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Production of hydrogen by autothermal reforming of biogas

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Abstract

In this paper the results of the operation of a pilot-plant with a hydrogen output of 50 Nm³/h are discussed. This plant shows the possibility of distributed production of hydrogen for the powertrains based on hydrogen. The focus of the investigations is the long-term behavior of the novel Nickel-based catalyst. This includes experimental studies of the impact of the start-up sequence on the reforming performance after the necessary activation of the catalyst. Additionally the prospective demand of hydrogen requires an analysis of the start-up time of the plant. The focus was a short start-up time without harming the catalyst.

Keywords: Autothermal reforming; hydrogen production; renewables

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1. Introduction

The enhanced efforts in the decarbonisation of the traffic sector is a strategy of the European Union to reduce the anthropogenic part of the climate change. Therefore several ways for the powertrains of the future have been developed. One option is the fuel cell. The fuel cell uses hydrogen and during the energy release only water is produced. To support the strategy, the scope of the project BioRobur (Biogas robust processing with combined catalytic reformer and trap), funded by the European Commission, is the decentralized production of hydrogen for these vehicles. To reduce the impact of this path of travelling on the environment, the production path for this project requires a location next to a biogas fermentation [1]. During the reforming of the biogas, which is supported by a catalyst, the hydrogen rich synthetic gas is produced. Several purification steps like water-gas-shift reaction or pressure swing adsorption can be added to fit the requirements of the fuel cell vehicles.

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In this paper the investigation of the boundary conditions for the efficient reforming of biogas to a hydrogen rich gas are summarized. Therefore the experimental results of a pilot-plant are analyzed. This plant takes the educt pretreatment and the autothermal reforming into account. The steps of hydrogen purification are skipped. The focus is the long-term behavior of the novel Nickel-based catalysts. This includes the investigation of the impact of the start-up sequence on the reforming performance after the necessary activation of the catalyst. Additionally the cold and the warm start time of the pilot-plant have been measured and optimized. Several investigations regarding the overall plant efficiency will finalize the paper.

2. Experimental method

The main part of the block flow diagram depicted in Figure 1 is the reactor (R-700) for autothermal reforming (ATR). The ATR of methane is taking place by following the chemical equation:

$$2CH_4 + {}^{1}\!/_{2}\, O_2 + H_2O \rightleftarrows 2CO + 5H_2$$

The required inlet flows of hydrogen, carbon dioxide, methane, air, nitrogen and water are shown on the left side. The hydrogen is for the activation of the Nickel-based catalysts. The carbon dioxide and the methane are mixed with a ratio of 40 vol.-% to 60 vol.-% to produce a representative synthetic biogas. The air is used for the partial oxidation (POX) of the reforming educts. In case of an emergency shutdown the nitrogen is used to flush all vessels and pipes and remove any combustible fluid. The last inlet flow is water, which is transformed to steam to have all inlet flows in gaseous state.

All educts for the ATR are entering the plant through flow controllers, are mixed in an ejector (J-700) and are preheated by heat integration with the heat exchanger (H-700) or by an electrical heater (E-700). The downstream following ATR reactor (R-700), the soot trap (S-700) as well as the educt heat exchanger (H-700) are one vessel made of Alloy 800H. The produced synthetic gas with a volume fraction of hydrogen in the dry gas of about 35 vol.-% is cooled down by superheating the steam in the heat exchanger H-100 and is finally combusted in a flare.

