

Catalyst performance in bio- methane (SNG) production

ECN contribution to BRISK WP8 final report

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Abstract

Methanation research at ECN aims at the production of Substitute Natural Gas (SNG), also called bio-methane, from producer gas obtained by gasification of solid biomass. The process involves three different catalysts for conversion of organic sulphur compounds and hydrogenation of unsaturated hydrocarbons, prereforming of aromatic hydrocarbons, and methanation. Test methods are described and representative results are given for catalysts exposed for more than 500 hours to biomass producer gas from a MILENA indirect gasifier after tar removal by an OLGA system. Some changes in performance or composition were observed, but no clear signs of catalyst degradation.

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Summary

Methanation research at ECN aims at the production of Substitute Natural Gas (SNG), also called bio-methane, from producer gas obtained by gasification of solid biomass. The work focuses on identifying and creating conditions which allow the use of commercially available catalysts, while aiming at maximum energy efficiency.

Research is performed with an integral test facility which includes a MILENA indirect gasifier, OLGA tar removal, sulphur removal by ZnO, and four fixed-bed reactors with three different catalysts. The test facility is described in chapter 2.

The use of real producer gas from a gasifier has the drawback that the gas composition and flow may vary over time, which may mask or cause changes in catalyst performance. On the other hand, it results in more realistic conditions and the opportunity to study the effect of trace compounds or contaminants which may not even have been identified yet. Chapter 3 describes the methods applied to evaluate the performance of the catalysts and methods used for post-test analysis.

Chapter 4 presents results obtained during and after a 500-hour test with real producer gas. Some changes in performance or composition were observed, but no clear signs of catalyst degradation.

1

Introduction

The aim of methanation research at ECN is to produce methane from biomass by gasification, gas cleaning and conversion to Substitute Natural Gas (SNG), i.e. gas with similar same properties as natural gas. The work focuses on identifying and creating conditions which allow the use of commercially available catalysts, while aiming at maximum energy efficiency.

ECN interest in SNG production from biomass dates back to before 2000 [1]. In 2006 the first integral tests were performed with a system consisting of a biomass gasifier, gas cleaning and a number of reactors with catalysts [2]. The first test lasted less than an hour, in which a nickel methanation catalyst was completely deactivated by carbon deposition. Catalyst activity could easily be monitored by analysis of the gas composition upstream and downstream the reactor. When conditions were improved, catalyst activity could be maintained for several days. During that time, the gas composition did not change, but the temperatures measured along the reactor clearly showed a reaction front moving downstream along the catalyst bed. Eventually, carbon deposition led to increasing flow resistance, observable by the pressure drop over a reactor.

Since then, gas cleaning has been improved and operating conditions have been optimized. Better gas cleaning requires more sensitive analysis techniques to detect and identify remaining traces of gas components which affect the performance of catalysts. Part of this work was performed within BRISK WP7 and is reported in deliverables 7.6 and 7.7 of that task (www.briskeu.com).

Within the Dutch national research program EDGaR (www.edgar-program.com) new test equipment was built for methanation research. In October 2014 an integral test was performed in which the methanation reactors operated for more than 500 hours [3, 4]. Here, the main features of the test set-up are summarized and results of catalyst testing are discussed.

2

Test set-up

Methanation research at ECN uses commercially available catalysts and cleaned gas from a biomass gasifier. The use of real producer gas from a gasifier has the drawback that the gas composition and flow may vary over time, which may mask or cause changes in catalyst performance. On the other hand, it results in more realistic conditions and the opportunity to study the effect of trace compounds or contaminants. These may be absent from a synthetic gas mixture because it can be difficult to include them, or because they have not even been identified yet. Post-test analysis can help identify the cause of changes in catalyst performance. Within BRISK WP8, project partner CERTH has assisted ECN in the analysis of fresh and used catalysts.

