Abstract

Reduction of anthropogenic CO₂ emissions poses several technological and ecological challenges. New CO₂-based processes for the production of base chemicals offer the opportunity to reduce CO₂ emissions by carbon capture and usage (CCU). The capture of CO₂ in traffic is not suitable for commercial exploitation due to many small emission sources. By contrast, CO₂-containing gas that is produced in very large amounts at point-sources in steel and energy production offers the potential to be converted into chemical products. This means that the CO₂-containing steel mill gas can be used almost completely in downstream chemical processes. In order to increase the production volume of base chemicals, however, large quantities of hydrogen are required in addition to CO₂, which are not available to the desired extent in the steel mill gases. This hydrogen can be produced environmentally friendly by means of water electrolysis and renewable electricity.

In the joint project Carbon2Chem®, technologies for chemical energy conversion are developed, which at the same time require competencies in the fields of catalysis, process engineering, energy systems and system control. The goal is the development of technologies which will be implemented in an industrial scale. It is intended in the medium term to develop technologies for the success of the energy transition and to reduce CO₂ emissions in a way that sustainable production processes can be designed and realized in an industrial scale. This should be done by collaborative work in interdisciplinary sub-projects in order to generate higher-quality solutions than is possible in separated projects.

The climate protection goals can be achieved by a cross-industry approach and application of optimized technologies for gas purification, catalysis and CO₂ activation. In this way, carbon-containing process gases or waste gases from industry can be converted into usable products and thus close carbon or CO₂ cycles.

This paper gives an overview of the Carbon2Chem® project as an example of a cross-industry approach and realizing carbon capture and usage (CCU) by proven technologies. The concept and project setup as well as the role of the individual partners are explained. An inside is given in the Carbon2Chem® technical center including the thyssenkrupp water electrolysis and gas treatment pilot plant. In addition an example of using steel mill gases for the production of ammonia and urea is presented.
Introduction
The new aspect of Carbon2Chem®, a cross-industrial network of different industries is depicted schematically in figure 1.

![Figure 1: Cross-industry approach in the Carbon2Chem project to reduce CO2 emissions](image)

Today, most of the steel making plants and chemical plants are operated independently from each other. Normally the steel mill gases are used either thermally in power plants to generate electricity for internal use in the steel mill or to heat processes, such as the coking plant. If there is enough surplus renewable energy, e.g. from wind, part of the steel mill gases can be used as a carbon, nitrogen and hydrogen source for making chemicals. In chemistry, metallurgical gases substitute the role of synthesis gas produced from fossil sources. In addition to the reduced demand of fossil fuels in the production of steel and chemical products, this also has a positive effect on CO2 emissions. In this case, carbon is not only used once, but passed on from one value chain to another. On the other hand surplus energy can be used to make hydrogen by electrolysis. To find an optimum a digital control system has to be developed.
Concept and Setup of Carbon2Chem® Project

Together with 17 partners from research and industry thyssenkrupp is conducting this cross-industry approach in the Carbon2Chem® project. The overall project is divided into seven sub-projects (L0 - L6) focused on different areas of research, as illustrated in Fig. 2. The simulations for system integration and the dimensioning of the overall system are being carried out in sub-project L0. Sub-project L1 is dealing with the production of hydrogen via water electrolysis and the integration of volatile renewable energies. Sub-project L2 is investigating the sustainable synthesis of methanol. In particular, catalytic systems are being tested and synthesis processes optimized. The central element of the Carbon2Chem® project is the clean-up of the steel mill gases in sub-project L3 for subsequent chemical synthesis. Alongside the use of the processed steel mill gases for the synthesis of methanol, the production of higher alcohols is also being considered. For this, new catalyst systems are being developed in sub-project L4. Sub-project L5 is investigating the production of isocyanates and polymers. Sub-project L6 is looking into the production of the diesel substitute oxymethylene ether (OME).

Sub-projects are coordinated by thyssenkrupp (L0 and L1), Akzo Nobel (L2), Linde (L3), Evonik (L4), Covestro (L5) and BASF (L6). Siemens takes part in L0, Clariant in L2 and Volkswagen in L6. Academic partners are Fraunhofer Umsicht, Karlsruhe Institute of Technology, Max Planck Institute for Chemical Energy Conversion, Ruhr University of Bochum, RWTH Aachen, TU Kaiserslautern, and The Hydrogen and Fuel Cell Center Duisburg. The BMBF funded project started in June 2016 and has a duration of 4 years.

