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STORE&GO

Innovative large-scale energy storage technologies and Power-to-Gas concepts after optimisation

D2.3

Demonstration plant Falkenhagen commissioned/ commissioning report

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Executive Summary

The methanation plant at Falkenhagen was commissioned according to the "**DIRECTIVE 2014/68/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 15 May 2014 on the harmonization of the laws of the Member States relating to the making available on the market of pressure equipment".** The commissioning works for the methanation plant were completed with the first injection of SNG into the ONTRAS transport gas grid in January 2019.

After delivery of all equipment, piping and cabling were installed in the methanation plant. In parallel, the connections between the hydrogen plant and the methanation plant were realized. Also, the infrastructure, needed for the measurement of gas quality and quantity before injecting SNG into the gas grid, has been assembled, and later tested and calibrated by authorities.

The overall project delay was mainly caused by issues during the procurement process of the catalyst-coated honeycombs and a consequently late delivery. After the catalyst was finally delivered, the required companies had to be re-mobilized into the project. This was quite complex due to general availability issues, which also resulted in a partial exchange of the involved key personnel. On top of that, the works on the interfaces were far more demanding than originally expected and required various iteration steps.

This document includes a process description and gives an overview of the manufacturing process and the applied commissioning procedures. These were implemented after mechanical completion was reached on site, according to the German "**Agreement Steam Boilers 0012010-10" (Guideline on the Risk Assessment of Putting into Operation).**

As outlined in the mentioned agreement the commissioning was carried out in the following steps:
– electrical, instrumentation and control equipment was put into operation
– functional testing of individual units,
– cold commissioning (without active firing/reaction system)
– hot commissioning (including active firing/reaction system, finalized in July 2018)
– trial runs by manufacturer (finalized in September 2018).

The activation of catalysts and the first methanation tests have been run according to the "**Agreement Steam Boilers 002 2010-10 "(Instructions for trial runs during the putting into operation as well as for trial runs during the operation of steam boiler plants)**.

In parallel, all tests have been reviewed and approved by TÜV Nord (Essen, NRW). The TÜV checked and approved the tightness of the associated pipe systems, the functional safety of the whole methanation plant and the applied measures for preventing water pollution.

After all successful tests the plant was commissioned under the number 101350-2-2431 with CE certificate from TÜV Nord in Essen.

1 Introduction

Methanation selection

Methanation is a chemical reaction converting carbon oxide and hydrogen into methane. A hydrogenation of a carbon oxide occurs. The product of this reaction is called SNG meaning either “Synthetic Natural Gas” or “Substitute Natural Gas”.

The mixture of carbon monoxide with hydrogen is a so-called synthesis gas. Synthesis gas is produced via gasification of solid or liquid carbon sources (e.g. coal, petrol coke, heavy liquid hydrocarbons or oil) in the presence of steam. Main drivers for SNG production from gasification are shown in Figure 1-1.

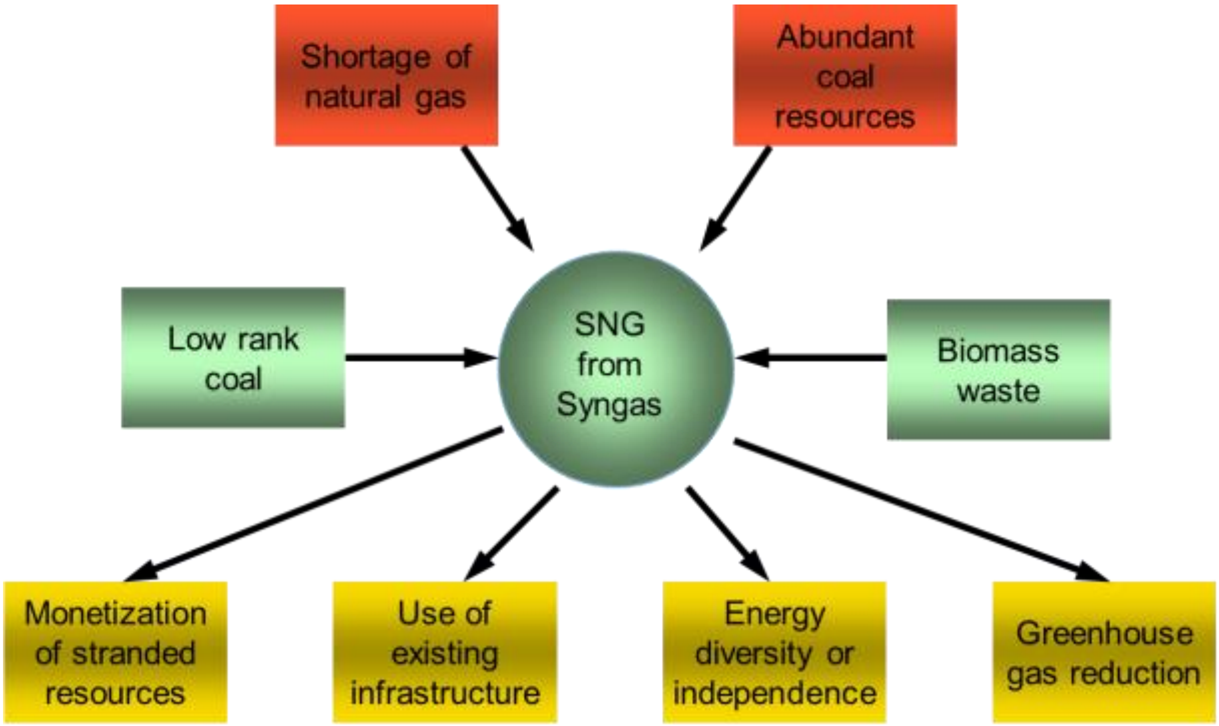


Figure 1-1: Main drivers for SNG production from Gasification.

In the year 1872 Brodie discovered the formation of methane gas out of a mixture of carbon dioxide, carbon monoxide and water in the presence of an electric discharge. 30 years later P. Sabatier and J. P. Senderens investigated the catalytic methanation process.
During this process the following chemical reactions occur:

1. Carbon monoxide conversion

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^0 = -206,2\,\frac{kJ}{mol}$$

2. Carbon dioxide conversion

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \qquad \Delta H^0 = -165,0\,\frac{kJ}{mol}$$

The first patents on the process were granted in England and Germany at the beginning of the 20th century to H. S. Ellworthy and H. W. Williamson.

First technical applications were realized in the Haber Bosch Process to produce ammonia. Within this process the relatively small fraction of carbon oxides is converted to methane. In the 1950's process technologies for the methane production were developed based on liquid and solid hydrocarbon containing fuels. This was done to reduce the dependency from natural gas and oil sources. [1] and [2] give a comprehensive overview of the relevant process technologies developed by companies Lurgi, Linde, Haldor Topsoe and others.

Process technology

The methanation of carbon oxides is based on a chemical equilibrium. Therefore, the maximum yield of a methanation reaction is defined by the three parameters pressure, temperature and gas composition.

On top of the reactions 1 and 2 there is a complex network of other equilibrium reactions running in parallel. Especially during higher temperatures these reactions would result in the generation of elementary carbon (soot) or carbon monoxide. While carbon monoxide is just an unwanted byproduct, the generation of soot on the catalyst surface might deactivate and irreversible damage the catalyst. Therefore, a proper temperature management is of utmost importance for the process design of the Sabatier reaction to ensure that the process temperatures remain on a sufficiently low level.

While the reaction kinetics of the carbon monoxide conversion are well known since decades, the kinetics of the carbon dioxide reaction was published in 2016 by Koschany [3] based on the results of the SEE project. For both reactions it was shown that the reaction velocity is increasing with increasing temperature and pressure. Both reactions are strongly exothermic, which is another reason for the importance of a proper temperature management to control the process. Temperature control measures could include a tailor-made reactor design, the selection of a proper cooling fluid for the chosen temperature range (e.g. thermal oil or steam) or the dilution of the feed gases to decrease the level of heat generation per volume. To improve the general process efficiency heat recovery / recuperation measures are to be established.

On top of the temperature control also the control of the pressure level in the process is important. Higher pressure levels are improving the methane yield of the Sabatier reaction. On the other hand, a higher process pressure also has a major impact on the design of the process equipment (e.g. piping, compressors, heat exchangers etc.) and will drive costs. To produce a high-grade gas (H gas) a gauss pressure level between 10 and 20 bar seems to be an ideal compromise considering both effects.

Current investigations

Since the 2000s, power-to-gas research gained traction due to its potential key role in the energy transition, first primarily the hydrogen pathway. Because the injection of hydrogen into the natural gas infrastructure is limited due to several technical restrictions [5], the original power-to-gas concept leaves room for improvements.

One option is to use the renewable hydrogen as a feedstock for a methanation process, where hydrogen and carbon oxides are converted to methane or „synthetic natural gas"(SNG).

A potential source for carbon monoxide might be biomass. Nevertheless, the carbon monoxide production process based on biomass is complex (thermal conversion to syngas) and includes various steps to clean up the produced gas. To protect the catalyst from poisoning potential sulfur and phosphor components must be removed from the feed gas by gas cleaning facilities.