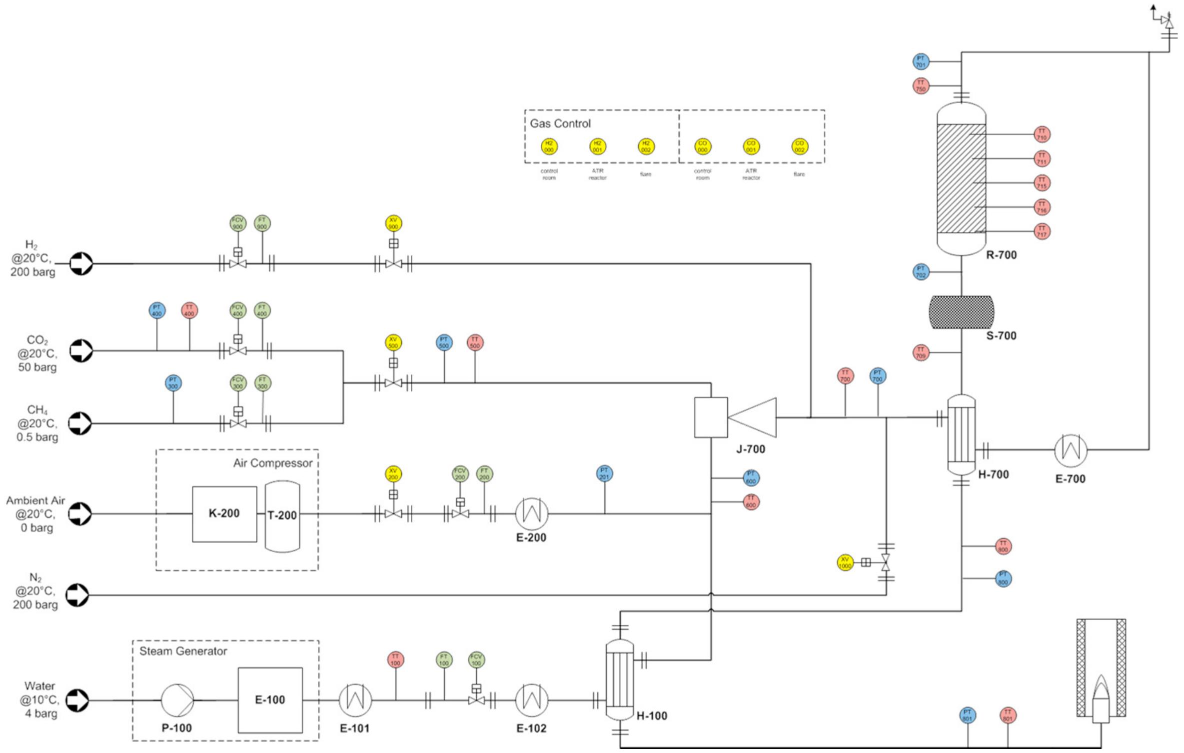


Figure 1 - Block flow diagram of the pilot-plant of the project BioRobur

Besides the main components of the plant, the block flow diagram shows the main measuring points. The red points are the temperature measurements. A thermocouple is located at the entrance of the reactor to monitor the temperature of the feed flow. In order to estimate the temperature profile in the reaction unit during the test, five thermocouples have been placed inside the reactor. The pressure drop over the catalyst and the soot trap is measured by pressure gauges shown in Figure 1 with blue dots. The flow controllers are depicted in green. Furthermore, the safety devices are the yellow plots, which are quick acting gate valves and gas sensors. The presence of an explosive or toxic environment is monitored by six sensors all around the plant. In case of an emergency state, the valves of biogas, air and hydrogen will be closed immediately and the nitrogen valve will be opened. All components, except the carbon dioxide storage and the flare, are placed in four containers. The plant is controlled by a DeltaV system from Emerson with a redundant control unit and an additional safety PLC. The system has 56 inputs and seven outputs. The safety PLC has separate inputs and outputs, in terms of numbers eight inputs and one output. The single output triggers several relays, which set the plant to a controlled state.

To control the reforming of the biogas three main parameters are used. The first one is the gas hourly space velocity (GHSV), which is the quotient of the volumetric flow rate of the reactants divided by the catalyst volume. It is the reciprocal of the residence time.

$$\mathrm{GHSV} = \frac{\dot{\mathrm{V}}_0}{\mathrm{Vcat}}$$

The second parameter is the steam to carbon ratio. The S/C-ratio describes the amount of steam compared to carbon. In the case of the ATR reforming in Freiberg, methane is stated as the single source for carbon. The carbon dioxide is disregarded.

$$\frac{\mathrm{S}}{\mathrm{C}} = \frac{\dot{\mathrm{n}}_{\mathrm{H2O}}}{\dot{\mathrm{n}}_{\mathrm{C}}} = \frac{\dot{\mathrm{n}}_{\mathrm{H2O}}}{\dot{\mathrm{n}}_{\mathrm{CH4}}}$$

