

Simulation of Methanol and Urea Production from Catalytic Conversion of Steel Mill Gases

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Supporting Information
available online

The time-dependent operation of methanol, ammonia, and urea production units embedded in a steel mill environment is analyzed with dynamic simulation models. From different process concepts and gas availability scenarios, a set of simulation cases is defined with blast furnace gas as carbon and coke oven gas as hydrogen source. Dynamic simulations indicate that significant CO₂ reductions require large amounts of additional H₂ from sustainable sources. From the results, global data such as carbon footprint or energy demands and details about process unit operation are obtained and processed.

Keywords: Carbon2Chem, Methanol, Simulation, Steel Mill Gases, Urea

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1 Introduction

The project working background of the Carbon2Chem[®] initiative is outlined in Fig. 1 and discussed in detail by Deerberg, Oles, and Schlögl [1]. Carbon2Chem[®] works on implementing a flexible carbon capture and utilization (CCU) concept by linking, e.g., the CO₂-emitting steel industry with the chemical and energy industry. Off-gases now serve as starting material and are combined with green hydrogen from electrolysis to produce basic chemicals and other products. As outlined in [1], the major challenges of this approach are high system dynamics, the supply of H₂-rich synthesis gas from steel mill gases and other H₂ sources, and the integration of chemical processing into the context of a steel production environment. Here, the goal is to enable effective chemical production simultaneously with effective steel production, avoiding serious technology changes in the steel making process. An essential part of the Carbon2Chem[®] integration strategy is dynamic simulation to investigate process dynamics and mass and energy demands in the frame of a cross-industrial production network.

With respect to this project background, our work focuses on modeling the lower right part of Fig. 1: 1) the synthesis of chemical products (methanol, ammonia, urea, and others) in connection with 2) the allocation and preparation of steel mill gases, 3) the supply of additional hydrogen from alkali electrolysis plants, and 4) the combustion of excess- and off-gases in the on-site power plant unit. As shown later in Sect. 2, the modeling of this cross-industrial system is done with detailed models of the process units. Referencing to a defined CCU scenario, time-dependent

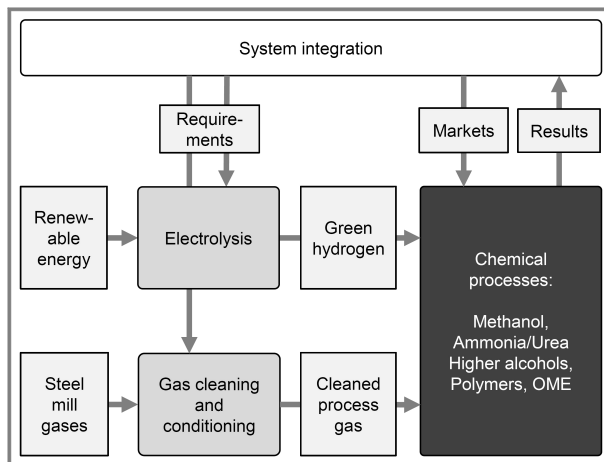


Figure 1. Working structure of the Carbon2Chem[®] joint research project. OME, oxymethylene ether.

flow rates of steel mill gases are considered to calculate, e.g., the demand for renewable energy to produce the required amount of green hydrogen. The resulting product flow rates are integrated to compare, e.g., the total product tonnage and its resulting CO₂ footprint between multiple simulation cases.

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The Carbon2Chem[®] initiative [1] works on the reduction of CO₂ emissions by CCU technology. Here, a short overview of recent contributions in this field is given. In most cases, the main aspects are hydrogen supply, gas cleaning, and gas conditioning [2]. Schlüter and Hennig [3] give the mathematical background for processing CO, CO₂, and H₂ from steel mill gases and H₂ from an electrolysis process to methanol and other chemicals. The dynamic modeling approach covers multiple levels of detail for the modeled unit operations. The results highlight the importance of the gas mixing and conditioning strategy and the energy demand of the electrolysis process. Girod et al. [4] investigated the methanol synthesis from steel mill gases in detail. They emphasize the importance of a suitable catalyst for the varying gas composition and the general dynamics of the process. Their tests determine a promising catalyst for long-term stability without noticeable deactivation over several weeks.

In [5], Schittkowski et al. also point out the role of a stable methanol catalyst for a cross-industry approach to reduce CO₂ emissions by methanol synthesis. The authors indicate the compounds that act as catalyst poisons and mention the need for a complex gas purification process. In [6], a case study for large-scale methanol production is demonstrated. The authors evaluate from a technical and economic perspective how methanol can be synthesized from natural gas or other light hydrocarbons as feedstock. The authors also point out a significant growth in the use of methanol as a fuel and additive. Therefore, the demand for methanol on the world market is expected to grow.

Yildirim et al. [7] give examples of urea production from various sources. It is shown how much carbon dioxide can be chemically fixed into urea for typical plant capacities. The authors also apply those process concepts to steel mill gases and determine the levels of hydrogen required for urea production. It is concluded that significant amounts of urea can be produced from a steel mill.

Stießel et al. [8] identify promising cross-industrial process concepts that use high levels of renewable energies that link carbon-intensive sectors like the steel industry with the chemical industry. The authors focus on economically and ecologically favorable configurations. Both methanol and urea are proposed as possible products for the carbon binding that can be produced on a large scale.

Abanades et al. [9] critically discuss whether CCU or carbon capture and storage (CCS) approaches promise a higher impact on carbon dioxide reduction. The authors state that the main challenge is not the conversion of carbon dioxide to methanol or fuel but the production of carbon-free electricity at very low cost. The authors conclude that CCS approaches are more viable mitigation options over a broad range of assumptions.

Görner et al. [10] calculate the benefits of the coupling of renewable energy sources and a combined cycle power plant with methanol production. The authors state that hydrogen production by electrolysis accounts for most of the power demand of the methanol plant (96 %). The combination of

a combined cycle power plant with methanol production generates an additional degree of freedom: the generated electricity can be directly sold or used to produce methanol. Therefore, with prognostic market data, the optimal operation of the whole plant can be identified.

In [11], the four CCU pilot projects MefCO₂, ALIGN-CCUS, OCEAN, and LOTER are discussed. The products for utilization are methanol and dimethyl ether, although the LOTER project proposes a direct electrochemical synthesis of methanol. The presented projects follow different approaches to the use of carbon dioxide, but all have in common that hydrogen and power demand are the key aspects. The authors also emphasize that products from CCU technologies cannot be expected to be more environmentally friendly *and* cheaper than conventional products at the same time.

The present work follows up the recent publication [3] and compares multiple process concepts and scenarios for the utilization of blast furnace gas (BFG) and coke oven gas (COG). In total, the results of seven simulation cases are analyzed under real time-dependent boundary conditions. The main limiting factors for the binding of carbon are identified and discussed. The importance of the hydrogen that is available or that is produced on-site is confirmed and highlighted.

2 Simulation Concept

2.1 Simulation Model Development

To simulate a specified cross-industrial network, the required model components of the process concept are combined from the unit model library [3], parametrized with suitable values, and coupled in the framework of simulation software. Here, the simulation framework COMSOL[®] Multiphysics 5.5 is used as discussed in [3]. The workflow is explained here for a generalized Carbon2Chem[®] process concept consisting of gas cleaning units, gas conditioning units, alkali electrolysis, and reaction units (Fig. 2).