Figure 1 shows the layout of the ECN test facility for SNG production. The gasifier is a 25 kW_{th} indirect gasifier of ECN design, referred to as MILENA. About 20% of the producer gas flow is led to the OLGA tar removal system. The equipment downstream OLGA was built with financial support from the EDGaR program. First, the gas is cooled to about 5°C to remove moisture. In principle, OLGA should remove tar so effectively, that no tar would condense on cooling. However, due to lack of space, the lab-scale system does not realize the potential and some naphthalene condenses in the cooler. The filter downstream the cooler removes tar aerosols which escape from OLGA and are responsible for the traces of heavy tar compounds detected downstream OLGA.¹

The compressor increases the gas pressure to about 6 bar for the fixed-bed reactors of the ESME test rig.² The gas flow is determined mainly by the frequency applied to the motor drive, the back pressure of the system and the compressor inlet pressure. The latter is the most difficult one to control, as it is influenced by pressure drop over the hot gas filter upstream OLGA and the aerosol filter upstream the compressor. These filters have to be cleaned or replaced by fresh ones once or twice a day. As a result, the gas flow is not constant during long test runs but varies by about 10%.

¹ Larger scale OLGA systems use an Electrostatic Precipitator (ESP) to remove tar aerosols.

² ESME = Ecn System for MEthanation.

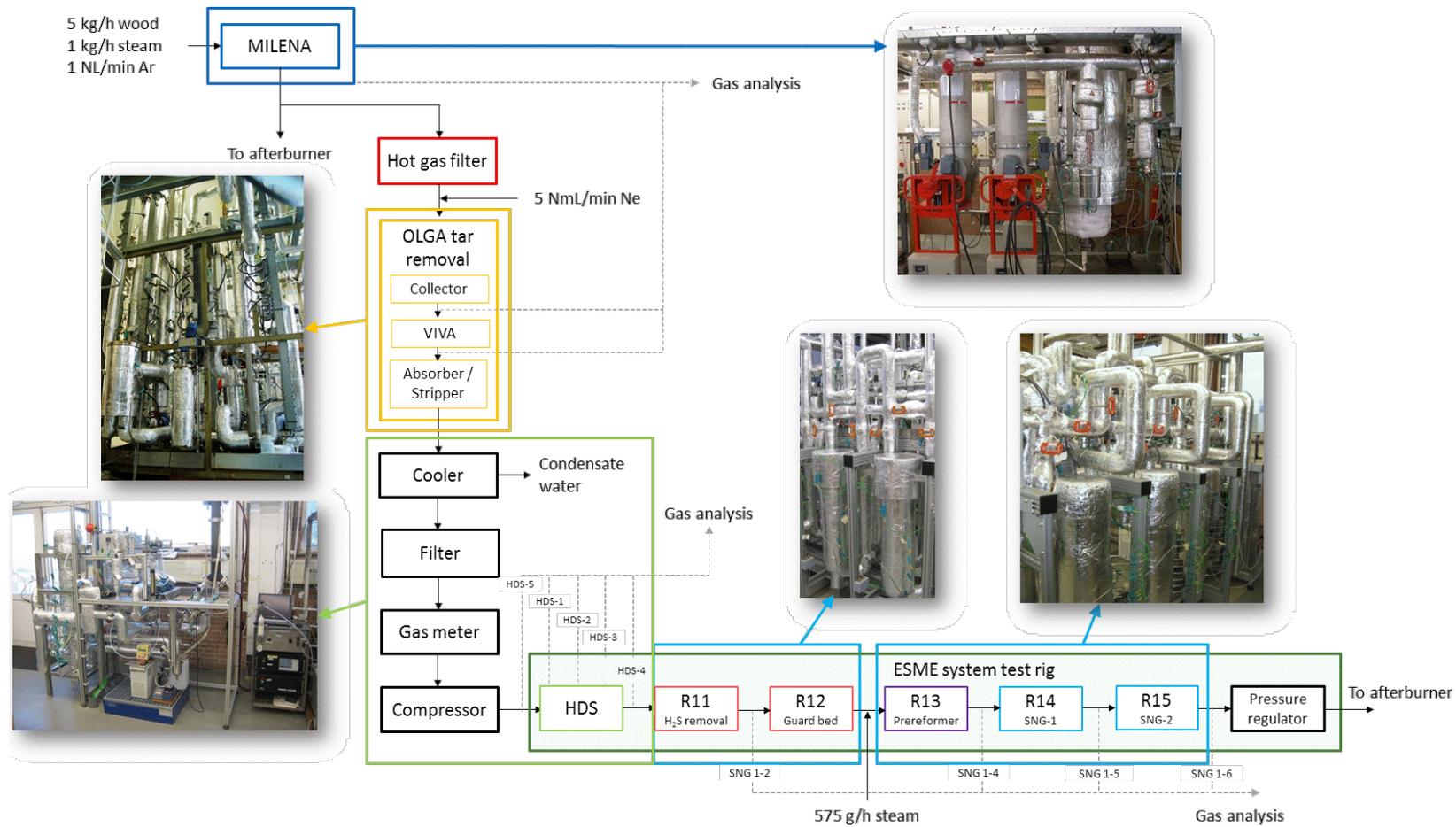


Figure 1 Lay-out of lab-scale SNG test facility at ECN.