The final control parameter is the oxygen to carbon ratio. The O/C-ratio describes the amount of oxygen in relation to carbon. The carbon source is methane, as described before.

$$\frac{\mathrm{O}}{\mathrm{C}} = \frac{\dot{\mathrm{n}}_{\mathrm{O}}}{\dot{\mathrm{n}}_{\mathrm{C}}} = \frac{2\dot{\mathrm{n}}_{\mathrm{O2}}}{\dot{\mathrm{n}}_{\mathrm{CH4}}} = \frac{2\cdot 0.21\cdot \dot{\mathrm{n}}_{\mathrm{Air}}}{\dot{\mathrm{n}}_{\mathrm{CH4}}}$$

Besides the three control parameters, three output parameters are selected to evaluate the quality of the input parameters and the catalyst. First, the hydrogen yield is indicated as the ratio of the amount of hydrogen in the product gas to methane in the educt flow. This parameter shows the selectivity of the catalyst to produce hydrogen instead of carbon monoxide.

$$\mathrm{Y} = \frac{\dot{\mathrm{n}}_{\mathrm{H2}}}{\dot{\mathrm{n}}_{\mathrm{CH4,0}}}$$

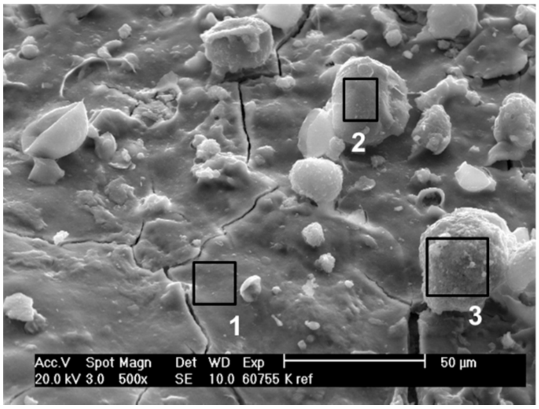
Second, the methane conversion is defined as the difference between the flow of methane going into the reactor (educt) and the one leaving the reactor (product) in relation to the overall methane flow. The methane in the product flow is produced due methanation or passed the catalyst without any reaction.

$$\mathrm{X} = \frac{\dot{\mathrm{n}}_{\mathrm{CH4,0}} - \dot{\mathrm{n}}_{\mathrm{CH4}}}{\dot{\mathrm{n}}_{\mathrm{CH4,0}}}$$

Another important parameter is the cold gas efficiency. The cold gas efficiency is defined as the ratio of the higher heating value (HHV) of the product gases to the HHV of the feed gases [2]. In addition to hydrogen, carbon monoxide is considered and can be used to produce more hydrogen by downstream water gas shift steps.

$$\eta_{\mathrm{cold\ gas}} = \frac{\dot{\mathrm{m}}_{\mathrm{H2}}\mathrm{HHV}_{\mathrm{H2}} + \dot{\mathrm{m}}_{\mathrm{CO}}\mathrm{HHV}_{\mathrm{CO}}}{\dot{\mathrm{m}}_{\mathrm{CH4}}\mathrm{HHV}_{\mathrm{CH4}}}$$

By taking the consumed electrical energy into account, the plant efficiency is calculated comparable to the cold gas efficiency. Only the electrical power consumption is added under the fraction bar.



Element	Pos. 1 [wt-%]	Pos. 2 [wt-%]	Pos. 3 [wt-%]
O	48.96	48.83	43.95
Mg	06.47	21.42	17.05
Al	30.84	19.98	17.94
Si	02.23	04.67	05.17
Ni	05.75	04.09	14.41
Zn	05.75	01.01	01.47

Figure 2 - REM (left) and EDX (right) of the Ni-based catalyst

3. Results and discussion

3.1. Investigated catalyst

Two different catalysts have been investigated. The first one is a noble metal catalyst with an amount of platinum and rhodium each below 1 wt.-% on the structure of a monolith. Since this catalyst only needs a temperature of about 450°C to start the reforming, this catalyst was used to prove the functionally of each plant component as well as the control and safety system. The measurements of the reforming start-up time have been performed with this catalyst.

