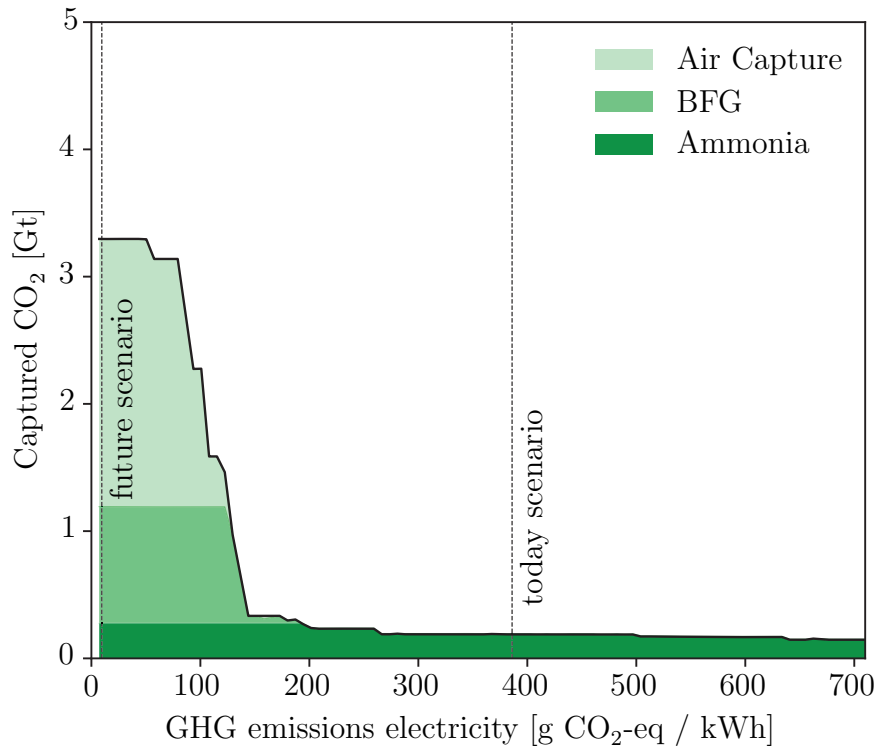


Figure 6: CO<sub>2</sub> captured from varying sources depending on the electricity impact. The decreasing electricity impact results in an increasing CO<sub>2</sub> demand in the chemical industry. As a result, CO<sub>2</sub> is not only captured from ammonia plants but also from less concentrated sources such as steel mill off-gases and via direct air capture.

the *today* electricity scenario. In the separation sequence, [firstly](#) 0.351 Gt CO are separated via TSA from the BFG/BOFG mixture [first](#). 0.32 Gt of [this](#) CO is shifted together with 0.21 Gt water in a water-gas-shift reactor to CO<sub>2</sub> and H<sub>2</sub>. The resulting stream is mixed with the remaining stream of the TSA and sent to a PSA to separate 0.92 Gt CO<sub>2</sub>. In a second PSA, 0.023 Gt H<sub>2</sub> are obtained from the remaining stream. The residual CO is mixed with a small amount of hydrogen to obtain syngas. This syngas is used as feedstock for syngas-based methanol, which is produced due to CO availability. However, the primary demand for methanol is supplied by CO<sub>2</sub>-based production. The COG is separated into 15.6 Mt methane and 5.1 Mt hydrogen via a PSA. Both gases are used as feedstock for the optimized chemical industry. [In total, the polygeneration system can achieve additional GHG savings of 79 Mt CO<sub>2</sub>-eq. compared to the optimized chemical industry in the future](#)

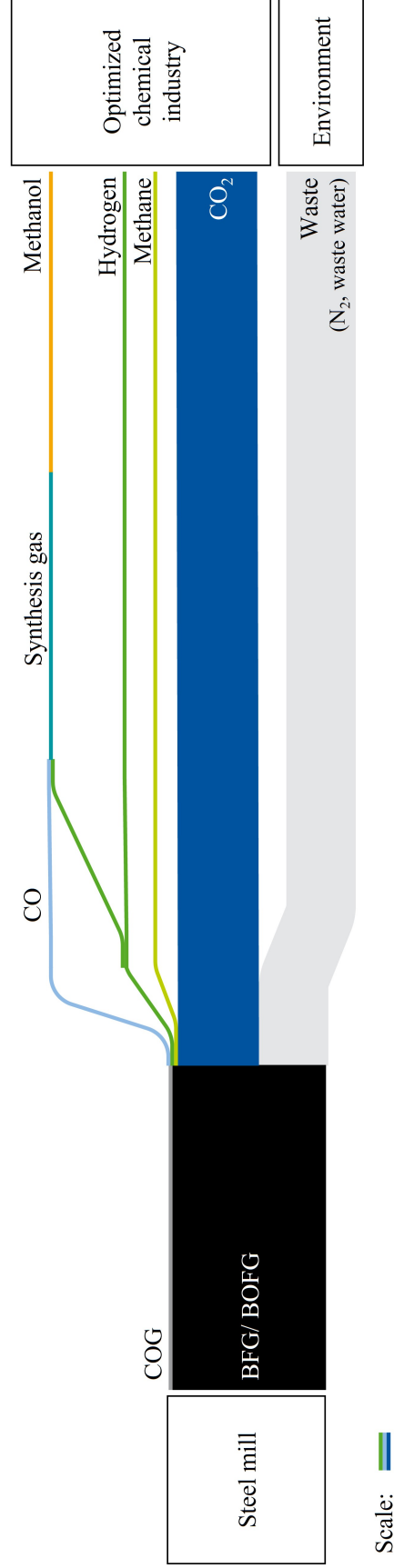


Figure 7: Sankey diagram of mass flows in polygeneration system for the *future* electricity scenario. For reasons of clarity, only flows that are added or increased in comparison to the optimized chemical industry without steel mill off-gas utilization are shown. A reference flow, consisting of 3 x 5 Mt, is given at the bottom left as a scale.

electricity scenario (i.e. 4.5% when related to the 1.74 Gt CO<sub>2</sub>-eq. of the stand-alone steel and optimized chemical industry).