The total gas flow to the compressor is measured with a gas meter. The instantaneous gas flow is determined by adding a small amount of neon to the gas upstream OLGA and measuring the resulting neon concentration. As the gas volume changes due to reactions promoted by the catalysts, the measured neon concentrations depend not only on the gas flow from OLGA but also on the gas sampling position.

The HDS reactor contains 2 L CoMoO catalyst which converts organic sulphur compounds (mainly thiophene, i.e. C₄H₄S) and hydrogenizes unsaturated hydrocarbons, e.g. C₂H₄ + H₂ => C₂H₆. Reactor R11 contains 2 L ZnO adsorbent which captures COS and H₂S. A guard bed (R12) is available to remove remaining contaminants, but was not used in this duration test.

The last three reactors each contain about 1 litre nickel catalyst. Steam is added upstream the prereformer R13 to allow conversion of aromatic compounds and produce H₂ by water gas shift. All three reactors R13, R14 and R15 produce methane. As the operating temperature decreases from R13 to R15, the CH₄ concentration increases and the H₂ concentration decreases. Gas produced by the test facility would still need further H₂ conversion and upgrading (i.e. CO₂ and H₂O removal, conversion of traces of CO) to meet SNG specifications for grid injection.

As indicated in Figure 1, the gas composition can be analysed downstream each reactor. Additional sampling points along the catalyst bed are available at the HDS reactor. Three sets of gas monitors and microGC's have been used for gas analysis: one set for MILENA and OLGA, one for the HDS reactor and one for the prereformer and methanation reactors. In addition, GC-FPD has been used to semi-offline measure sulphur compounds and GC-FID for hydrocarbons.

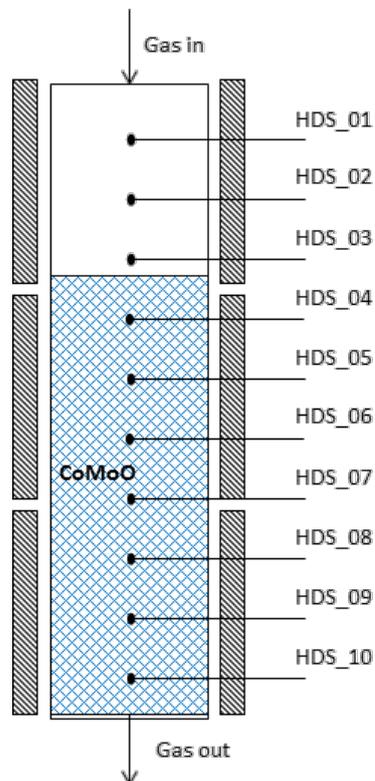


Figure 2 *Schematic representation of HDS reactor with position of thermocouples for temperature measurements and heating elements with respect to catalyst bed.*

All reactors allow temperature measurement along the axis of the adsorbent or catalyst bed (e.g. see Figure 2). In order to limit heat loss the reactors are insulated and heated externally. The set point temperatures of the heating elements were chosen to reach the intended gas entry temperatures and to maintain a constant temperature in the second half of the catalyst beds where no heat production is expected. The pressure drop over each reactor can be derived from pressure measurements in between reactors.

3

Test methods

This chapter describes the methods applied to evaluate the performance of three different catalysts of the ESME process and methods used for post-test analysis.

HDS catalyst

The main HDS performance parameter is the efficiency of thiophene conversion. This requires reliable measurement of sub-ppm concentrations. Extreme care is required to prevent contamination when equipment is also used for analysis of gas with higher thiophene content. The HDS reactor at ECN allows gas sampling at three positions along the reactor to monitor how the reaction proceeds. These positions correspond to about 10%, 40% and 100% of the catalytic bed. BRISK research on the analysis of organic sulphur compounds (WP7.3) allowed further optimization of operating conditions for the HDS catalyst.