To simulate this concept, the following components are required from the model library:

- Gas supply from steel mill H1, time-dependent over a period of one production year
- Water electrolysis E1, hydrogen supply of the synthesis
- Power plant PP1, processing and combustion of excess gases
- Separators S1, S2, S3, cleaning of steel mill gases
- Compressors S1.P1, S2.P1, S3.P1, E1.P1, R1.P1, R1.P2, R8.P1, S5.P1, S6.P1, compression of steel mill gases, hydrogen, carbon dioxide, and synthesis gas
- Splitters and mixers, regulation and mixing of gas flows
- Pressurized gas tanks and buffer tanks for synthesis gas and hydrogen
- Synthesis R1, methanol/ammonia/urea synthesis process with product gas recirculation and reprocessing

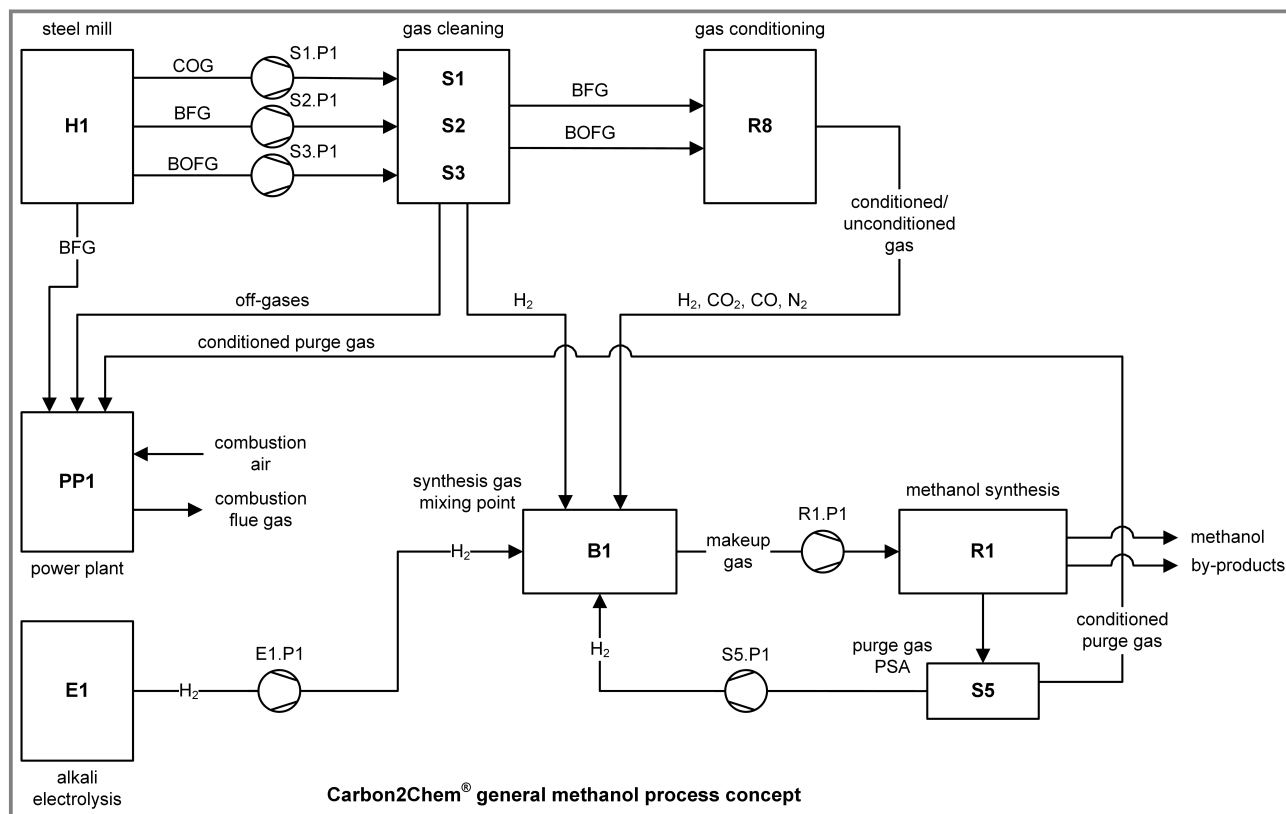


Figure 2. Carbon2Chem[®] process concept C1/C2, CCU concept based on cleaned BFG/BOFG and H₂ from COG, additional H₂ from water electrolysis.

The generalized concept includes the usage of basic oxygen furnace gas (BOFG), but this carbon source is not used in the process concepts presented later. The methanol synthesis process R1 as used in the Carbon2Chem[®] simulations is shown in more detail in Fig. 3. The interconnection of the components is defined in the process concept (Fig. 2) and has to be realized in the COMSOL[®] simulation software. Simulations can be run stationary with the yearly averages of mill gases or time-dependent with the transient steel mill gas flows from component H1 (representing the gas availability for chemicals at a specific production site). In

dynamic mode, the simulation is the system answer to the time-dependent gas flow conditions at the gas transit station under consideration of initial and boundary conditions and the definition of the component models. The starting point of the time-dependent simulation is the converged solution of the stationary simulation with the steel mill gas rates for $t = t_0$. For the simulations presented here, time derivatives arise in the buffer tank models only, but it is possible and tested to connect COMSOL[®] reactor simulation models containing real time derivatives (the buffering terms of the heat and mass balances).

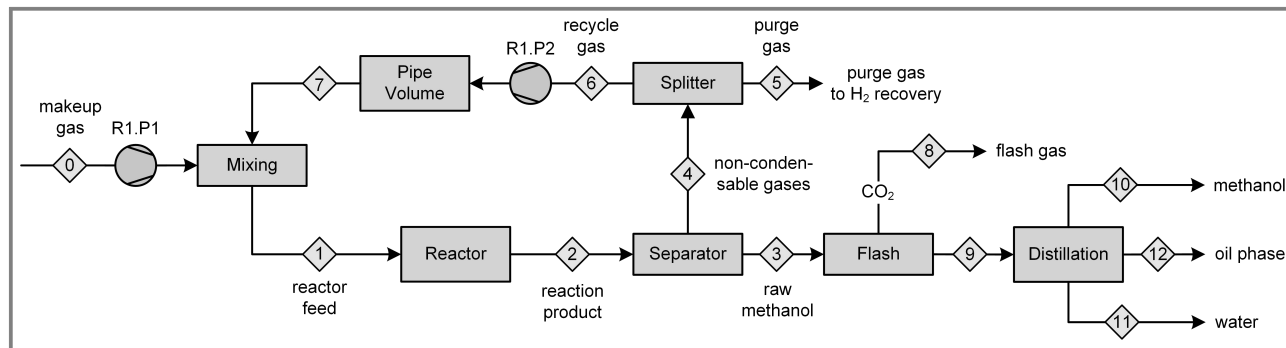


Figure 3. Methanol process block flow diagram used for Carbon2Chem[®] process concepts (unit R1).

2.2 Process Concepts

The concepts investigated by dynamic simulation mainly differ in synthesized product, used type and quantity of steel mill gases, and used technical components, e.g., gas conditioning units and gas buffers. A simulation case is defined from these elements and provides an answer to the mass and energy flows in the process diagram, which can then be used to draw conclusions on economic and ecologic efficiency (see Thonemann et al. [12–14]). Here, four process concepts C1 to C4 for the production of methanol and urea are developed for simulation.

The standard methanol process concept C1 shown in Fig. 2 is based on the usage of BFG in methanol synthesis without further gas conditioning (skip unit R8). Here, the synthesis gas includes higher contents of N_2 . H_2 -rich COG is used to provide hydrogen by a pressure swing adsorption (PSA); additionally, required hydrogen is produced by water electrolysis. H_2 from COG depends on the time-dependent COG flow and the separation process at S1. H_2 from electrolysis is controlled to ensure a hydrogen content in the methanol synthesis gas which is slightly above the stoichiometric level (see [3] and Eq. (7)). In the methanol process (Fig. 3), hydrogen from purge gas is separated in a PSA process and recycled to the synthesis gas inlet; the remaining H_2 -poor purge gas is routed to the on-site power plant, occasionally after enrichment by natural gas.

The disadvantage of this concept is the high nitrogen content in the methanol makeup gas originating from the BFG ($\approx 50\% N_2$). In the second process concept C2, this problem is treated with a water-gas shift process (R8) in the BFG/BOFG line (see unit R8 in Fig. 2 and the R8 process block diagram in Fig. 4). CO is shifted to CO_2 and separated together with a part of H_2 (the methanator and dryer units are not active here). CO_2 and H_2 are routed to the makeup gas mixing point and the methanol synthesis is run with a CO_2 -rich gas composition. The inert gas fraction is small

in this case, thus, the carbon efficiency of the synthesis will be in the range of industrial standards ($> 90\%$). The purge gas contains CO_2 and is recycled to the downstream processing of the water-gas shift reaction to recover CO_2 and H_2 .

