GasHUB final report

TEBE116178

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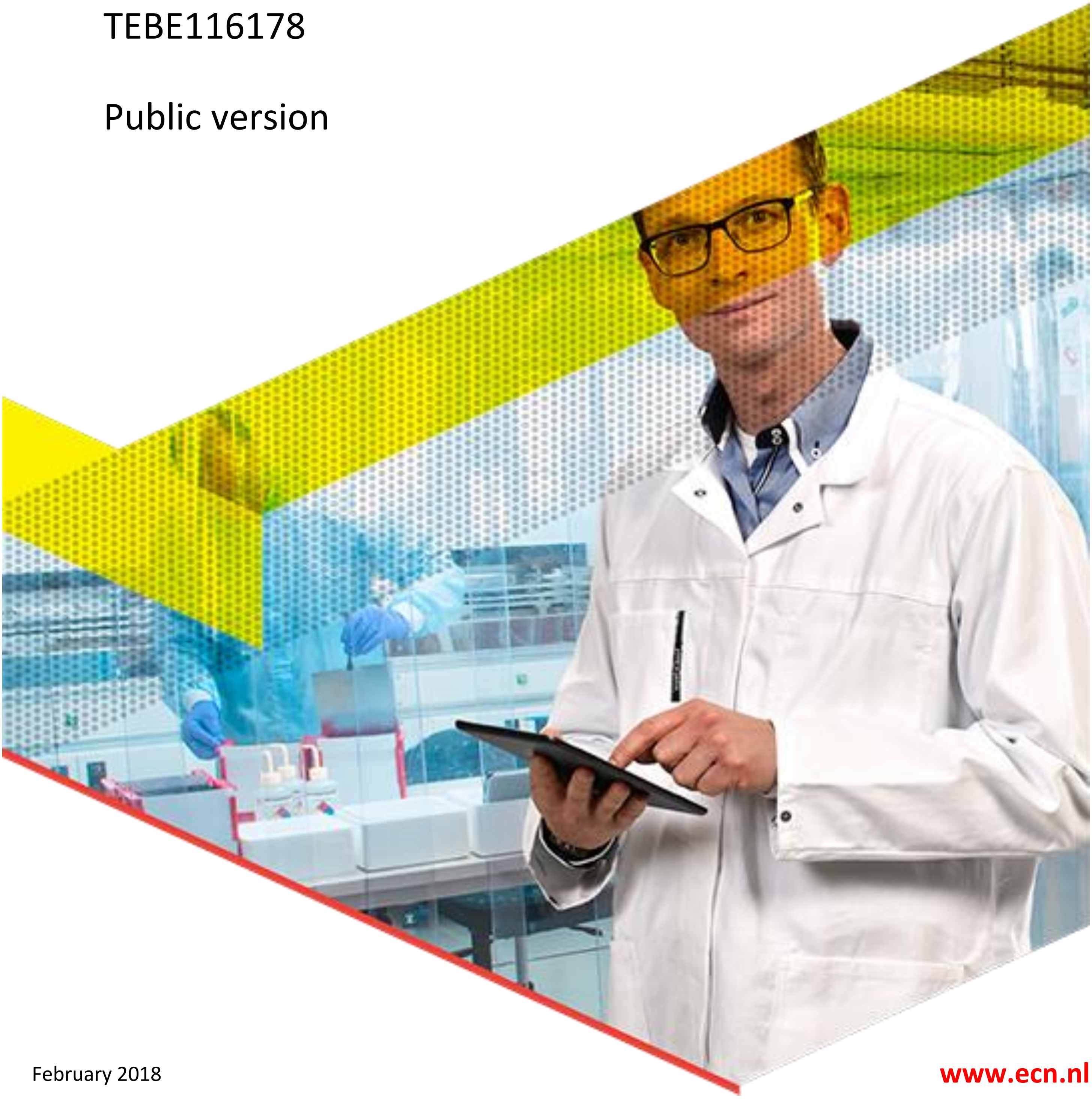

February 2018

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GasHUB progress report

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Abstract

The GasHUB project (reference TEBE 116178) focuses on the testing and optimization of sorbents and catalysts for the development of a robust, flexible gas upgrading train for the conversion of biomass (via gasification) into a range of energy carriers (such as biofuels, green gas and hydrogen) and chemicals. The gas upgrading includes the conversion and removal of sulphur contaminants and the conversion of higher hydrocarbons into syngas. All in all, the tests performed have resulted in extensive knowledge gained on the performance of sorbents and catalysts, in terms of activation procedures, window of operating conditions, long-term performance, and effect of the type of gasification feedstock.