HDS catalyst performance can also be monitored by the efficiency of C_2H_4 hydrogenation to C_2H_6 . MILENA producer gas contains 3 to 4 vol% C_2H_4 , which can easily be measured with a microGC. Thiophene and C_2H_4 conversion appear to be simultaneous processes, i.e. they seem to require identical conditions to reach a certain conversion level. The HDS catalyst also promotes water gas shift if the gas contains sufficient H_2O . However, as the H_2/CO ratio of the MILENA producer gas can also vary due to e.g. changing catalytic activity of bed material, the H_2/CO ratio cannot be used to monitor HDS catalyst performance.

Hydrogenation and water gas shift reactions produce heat and increase the gas temperature. Hence, reactor temperature is another parameter to monitor catalyst performance. As the gas temperature increase is sensitive to changes in the producer gas composition, it is not an easy parameter for assessment of catalyst activity. However, the reactions produce a jump in temperature at the reaction front. Although steepness and position of the jump may vary with gas flow, movement of the reaction front downstream the reactor usually is a clear indication of catalyst deactivation.

Prereformer catalyst (R13)

In case of the prereformer catalyst, the main problem is carbon formation from aromatic compounds.³ The choice of catalyst, temperature and amount of steam were the main parameters considered previously. Carbon deposition can reduce the available area for gas flow to the extent that pressure drop over the reactor increases notably.

Reactions in the prereformer change the gas composition considerably: benzene, toluene and C₂H₆ are completely converted, CO decreases and CH₄, H₂ and CO₂ increase. Gas analysis would allow to monitor changes in catalyst performance, if gas sampling along the reactor were available. At ECN, measurements can be performed downstream the reactor only. This limits the usefulness of gas analysis as a tool to follow catalyst deactivation. The break-through of benzene, toluene and C₂H₆ are clear indications of insufficient remaining catalyst activity. In principle, gas analysis combined with flow measurement can be used to determine the carbon balance over the reactor. However, it is difficult to reach the required accuracy.⁴

Although reforming of benzene and toluene is endothermic, methanation and other reactions produce more than enough heat to increase the gas temperature considerably. Again, the gas temperature is not an easy parameter for assessment of catalyst activity, because of its sensitivity to the inlet gas composition, flow and pressure. However, movement of the reaction front downstream the reactor would be a clear indication of catalyst deactivation.

Methanation catalysts (R14 and R15)

The prereformer acts as effective adsorbent for most, if not all, contaminants. Hence, changes in performance of the methanation catalysts can be attributed to operating conditions or the catalyst itself. As the prereformer tends to deliver a more constant gas composition than the gasifier, gas analysis downstream a reactor provides little information on changes in the catalyst activity until deactivation reaches deep into the reactor. Again, reactions produce heat and a reaction front can be defined and monitored. In the last reactor (R15), the temperature increase is relatively small. The reaction front is less well defined, but still good enough to monitor catalyst activity.

Post-test analysis of catalysts

Test methods described above are useful to observe changes in catalyst activity during testing. However, the absence of noticeable change within a given test does not prove that activity can be maintained over a practical length of time for the application envisaged, which usually means several years. Post-test analysis and comparison of properties before and after a test can provide information needed to extrapolate test results to relevant time frames. Typical properties to be considered are the available surface area, surface structure and composition. Some examples will be given of analyses performed by ECN and CERTH on samples provided by ECN.

³ The prereformer can also be deactivated by carbon formation from unsaturated hydrocarbons, but not if an upstream HDS catalyst has removed these compounds by hydrogenation.

⁴ At 1% accuracy and GHSV = 1000 h⁻¹, a carbon loss of 3 kg/hr per m³ catalyst volume could go unnoticed. At that rate, the reactor volume would be filled with carbon in 100 to 200 hours. Pressure drop would then be a more easily checked variable.

4

Test results

Results are presented of the performance and post-test analysis of catalysts used in a duration test which was performed in October 2014 with the configuration described in chapter 2. The test was interrupted several times by failures in part of the system (see Figure 3). Most of the time was lost for regular maintenance of the afterburner for surplus MILENA gas. All the catalytic reactors were in operation for more than 500 hours in total, with 100% availability over the time that producer gas was available.