A third methanol process concept C3 captures the CO_2 from the power plant exhaust gas and makes it available to a methanol synthesis running with a pure CO_2/H_2 makeup gas mixture (see Fig. S1 in the Supporting Information). This concept is simulated as a classical benchmark in comparison to the other CCU routes. Hydrogen is supplied by COG gas (PSA treatment) and by water electrolysis; the amount of produced hydrogen is controlled by the designated ratio H_2/CO_2 in the makeup gas (slightly above 3.0). As shown in Fig. S1, recovered H_2 from purge gas is recycled to the synthesis, and the remaining purge gas is routed to the power plant. In this concept, the only remaining carbon exit is the CO_2 scrubbing unit and, therefore, high CO_2 reductions are possible depending on the efficiency of this unit ($> 90\%$ is assumed in our simulations).

All methanol production simulations were set up using one of these three concepts. For the production of ammonia and urea from steel mill gases, the concept has to be changed only in a few points (Fig. 5). Process concept C4 corresponds to the classical ammonia/urea route and uses a water-gas shift treatment of BFG (R8, Fig. 4) for the supply of a H_2/N_2 synthesis gas for ammonia synthesis (R3) and the separated CO_2 gas from R8 for urea synthesis from NH_3 and CO_2 (Fig. 5). The hydrogen supply follows the methanol concepts (H_2 from COG and from alkali electrolysis); the H_2/N_2 ratio is controlled in the range of 2.9 to 3.0. From purge gas, H_2 and NH_3 is recovered; the remaining H_2 -poor purge gas is combusted in the power plant. From the molar ratio of $([CO] + [CO_2])/[N_2]$ in BFG it can be expected that all ammonia produced from N_2 can be synthesized to urea, leaving only a minimal CO_2 excess.

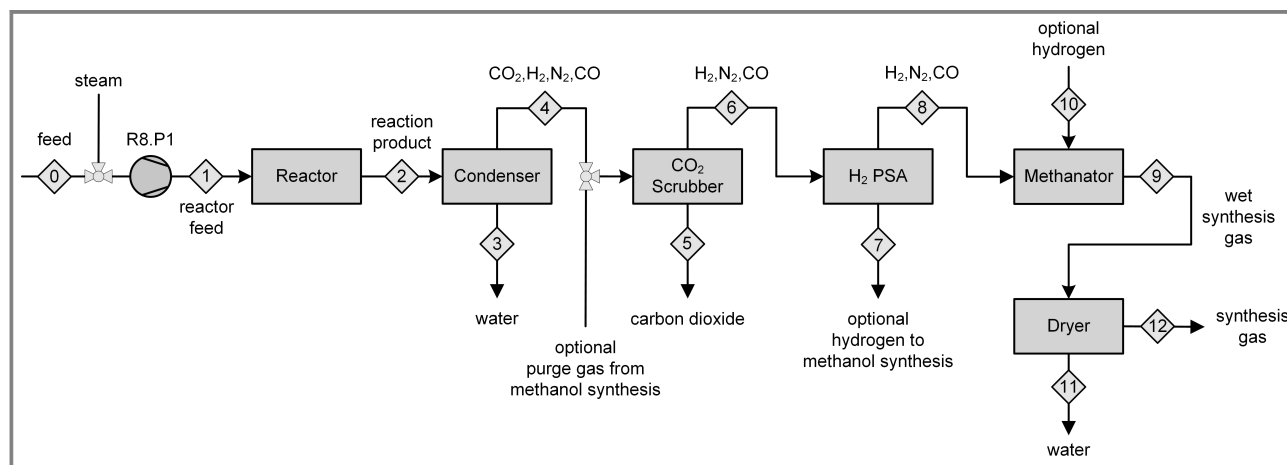


Figure 4. Water-gas shift process (unit R8), generic block flow diagram designed for Carbon2Chem[®] methanol and ammonia process concepts.

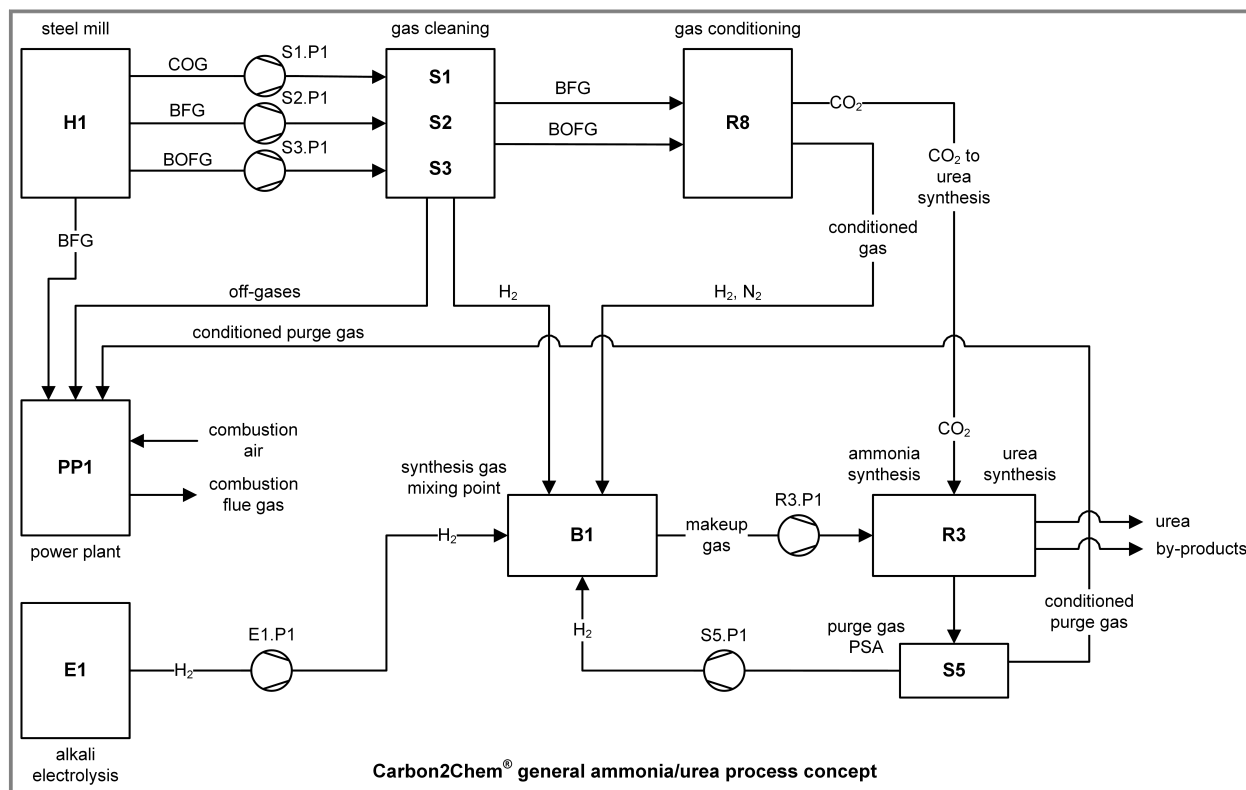


Figure 5. Carbon2Chem® process concept C4 for ammonia and urea, CCU concept based on cleaned BFG/BOFG and H₂ from COG, additional H₂ from water electrolysis.