The first exploratory short tests performed within WP2 revealed proper performance of sorbents and catalysts. The tested ZnO materials can remove COS below detection limits, and also largely H_2S. Overall good and stable performance of the catalysts (i.e. practically complete conversion of organic S compounds in the HDS, removal of H_2S and COS in the HDS catalyst, and aromatics conversion in the pre-reformer) was observed during the first short experiment with the whole ESME train.

Complementary TPR and activity tests were carried out within WP2 to shed more light on activation procedure and window of operating conditions, relevant information in view of shutdown/re-start procedures at the AMBIGO plant. The activity tests showed that the pre-reformer catalyst and methanation catalyst start to become active (in terms of methane production, CO conversion, and CO_2 production) at temperatures above the onset temperature. Slight hysteresis temperature effects were observed for the pre-reformer catalyst, whereas stronger hysteresis effects were observed in the methanation catalyst. Steam/carbon (S/C) values above 0.5 mol/mol (equivalent to > 40 vol.% water in the inlet gas) can be preliminarily considered as an acceptable operating region for both catalysts where a trade-off between large methanation and WGS activity, and (low) carbon formation is reached.

The knowledge gained within WP2 resulted in the selection of the final configuration (sorbents and catalysts) for the final duration test of WP3. The objective was to demonstrate the long-term performance of the selected materials under relevant gasification conditions in view of the operation of the AMBIGO plant. The total duration test (whole ESME system on stream for 222 hours), was split in 2 periods (94 hours in December 2017 and 128 hours in January 2018), with overall availability above 90%. All in all, stable operating conditions were achieved in the gasifier, the tar removal unit and the methanation train throughout the endurance experiments. Total conversion of CO was observed during test 2 after the second methanation reactor. The raw bio-SNG gas at the outlet of the second methanation reactor contained approximately 40 vol.% CH_4, 3 vol.% H_2 and ~ 50 vol.% CO_2. The HDS reactor showed all in all satisfactory operation, with complete conversion of organic sulphur compounds and of unsaturated hydrocarbons. The ZnO bed was able to reduce the H_2S concentration down to the accuracy limits of the current detection equipment, which can be considered as an acceptable value for the AMBIGO plant. In the HDS catalyst, thiophene derivatives and mercaptans derivatives were observed to be largely converted in the top part of the HDS catalyst bed, the rest being converted below detection limits in the rest

of the bed. No signs of deactivation due to carbon deposition were observed in the pre-reforming and methanation reactors throughout the test.

The research work was complemented with a business case roadmap for the development of the GasHUB gas upgrading train. A number of routes have been thus selected and described, as well as background considerations relevant to the deployment of bio-based routes in general. The analysis indicates that the bio-SNG route is at this stage the furthest advanced one. For each route (green gas, hydrogen, chemicals or fuels), the inclusion of economics or LCA as selection factors will influence the ranking. Complementary and in parallel with the progress in milestones of each route, the drivers and risks need to be constantly monitored. Relevant factors identified in the analysis include the availability of biomass feedstock, the process scale, and process flexibility.

The knowledge gained within the GasHUB project on the sorbents and catalysts (activation procedure, window of operating conditions, long-term performance) will be firstly applied in the AMBIGO project.

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1. Project overview

1.1 Project background

The GasHUB project ("Gasreinigingsmodule voor Hoogwaardige Utilisatie van Biomassa", reference TEBE 116178, 5.4689) is a 17-month project started in October 2016 and finalized in February 2018[1]. The project focuses on the testing and optimization of sorbents and catalysts for the development of a robust, flexible gas upgrading train for the conversion of biomass (via gasification) into a range of energy carriers (such as biofuels, green gas and hydrogen) and chemicals. The gas upgrading includes the conversion and removal of sulphur contaminants and the conversion of higher hydrocarbons into syngas. Figure 1 plots the schematic value chain considered in the project. Within this scheme, GasHUB focuses on the gas cleaning section, flexible in terms of biomass feedstock and application.