Another technical option is the use of carbon dioxide as a feedstock for the methanation process. Carbon dioxide is a common byproduct of various industry processes and is often emitted into the atmosphere. To use waste gas carbon dioxide as a feedstock this gas also has to be properly cleaned (e.g. by removing potential catalyst poisons as described above). The technology for the separation of the Carbon dioxide is well understood and already used in various carbon capture and storage (CCS) or carbon capture and utilization (CCU) processes.

To demonstrate the methanation-based power-to-gas concept ZSW Stuttgart realized an alpha plant. The company Etogas (a ZSW spin-off) designed and installed this demo plant located in Werlte, Germany. This project was sponsored by Audi and has an electrical capacity of 6 MW. The required carbon dioxide is provided by a biogas plant and the produced SNG is injected into the local natural gas infrastructure.

The catalytic reactions required for the methanation process were further investigated and optimized in various other research and development projects. The iC4-project was focused on catalyst optimization, reaction kinetics and process simulation while the SEE project developed and investigated innovative reactor concepts (e.g. tray type reactors, 3-phase methanation and honeycomb reactors).

The results of these projects clearly show that the carbon dioxide based methanation can be used in industry applications. Current research activities are optimizing the process, investigating scalability and improving the heat recovery to improve the efficiency of the whole process.

2 Process Description

Methanation Plant - Overview

The new methanation plant at the Falkenhagen power-to-gas site is used to produce Synthetic Natural Gas (SNG) from carbon dioxide and hydrogen generated from regenerative electrical power sources by water electrolysis. This hydrogen is mixed with CO_2 and converted into methane by the Sabatier reaction in a novel reactor on suitable catalysts. The generated SNG is fed to the natural gas transport pipeline system of ONTRAS via the existing compression and feed-in infrastructure.

The hydrogen required for the methanation is provided by electrolysis plants already existing in Falkenhagen. In the plant described below, a maximum of 210 m^3/h (at normal temperature and pressure, "NTP") of hydrogen are used for the methanation. This quantity corresponds approximately to an absorbed electrical load of about 1 MW. The CO_2 (52.5 m^3/h at NTP), required for methanation of the hydrogen, was generated in a bioethanol plant in Zeitz (Germany) and is provided by the company "SOL Kohlensäure" in liquid form in a CO_2 tank at site.

The methanation reaction is carried out in two stages. The first reaction stage generates about 80% conversion rate. A second polishing reactor completes the methanation reaction to achieve the SNG product quality required for the injection into the natural gas grid.

Methanation Plant - Detailed Description

The hydrogen produced by the electrolysis is provided at an absolute pressure of about 9 bar. Since a higher operating pressure is advantageous for the methanation reaction, the hydrogen is compressed together with the CO_2 by the Feed Gas Compressor 36K001 to an absolute pressure up to 15 bar.

The CO_2 is provided in liquid form at a temperature of -20 °C and an absolute pressure of 21 bar in the CO_2 tank B 801 (28 t storage capacity). The liquid carbon dioxide is evaporated in the CO_2 evaporator W 802 by using a heat transfer medium (water glycol mixture coolant). Downstream of the evaporator the CO_2 has an absolute operating pressure of approx. 9 bar and a temperature of 40 °C and is mixed with the hydrogen in buffer vessel 36D001.

The compressed gas mixture is then preheated in the Feed Effluent HX I (36E001) with the product gas leaving the reactor and heated to the reaction temperature of 250 °C in the following Preheater I (36E002).

In the first reaction stage of the process the gas mixture enters the Honeycomb Methanation Reactor 36R002. Reactor 36R002 is a tube type reactor whose tubes contain honeycomb-like structures coated with catalyst. The gas flows through the tubes while the reaction heat is dissipated through the cooling medium (thermal oil) located on the shell side. The reaction heat is transferred to the cooling medium (thermal oil) via the walls. The outlet temperatures of the reactors are regulated by the throughput of the cooling medium, which allows nearly isothermal operation.

The methanation reaction (Sabatier reaction) takes place according to the following equation:

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O \qquad \Delta H_R = -165 \text{ kJ/mol}$$

The heated thermal oil is delivered by pump 36P001 to the heat exchanger W 902 in which the oil is cooled by hot water from the adjacent veneer plant heating system. This system is also used during the start-up and during idle or shutdown periods of the plant for heating of the reactors. The thermal oil circuit is operated at a pressure below the process pressure as well as below the operating pressure of the hot water circuit. Leakages of gas or hot water into the thermal oil system are detected by pressure and level monitoring.

The product gas leaving the first reactor stage is first cooled in the heat exchanger 36E001 against the feed gas. Subsequently, the gas stream in the Air Cooler I 36EA01 is cooled to about 60 °C and further through the following Gas Chiller I 36E004 to 10 °C, a large portion of the reaction water formed is condensed and separated from the product gas in the following Liquid Separator I 36D002. A water/glycol mixture is used as the cooling medium in the Gas Chiller I 36E004, which in turn is cooled in the CO_2 evaporator W802 by evaporation of the liquid CO_2. The separated process condensate is fed to the expansion vessel 36D009 on level control.

The gas stream exiting from the Liquid Separator I 36D002 is further heated in the Feed Effluent HX II 36E006 against the product gas of the reactor Polishing Reactor FB 36R003 and subsequently in the Preheater II 36E007. The methanation reaction is continued in the Polishing reactor 36R003. This reactor is furnished as a cooled tube reactor with a catalyst pellets filling in the tube bundle tubes and hot oil cooling medium at the shell side which allows an isothermal reaction regime. In this reactor the required conversion rate is achieved to supply the product gas to the natural gas network.

After exiting the Polishing Reactor FB 36R003 the gas stream is again cooled in the heat exchanger 36E006 against the feed gas. Subsequently, the gas flow is cooled further by the Air Cooler II 36EA02 and then the Gas Chiller II 36E008 against coolant. In the Liquid Separator II 36D005, the condensed process condensate is separated and, together with condensate, is discharged from the Liquid Separator I 36D002 into the Process Water Flash Vessel 36D009, where the condensate is expanded and subsequently conveyed with the Process Water Pump 36P003 for water electrolysis, where it is processed and reused. During the decompression process, a small gas flow is delivered to the flare, which mainly contains methane.

To feed the produced methane gas into the existing natural gas network, this needs to be treated further according to the DVGW rules (G 260) for drying. Dryers Vessels I and II (36D006 and 36D007) are used to adjust the residual moisture content required for feeding the natural gas network.

One of the two dryers is passed through with product gas and withdraws the moisture from the gas, while the second is heated for regeneration and is treated with dry product gas.

Subsequently, the SNG product gas is sent to the existing compression unit for final supply to the natural gas network.

Gas measurement and injection facilities

For the tie-in of the new methanation plant into the system of the existing power-to-gas plant, the gas metering and injection facilities had to be modified. On top of the existing hydrogen metering and injection, a second operating mode had to be established to allow the feed-in of synthetic natural gas into the ONTRAS gas grid. Therefore, a parallel metering infrastructure was installed, which allows fiscal metering and gas quality measurement of the produced SNG. Now the plant can be either used to produce and inject hydrogen (existing) or SNG (new). A simultaneous injection of green hydrogen and SNG is not foreseen yet.

For the gas quality measurement, the system was equipped with an additional process gas chromatograph able to analyse 14 gas components including methane, carbon dioxide, hydrogen, nitrogen, C2 – C4 and carbon monoxide. The dew point of the injected gas is monitored by an additional sensor provided by company BARTEC. The fiscal flow measurement is realized by a rotary flow meter of company Elster.

Due to the significantly reduced volume flow – the SNG plant can produce up to 57 Nm³/h (NTP) in contrast to up to 360 m³/h (NTP) of green hydrogen – also the pipeline compression system must be modified. The original hydrogen injection installation consists of two parallel compressors with 70% of the original capacity each. For SNG production only one of these compressors will be used, the other will be temporarily shutdown and blocked in under hydrogen atmosphere.

The original tie-in line for the hydrogen injection is equipped with an additional leakage detection system monitoring the gas amounts entering and leaving the pipeline. This system is calibrated for hydrogen and will be temporarily bypassed during SNG production.

Depending on the mode of operation, there are two different data matrixes, where the important measurement parameters are constantly monitored and an alarm or shutdown is triggered, when the value is not in the expected range for a defined period. For SNG production, the most important monitored parameters are pressure, water dew point, heating value, and content of methane, carbon dioxide, hydrogen and carbon monoxide.

Process Flow Diagram of Power to Gas Plant in Falkenhagen

The following Figure 2-1 shows a simplified process flow diagram. It includes all main equipment installed at the site of Falkenhagen. It also gives an overview of the scope of the partners TKIS (green) and Uniper (blue) the existing equipment parts are shown in black: electrolysis units, pipeline compressors, injection line and heating system of the veneer mill.