3 Simulation Scenarios

3.1 Gas Availability Data

The simulation scenarios for the distributed cross-industrial network are based on the time-dependent gas availability data from the Duisburg site of thyssenkrupp AG. In the simulation cases presented here, BOFG is not part of the utilization concepts. Three main availability scenarios were investigated in the frame of the Carbon2Chem® project:

- Scenario 1: H₂ from COG, total COG usage, no additional H₂ source, BFG supply is controlled by chemical demand for the specified synthesis process, no BOFG usage
- Scenario 2: H₂ from COG, partial COG usage, available BFG, additional H₂ source, H₂ supply is controlled by chemical demand for the specified synthesis process, no BOFG usage
- Scenario 3: H₂ from COG, partial COG usage, available BFG present today at the exhaust line of the power plant (post-combustion), additional H₂ source, H₂ supply is controlled by chemical demand for the specified synthesis process, no BOFG usage

Total COG means the COG produced at the coke oven; partial COG is the coke oven gas not used in the steel mill. Scenarios 2 and 3 are using the off-gases of the steel mill

process for chemical production. In scenario 1, a significant amount of COG prior used in the steel mill is diverted for CCU and has to be substituted. In scenario 3, the power plant operation with BFG remains in the present state; only the exhaust gases are used in a CCU operation. The used composition of COG and BFG is given in Tab. 1; the composition remains constant in time-dependent simulations (only the flow rates vary).

Table 1. Molar composition [mol mol⁻¹] of COG and BFG.

Component	Coke oven gas	Blast furnace gas
Hydrogen	0.63	0.04
Carbon monoxide	0.07	0.25
Carbon dioxide	0.02	0.23
Methane	0.22	0.00
Nitrogen	0.06	0.48

3.2 Simulation Cases

In the Carbon2Chem® simulation plan, gas availability data and process concepts are combined to specific simulation scenarios. The present work considers different BFG usage

flow rates (JUMBO, INDUSTRIAL), different BFG gas conditioning (cleaning only, water-gas shift (WGS)), classical CCU from power plant exhaust gas (POSTC) and hydrogen supply from total available COG only (COG MAX). The CO-rich BOFG is not considered in any case, as this gas is a relevant part of the steel mill processing and should be taken into account in later Carbon2Chem[®] phases. The chemical product in cases 1–6 is methanol, in case 7 urea (synthesized from ammonia and CO₂).

For the presentation of relevant simulation results the following seven simulation cases (addressed as case 1 to case 7) are prepared:

- 1) Methanol concept C1 JUMBO – gas availability scenario 2, use of total available BFG without conditioning, H₂ from COG and from electrolysis, block flow diagrams see Figs. 2 and 3.
- 2) Methanol concept C1 INDUSTRIAL – gas availability scenario 2 with BFG limitation to 330 000 m³h⁻¹ (STP, dry), use of BFG without conditioning, H₂ from COG and from electrolysis, block flow diagrams see Figs. 2 and 3.
- 3) Methanol concept C1 COG MAX – gas availability scenario 1, use of BFG without conditioning, H₂ from COG only, no external H₂ source, higher recycle gas ratio of 5.0 due to significantly lower flow rates, block flow diagrams see Figs. 2 and 3.
- 4) Methanol concept C2 JUMBO WGS – gas availability scenario 2, use of total available BFG and water-gas shift conditioning, H₂ from COG and from electrolysis, block flow diagrams see Figs. 2–4.
- 5) Methanol concept C2 INDUSTRIAL WGS – gas availability scenario 2 with BFG limitation to 330 000 m³h⁻¹ (STP, dry), use of BFG and water-gas shift conditioning,

H₂ from COG and from electrolysis, block flow diagrams see Figs. 2–4.

- 6) Methanol concept C3 JUMBO POSTC – gas availability scenario 3, use of total CO₂ from power plant exhaust gas (post-combustion), H₂ from COG and from electrolysis, block flow diagrams see Figs. 3 and S1.
- 7) Ammonia/urea concept C4 JUMBO – gas availability scenario 2, use of available BFG and water-gas shift conditioning, H₂ from COG and from electrolysis, use of separated CO₂ in urea synthesis, block flow diagram see Figs. 4 and 5.

The simulation cases were set up and parametrized in COMSOL[®] Multiphysics 5.5; important settings are given in Tab. 2. In a first steady-state run, the process flow sheet data are calculated with the yearly average values of the steel mill gas flow rates. Most relevant result flows like makeup gas, synthesis product, hydrogen production, or power plant operation are checked and validated against previous results and feasible data (computation time in the range of minutes). Next, a time-dependent simulation run over a whole production year is started on a Fujitsu simulation cluster running COMSOL[®] (computation time 1–2 days). In the simulation community of Carbon2Chem[®], the reference periods January 21–February 08 and July 07–14, 2016, were simulated in some cases to discuss and compare results from different simulation tools developed and used in the project – some results are shown in Sect. 4. The input variables of the time-dependent simulations are the transient flow rates of BFG and COG at the compressors S1.P1, S2.P1 (compositions see Tab. 1). Compressors, electrolysis and synthesis units are designed with certain limits oriented at the whole year processing.

The results from time-dependent simulations are post-processed in two ways:

Table 2. Important settings for simulation cases 1–7.

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
Product	Methanol	Methanol	Methanol	Methanol	Methanol	Methanol	Urea
COG availability, scenario	2	2	1	2	2	3	2
BFG availability, scenario	2	2	1	2	2	3	2
BOFG availability	–	–	–	–	–	–	–
Process concept	C1	C1	C1	C2	C2	C3	C4
Additional hydrogen	yes	yes	no	yes	yes	yes	yes
Recycle gas factor at design	4.0	4.0	5.0	4.0	4.0	4.0	4.0
Recycle gas flow rate	const.	const.	const.	const.	const.	const.	const.
S1 COG H ₂ recovery	0.70	0.70	0.70	0.70	0.70	0.70	0.70
S5 purge gas H ₂ recovery	0.70	0.70	0.70	0.70	0.70	0.70	0.90
S6 flue gas CO ₂ recovery	–	–	–	–	–	0.90	–
Water-gas shift H ₂ recovery	–	–	–	0.70	0.70	–	–
Stoichiometric coefficient S	2.05	2.05	2.05	2.05	2.05	2.05	3.00

- Processing of yearly average values and derived parameters to prepare the most relevant process efficiency parameters and data required for further economic and ecologic calculations. These values are different from the results of a steady-state simulation due to the modeled operation characteristics of process elements (see Sect. 4, discussion of time-dependent results).
- Processing of time-dependent courses of mass and energy flows (tables and diagrams) to prepare the discussion of process challenges resulting from strong fluctuations. These data were extracted from the total year simulations (10-min resolution) and also in deeper time resolution (2-min) from the reference week results. Both result types are presented and discussed in Sect. 4.

4 Results

4.1 Methanol Process Simulations

The methanol production route from CO/CO₂/H₂ mixtures is a combination of three chemical equilibrium reactions:

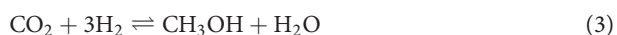
CO reaction:



Reverse water-gas shift:



CO₂ reaction:



The chemical equilibrium of the reaction mixture is given by the equilibrium definitions:

$$K_1(T) = \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{CO}}f_{\text{H}_2}^2} = \frac{\varphi_{\text{CH}_3\text{OH}} y_{\text{CH}_3\text{OH}}}{\varphi_{\text{CO}}\varphi_{\text{H}_2}^2 y_{\text{CO}}y_{\text{H}_2}^2} \frac{1}{P^2} \quad (4)$$

$$K_2(T) = \frac{f_{\text{CO}}f_{\text{H}_2\text{O}}}{f_{\text{CO}_2}f_{\text{H}_2}} = \frac{\varphi_{\text{CO}}\varphi_{\text{H}_2\text{O}} y_{\text{CO}}y_{\text{H}_2\text{O}}}{\varphi_{\text{CO}_2}\varphi_{\text{H}_2} y_{\text{CO}_2}y_{\text{H}_2}} \quad (5)$$

$$K_3(T) = K_1 K_2 \quad (6)$$

An equilibrium model was used in the methanol process simulation cases 1–6 solving Eqs. (4)/(5) together with the methanol process flow sheet shown in Fig. 3; equilibrium conditions are set to 83.5 bar and 250 °C. The makeup gas conditions are set as:

$$S = \frac{y_{\text{H}_2} - y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2}} = 2.05 \quad (7)$$

All other flow characteristics result from the flow sheet simulation for the specified process concept linked with the simulation case (see Sect. 3.2). The most important yearly time-averaged results are summarized in Tab. 3 (methanol runs in cases 1–6).