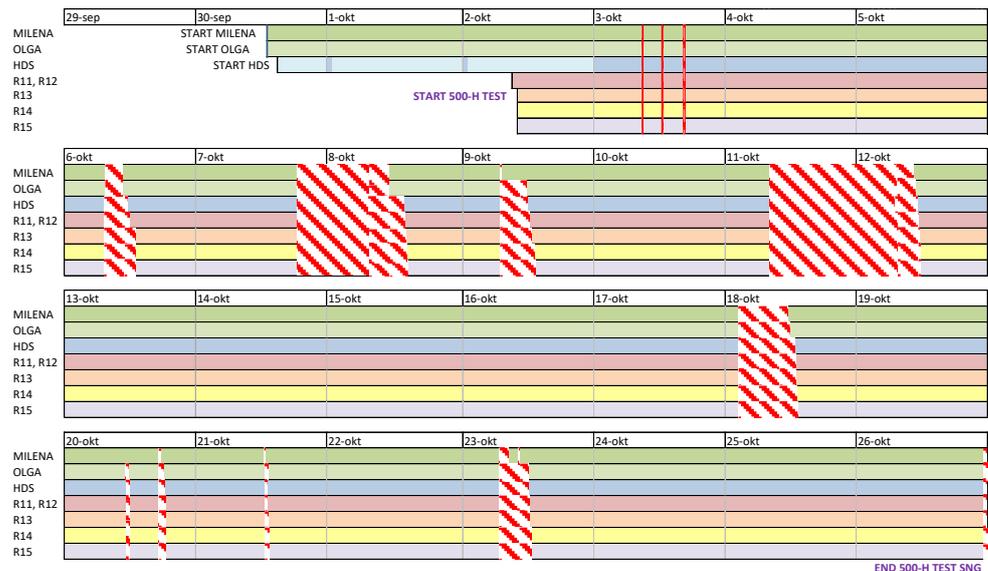


Figure 3 Up and down time of components of the SNG test facility during 500 h duration test.

HDS catalyst

Initially, the HDS catalyst removed all sulphur compounds from the gas. This had been observed before and is caused by sulphidation of the catalyst, i.e. (partial) replacement of oxygen in CoMoO_x by sulphur. After 200 hours H_2S and COS start to break through and after 300 hours no more sulphur is retained by the catalyst.

The performance of the HDS catalyst was monitored by regular measurement of the thiophene concentration at the HDS entry, after about 10% and 40% of the reactor length and at the reactor exit. No thiophene was detected at the reactor exit. Figure 4 and Figure 5 show results for thiophene and $C_2H_4/(C_2H_2+C_2H_4+C_2H_6)$ at the other positions.

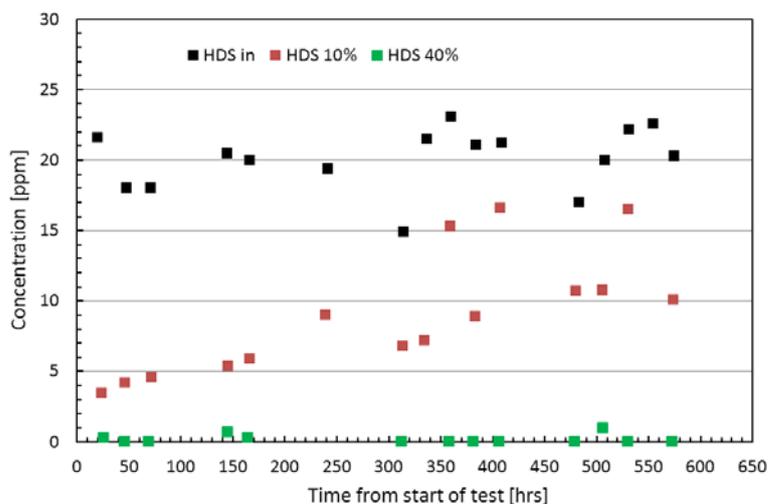


Figure 4 Thiophene concentration at HDS reactor entry and after 10% and 40% of the catalyst bed.