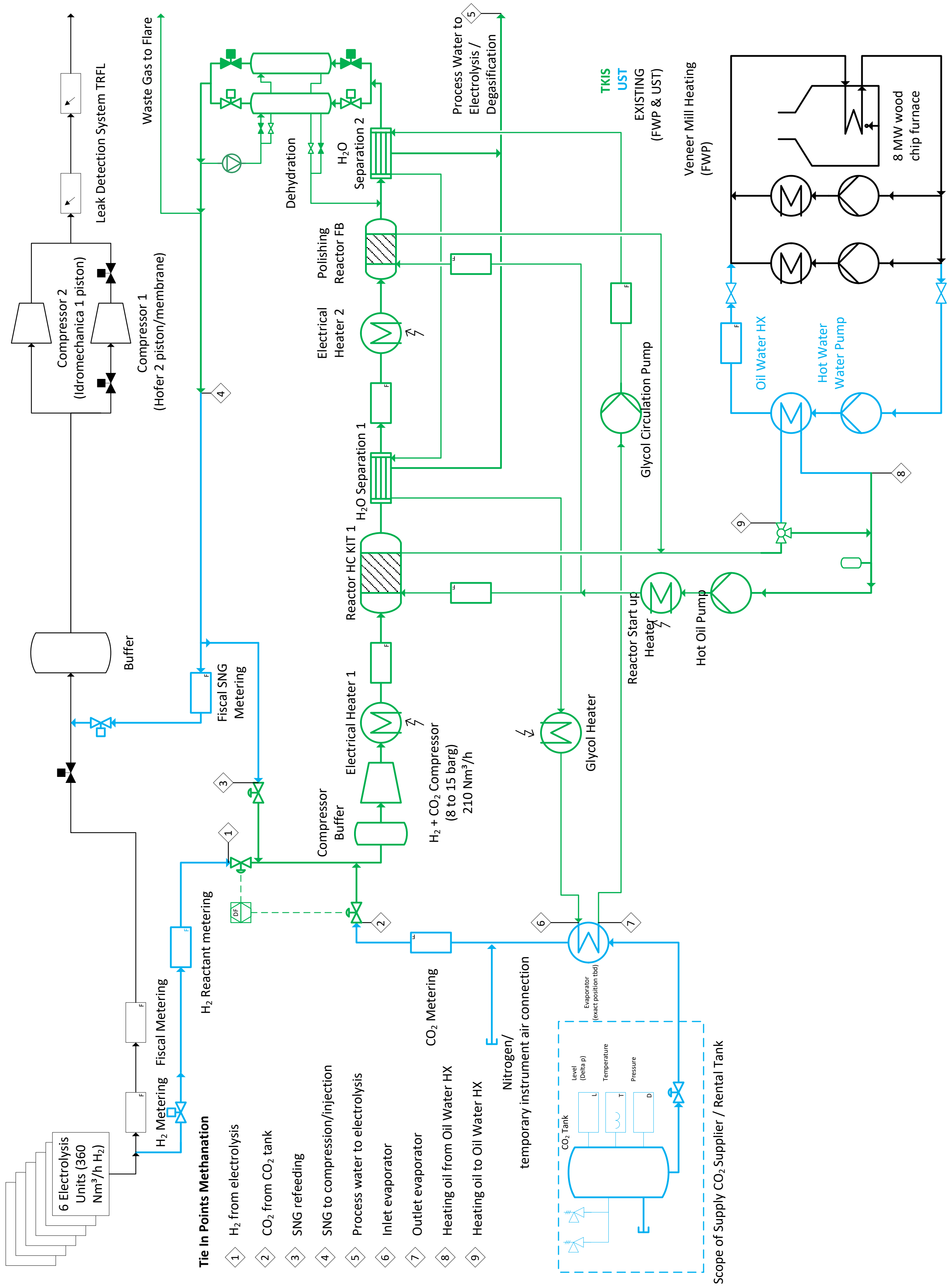


Figure 2-1: Process flow diagram of power-to-gas plant Falkenhagen

Control philosophy

The overall process control system of the power-to-gas plant Falkenhagen hast to integrate two independent, self-sustaining process control systems, which are developed based on different technology platforms. The general structure is shown in Figure 2-2.

The green box shows the process control system of the methanation plant itself, which was realized by company Silica Verfahrenstechnik GmbH. The system is realized based on a Siemens platform (SIMATIC STEP 7, WinCC for visualization) and controls the methanation plant via three remote I/Os. These are connecting all measurements and valve gears to the methanation control room. In addition, there are direct electrical connections to the aggregates (pump, compressor) and the installed heating devices (electrical heat exchanger and trace heating). The methanation control system is programmed to process a hydrogen flow between 80 and 210 m^3/h (NTP). During production the composition of the produced SNG is constantly monitored to decide if the gas is fed to the injection facilities or disposed in the associated flare.

In parallel, there is the process control system of the electrolysis and pipeline compressor system, which was realized by the company Hydrogenics It is based on the Siemens platform (SIMATIC STEP 7). The visualization of this system is realized via separate operating/HMI panels of the company Beijer Electronics. Here the internal control of the electrolysis units is realized. Furthermore, the requested hydrogen capacity is distributed between the available electrolysis units, and the pipeline compressor is switched on and switched off when required. For the integration of the new methanation unit, the compressor operation was decoupled from the actual hydrogen production. Furthermore, one of the pipeline compressors, the membrane compressor of company Hofer, was mothballed, since this compressor could not be used for SNG service without major modifications. One of the two compressors is more than sufficient to deliver the produced SNG flow of not more than 60 m^3/h (NTP) into the ONTRAS transport grid (design capacity of the compressor is ~ 210 m^3/h (NTP)).

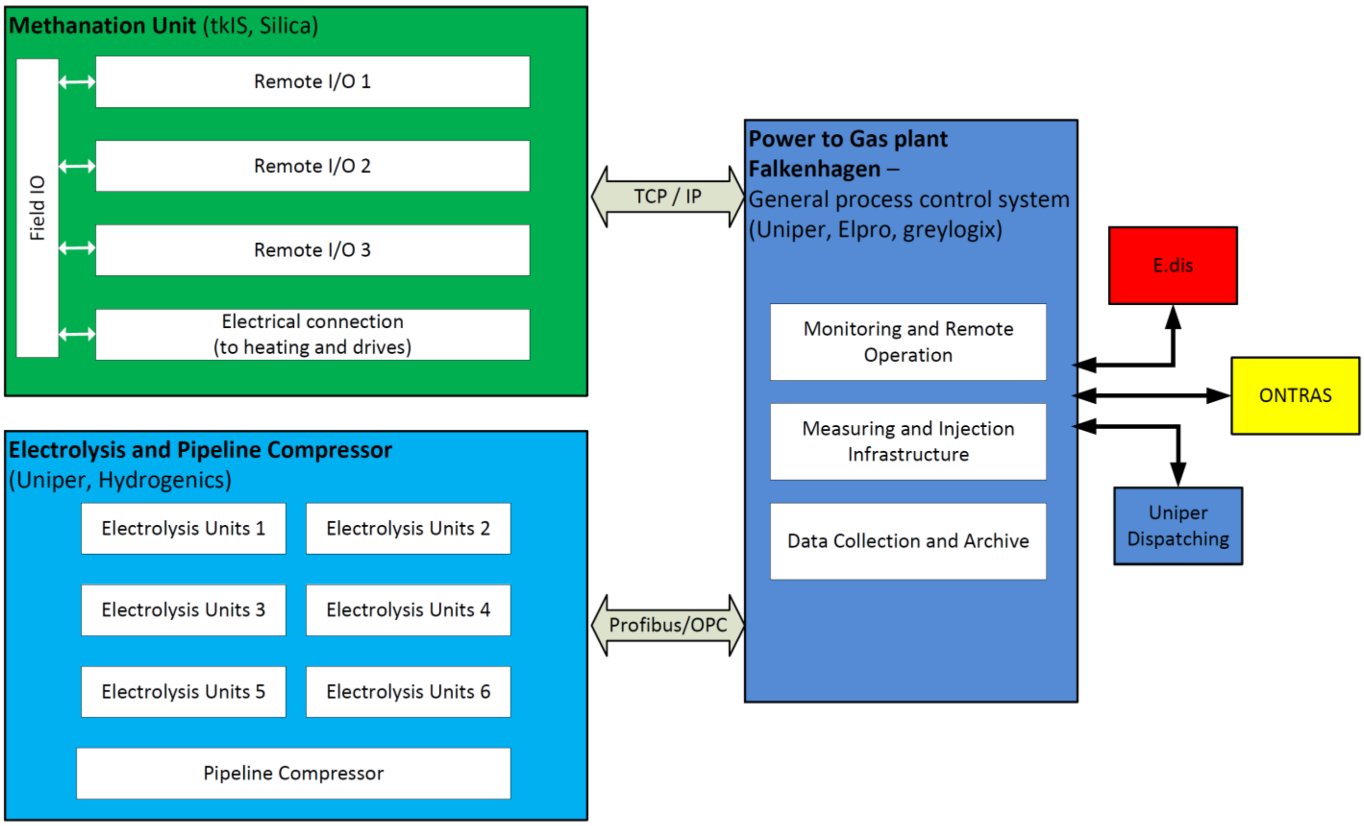


Figure 2-2: Process control system

In the new methanation mode, also some additional control parameters are required for the hydrogen production. During methanation, the original humidity and oxygen content measurements of Hydrogenics will see only SNG and could therefore not be used to monitor the actual hydrogen quality. For this purpose, Unipers hydrogen PGC infrastructure will be used and the provided data must be processed by the Hydrogenics control system.