To reduce the investment and running cost of a biogas reforming plant, the second tested catalyst was a nickel-based catalyst. This catalyst has a lower production cost but needed to be activated. The composition of the catalyst has been investigated by the project partner IRCE Lyon [3]. The idea was to have a composition of 15 wt.-% of nickel and 0.05 wt.-% rhodium on a support of magnesium spinel ($MgAl_2O_4$) on a SiSiC foam structure. But with the combination of REM and EDX the composition of the coated surface at different positions was investigated. The results are shown in Figure 2. On the left side of the figure, the surface of the catalyst was recorded at a magnification of 500. The measurement of the composition on spot 1 is comparable to the composition measurement of IRCE Lyon and shows a composition of only 5.75 wt.-% Ni instead of the stated 15 wt.-%. No Rhodium was found. So the following investigations have been performed with a pure Nickel catalyst with about 6 wt. % load of Nickel and without the support of any noble metal.

3.2. Activation and start-up procedure

It is important to activate the Nickel catalyst before operation, otherwise no reforming activation can be observed. Therefore a hydrogen flow is required to reduce the oxidized nickel to metallic nickel. The temperature inside the catalyst has to be at least 500°C and then the activation is taking place for at least one hour.

At the BioRobur plant at the TUBAF in Freiberg the standard activation procedure starts with an air flow until the catalyst reaches a maximum temperature of 300°C. At this temperature no deactivation of the catalyst with the oxygen from the air occurs. Also steam tends to deactivate the nickel catalyst at higher temperature. Therefore only a mixture of 75 vol. % nitrogen and 25 vol.-% hydrogen until a catalyst temperature up to 700°C is used for the further activation procedure. The gas flow velocity through the catalyst is kept equal to previous tests to reduce the required amount of nitrogen and hydrogen, which results in 83.0 Nl/min nitrogen and 27.7 Nl/min hydrogen for the Nickel catalyst of a diameter of 260 mm and a height of 250 mm. After reaching the 700°C, the activation procedure is continued for at least two hours.

Even more important than the activation procedure is the start-up sequence. The start-up sequences investigated for the BioRobur plant are partly shown in Figure 3.

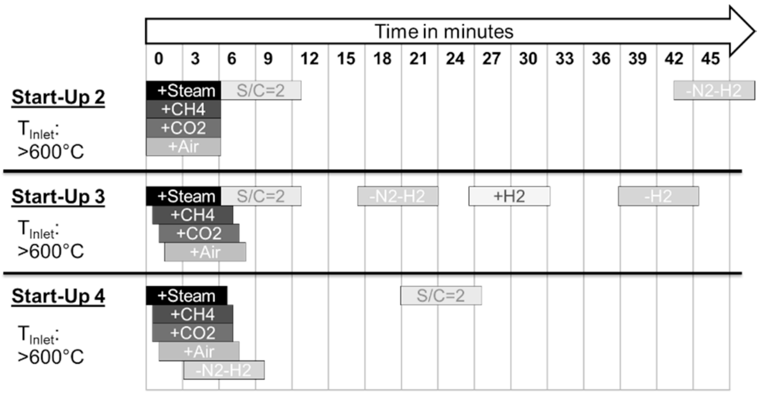


Figure 3 - Most reliable start-up sequences

The depicted start-up sequences are the most reliable ones, which reduce the deactivation during the switch from activation to start-up to a minimum. For example, the start-up sequence 3 starts with steam followed by methane, then carbon dioxide and finally air, always 30 seconds between the start of a new flow. Beginning from minute six, the nominal conditions are set, which are an O/C ratio of 1.1 and an S/C ratio of 2.0. After further ten minutes the activation flow of hydrogen and nitrogen is stopped, to maybe see some changes in the synthetic gas composition. To investigate, if pure hydrogen can result in a higher catalyst activity, the flow of hydrogen is added again.