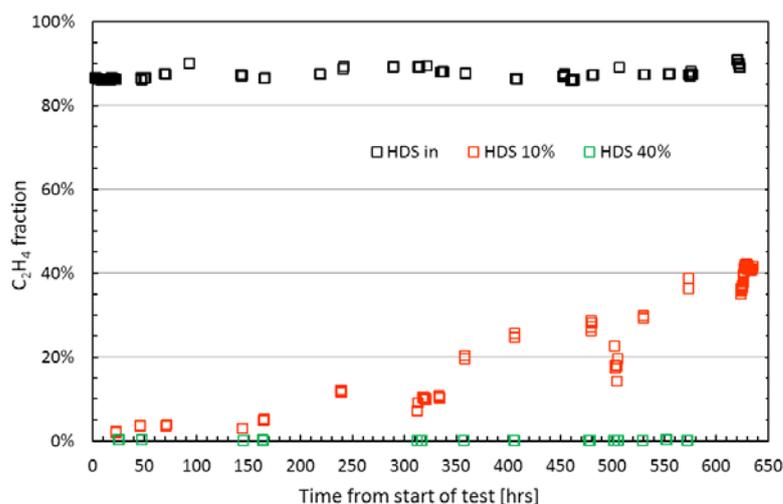


Figure 5 Fraction of C_2H_4 in total C_2H_x at HDS reactor entry and after 10% and 40% of the catalyst bed.

The performance of the top part of the catalyst bed seems to deteriorate over the course of the test, both for thiophene conversion and for C_2H_4 hydrogenation. There is no obvious correlation with the sulphidation of the catalyst. However, afterwards it was noted that the top of the catalyst bed had moved down a little, effectively bringing the first gas sampling point closer to the reactor inlet. Hence, the effects observed may reflect a change in the actual catalyst volume rather than a change in catalyst activity.⁵

⁵ If the total bed shrinks by 3%, the top gas sampling point moves from a nominal 10% to 7% position. As the top surface of the catalyst bed is relatively cold, the first few percent of the catalyst bed hardly contribute. Hence, the sampling point may actually move from e.g. 8% to 5%.

SEM EDX analysis of a catalyst sample taken from the top of the HDS reactor showed that the active material had changed from CoMoO_x to (approximately) CoMoSO_{x-1} .

Prereformer catalyst

Figure 6 shows the pressure and pressure drop over the three reactors with nickel catalysts, i.e. prereformer and two methanation reactors, over the course of the duration test. Clearly there is no change in pressure drop which would point at significant carbon deposition.

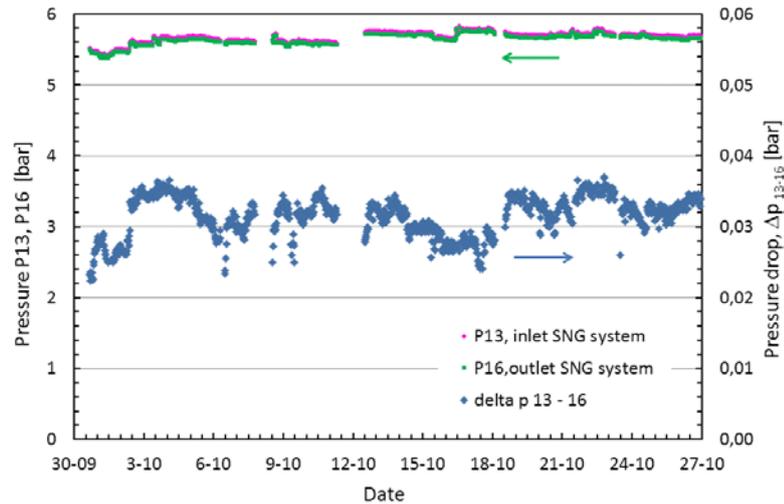


Figure 6 *Pressure upstream prereformer (P13), downstream methanation reactors (P16) and pressure drop over prereformer and methanation reactors during duration test.*

Figure 7 shows the temperature increase in the prereformer with respect to the gas temperature measured at position 3, just above the catalyst bed. At the top of the catalyst bed (T4) and from about halfway (T7), the temperature increase remains about stable. At position 5, which is near the centre of the heat producing region, there are periods of gradual cooling which could point at loss of activity. However, after interruptions the temperature increases again. Either activity is restored or the observed effect is caused by the external heating, which switches on if the reactor is not operating and switches off again when sufficient heat is produced by reactions.

