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Spring 2023

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GaSEM: Sorption Enhanced Methanation Enabled by Smart Sensors

Introduction

The variability of natural gas composition is increasing with the diversification of sources, the transition away from fossil sources and hydrogen blending. This is fueling a demand for smart sensors able to monitor gas quality and control gas production processes. The most appropriate sensor for the task depends heavily on the specific requirements, with many applications benefiting from customized sensor solutions. In this article the usefulness of custom sensors will be demonstrated using the example of the recently successfully completed GaSEM project co-developed by Mems AG and UMTEC (Institute for Environmental and Process Engineering, OST - Eastern Switzerland University of Applied Sciences). In the project a fully automated sorption enhanced methanation (SEM) plant was developed, which was controlled based on the response of several smart gasQS static measuring instruments.

SEM Operating principle

The production of methane from hydrogen and carbon dioxide is based on the following chemical reaction:

$CO_2 + 4{\cdot}H_2 = CH_4 + 2{\cdot}H_2O$

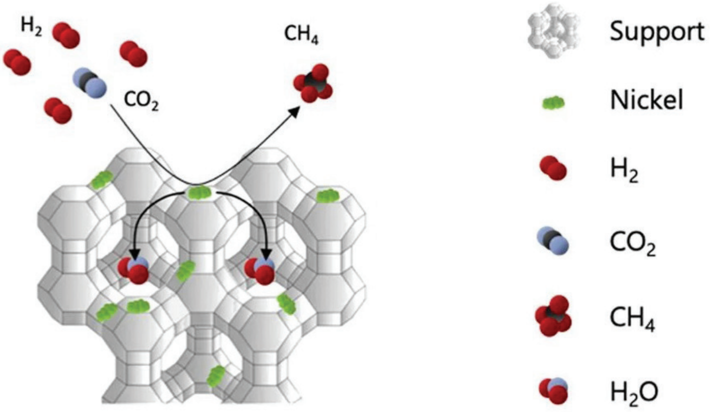
Thus, not only methane is produced during methanation, but also water. SEM enables the complete conversion of carbon dioxide and hydrogen to methane by adsorbing the produced water in a zeolite. The applied Ni-zeolite catalyst, named SmartCat, shifts the reaction equilibrium to the product side and enables a 100% conversion, even at atmospheric pressure.

The optimized SmartCat catalyst allows 100% conversion even if a CO_2/H_2 mixture is mixed with more than 70 % of other "ballast gases", such as methane in the case of biogas. It is therefore not necessary to separate CO_2 beforehand, which results in an economic advantage for power-to-gas (PtG) plants. The technology can be used advantageously as an in-line biogas upgrade, to which only H_2 is added to biogenic CH_4/CO_2 mixtures.

The sorption reactor is integrated into a larger system. This system starts with the feed of the reactant gases (CO_2, H_2) and ends with the supply of the product gas (CH_4) into the gas grid, as shown in Figure 2.

Mems AG is a leading supplier of high-quality measuring instruments for the determination of gas quality parameters via correlation. GasQS products are characterized by their accuracy, stability and longevity and are tailored to the demands of the application.
Under the direction of Prof. Dr. Andre Heel, the "Advanced Materials & Processes" group at the OST (Eastern Switzerland University of Applied Sciences) deals with the development of innovative materials & processes in environmental and energy process engineering. A particular focus is on the development of high-performance processes for "biofuels" and "synfuels" and their transfer into industrial processes.

Figure 1 - Principle of sorption-enhanced methanation.



In the process schematic measuring devices and sensors are represented by circles and are used to provide data for the monitoring and controlling of the system. The system is controlled using a programmable logic controller (PLC). The PLC is responsible for setting the flow rates on the mass flow controllers (MFCs) and controlling the state of the system by switching the appropriate valves.

gasQS static

The gasQS static from Mems AG is a measuring instrument that operates on the basis of thermal conductivity (λ) measurements. It is equipped as standard with a 4-20 mA analog output and is pressure-compensated over the entire pressure range up to 15 bar(g). Each SEM reactor is equipped with a gasQS static at its output to monitor the various phases of the reaction. An additional gasQS static at the system input is used to monitor the mixing ratio of the reactant gases.