The carbon binding efficiencies used here are defined as:

$$\eta_{\text{CO}_2,\text{scen}} = \frac{M_{\text{CO}_2,\text{bound,scen}}}{M_{\text{CO}_2,\text{COG,scen}} + M_{\text{CO}_2,\text{BFG,scen}} + M_{\text{CO}_2,\text{BOFG,scen}} + M_{\text{CO}_2,\text{NG}}} \quad (8)$$

$$\eta_{\text{CO}_2,\text{total}} = \frac{M_{\text{CO}_2,\text{bound,scen}}}{M_{\text{CO}_2,\text{COG,total}} + M_{\text{CO}_2,\text{BFG,total}} + M_{\text{CO}_2,\text{BOFG,total}} + M_{\text{CO}_2,\text{NG}}} \quad (9)$$

Table 3. Methanol and ammonia/urea process simulation results, yearly average data of time-dependent runs.

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
Electrolysis hydrogen [Mm ³ a ⁻¹ STP]	8000	2530	0	10 090	3210	12 660	8620
Electrolysis oxygen [Mm ³ a ⁻¹ STP]	3990	1260	0	5030	1600	6320	4310
Electrolysis electric power [TWh a ⁻¹]	35.7	11.5	0	44.9	14.5	56.2	38.4
Compression power [TWh a ⁻¹]	4.01	1.33	0.36	4.55	1.50	5.67	4.68
PP1 electric power [TWh a ⁻¹]	3.16	3.74	4.93	1.98	3.35	4.51	0.997
Methanol production [Mt a ⁻¹]	4.42	1.48	0.310	5.51	1.83	5.80	–
Ammonia production [Mt a ⁻¹]	–	–	–	–	–	–	5.67
Urea production [Mt a ⁻¹]	–	–	–	–	–	–	10.0
Natural gas [Mm ³ a ⁻¹ STP]	281	94.2	432	0	0	0	0
Carbon bound [Mt a ⁻¹]	6.07	2.04	0.43	7.56	2.52	7.97	7.33
Carbon bound/scenario C [%]	66.4	23.1	4.3	87.4	29.1	92.1	84.7
Carbon bound/total C [%]	36.0	12.3	2.5	46.1	15.4	48.6	44.7

Here, M_{CO_2} is the CO_2 equivalent mass of carbon in the specified gas in relationship to the equivalent mass bound in the products (methanol, urea). The simulation key results for the methanol process concept cases 1–6 are summarized as follows:

- CO_2 elimination rates above 60 % of scenario-based CO_2 (5 Mt a^{-1}) can be realized with the JUMBO scenarios only (cases 1, 3, 6); the mid-term focus on INDUSTRIAL concepts (cases 2, 5) can realize elimination rates in the range of 20–30 % (about 2 Mt a^{-1}).
- Total CO_2 emissions of the Duisburg site of thyssenkrupp AG can be reduced to a maximum of 50 %, because only a certain proportion of the steel production gases is available for chemical production in the scenarios considered.
- Process concepts without additional H_2 supply (case 3) cannot realize noteworthy CO_2 reductions in the steel mill; such plants produce in the range of $300\,000 \text{ t a}^{-1}$ methanol with hydrogen from total COG; a substitution of used COG in the steel mill is necessary in this case.
- The process concept C1 with N_2 -rich synthesis gas achieves a CO_2 reduction of 67 % – the large nitrogen charge limits the methanol carbon efficiency in the synthesis to about 70–75 %. The overall CO_2 reductions are in the range of 6 Mt a^{-1} . The process concept C2 with low- N_2 /high- CO_2 synthesis gas achieves higher CO_2 reductions of up to 88 % (7.6 Mt a^{-1} in total). This technical advantage (reduction of N_2 load in the synthesis gas) needs to be evaluated against additional capital expenditure (CAPEX) and operational expenditure (OPEX) for this concept.
- The alternative scenario JUMBO POSTC (concept C3, case 6) achieves the highest CO_2 reduction of 92 % (8 Mt a^{-1} in total). As a result of the design, reduction depends strongly on the CO_2 separation efficiency of the scrubber unit after the power plant exhaust outlet (95 % of efficiency savings are made here). Hydrogen demand is considerably higher than in other concepts, because burned BFG reaches the synthesis gas mixing point as pure CO_2 (all internal hydrogen is oxidized to water). The overall power demand is therefore in the range of 60 TWh a^{-1} . Produced methanol tonnage is comparable to simulation case 4 with nearly pure CO_2 as carbon source in the synthesis.
- Addition of natural gas (NG) is necessary in concepts C1 and C2 to raise the purge gas energy content to BFG specific heat of combustion (3.6 MJ m^{-3}). Moreover, in concept C3 additional NG is calculated to close the COG gap of the steel mill (see Sect. 3.1).

- The methanol production has to be realized in the JUMBO concepts with very large multi-line synthesis units; the yearly production is in the range of 5 Mt. The INDUSTRIAL concepts correspond to present-day world-scale plants with a yearly production of 1.5 Mt and can be realized in a medium-term strategy. The reprocessing, storage, and shipment of such large product quantities has to be analyzed and planned carefully.
- Power consumption for H_2 production and process compressors is in the range of 50 TWh a^{-1} for JUMBO scenarios (except in case 6; see above) and at one third of this value for INDUSTRIAL scenarios. The process concept C2 (cases 4, 5) shows a 25 % higher power demand than the standard concept C1 (cases 1, 2). This fact can be explained by the higher synthesis yield and the incomplete recovery of hydrogen after the water-gas shift process in concept C2. The provision of such high power demand at the site (or the availability of equivalent external hydrogen) is a technical challenge and has to be tackled by a multi-strategy approach combining electrolysis technology and additional external hydrogen sources.

In Fig. 6, the main time-averaged data for power consumption, product mass, and relative carbon reduction (scenario and total) are shown. The dominance of the JUMBO scenarios (cases 1, 4, 6) is evident as well as the insignificant scale of the COG MAX scenario (case 3) running without additional hydrogen.

Time-dependent results for the methanol simulation campaign are shown in Figs. 7–9. The pumping rate of the BFG compressor (Fig. 7, one-year period) is limited to a maximum output rate. The BFG flow maxima are therefore truncated at this value and excess gas is led to the power plant. Truncation is important, as subsequent units receive

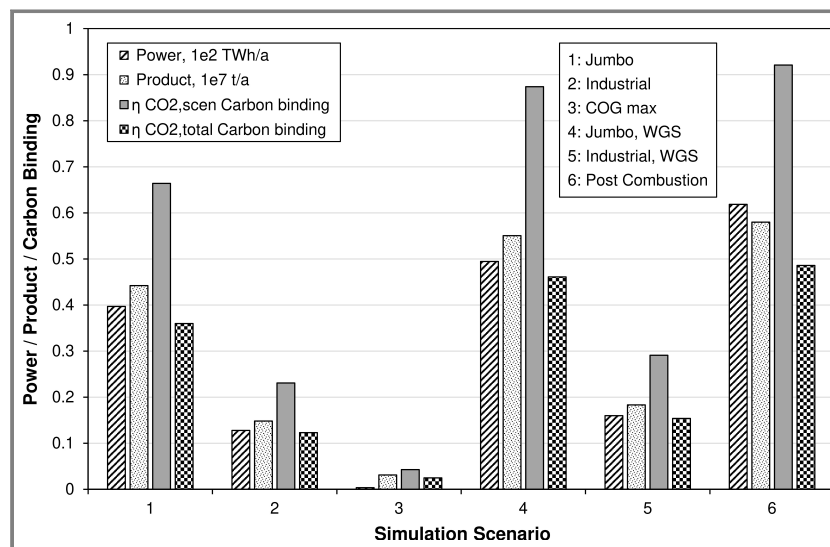


Figure 6. Methanol simulation cases 1–6: selected time-averaged results, derived from time-dependent simulation of production year 2015/2016, note the vertical axis definitions given in left legend.