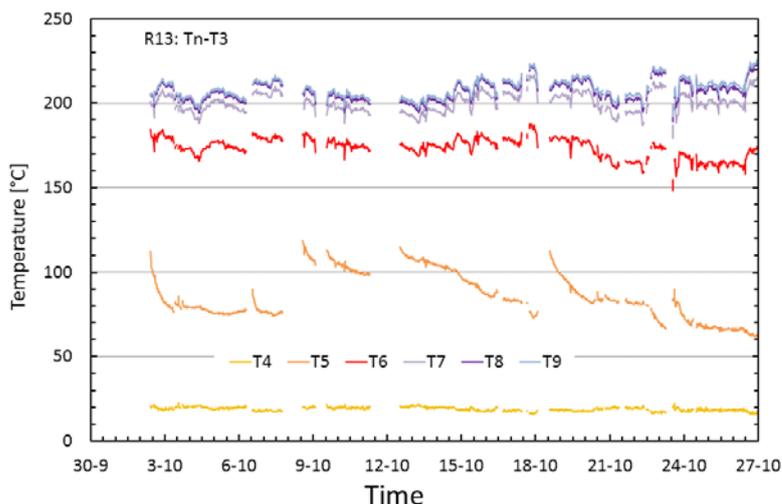


Figure 7 Temperature increase along the axis of the prereformer reactor during duration test.

SEM EDX analysis showed that used catalyst contained some carbon, but actually less than fresh catalyst. A tiny amount of sulphur was detected at the surface, which may indicate there is still some organic sulphur left downstream the HDS reactor.

Temperature programmed reduction (TPR) showed two nickel reduction peaks at about 250°C and 450°C in fresh catalyst. Used catalyst showed only a high temperature peak. Apparently, fresh catalyst contains some nickel particles which are more easily reduced, but which disappear by sintering or other causes. Figure 8 shows results of temperature programmed oxidation (TPO) by CERTH for samples of the same catalyst from earlier experiments. Used catalyst samples (R13-M and R13-B) show two oxidation peaks, whereas the fresh catalyst sample (R13-V) shows only one.

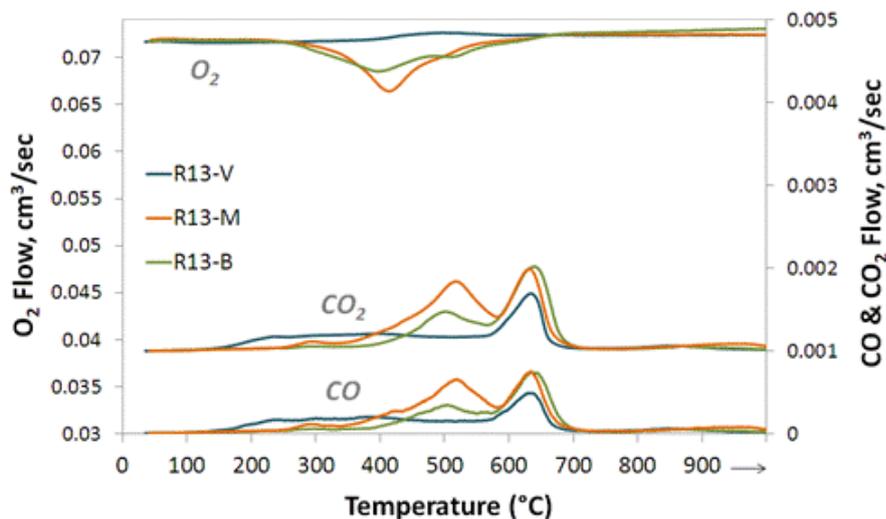


Figure 8 Temperature programmed oxidation of fresh (V) and spent catalyst from the top (B) and middle (M) of the prereformer catalyst bed. Work performed by CERTH.

Results of SEM EDX carbon analysis, TPR and TPO are discussed here to show their use in catalyst evaluation. However, the results shown may not be representative for changes due to catalyst use. Instead, the results might just show that different

treatments have been applied to make the catalyst safe for handling in air. Fresh catalyst was taken from a batch as supplied. Used catalyst has first been reduced with H₂, then exposed to producer gas, and finally oxidized with air. During oxidation, the reactor temperature was kept below 200°C by N₂ dilution. The air/N₂ ratio was increased when the temperatures indicated that the oxidation rate decreased.