The final decision of the best start-up sequence is deduced from the performance of the same catalyst after the sequences in terms of cold gas efficiency, methane conversion and hydrogen yield. In Figure 4 the results of the three start-up sequences of Figure 3 are compared to the noble metal catalyst, which is used as a reference since noble metal catalysts do not require an activation. The shown results are the average values of an increasing and a decreasing GHSV ramp. The start-up sequence 2, which add hydrogen and nitrogen for about 45 minutes to the educt flow, results in a very good methane conversion, even higher than the noble metal catalyst. The cold gas efficiency and the hydrogen yield show very good results compared to the two others. These two could also not reach the desired GHSV of 10 000 1/h to produce 50 Nm³/h hydrogen.

3.3. Reforming start-up time

The catalyst requires, besides the activation in terms of a Nickel-based catalyst, a specific temperature to start the reforming of biogas to synthetic gas. If the inlet temperature is too low, no reaction is taking place, since the ignition energy for the partial oxidation is not reached. A high inlet temperature would result in a deactivation of the catalyst trough for example coking or sintering. For the noble metal catalyst the temperature of the educts entering the ATR vessel has to be at least 450°C. For the Nickel-based catalyst the temperature has to be at least 50 K higher.

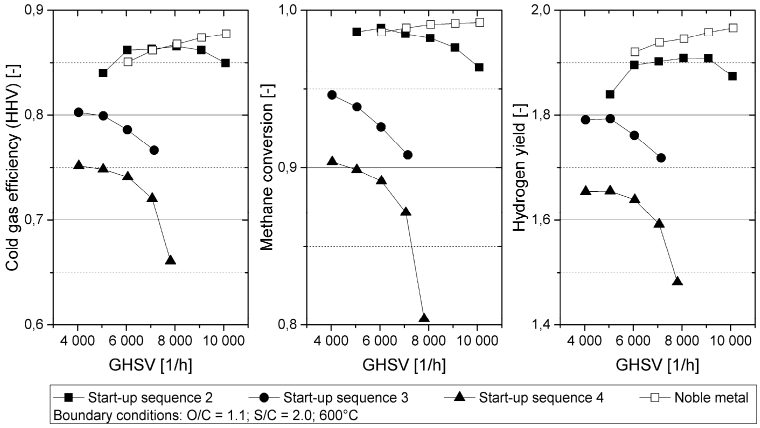


Figure 4 - Results of different start-up sequences

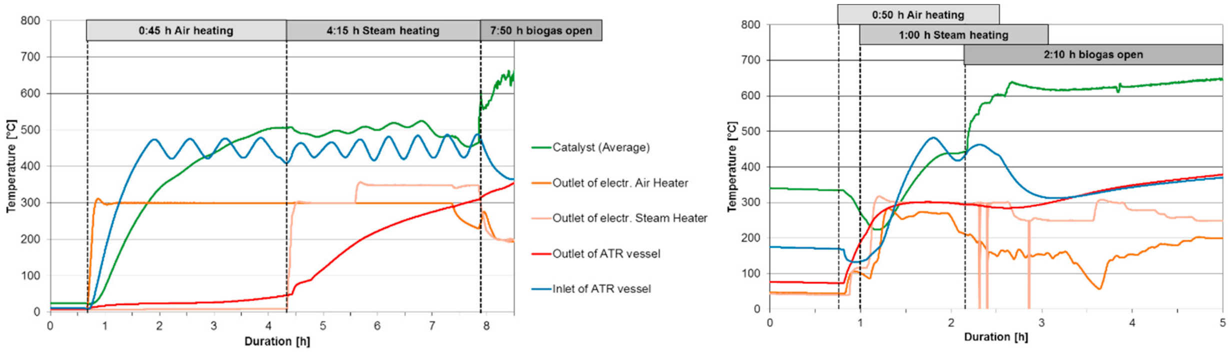


Figure 5 - Reforming start-up time - cold start (left) and warm start (right) for the noble metal catalyst

These inlet temperatures are achieved by electrical heaters. The BioRobur plant at TUBAF in Freiberg has four heaters for the start-up and for conditioning the educt inlet temperature. The first is an air heater with a power of 8.5 kW, the second is a steam heater with 10 kW, the third is the educt heater at the ATR vessel inlet with a power of 14 kW and finally the heater for the ATR vessel walls at the height of the catalyst with a power of 4 kW.