The overall process control system of the power-to-gas plant is the major interface between these two units. This process control system is also using a Siemens platform similar to the process control system of the methanation plant (STEP 7 and WinCC). Due to the time span between erection of the hydrogen part of the power-to-gas plant and the erection of the methanation, an older version of the Siemens software was used, which has to be considered for the interfaces and is the reason for some compatibility issues. Here, the data is processed collected and provided to all major stakeholders. The overall process control system shall also allow remote operation of the power-to-gas plant from Uniper's dispatching infrastructure located in Düsseldorf. The major stakeholders here are the transport grid operator ONTRAS, the technical service provider e.dis and Uniper's dispatching department, which shall monitor the plant and ensure safe operation 24/7.

3 Contractors/Supplier

The following companies were involved in the commissioning process

<u>Methanation Plant</u>

1. Silica Verfahrenstechnik GmbH, Berlin

   Based on the general specification and design guidelines of the project partners TKIS, KIT and Uniper the company Silica carried out the detail engineering and manufacturing of the methanation plant, and was deeply involved in the successful commissioning of the methanation plant, and supported first operational tests.

2. SMB Rohrleitungsbau Wildau GmbH & Co. KG, Ludwigsfelde

   The company SMB was responsible for the main civil works and the piping installations not included in the scope of the company Silica. Like Silica, SMB provided the detail engineering for the required foundations, steel structures and pipelines and carried out the manufacturing works. They realized the hydrogen and SNG pipeline connecting the new and the existing plant and the heat transfer pipeline to the adjacent veneer mill. The company SMB was also closely involved in the execution of the pressure/tightness tests witnessed and monitored by the TÜV.

<u>Tie-in works, Metering and Injection Facilities</u>

3. Elster GmbH, Dortmund

   Elster is the selected supplier of the gas metering equipment (mainly 14 component process gas chromatograph and rotary volume measurement) required for the SNG injection facilities. They were responsible for the delivery and installation of the equipment. On top of that they were responsible for the tie-in of the new measuring devices into the process control system and supported commissioning and official calibration witnesses by the responsible authorities (Landesamt für Mess- und Eichwesen Berlin-Brandenburg, Fürstenwalde).

4. Hydrogenics

   Hydrogenics delivered the main components of the existing power-to-gas plant including the 6 electrolysis systems and the two pipeline compressors. For the STORE&GO project the support of Hydrogenics was required for the recommissioning of the electrolysis systems and for the modification of the original process control system. The SNG production mode must also be established within the Hydrogenics system. When SNG is produced the control of the pipeline compressors needs to be independent from the hydrogen production process. On top of that, the start-up conditions and the alarm/shutdown matrix are to be updated to reflect the new mode of operation.

5. TÜV Nord, Essen

   TÜV Nord was already involved in the permitting and approval process of the original hydrogen producing power-to-gas plant. Also, within the STORE&GO project, experts of the TÜV Nord were involved for reviewing functional plant safety and the proper treatment of potential water pollutants. Also they witnessed and reviewed the pressure and tightness testing for plant piping and the installed pressure vessels.

6. Elpro

Company Elpro is the selected service provider for the required electrical installations and for the programming works aiming to modify the existing process control system for the tie-in of the methanation. Due to the fact that these tie-in works are to be completed after all other works are finalized, Elpro is closely involved in the commissioning works, test operation and start of normal operation. They must provide and maintain the interfaces between the existing process control system, the Hydrogenics control system and the control system of the methanation plant itself provided by Silica.

4 Plant layout

Figure 4-1 shows the actual plant layout in Falkenhagen. In the foreground of the picture the methanation plant is shown including local control room, gas treatment, reactor vessels, CO_2 supply and heat transfer system. The background of the picture illustrates the layout of the existing plant including electrolysis units, pipeline compressor container, general control room, transformer building and injection facilities.

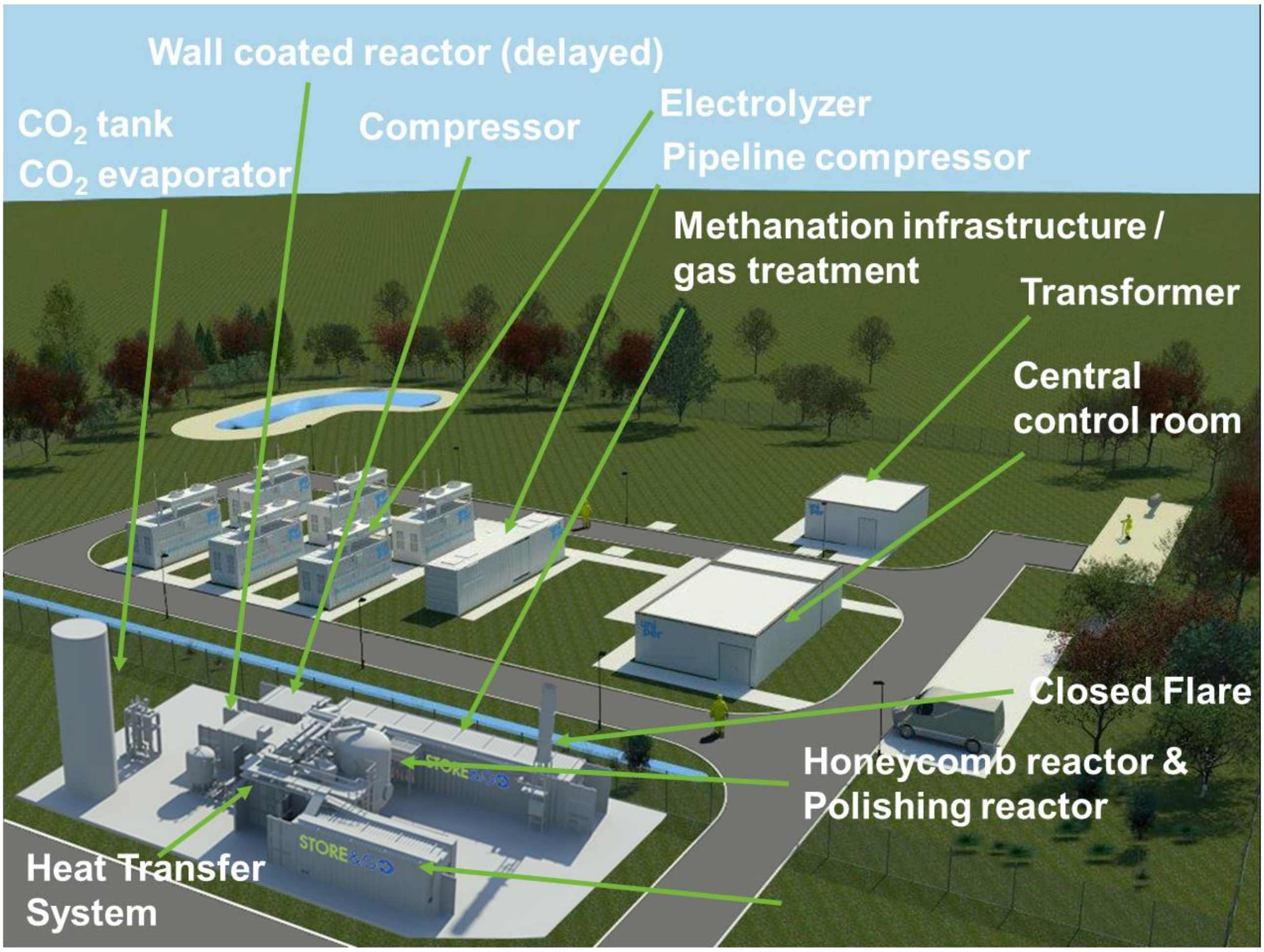


Figure 4-1: Plant layout for hydrogen and methanation plant

5 Plant erection

The manufacturing and inspection processes for all required equipment parts and services (including electro and instrumentation) were completed in October 2017 and the various parts delivered to site and installed since November 2017 after completion of the major ground works. During the design phase it was decided to aim for the highest prefabrication level possible. This decision allows to minimize the installation works on site.

The following pictures give a chronological impression of the erection works in Falkenhagen executed in Q4 of the year 2017 starting with the completion of the foundation works and ending with a mechanical complete plant.

Figure 5-1: Finalization of foundation works

Figure 5-2: Delivery of gas treatment container

Figure 5-3: Delivery of control room container of methanation

Figure 5-4: Erection process of methanation plant (heat transfer container and skid, CO_2 evaporator)

Figure 5-5: Erection process of methanation plant (foundation for CO_2 tank)

Figure 5-6: Front view of the delivered equipment on site

Figure 5-7: Roof of heat transfer container showing top of honeycomb reactor and economizer – in the background the trench for the hydrogen and SNG line for the tie-in to the existing plant is shown

Mechanical completion

Mechanical completion was officially achieved in December 2017.

After mechanical completion of the unit, pre-commissioning and commission procedures need to be implemented to start normal operation of the unit. Further below a short overview about the required activities will be given.