The groundbreaking ceremony for the Carbon2Chem® Technical Center in Duisburg took place on 2nd of November 2016 and the opening on 20th of September 2018.

The Carbon2Chem® project is being supported by the Federal Ministry for Education and Research with a total of 60 million Euro in the period 2016 to 2020. The total project volume including all partners from research and industry amounts to more than 120 million Euro.
Proven Technology in a New Landscape – The Carbon2Chem® Pilot Plant

The scheme in Fig. 3 explains the concept of our pilot plant. Steel mill gases are purified and mixed in the gas treatment unit. The gases are mixed with hydrogen from the water electrolysis and used for chemical production in catalytic test units located in the Carbon2Chem® laboratory building. Thinking in terms of cross-sectoral networks and renewable energy it becomes clear that the water electrolysis must be able to run under non-steady state conditions. To check this we run a 2 MW alkaline water electrolysis unit at the Duisburg Carbon2Chem® pilot plant site based on the well developed alkaline technology of thyssenkrupp Uhde Chlorine Engineers (tkUCE).

Fig. 3 Concept of Carbon2Chem® Pilot Plant in Duisburg

Water Electrolysis

The objective of the overall Carbon2Chem® project is to link the energy, steel and chemical industries into a cross-industrial production network. In this case the process of water electrolysis plays a key role, as hydrogen is required for almost all subsequent synthesis routes. The availability of this gas must be ensured notwithstanding the use of fluctuating, renewable energies and the varying hydrogen content in the top gases. These requirements inevitably lead to rethinking the previously known mode of operation of electrolyzers. A distinction must be made between the two competing electrolysis technologies (PEM and alkaline), as these behave differently on applying the same operating profiles. The effects of load profiles in a renewable energy grid on the efficiency and life time of electrolyzers have to be analysed and optimized. The quantities of hydrogen required in the planned industrial application amount between a few hundred thousand and one million Nm³ of H₂ per hour. Hence, a GW scale plant is conceivable at one location and justifies the necessary technical and economic scale-up process in order to make significant statements for later real operation at a steel mill. The realization of such large plants requires solutions for the integration of renewable energies and network stabilization of an entire region.

Operational and performance data of common electrolysis technologies will be analyzed and validated by an independent institute (Center for Fuel Cell Technology, ZBT). For this purpose, ZBT procured three representative electrolysis systems (PEM, alkaline and high-temperature solid oxide) in kW scale and put them into operation. The long-term operation of 1-2 years under load changes and resulting damage mechanisms will be investigated. Results of these investigations will be taken into account in the selection of appropriate electrolysis systems.
Following the kick off of the Carbon2Chem® project in June 2016, thyssenkrupp Uhde Chlorine Engineers (tkUCE) started the engineering and construction of a 2 MW alkaline electrolysis plant (see figure 4). The plant has been put on stream and shows stable operation.

![2MW alkaline water electrolysis at Carbon2Chem® pilot plant site Duisburg](image)