To express the time span between the start of any of the electrical heaters and the first reforming activities of the catalyst, the reforming start-up time is defined. The reforming start-up time does not take into account, that further hydrogen purification steps need time to start as well. Depending on the temperature of the catalyst, the reforming start-up time is divided into cold start and warm start.

A typical reforming start-up is depicted on the left side of Figure 5. The cold start of the noble metal catalyst starts at 0:45 h with the activation of the air heater and the educt heater. The air heater (E-200) reaches the desired temperature of 300°C very fast and is used to heat up the educt piping to avoid condensation of steam. The electrical educt heater (E-700) is used for heating the catalyst and two heat exchangers (H-700 and H-100), which are used for the heat integration and therefore also need to reach a temperature above the condensation temperature of steam. After 3:30 h of air heating, the temperature at the outlet of the ATR vessel and therefore the temperature of the educt heat exchanger (H-700) have the required temperature to add steam to the heating sequence. It is possible to start the reforming process at this time, but since the synthetic biogas is entering the process at a temperature below 20°C and then mixed with air and steam, the steam would condensate. With the resulting reduction of the steam flow, a destruction of the catalyst could be the consequence, since the heat of the POX is increasing the temperature of the catalyst even above the destruction temperature. Additionally further investigations showed, that a temperature drop at the inlet of the ATR vessel of 150 K occurred during the addition of synthetic biogas, even with a starting autothermal reforming reaction. So the heating is continued until the outlet temperature of the ATR vessel and therefore also the temperature of the educt heat exchanger reaches a safe start temperature. This results in a reforming start-up time for a cold start of about 7:00 h. For a Nickel-based catalyst the time would be the same, since the steam heating would be partially replaced by an activation phase.

The warm start of the noble metal catalyst is shown at the right side of Figure 5. The time of air heating is now reduced from 3:30 h to 0:10 h, because the temperature of the components are still above the condensation temperature. So the only scope was to reach a catalyst temperature of 450°C. This was done with the addition of steam for about 1:00 h. The reforming start-up time for a warm start is reduced to about 1:30 h, for a plant stop of about 12:00 h.

After further improvements of the insulation and the piping as well as the increase of the heater temperatures to their maximum allowed temperature (E-102, E-200: 500°C and E-700: 800°C) the reforming start-up time for a cold start is currently 2:35 h and for a warm start 0:40 h.

3.4. Long-term test of the Nickel-based catalyst

The main goal of the full-scale plant was the investigation of the long-term stability of the catalyst, developed by the BioRobur team. Therefore this chapter shows the results of the Nickel-based catalyst on a foam structure.

The long-term test of the catalyst was performed with a coated soot trap installed. The boundary conditions were a space velocity of 4 000 1/h, which is comparable to a 40% load. The O/C ratio was set to 1.1 and the S/C ratio was 2.0. The results in terms of the composition of the synthetic gas without water are plotted in Figure 6 and are measured mostly directly after the catalyst. The plot is a composition of two preliminary tests and a final 20:00 h test. The preliminary tests have been performed at an inlet temperature of 500°C and the 20:00 h test at 650°C. The accumulated test time is 52:00 h and only takes the reforming time of the catalyst into account, so the time for heat-up and activation is not considered.

The first preliminary test on Figure 6 for 1:30 h is after the external preparation of the catalyst, so no deactivation on the whole catalyst is present. The composition of the synthetic gas matches the calculation in terms of thermodynamic equilibrium very well. During the next 1:30 h test, the measuring results for the synthetic gas composition differs, since the catalyst already starts degrading. At the beginning and until 1:00 h the measuring point was the usual one, which is directly after the catalyst. Then the measuring point was switched to downstream of the soot trap, which is a wall flow filter with an iron coating. The amount of methane increases, so the evidence leads to a methanation of the soot trap, since during the tests with the uncoated soot trap no methanation was observed. The measuring point was switched again, this time to upstream of the catalyst. The gas composition shows, that no reforming is taking place inside the piping before the catalyst, even with wall temperatures of about 600°C and a nickel amount of the pipes of 30 to 35%. The final switch back to downstream of the soot trap shows again the methanation. During the 20:00 h test all educt flows were constant, so the shape of the amount of methane at about 40:00 h cannot be explained with fluctuation educt flows. But what is clear is that the increasing amount of methane in the product gas, measured directly after the catalyst, shows the reduction of the catalyst. Even with an increase of the inlet temperature of 150 K for the third test, the amount of hydrogen should be in the range of the first test run in terms of thermodynamic equilibrium.