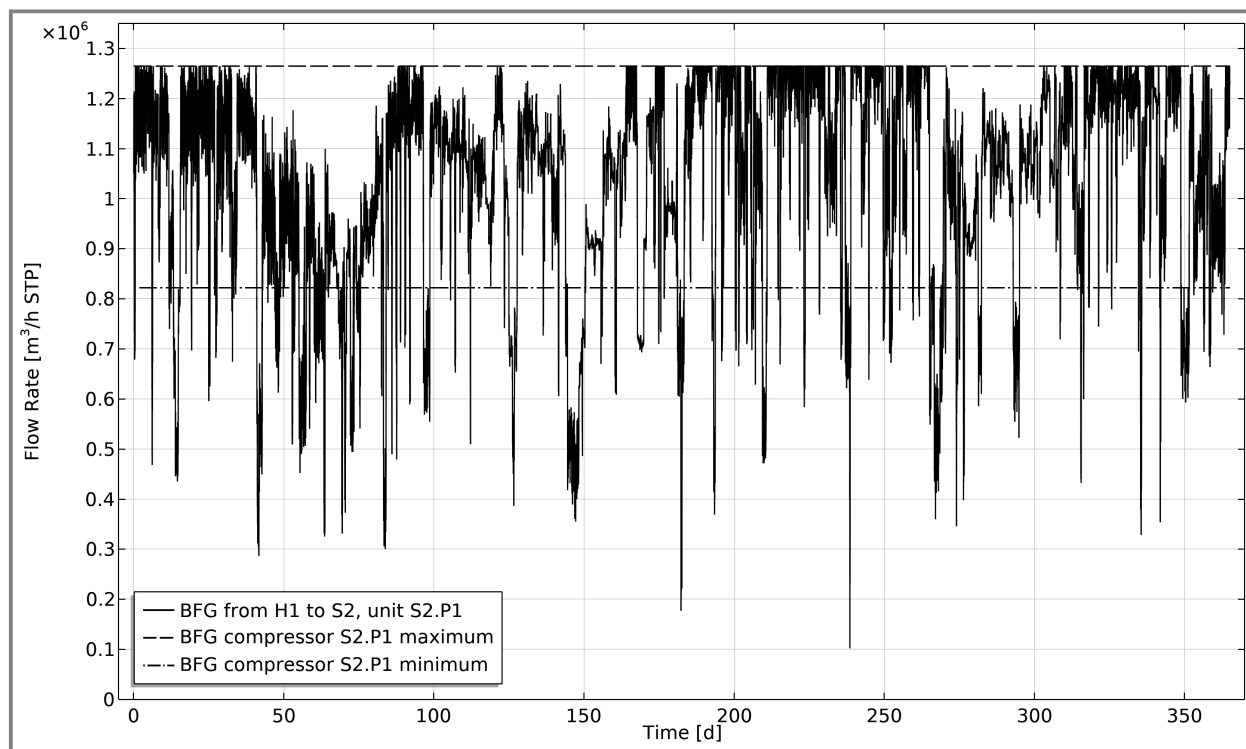


Figure 7. Methanol simulation case 1: pumping rate of BFG compressor S2.P1, time-dependent simulation of production year 2015/2016, note the truncation at $1.27 \cdot 10^6 \text{ m}^3 \text{ h}^{-1}$ (STP).

only limited rates. Below a minimum pumping rate, gas is recycled inside the compressor (recycle mode), thus, lower capacities are realized at constant compression power without a shutdown of compressor and synthesis train at the minimum rate (shutdown scenarios are not considered here).

The methanol raw product flow rate (methanol-water mixture from synthesis gas-liquid separator, see Fig. 3) for the production week July 07–14, 2016, is given in Fig. 8 in high time resolution. The product flow rate follows the time fluctuations in the BFG feed gas at mixing point B1, because no active buffers are integrated in the process concept – note the 40 % decrease during day 281. On the right axis of Fig. 8, the carbon efficiency of the methanol process is shown; a constant gas recycle flow is responsible for slightly higher carbon efficiencies at lower makeup gas flow rates. The power demand at the water electrolysis plant (Fig. S2) shows a strong decrease from 4.2 to 2.6 GW (–40 %) in 1 h and vice versa 24 h later. It can be seen that electrolysis power is running synchronously with the BFG flow rate, too.

The transient conditions expected at the methanol reactor inlet are important for the design of experimental work in Carbon2Chem[®] related to methanol catalyst testing. In Fig. 9, the flow rate and the molar fraction of the flow at the reactor inlet is given, as calculated by the reference week simulation of case 1. Firstly, the flow rate fluctuations at the inlet are relatively low, because the process is operated with a constant recycle flow rate (four times the process design

makeup gas flow rate). Secondly, inert fractions increase and reactant fractions decrease with lower inlet flow rates; this effect is also explained by the constant recycle flow rate (higher recycle ratio for lower makeup gas flow, consecutively increasing chemical conversion rate). Data as specified in Fig. 9 are used from the experimental teams to design their experimental conditions for catalyst testing campaigns.

4.2 Ammonia/Urea Process Simulations

The ammonia and urea syntheses are set up by the following reactions:

Ammonia reaction:



Basaroff reactions:



The chemical equilibrium of the ammonia reaction (Eq. (10)) is given by the definition

$$K_1(T) = \frac{f_{\text{NH}_3}^2}{f_{\text{N}_2} f_{\text{H}_2}^3} = \frac{\varphi_{\text{NH}_3}^2}{\varphi_{\text{N}_2} \varphi_{\text{H}_2}^3} \frac{y_{\text{NH}_3}^2}{y_{\text{N}_2} y_{\text{H}_2}^3} \frac{1}{P^2} \quad (13)$$

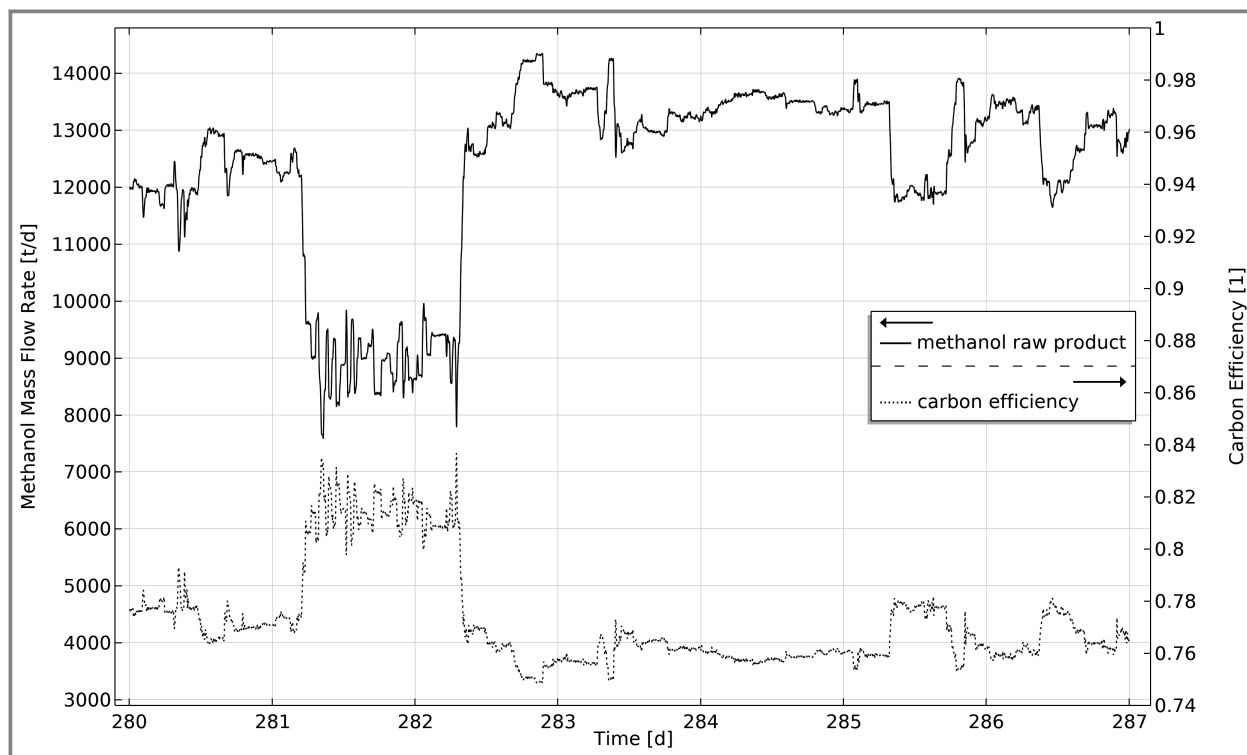


Figure 8. Methanol simulation case 1: methanol production rate before reprocessing (left), carbon efficiency of methanol process (right), time-dependent simulation of week July 07–14, 2016.