**Fig. 4  2MW alkaline water electrolysis at Carbon2Chem® pilot plant site Duisburg**

**Purification of Steel Mill Gases**

In steel mills, a continuous gas stream is produced in the blast furnace, converter and coking plant, which contains large quantities of hydrogen, nitrogen, carbon monoxide and carbon dioxide. These are typical components of synthesis gas. In the Carbon2Chem® cluster it will be investigated under which conditions these metallurgical gases can be treated, cleaned and used as synthesis gas for the chemical synthesis of base chemical. In addition to CO, CO₂, H₂ and N₂, steel mill gases contain other elements such as sulfur compounds, aromatic and non-aromatic hydrocarbons, halides, nitrogen compounds and various metals, which are undesirable and also potential poisons for catalysts in the chemical synthesis. The catalyst poisons must therefore be removed. Hence sorptive as well as catalytic gas purification and subsequent gas conditioning are the main research topics of this subproject. For this purpose thyssenkrupp Industrial Solutions AG started engineering of a gas treatment pilot plant in the initial phase of Carbon2Chem®. Sub-project partner Linde AG is responsible for coken oven gas purification by PSA which is integrated in the pilot plant. After construction and mechanical completion the plant has been commissioned at the Carbon2Chem® technical center in Duisburg (see figure 5). The pilot plant is supplied with a slip-stream of blast furnace, converter and coke oven gas from the thyssenkrupp steel mill. The challenges in the field of gas purification consist in the provision of a synthesis gas with appropriate composition, quality and quantity. In this context, economics, life time, and the interface to the power grid are also investigated.
Suitable methods for removing potential catalyst poisons and suitable catalysts, adsorbents and solvents are identified. The influence of fluctuations in steel mill gas supply on the composition and quality of synthesis gas is being examined, too. Therefore dynamic simulations have to performed. Pilot plant investigation will be accompanied by laboratory research of the academic project partners.

**Conversion of Steel Mill Gases to Base Chemicals**

At first a synthesis gas has to be produced which is pure enough and has the appropriate composition for the chemical processes, such as methanol, ammonia, Fischer-Tropsch, CO- conversion or methanation. These products can be used to make polymers, fuels, fertilizer or synthetic natural gas (SNG). Thus, main challenges in the project are the gas purification and synthesis strategies. In difference to natural gas, steel mill gases contain a lot of impurities. Synthesis strategies means that possible chemical products should be chosen in dependence of available off-gases and on optimum of mixing of available stell mill gases has to be determined.

In the context of chemical synthesis based on steel mill gases, it would be necessary on the one hand to remove a wide variety of trace components and at the same time to select a clever combination of the partial streams of blast furnace gas, converter gas and coke oven gas in order to achieve the above-mentioned synthesis gas ratios. The steel mill gases are cleaned using process steps specially developed for this purpose. When designing and
operating such a gas cleaning system, the respective purity requirements of the catalysts used for the different chemical syntheses and the resulting gas composition must be taken into account. To adjust the required synthesis gas ratios of CO₂/CO/H₂ to the desired values, technologies already available today, such as water gas shift (WGS) technology, can be used. In Fig. 6 different steps and options of converting steel mill gases to chemicals are shown. Chemical synthesis on basis of purified steel mill gases, will be performed in the Carbon2Chem® laboratory testing units, connected to the gas treatment pilot plant.

Due to the large quantities of steel mill gases to be utilized, the downstream chemical plants must operate with high availability. If the hydrogen from water electrolysis is not continuously available due to the use of fluctuating renewable energies, process engineering concepts must be used which ensure stable plant operation. A simulation of such an integrated network of steel, chemical and energy plants offers the possibility of optimizing operating models and achieving the highest possible capacity of the plants despite a fluctuating supply of renewable energies. The dimensioning of the equipment and machines is one of the most important challenges.

### Ammonia and Urea from Steel Mill Gases

As an example for the conversion of steel mill gases to base chemicals, ammonia and urea are chosen. Ammonia and urea are one of the core technologies of thyssenkrupp Industrial Solutions AG. This process is capable of fixing high amounts of CO₂ and using nitrogen from the blast furnace gas. Usually nitrogen cannot be used in most chemical processes because it is inert. However, in the case of ammonia production, nitrogen is converted and blast furnace gas is a valuable feedstock. In addition large quantities of CO₂ are consumed by making urea.
In figure 7 a block flow diagram for the production of 3,500 tons of Urea per day is shown. In this case, all three types of steel mill gases, blast furnace gas, converter gas and coke oven are used.

![Block flow diagram for the production of urea from steel mill gases][2]

**Conclusion and Outlook**

Efforts in the project Carbon2Chem® are directed towards reducing CO₂ emissions by applying CCU (carbon capture and usage) on basis of proven technologies. Main focus is on water electrolysis and gas purification. Due to the fact that steel mills deliver massive amounts of CO₂ and other valuable building blocks for chemical synthesis the Carbon2Chem® technical center has been placed adjacent to the thyssenkrupp Steel site in Duisburg. The actual proof of concept phase will continue until June 2020. Results obtained are used for planning the second project phase which will mainly be directed towards realization of plants in an industrial scale.

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**References**