During the project the implementation of the HART protocol (highway addressable remote transducer) for the gasQS static was investigated. The HART protocol allows digital communication on the analog current loop enabling substantial additional features such as the ability to communicate multiple signals (e.g., pressure or temperature), switch between calibration ranges (0-100% to 92-100%, or H_2 in CH_4 to CO_2 in CH_4, for example), calculated output values (e.g., calorific value, Wobbe index, etc.) or to upgrade the instrument in the field.

System control and monitoring

Each SEM reactor in the system periodically passes through three phases of operation, which are well described with a three-stage state machine (Figure 3). Within the project a methanation to drying ratio of approximately 1:1 could be established. Hence, the reactors can be operated sequentially, so that one reactor is dried of reaction water while the other produces methane. In this way, a continuous methanation reaction and operation is established. Also shown in Figure 3 is the thermal conductivity of the gas exiting a reactor during the three process phases.

The phases of reactor operation are:

Methanation phase

If the reactor is fed with a stoichiometric mixture of H_2 and CO_2, the conversion to methane depends upon the reactor efficiency "x" according to the following equation ($0 \le x \le 1$):

$4{\cdot}H_2 + CO_2 \rightarrow x{\cdot}(CH_4 + 2{\cdot}H_2O) + (1\text{-}x){\cdot}(CO_2 + 4{\cdot}H_2)$

In a conventional atmospheric methanation reactor, "x" is about 0.82 (82%) in the best case, resulting in a considerable amount of unused H_2 and CO_2. For SEM under ideal conditions the conversion efficiency can reach 1 (100%). As the water is adsorbed by the zeolite, the product gas is dominated by methane and so the thermal conductivity remains constant at this level during this phase. During the production phases (methanation and saturation) a HART enabled gasQS static could be programmed to additionally output calorific value or the Wobbe index of the produced gas, enabling the possibility of automatic billing of customers.

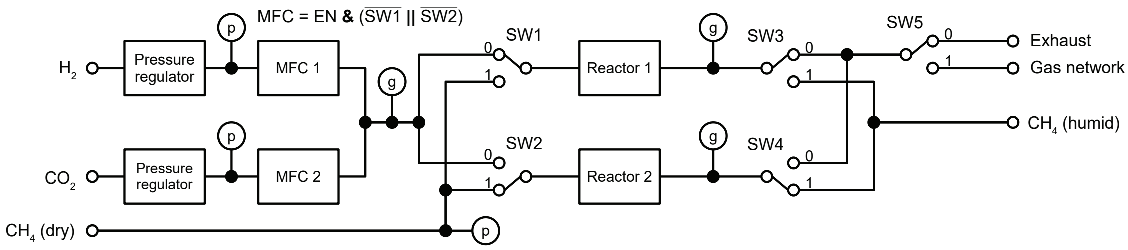


Figure 2 - Block diagram of the sorption enhanced methanation plant.