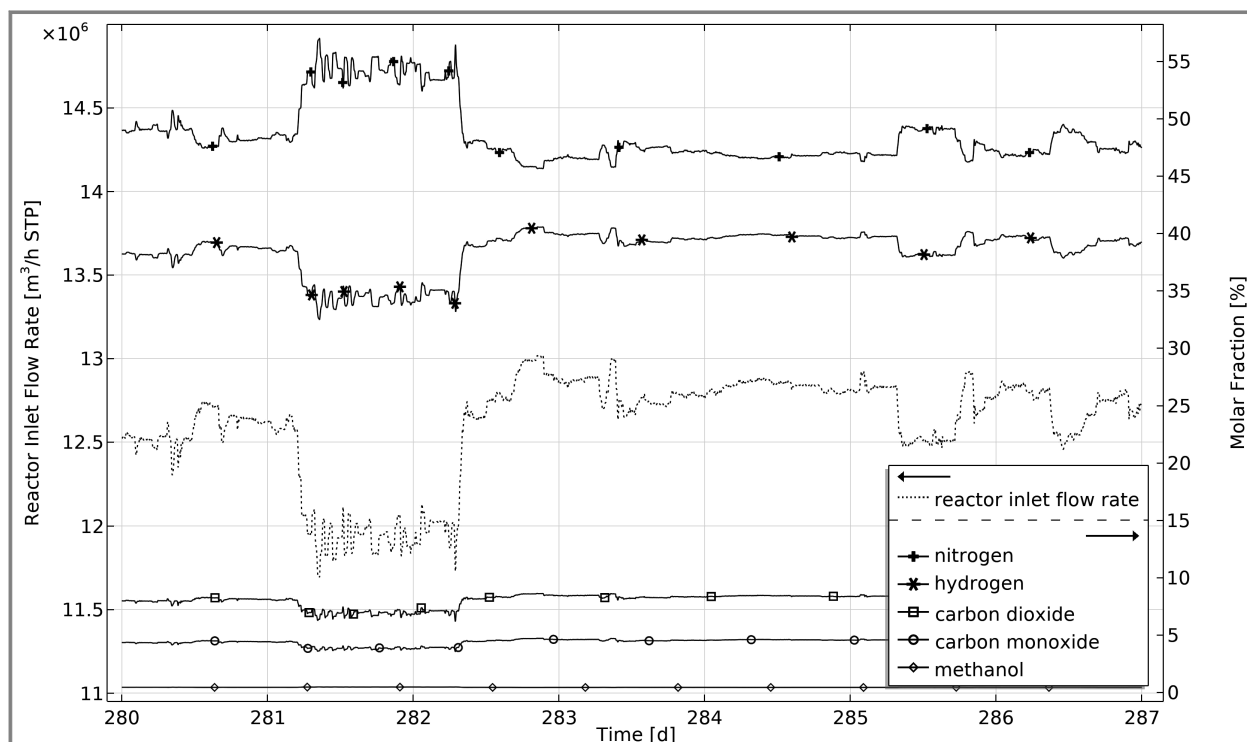


Figure 9. Methanol simulation case 1: reactor inlet molar flow rate (left) and molar fractions (right), time-dependent simulation of week July 07–14, 2016.

The process flow sheet of the ammonia synthesis is very similar to the block diagram for methanol given in Fig. 3. An equilibrium model based on this flow sheet was used for solving Eq. (13) at the reactor outlet with equilibrium conditions set to 200 bar and 485 °C. With makeup gas conditions set as

$$S = \frac{y_{\text{H}_2}}{y_{\text{N}_2}} = 3.0 \quad (14)$$

and a recycle ratio of 4.0, the results of equilibrium model calculations show that the overall process conversion of nitrogen to ammonia is in the range of 90 %. This value is used further in the simulation of case 7. The two Basaroff reactions (Eqs. (11) and (12)) to urea are set as a stoichiometric model. Other settings are shown in Tab. 2.

The most important yearly time-averaged results for the underlying production year 2015/2016 are summarized in Tab. 3 given above (see case 7). Hydrogen and power demand of this process are similar to case 4 (methanol from conditioned BFG); an electrolysis plant for 1.2 Mm³h⁻¹ (STP) is required. Under the consideration that all ammonia is synthesized to urea, CO₂ reduction reaches 85 % of the available carbon (7.3 Mt a⁻¹) and a production of 5.6 Mt a⁻¹ ammonia and 10 Mt a⁻¹ urea is achieved.

Time-dependent simulation results for the ammonia/urea process concept are given in Figs. 10, 11, and S3 for an 18-day period from January 21 to February 08, 2016. Fig. 10

shows the N₂/H₂ and CO₂ gas flow rates from water-gas shift process (see Fig. 4, flow sheet points 5 and 12); the H₂ molar fraction reaches 37 % in the synthesis gas and has to be considerably increased by external hydrogen. There are remarkable flow rate fluctuations up to ±60 % in this time period. The makeup gas for ammonia synthesis and the resulting ammonia production of the process are given as crucial process design information in Figs. S3 and 11. Both curves correspond to the gas flow rate variations in Fig. 10 (no active buffering set). The process has to be designed for a makeup gas flow rate of 2.3 Mm³h⁻¹ (STP) and produces up to 19 000 t d⁻¹ ammonia with fluctuations of ±60 % over several days.

5 Conclusion

The dynamic simulation of methanol and ammonia/urea production from steel mill gases shows the feasibility of this CO₂ reduction method. Main limiting factors are the availability of raw gases, the availability of external hydrogen for synthesis gas conditioning and certain thermodynamic synthesis conditions like pressure and inert gas content. We confirm and highlight the importance of the green hydrogen for the large-scale process concepts as mentioned in [2].

The total flow rate of H₂-rich coke oven gas is only 1/7 of the blast furnace gas available in scenario 2. Acceptable CO₂ reductions from BFG can therefore only be realized by the