The hydrogen yield, the methane conversion as well as the cold gas efficiency were calculated with the measured synthetic gas composition, see Figure 6 right side. The methane conversion stays at the high level of 99% to 96%. But the hydrogen yield is dropping from 2.2 to 1.7. The cold gas efficiency starts with 90% at the ASPEN-calculated level for thermodynamic equilibrium. During the 20:00 h test the inlet temperature is 150 K higher and this should result in a cold gas efficiency of about 92%. But the measurements lead to a cold gas efficiency in the range of 70% to 80%, indicating the degradation of the catalyst.

To visualise the position of the partial oxidation, two thermocouples were placed between the layers of the catalyst, one between layer 1 and 2 and the other one between layer 2 and 3, as depicted on the left side of Figure 7. The temperature profile of the 20:00 h test as well as the start-up and partially the shut-down sequence are shown in the diagram. At the bottom of the diagram the hydrogen flow is plotted in Nl/min. The inlet temperature of the ATR vessel (T preheat) starts at 200°C, while the catalyst has a temperature of about 400°C. Both temperatures, of the gas phase (T preheat) as well as of the solid phase (T begin cat), are reaching the desired activation temperature of 850°C, which reverses most of the deactivation phenomena of the Nickel-based catalyst. After 3 h of 20/80 H_2/N_2 flow, the reforming is started. The temperature at the first two layers of the catalyst reaches temperatures of about 1 000°C and indicates the POX layer at this position. After stopping the hydrogen addition to the educt flow, the reduction of the catalyst is visible. After about 14:00 h the temperature between layer 1 and 2 falls below the temperature between layer 2 and 3.

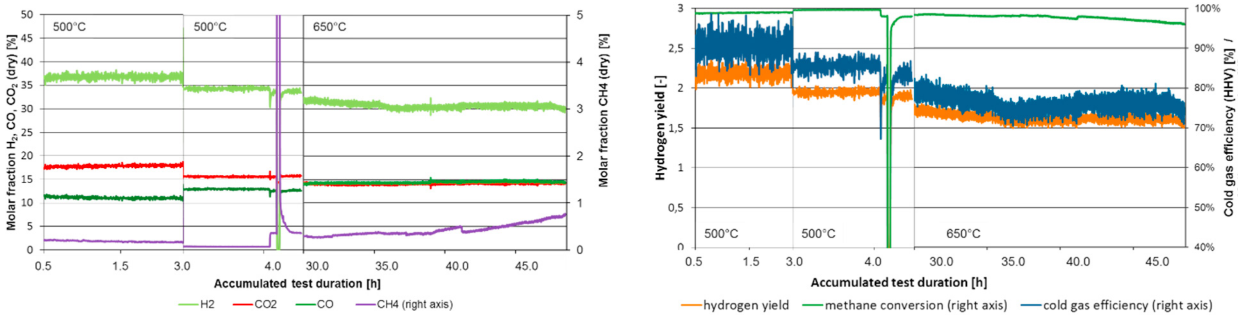


Figure 6 - Synthetic gas composition (left) and analysis (right) of the long-term test of the Ni-based catalyst at GHSV = 4 000 1/h, O/C = 1.1, S/C = 2.0 with two different inlet temperatures