## Discussion

Our optimization shows that polygeneration systems can be climate beneficial compared to the current practice of thermal usage of the steel mill off-gases, although the polygeneration presented only makes a small contribution. Using the coke oven gas from the steel mill as feedstock for polygeneration systems could reduce greenhouse gas emissions globally by up to 115 Mt CO<sub>2</sub>-eq. already today by supplying hydrogen and synthesis gas. With future low-carbon electricity, the utilization of steel mill off-gases can contribute to a changing chemical industry as an additional point source of CO<sub>2</sub>. GHG savings up to 3.6 Gt CO<sub>2</sub>-eq. can be achieved compared to the business-as-usual, fossil-based chemical industry. However, these GHG savings are largely due to transformation of the chemical industry. The integration of steel mill off-gases saves only additional 79 Mt CO<sub>2</sub>-eq. compared to a stand-alone steel and chemical industry. In percentage terms, the optimization of the chemical industry achieves a GHG emissions reduction of 33%, which can be increased only by additional 4.5% when considering the industrial symbiosis of steel and chemical industry. Although the savings for the global steel industry are quite low compared to the potential savings when optimizing the chemical industry, the results show that individual steel mills can certainly contribute significantly.

The feedstock demand of the chemical industry depends on the electricity impact since the climate-optimal chemical industry moves from syngas-based to CO<sub>2</sub>-based production as the electricity carbon footprint decreases. As a result, the optimal separation system of steel mill off-gases also strongly depends on the electricity impact.

Overall, the steel industry cannot become carbon neutral as long as the inputs to the coke oven are fossil-based. Further technological changes are required within the steel mill to

enable the carbon neutrality of the steel industry. One possibility is to switch to non-fossil reduction agents, e.g., hydrogen from electrolysis with renewable energy, which can be used in the direct reduction process. Additionally, carbon capture and storage can be considered at the end of life of the chemicals produced to avoid re-emitting the carbon content of the steel mill off-gases.

Nevertheless, the results show that, already today, the use of steel mill off-gases can reduce GHG emissions. Thus, the presented polygeneration can serve as a bridging technology until sufficient green hydrogen is available for direct reduction processes. Another advantage is that existing blast furnaces can be further used, without the immediate need for the cost-intensive transition to direct reduction processes. Therefore, future work should be to determine the cost-optimal investment path towards direct reduction processes with availability constraints for green hydrogen. At this point, the steel mill has to be included in the system boundaries to allow for the environmental assessment of technological changes. Furthermore, the results have shown that the [already limited](#) GHG savings through steel mill off-gas utilization strongly depend on the chemical industry’s development. [If the chemical industry would change substantially, e.g. through the use of bio-based processes, the benefits of polygeneration could decrease further.](#) Further work should therefore address other technologies for a low carbon chemical industry, such as the increased use of biogenic resources or recycling.

## Acknowledgement

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## Supporting Information Available

Further information regarding the details of the optimization problem can be found in the electronic support information. The code including the Excel exports for the results used in this paper is available on Github: <https://github.com/jkleinekorte/millgas2what>

## List of abbreviations and mathematical symbols

Abbreviation	Explanation
BFG	Blast Furnace Gas
BOFG	Basic Oxygen Furnace Gas
CCU	Carbon Capture and Utilization
CCA	Carbon Chemical Absorption
CDR	Carbon Dioxide Reforming (of Methane)
CHP	Combined Heat and Power Unit
COG	Coke Oven Gas
GDP	Generalized disjunctive (optimization) program
GHG	Green House Gas
GW	Global Warming Impact
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LTSR	Low Temperature Shift Reaction
LP	Linear (optimization) program
MEA	Monoethanolamine
MGS	Steel Mill Off-Gas Separation
MINLP	Mixed-integer non-linear (optimization) program
MSP	Membrane Separation Process
MIP	Mixed-integer linear (optimization) program
NLP	Non-linear (optimization) program
SMR	Steam Methane Reforming
TCM	Technology Choice Model
TRL	Technology Readiness Level
TSA	Temperature Swing Adsorption
POR	Partial Oxygen Reforming (of Methane)
PSA	Pressure Swing Adsorption

Symbol	Explanation	Unit
$A$	Technology matrix	—
$B$	Environmental flow matrix matrix	—
$f$	Final demand vector	—
$h$	Impact vector	—
$p$	Production volume	—
$Q$	Characterization matrix	—
$s$	Scaling vector	—
$v$	End-of-life vector	—

Subscripts	Explanation
$i$	Disjunct $i$ in separation superstructure , i.e., in unit operation
$k$	Disjunction $k$ in separation superstructure, i.e., all unit operations available for a specific separation task

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Can an industrial symbiosis of the steel and chemical industries support the fight against climate change by using waste gases from steelworks as feedstock for the chemical industry?