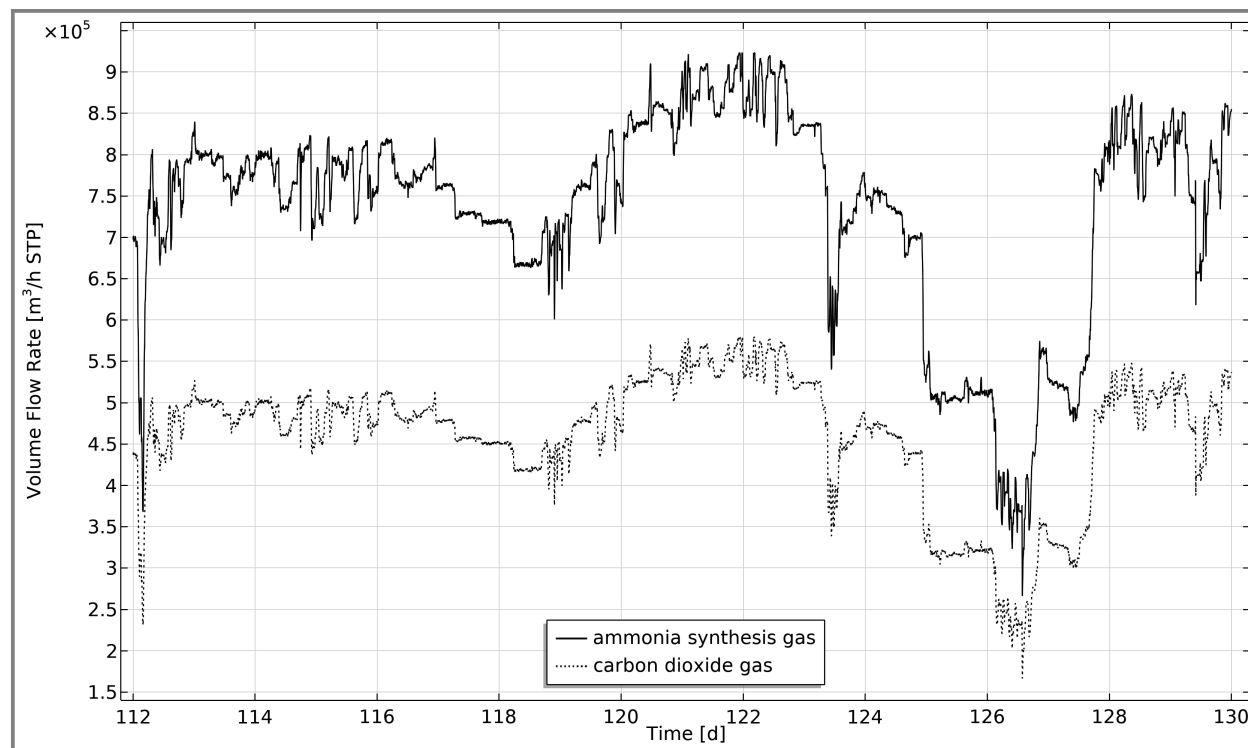


Figure 10. Ammonia/urea simulation case 7: water-gas shift process gases H₂/N₂ and CO₂, time-dependent simulation of 18-day period January 21–February 08, 2016.

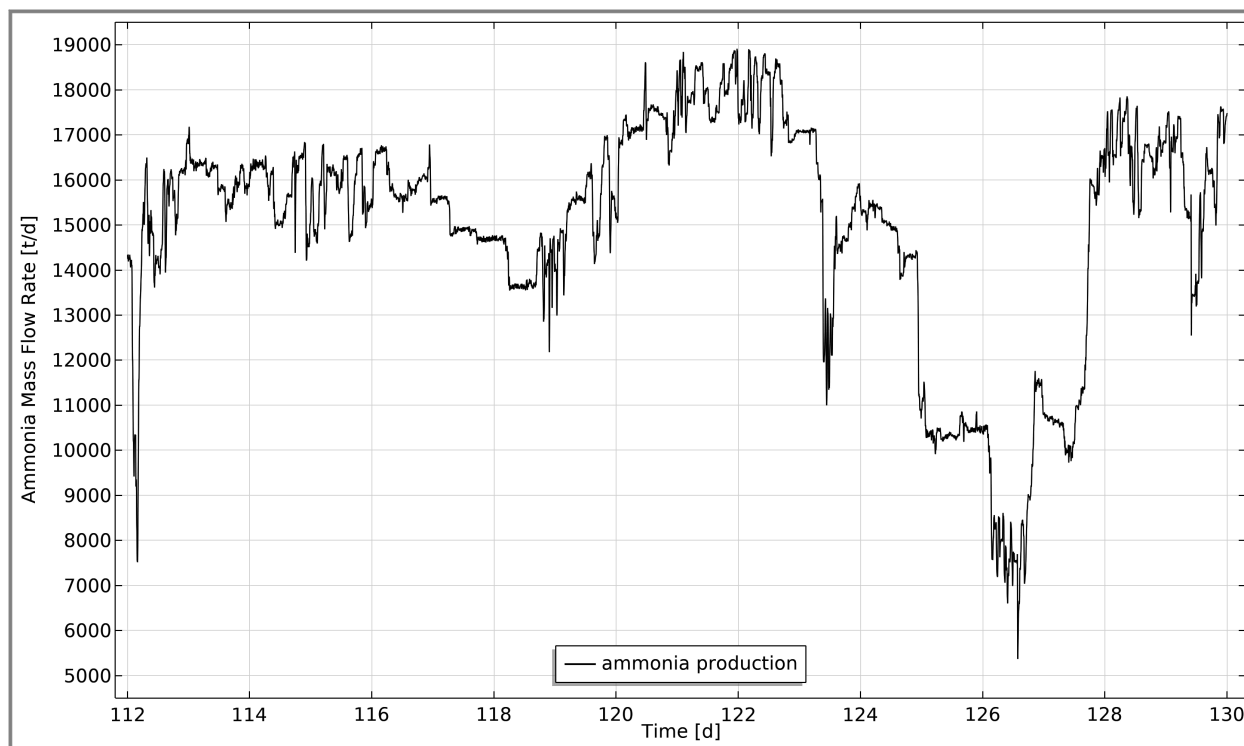


Figure 11. Ammonia/urea simulation case 7: ammonia mass production rate, time-dependent simulation of 18-day period January 21–February 08, 2016.

provision of additional hydrogen (see reduction result of 4.3 % in case 3). If external hydrogen is available, CO₂ reductions can be increased by up to 30 % for an industrial-scale plant (see case 5, 1.5 Mt a⁻¹ methanol) or by up to 90 % for a super-scale plant (see cases 5 and 7) consisting of several lines of industrial scale and utilizing total available BFG.

The process concept using power plant exhaust gases gives results comparable to concepts with total BFG utilization (CO₂ reduction above 90 %), but the overall CO₂ reduction result strongly depends on the gas scrubbing efficiency behind the power plant. Urea from ammonia (case 7) is a promising alternative CCU route for steel mill gases and achieves comparable CO₂ reduction results of up to 85 %. A characteristic feature of this process is the low flow rate of purge gas feeding the power plant, which will decrease its electric output to 20 % or lower of the present-day value (further considerations necessary).

Higher CO₂ reduction results above 50 % require high electric energy throughputs in the range of 35–55 TWh a⁻¹ if hydrogen is produced on-site by water electrolysis. In our simulations, electric power was considered to be fully available at all times, so these simulation results represent a best-case scenario. Electric power characteristics like carbon fraction or price can in principle be coupled with the chemical production (see van Beek and Sadlowski [15–17]), but it is clear that overall CO₂ reduction at the site will decrease with relevant CO₂ footprints applied to electric power used

for hydrogen production at the water electrolysis. Thus, the on-site reduction of CO₂ strongly depends on off-site CO₂ reduction in the power mix by pushing the amount of sustainable generation.

Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/cite.202000068>.

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Symbols used

f	[-]	fugacity
K_1	[bar ⁻²]	equilibrium constant, Eqs. (1) and (10)
K_2	[-]	equilibrium constant, Eq. (2)
K_3	[bar ⁻²]	equilibrium constant, Eq. (3)
M	[kg]	mass

P	[Pa]	pressure
S	[-]	stoichiometric coefficient
t	[s]	time
T	[K]	temperature
y	[-]	molar fraction

Greek letters

η	[-]	CO ₂ reduction efficiency
φ	[-]	fugacity coefficient

Subscripts

bound	carbon bound in chemicals
scen	gas availability scenario
total	total gas production at steel mill

Abbreviations

BFG	blast furnace gas
BOFG	basic oxygen furnace gas
CAPEX	capital expenditure
CCS	carbon capture and storage
CCU	carbon capture and utilization
COG	coke oven gas
E1	water electrolysis plant
H1	steel mill
NG	natural gas
OME	oxymethylene ether
OPEX	operational expenditure
PP	power plant
PSA	pressure swing adsorption
R	reaction process
S	gas separator unit
STP	standard temperature and pressure
WGS	water-gas shift process

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Simulation of Methanol and Urea Production from Catalytic Conversion of Steel Mill Gases

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Research Article: Time-dependent operation of methanol and urea plants embedded in a steelworks environment is analyzed with dynamic simulation models. Different process concepts and gas availability scenarios are considered to study the chemical production from blast furnace gas, coke oven gas, and external hydrogen.



Supporting Information
available online