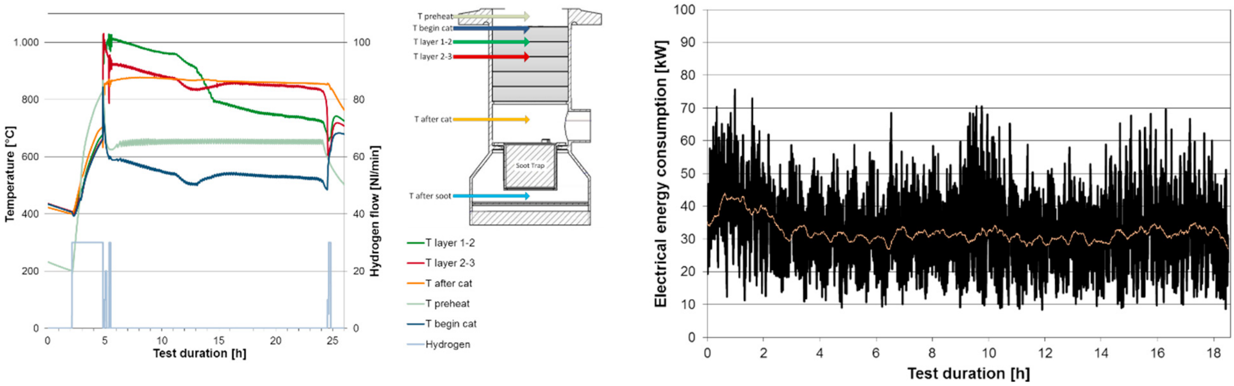


Figure 7 - Temperature profiles (left) and energy consumption (right) of the third long-term test at GHSV of 4 000 1/h, O/C of 1.1, S/C of 2.0 and an inlet temperature of 650°C

This indicates that the oxidation zone is now closer to the temperature measurement between layer 2 and 3 than between layer 1 and 2. While the temperature inside the catalyst is dropping, the inlet flow and inlet temperature as well as the outlet temperature are constant. After 20:00 h of testing, the hydrogen flow is added again at this high temperature. Only nitrogen and hydrogen are used for the following cool-down to room temperature to “freeze” the current condition of the catalyst for further investigations.

3.5. Efficiency of the pilot-plant

The BioRobur pilot-plant at TUBAF is equipped with a power metering for all electrical devices. The main consumers for electrical power are the steam generator, the air compressor as well as the heaters for air, steam and biogas. Minor consumers are the ATR wall heater, the control system, the air dryer, the lightning, the temperature and pressure transmitters and the flow controllers. The monitoring of all these consumers lead to a plot like the right side of Figure 7 for the long-term test of the Nickel-based catalyst. The average value is 35 kW. The maximum required energy is about 70 kW, since the main consumers are controlled by pulse width modulation. With the values and conditions of Figure 7 the average plant efficiency is calculated and it is about 55%.

If the inlet temperature is reduced to 500°C, the produced amount of carbon monoxide as well as of hydrogen is lower compared to 650°C. But the heat integration reaches a level, which allows the deactivation of the electrical educt heater. The pilot-plant has a plant efficiency of about 68% for the design condition (GHSV 10 000 1/h, O/C 1.1, S/C 2.0) and an inlet temperature of 500°C, no matter which catalyst, Nickel-based or noble metal, is used.

4. Conclusion

The decentralized production of hydrogen with a Nickel-catalyst as well as with a noble metal catalyst has been successfully investigated. The cheaper Nickel-catalyst showed promising results during the long-term test. The investigations showed that the problem of the deactivation of the catalysts during the start of the plant are manageable. The omission of a reliable hydrogen source, the activation procedure, the deactivation as well as lower start temperatures are very important advantages of a noble metal catalyst. So the deciding fact will be the economical part.

The pilot-plant showed already a high plant efficiency of 68% at a low level of heat integration. Further investigations showed, that for the best heat integration three additional heat exchangers are required. After that, the results for the plant efficiency will be very close to the cold gas efficiency.

References

[1] Naijjar Y. S. H. Hydrogen safety: The road toward green technology. *Int J Hydrogen Energy* 2013;38:10716–10728.

[2] Higman C, Van der Burgt M. *Gasification*. 2nd ed. Burlington: Gulf Professional Publishing; 2003.

[3] Luneau M, Schuurman Y, Meunier FC, Mirodatos C, Guilhaume N. High-throughput assessment of catalyst stability during autothermal reforming of model biogas. *Catal. Sci. Technol.* 2015;5:4390-4397.