Figure 5-8: Mechanically complete plant in January 2018

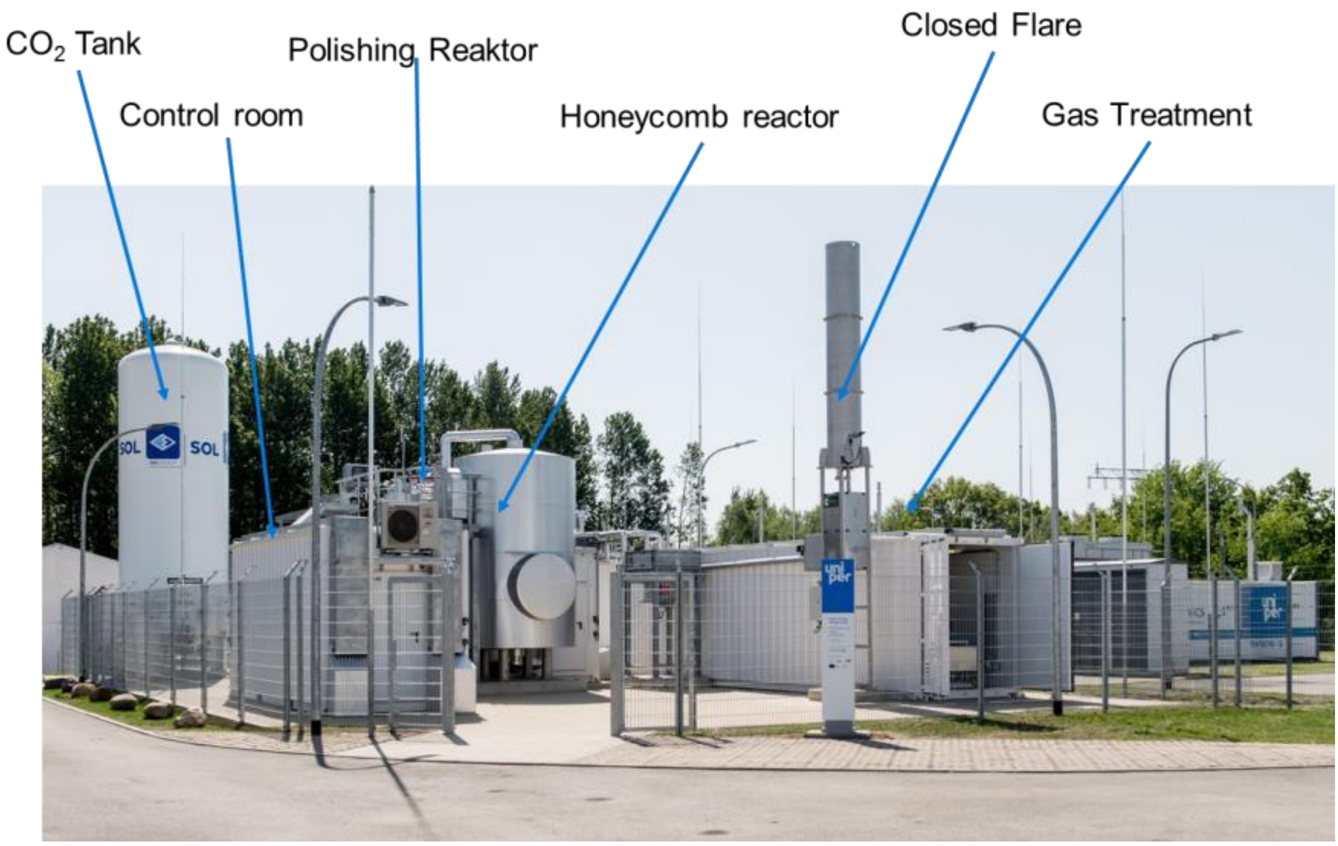


Figure 5-9: The finalized methanation plant – ready for commissioning

Figure 5-10: Methanation plant with connection to the veneer mill

6 Commissioning activities

The commissioning activities could be divided into four different phases, which are pre-commissioning, cold- and hot commissioning and the operating tests. The operating test were carried out to collect first operational experiences and to investigate and understand the process in detail and establish/develop improved automation and control algorithms.

Pre-Commissioning

Before the start of the pre-commissioning, the process piping has been cleaned by blowing out procedures where compressed air or nitrogen was blown through the process lines with flange connections dismantled. For this procedure sensitive piping elements such as flow meters, analysers, control valves, check valves were replaced by respective fitting pieces.

After mechanical and electrical completion of the methanation unit at the end of January 2018, all equipment and piping have been checked for cleanliness and completeness. In a next step, electrical, instrumentation and control equipment was re-installed and set into operation. After this status was achieved, functional tests of individual units have been executed.

During pre-commissioning, main documentation has been compared with the installed equipment. All commissioning procedures in the operating manual have been checked and modified if required added. Also, the flow charts in the process control system were checked to show all measurements, control parameters and information on process units. The cause and effect diagram was checked for the four plant operation modes of the methanation

- Cold standby
- Warm standby
- Hot standby
- Plant operation

Cold Commissioning

In Calendar week 7 in 2018, all pipes of the auxiliary systems were checked for tightness. The tightness of the hot water system, thermal oil system and chilling water system were documented by TÜV. Then, all air which might be trapped in the piping and in the equipment was removed and replaced by extensive nitrogen purging.

Heating water, water/glycol cooling agent and thermal oil Therminol 66 were filled into the units and the respective operation circuits have been pressurised. The auxiliary systems were checked and started. All stand by procedures were tested to check the warming up and cooling down procedures. During these check-up procedures it was shown that all electrical heaters had to be adjusted.

Hot Commissioning

In a first step of the hot commissioning phase, the reactors were equipped with the catalysts. This was done after the catalyst coated honeycombs arrived in Falkenhagen in CW 15.

In the Honey comb reactor 36R002 176 catalyst elements have been installed on April 19th. In parallel the temperature measurements for monitoring the catalyst element temperature were mounted in the expected hot-spot zone of the honeycombs and fixed properly.

The Polishing Reactor 36R003 was filled on April 20th with catalyst granules and the catalyst temperature element was mounted.

After filling the reactors with the catalysts, the reactors were closed and a tightness test was performed. For this purpose, nitrogen batteries were used. Under pressurised condition the gauss pressure of 18 bar in the unit has been monitored for 72 hours by TÜV Nord and the flange connections have been checked by application of a leak detection fluid. After this process was completed the complete plant was depressurized and left under nitrogen atmosphere.

With all the process media and catalysts in place, a procedure has been implemented to convert the catalyst in the reactors from the catalyst delivery/normal supply condition (oxidised stage – NiO) into the operating condition (reduced stage – elementary Ni). This was achieved by the application of hydrogen for 48 hours at a temperature of the catalysts of 300 °C and a pressure of 8 bar.

To complete the reduction process, the unit was purged with nitrogen for inerting and was slightly pressurised up to 8 bar gauss pressure. By operation of the Feed Gas Compressor 36K001 and opening of a recirculation line the inert nitrogen gas flow was established across the reactors. The unit and especially the reactors were heated up by the hot oil system and its electrical heater to a temperature of 300 °C. After reaching the reduction temperature small amounts of hydrogen were gradually introduced into the circulating gas flow to reduce the catalyst. As the reduction reaction is exothermic this procedure needs to be performed cautiously with intensive monitoring of the catalyst temperatures. When no further heat development was observed this procedure was stopped and the unit was ready for operation. The hot commissioning works were completed in July 2018.

Trial runs by manufacturer

First test runs of the plant were executed to check the gas supply of the methanation system. Both feed gases hydrogen and carbon dioxide were checked, and the required supply pressure of these gases assured.

The start-up of the methanation begins with heating up the unit and especially the reactors to the required operating temperature. This is achieved by the hot oil system. At the beginning of the process the heating is realised by the hot water from the veneer mill. By using the veneer mill heating up to 155 °C can be reached (also during the warm standby phases). To further increase the temperature the hot water system is switched off and the thermal oil was heated up to 220 °C by the electrical heater in hot standby mode. The first test runs proved that all heating systems worked properly.

The chilled water system automatically was started during the operation phase to provide the necessary gas cooling and supports the evaporation of the liquefied CO_2 feed.

In parallel Feed Gas Compressor 36K001 is started and the process gas content of the unit – mainly hydrogen – is circulated across the reactors by a recirculation line. In this way the electrical heaters upstream of the reactors are used for heating up the whole system to the reaction start temperature. These tests were finalized in September 2018.