Methanation catalyst

As expected, the methanation catalysts showed stable behaviour. The temperature profiles showed small changes (see e.g. Figure 9) but no indication of catalyst degradation.

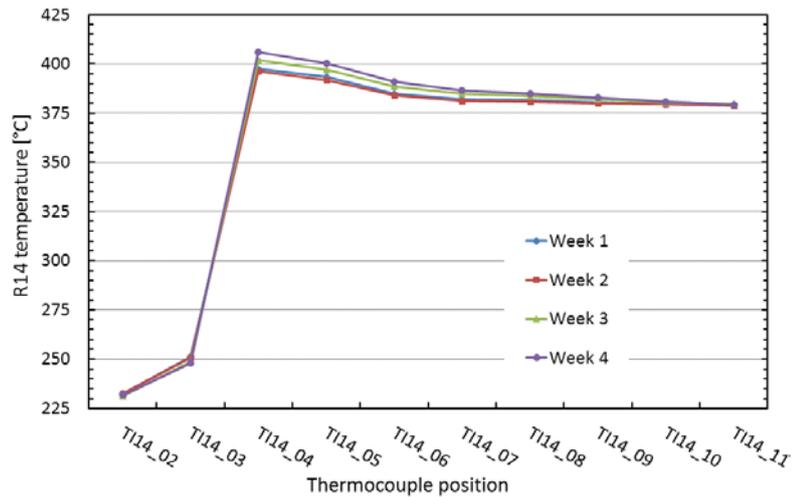


Figure 9 *Temperature profile of methanation reactor R14 in duration test.*

SEM EDX analysis shows that both fresh and used catalyst contain a considerable amount of carbon. No sulphur or other contaminants are detected on used catalyst. TPR shows that nickel in used samples is more easily reduced. TPO (by CETH) shows more O₂ consumption by Ni in used catalyst than in fresh catalyst. Both TPR and TPO indicate that methanation catalyst as supplied has undergone more harsh oxidation treatment than applied to used catalyst by ECN.

TPR also shows that the amount of carbon in fresh and used samples may be similar, but their reaction with H₂ is not. Only used samples produce CH₄. Apparently, carbon in fresh catalyst is a residue of the production process, while in used catalyst it is deposited close to active nickel particles. Carbon in used catalyst reacts with H₂ at the operating temperature of methanation catalyst.

5

Conclusion

Catalyst research with producer gas from a biomass gasifier is discussed. Test methods are explained and illustrated with examples from a 500 hr test performed in October 2014 with a system consisting of a biomass gasifier, tar removal, gas cleaning and reactors with three different types of catalyst. Part of the analysis methods were developed or optimized in BRISK WP7. CERTH contributed to the post-test analysis in BRISK WP8. Some changes in performance or composition were observed, but no clear signs of catalyst degradation.



References

- [1] Mozaffarian, M.; Bracht, M.; Uil, H. den; Woude, R.R. van der: *Hydrogen conversion in substitute natural gas by biomass hydrogasification*. Report ECN-RX--99-016 (1999). Contribution to the 4th International Conference on New Energy Systems & Conversions (NESC '99), 27-30 June 1999, Osaka, Japan.
- [2] Boerrigter, H.; Zwart, R.W.R.; Deurwaarder, E.P.; Meijden, C.M. van der; Paasen, S.V.B. van: *Production of Synthetic Natural Gas (SNG) from biomass; development and operation of an integrated bio-SNG system*. Report ECN-E--06-018 (2006).
- [3] Rabou, L.P.L.M.; Aranda Almansa, G.: *500 hours producing bio-SNG from MILENA gasification using the ESME system*. Report ECN-E--15-008 (2015).
- [4] Aranda Almansa, G.; Rabou, L.P.L.M.; Meijden, C.M. van der; Drift, A. van der: *ECN System for MEthanaion (ESME)*. Report ECN-L--15-044 (2015). Contribution to the 23rd European Biomass Conference and Exhibition, 1-4 June 2015, Vienna, Austria.

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