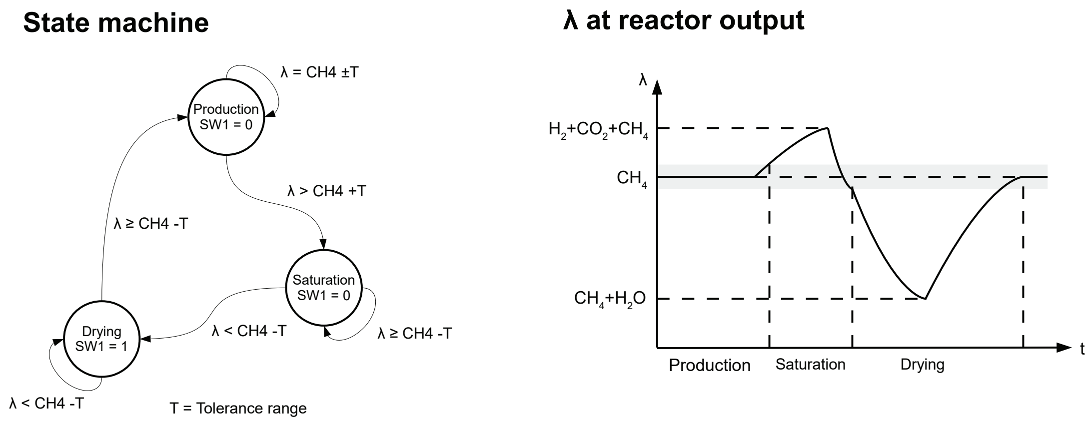


Figure 3 – The production process and associated conditions. λ: Thermal conductivity value of the gases measured by the sensors.

Saturation phase

As the zeolite-based SmartCat catalyst reaches the end of its water adsorption capacity, the conversion efficiency decreases. In addition to methane, water, H_2 and CO_2 are also present in the product gas, as in conventional methanation. The thermal conductivity changes with the product gas composition and is monitored with the gasQS static. The allowable tolerance of the thermal conductivity is adjusted based on application requirements. In the current case it was set to ensure a methane concentration of >96%, the current methane gas quality limit in Switzerland for gas grid injection. Once the tolerance limit is reached the methanation process is terminated and the reactor is switched to the drying phase.

Drying phase

In order to remove the water from the saturated zeolite, a dry gas is flowed through the reactor. Methane is used for drying due to its availability at methanation plants and compatibility with standard sensors, but with HART enabled gasQS statics the calibration range could be adjusted on the fly, enabling the use of other gases for drying. Water has a lower thermal conductivity than methane, allowing the drying progress to be tracked with the gasQS static. The wet gas can then be dried by separating the water out in the post-processing stage (with e.g., a cold trap or molecular sieve).

Figure 4 – The prototype methanation reactor and thermal oil heat exchanger.

Commissioning and de-commissioning

Prior to and following operation the reactors must be flooded with inert gas, for which CO_2 is typically chosen. The thermal conductivity of CO_2 is considerably lower than that of methane, making it difficult to cover both operating ranges accurately with a single calibration range. Here the additional capability of HART enabled gasQS statics to switch calibration ranges would be advantageous, enabling accurate determination of the thermal conductivity over two quite different ranges.

Industrial and scalable reactor design

Various reactors and catalysts exist on the market; however, these are restricted to operation at higher pressures to realize higher conversion. In order to enable low pressure operation a new and scalable reactor design was developed in close cooperation with the company Fluitec AG. The first prototype fixed-bed reactor has an empty volume of about 10 liters at a length of just under 1 m. Future reactors will be longer and can be produced with diameters up to 2m. To combat the hotspots typical of PtG reactors, an innovative heat exchanger design was employed. Fluitec's invention is used to ensure a homogeneous and efficient temperature distribution, since the SmartCat's water adsorption capacity is very temperature sensitive. Even hot spots of 10 Kelvin result in a substantial reduction of SEM operation time. An industrial thermal oil heat exchanger from Regloplas was employed to efficiently transfer heat generated during the exothermic methanation phase of one reactor to aid the endothermic drying of the other reactor.

Summary

With the successful completion of the GaSEM project, a fully automated, stand-alone sorption enhanced methanation plant has been demonstrated. Through knowledge of the process stages and measurements of thermal conductivity, a state machine was constructed to monitor the reactors and control their state. Future gasQS statics upgraded with the HART protocol would provide additional flexibility regarding the gases employed for drying and commissioning the reactor, improve measurement accuracy and enable the output of additional gas quality factors such as calorific value or Wobbe index for billing purposes. •

Contact Information:
Mems AG
Telephone: +41 (0)56 470 92 00
E-mail: info@mems.ch
Website: www.mems.ch

Figure 5 – The gasQS static from Mems AG.