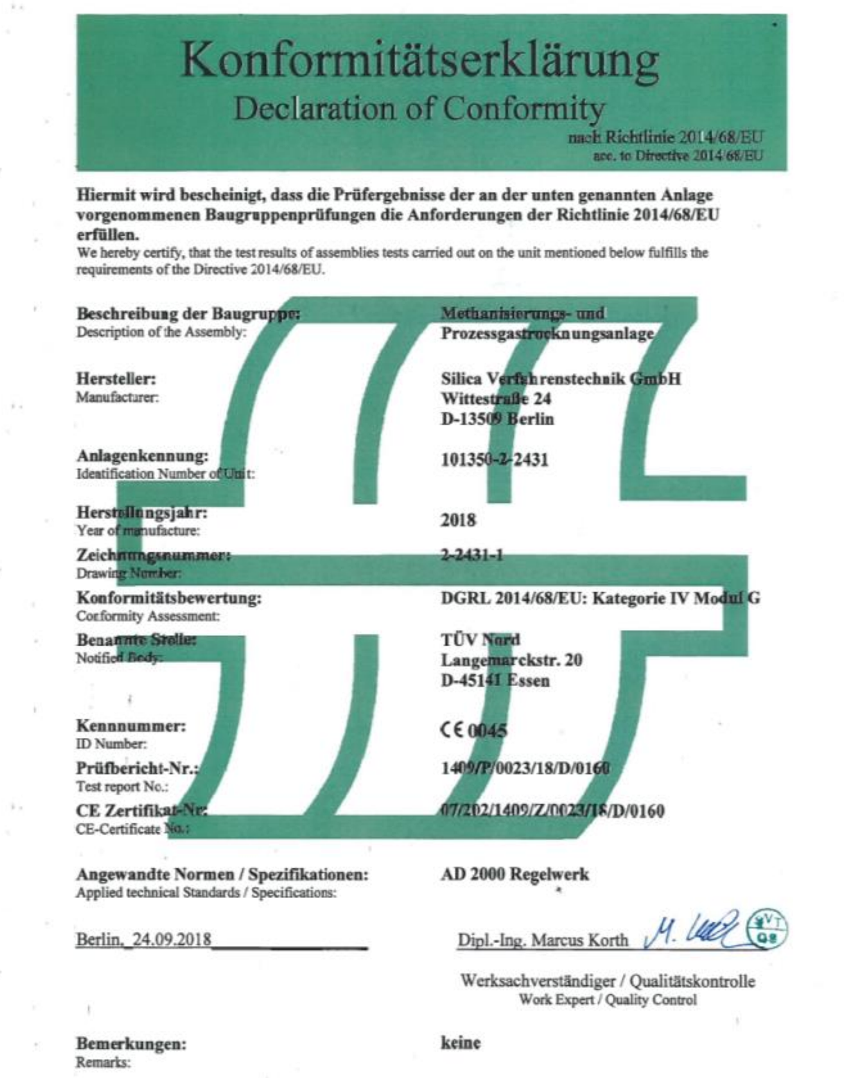
First methanation test runs

After checking the availability of the two feed gases hydrogen and carbon dioxide, the start-up of the plant begins with heating up the unit and especially the reactors to the required operating temperatures. This is done via the hot oil system. The chilled water system is also started to provide the necessary gas cooling and supports the evaporation of the liquefied CO_2 feed gas.

With the operating temperatures attained, the Feed Gas Compressor 36K001 is started and the process gas content of the unit is circulated across the reactors by operation of a recirculation line.

The feed gases hydrogen and CO_2 are gradually fed to the unit and the methanation reaction is started. In the first phase off-spec product gas will be produced, which will be flared. When stable reaction conditions (reactor temperatures) and the required methane content as well as the moisture content in the product gas are reached, the process gas circulation can be closed and the product gas can be sent to the downstream pipeline compressor for injection of the gas into the adjacent natural gas pipeline system. The heat of reaction generated by the methanation reaction will be used for the heating of the adjacent veneer mill. First gas with required quality was produced in August 2018.

After all test runs during the commissioning phase, after the final check up by TÜV Nord, the "Declaration of Conformity" (see Figure 6-1) and the CE sign for the methanation unit were achieved in September 2018.



Konformitätserklärung
Declaration of Conformity
nach Richtlinie 2014/68/EU
acc. to Directive 2014/68/EU

Hiermit wird bescheinigt, dass die Prüfergebnisse der an der unten genannten Anlage vorgenommenen Baugruppenprüfungen die Anforderungen der Richtlinie 2014/68/EU erfüllen.
We hereby certify, that the test results of assemblies tests carried out on the unit mentioned below fulfills the requirements of the Directive 2014/68/EU.

Beschreibung der Baugruppe: Description of the Assembly:	**Methanisierungs- und Prozessgastrocknungsanlage**
Hersteller: Manufacturer:	**Silica Verfahrenstechnik GmbH Wittestraße 24 D-13509 Berlin**
Anlagenkennung: Identification Number of Unit:	**101350-2-2431**
Herstellungsjahr: Year of manufacture:	**2018**
Zeichnungsnummer: Drawing Number:	**2-2431-1**
Konformitätsbewertung: Conformity Assessment:	**DGRL 2014/68/EU: Kategorie IV Modul G**
Benannte Stelle: Notified Body:	**TÜV Nord Langemarckstr. 20 D-45141 Essen**
Kennnummer: ID Number:	**CE 0045**
Prüfbericht-Nr.: Test report No.:	**1409/P/0023/18/D/0160**
CE Zertifikat-Nr.: CE-Certificate No.:	**07/202/1409/Z/0023/18/D/0160**
Angewandte Normen / Spezifikationen: Applied technical Standards / Specifications:	**AD 2000 Regelwerk**

Berlin, 24.09.2018 Dipl.-Ing. Marcus Korth

Werksachverständiger / Qualitätskontrolle
Work Expert / Quality Control

Bemerkungen: Remarks:	**keine**

Figure 6-1: Declaration of conformity

After achieving the declaration of conformity for the methanation plant, the plant was run for process optimization. During that period parameter sets, switch points and control loops were modified and improved. In parallel, start-up and shutdown procedures were investigated and partly implemented.

The following paragraph shall give some impressions on the gained experiences in operating the methanation plant.

One issue, which was already observed during the first operating hours, was the relatively high temperatures detected in the catalyst hotspots. The exact position of the thermo-elements in the tube sheet are shown in Figure 6-2. In the picture the hot oil flow is indicated as red marks, while the 3 hotspot elements are indicated in blue (T201), orange (T202) and green (T203). During the first 500 hours of plant operation, the hotspot temperatures easily reach 500 °C and more. In the same time the overall gas temperature of the gas leaving the reactor remains well below 200 °C.

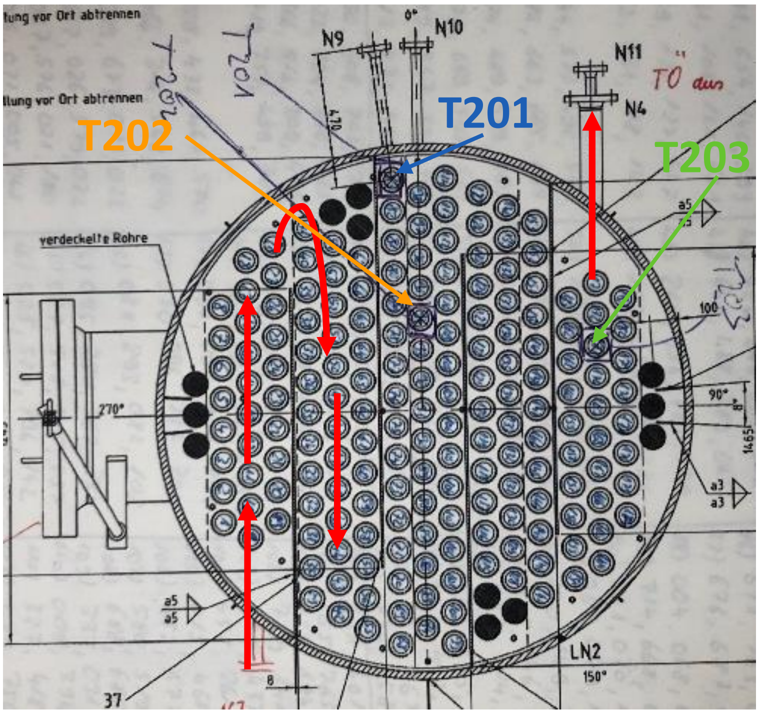


Figure 6-2: Position of temperature elements in honey reactor tube sheet

A typical temperature profile from end of August 2018 is shown in Figure 6-3. Today, after more than 500 hours of plant operation, no deactivation of the catalyst was observed. The hotspot temperatures remain around 500 °C, while the gas temperature directly in the reactor outlet (T304 indicated in yellow) is not exceeding 200 °C.

One explanation for this behaviour might be that the hydrogen purging procedures, which are carried out prior to production stops, regenerate the catalyst surface and maintain the high level of reactivity. One of the first steps of the process optimization was the modification of the temperature set points for the reactor control system to consider this system characteristics.

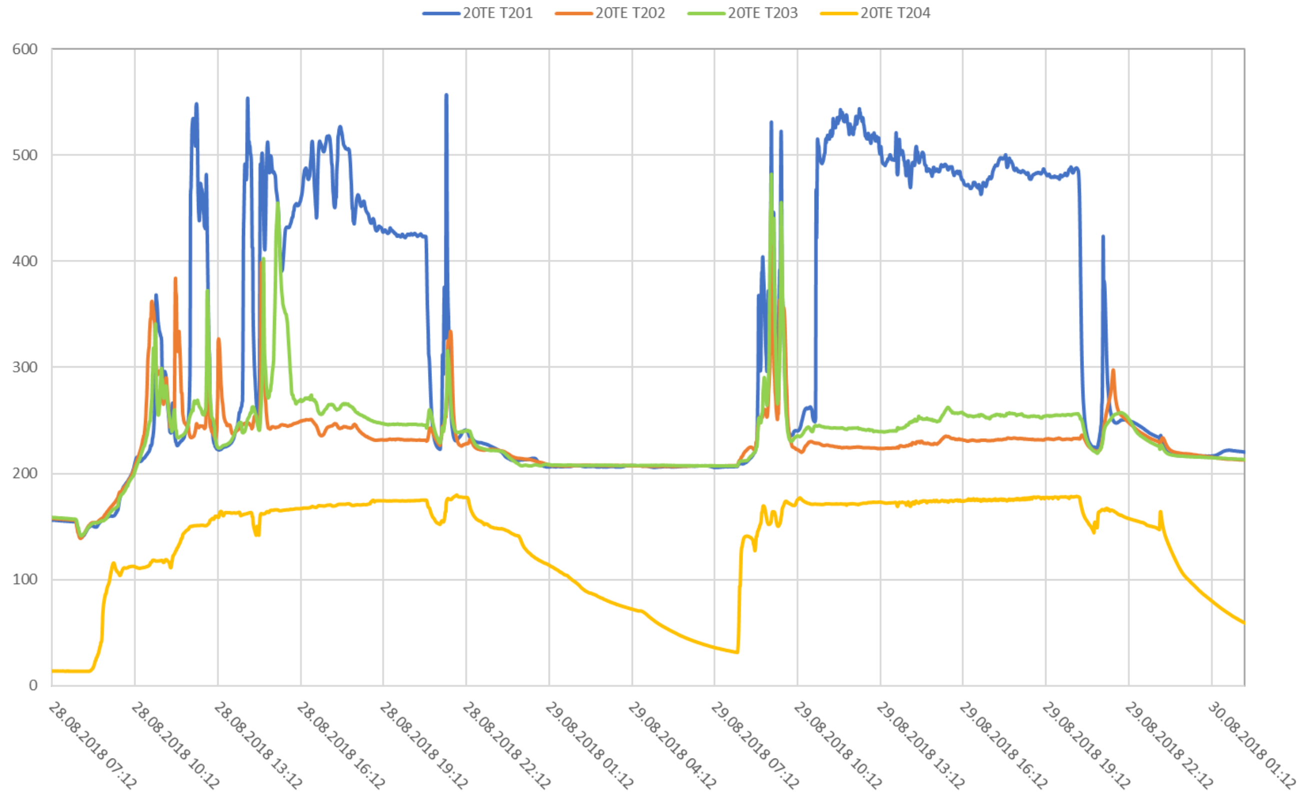


Figure 6-3: Typical temperature profile of honeycomb reactor

Also, in August 2018 it was shown that the SNG gas qualities achieved by the methanation system were extremely promising. Although there were challenges in automatically maintaining the exact CO_2/H_2 ratio over longer time periods, methane concentrations of more than 98 % were reached and reproduced repeatedly. Table 6-1 shows the result of a SNG gas analysis from August 2018. All other monitored gas components were not detected in the produced SNG (C3 – C12, benzene, toluene, cyclohexane, methylcyclohexane, carbon monoxide, H_2S).

Table 6-1: SNG composition measured by Elster PGC

No.	Component	Norm. Concentration [%]
1	Hydrogen	0,483
2	Nitrogen	0,117
3	Methane	99,374
4	Carbon Dioxide	0,017
5	Ethane	0,008
	Total	100,000

One major issue in the start of the plant operation was the reliability of the used flow measurements. The originally installed devices (rotameter type flow meters of company Krohne shown in Figure 6-4) were stuck regularly and delivered wrong figures, which resulted in serious control issues. With the originally installed flow meters, it was impossible to control the CO_2/H_2 ratio with the required precision.

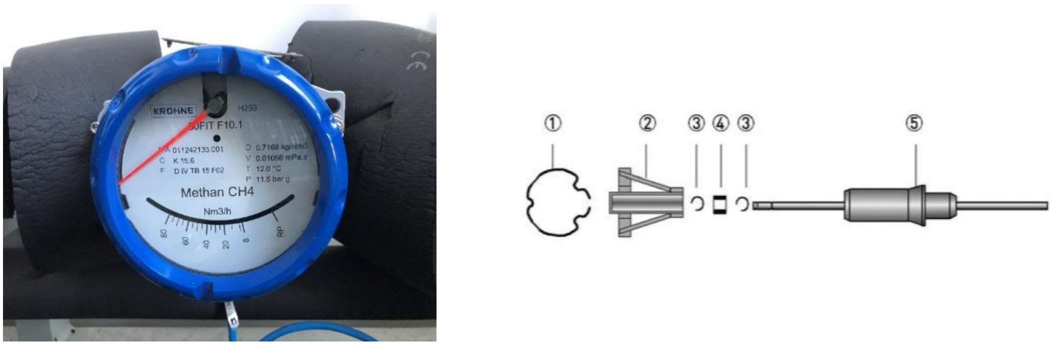


Figure 6-4: Rotameter type flow measurements of company Krohne (isolated device and inlays)

After the devices were dismounted, cleaned, repaired and re-installed several times, it was decided to exchange two of these devices – the flow measurements in the hydrogen supply line and in the recycle line connecting the outlet of polishing reactor and the suction side of the methanation compressor. The issues with the original measurements were mainly caused by pressure hammer issues and the occurrence of small amounts of metal dust and undefined dirt.

The proposed solution of the supplier was the exchange of the measurements against more robust versions with a slightly increased inner diameter. The new devices were installed in December 2018 and extensively tested afterwards. The tests proved that the new measurements are working as expected and that the CO_2/H_2 ratio is accurately measured and controlled in a reliable way.

Since the flow metering issue was solved the plant has been further optimized in various ways:

One example for this optimization was the implementation of a procedure to allow automatic start-up of the CO_2 supply. This was required to prevent dry ice formation and therefore reduced CO_2 supply, if the CO_2 valve is opened to fast.

Another example was the programming of additional control loops to ensure the supply of a constant gas quality even under changing conditions in the feed gas supply. This control loop monitors the CO_2/H_2 ratio downstream of the first reactor stage and modifies the inlet ratio continuously to ensure that the ratio at this point stays in a range between 0.235 & 0.280, which is sufficient to reach injection gas quality. Such a control mechanism needs to consider the significant delays between the modification of the set point and the actual system reaction. For the tested gas flows (around 50 % of the total capacity of the plant), these delays are 45 minutes and more.

Figure 6-5 shows process temperatures, corresponding gas flows and concentrations in CW 2 of year 2019. Here the plant was operated for a period of more than 72 h without major interventions. Although injection quality was not always met, the tests show that the plant could be operated under stable conditions for a significant period. Again, the hotspot temperatures in the honeycomb reactor remain at the high level of around 500 °C for nearly the complete test period.

During the 72 hours test, the produced gas was completely flared. This mode of operation implies some special demands, which are caused by restrictions in the flare design. The regular switch between flare stage 1 (low gas amounts) and flare stage 2 (full capacity) results in frequent changes in the gas flows through the reactors, which result in frequent disturbances of the stable operation.

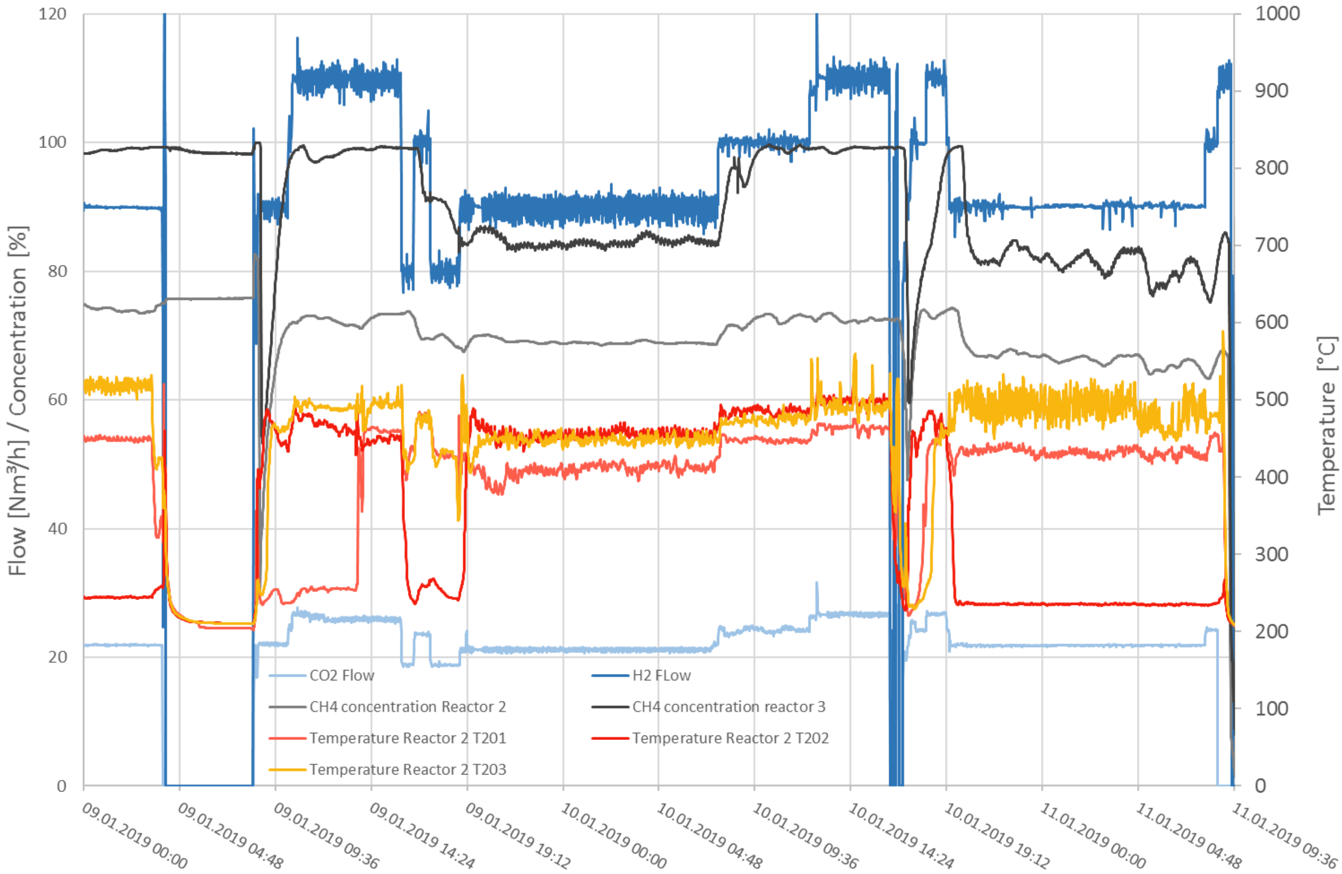


Figure 6-5: Test operation in calendar week 2 (09.–11.01.2019), part of 72 hours test

The official approval of ONTRAS for the injection of the SNG was achieved end of CW 2. Shortly after this milestone was reached, injection operation was tested. The first SNG gas (~ 60 m³ (NTP)) was injected into the ONTRAS grid on the 16th of January 2019. Figure 6-6 shows the process conditions during this first injection test.

While two of the hot spot temperatures are constantly around 500 °C, the third hotspot temperature element is limited to 250 °C (T 2b indicated in grey). This behaviour was observed during various tests and might be an indication for issues in the gas distribution. It might be that there is not an even distribution of the feed gas through all catalyst pipes.

The methane concentration downstream of the honeycomb reactor is around 70 % (indicated in blue). Downstream of the polishing reactor CH_4 concentrations of more than 98 % are reached. As discussed before in general the measured data points seem to be more stable than in the experiments before, where the flare was used to dispose the produced gas.

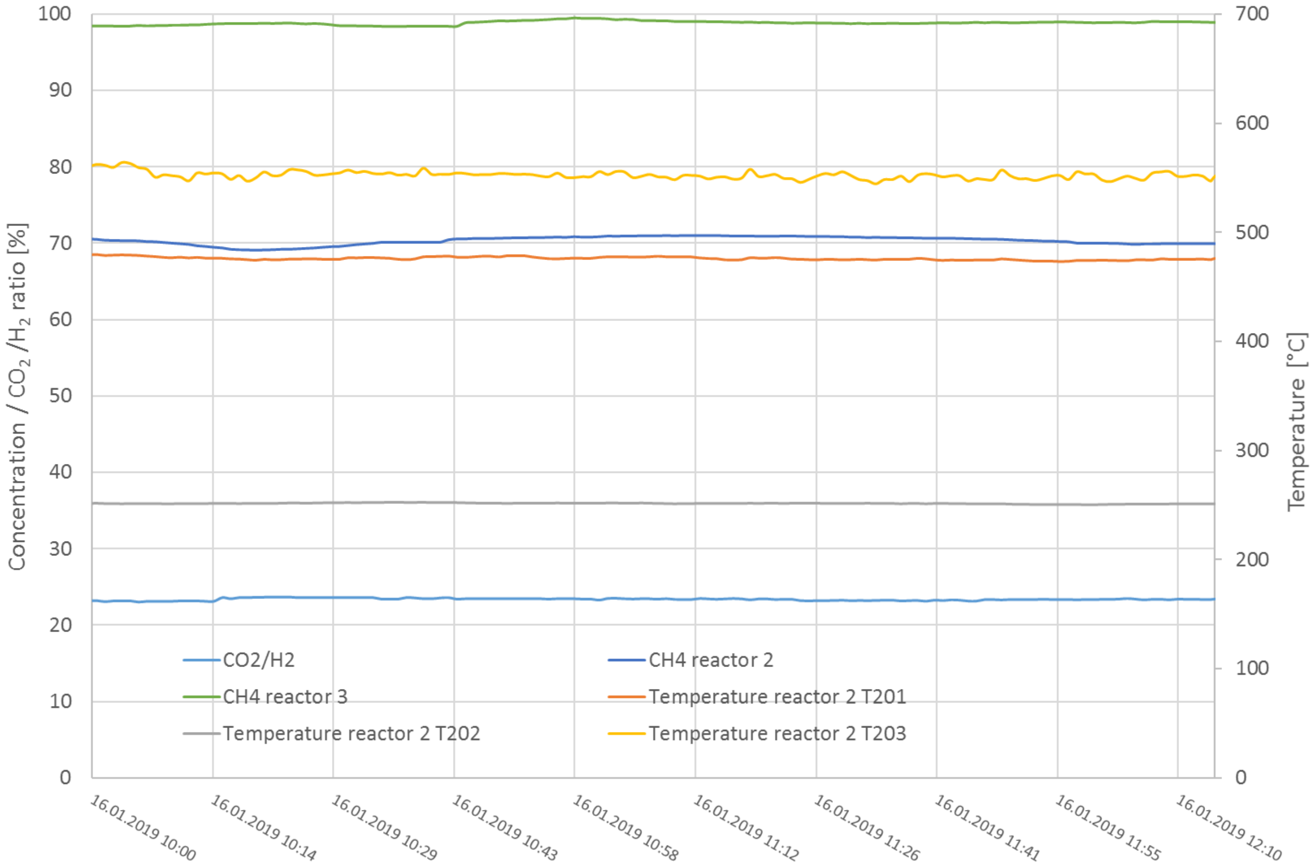


Figure 6-6: First injection into ONTRAS gas grid (CW 3 2019)

The CO_2/H_2 ratio in the gas feed was set and maintained at a value of ~ 0.235. In this way, downstream of the honeycomb reactor a stable ratio around 0.25 in the inlet of the polishing reactor is reached, which leads to injection quality downstream of the dehydration unit (as shown in the simplified PFD Picture 2). It seems that the calibration of the hydrogen and carbon dioxide flow sensor leaves room for further optimization.

7 Next Steps

By reaching the milestone “first gas injection” into the ONTRAS grid in January 2019, the commissioning works for the methanation plant were finalized.

Nevertheless, there are still open points concerning the tie-in works of the methanation system into the overall plant, which are required to reach fully automated operation. The programming considering the interaction between the “old” hydrogen part of the existing plant and the STORE&GO project equipment requires additional finetuning works. Current activities are focussing on checking of the various interfaces between the involved process control system (overall, methanation and electrolysis systems) and finalizing the overall process control system, which allows to run the complete plant solely from the Uniper control room and later completely automated remotely controlled.

During the next weeks, further injection tests will be carried out within the STORE&GO project. On top of that, the increase of the plant production to its design capacity shall be investigated. The key question here will be how the temperature management of the hot-spot areas can prevent exceeding 520 °C for longer periods. If the temperature is further increased, damages of the catalyst might occur.

For CW 13 2019 there is the second site visit of Work Package 5 planned, with the aim to produce data for further investigations. Here, the discussions on the desired test program for the demonstration plants also must be intensified. Based on the collected experiences, it seems highly questionable if the methanation will be able to follow the proposed stress tests. The observed reaction time of the system may prevent at least some of the originally planned tests and may hinder the quick modulation of input power from the electrical grid.

Bibliography

Literature

[1] J. Kopyscinski, et al., "Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009," Fuel, vol. 89, pp. 1763-1783, 2010.

[2] S. Rönsch and A. Ortwein, "Methanation of Synthetic Gas – Fundamentals and Process Development (in German)," Chemie Ingenieur Technik, vol. 83, pp. 1200-1208, 2011.

[3] F. Koschany et al., "On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)x," Applied Catalysis B: Enviromental 181, pp 504-516, 2016

DE102009018126 (A1).

[4] Müller-Syring, Gert et al: „Forschungsbericht G 1/07/10 - Abschlussbericht zur Entwicklung von modularen Konzepten zur Erzeugung, Speicherung und Einspeisung von Wasserstoff und Methan ins Erdgasnetz", DVGW, 2013.