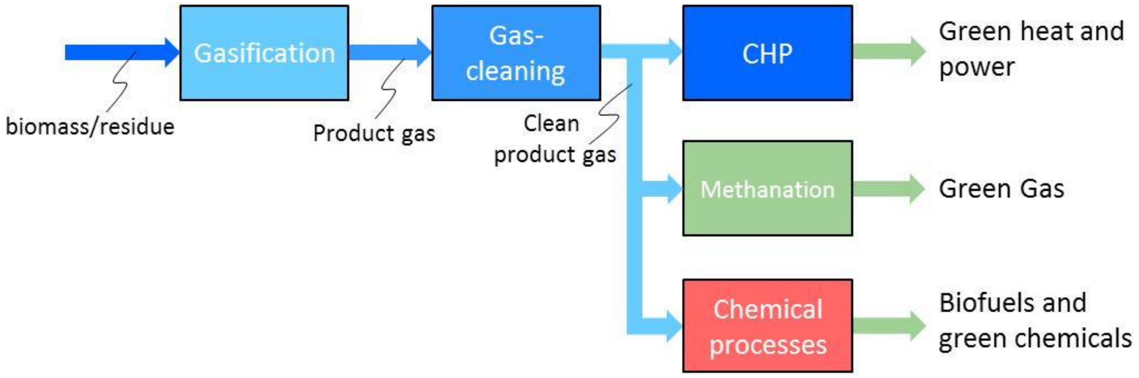

Figure 1. Value chain considered in GasHUB project: gasification + gas cleaning/upgrading (focus of GasHUB) + application of the upgraded gas.

The knowledge gained within the GasHUB project on the sorbents and catalysts (activation procedure, window of operating conditions, long-term performance) will be firstly applied in the AMBIGO project, a bio-SNG plant based on biomass gasification which will be located in Alkmaar[2].

The project consortium is composed of 2 partners: Albemarle (supplier of sorbents and catalysts), and ECN (testing of materials under real gasification conditions). For Albemarle, this project is relevant for the application of their products in the deployment of the bio-based economy; ECN

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[1] After the 2-month extension granted in November 2017.

[2] https://www.ambigo.nl/en/

pursues the broadening of applications of gasification technology into transport biofuels and chemicals through the development of a flexible gas upgrading unit. In the end, the results of the project will contribute to the speed-up of the implementation of large-scale production of green gas, transport fuels and chemicals, thus contributing to the realization of the bio-based economy, with the main advantage of large potential reduction of CO_2 emissions.

With this background, the present report summarizes the progress of the project in the period October 2016-January 2018. This report is structured as follows: after the overview of the project status in Section 1, Sections 2-4 show the most relevant results obtained so far within the project. Section 2 describes the results of the short tests carried out within WP2; Section 3 contains the main findings of the micro-flow experiments performed in WP2 to gain more insight about the reduction and activity of the pre-reformer and methanation catalysts; finally, Section 4 contains the most significant results from the final duration tests carried out within WP3.

1.2 Project overview and overall status

Table 1 summarizes the status of the work packages in which the project is structured. The core of the project, composed by WP2 (catalyst testing) and WP3 (final duration tests), and WP4 (business case and roadmap) has been completed in time. The results obtained in the different tests have been reported in a number of deliverables (see Section 1.3), and are expected to be disseminated in international conferences (REGATEC 2018).

Table 1. Overview of work packages of GasHUB project, and status of work.

WP	Name WP	Status
1	Project management	Completed
2	Catalyst testing	Completed
3	Duration testing	Completed
4	Business case development	Completed

As for project management, in November 2017 a 2-month extension to the project was granted by RVO, thus the termination of the project was extended to 28/02/2018.

1.3 Status of deliverables

D1.1 and D1.2 (public and confidential end reports): present report.
D1.3: Conference contributions:

- B.J. Vreugdenhil. Gasreinigingsmodule voor Hoogwaardige Utilisatie van Biomassa “GasHUB”. TKI dag, Geertruidenberg, 8th March 2017.
- G. Aranda Almansa, B.J. Vreugdenhil, L.P.L.M. Rabou.Bio-SNG production from biomass gasification - duration tests with MILENA/ OLGA/ ESME for selection of catalysts and sorbents. Abstract accepted as poster contribution at REGATEC 2018 (Tolouse, 2-4 May 2018)

D2.1:

- L.P.L.M. Rabou. Verkennende test ZnO voor AMBIGO. ECN-BEE-2016-164 (2016)
- L.P.L.M. Rabou. HDS test week 51, ECN-BEE-2017-010.
- L.P.L.M. Rabou. GasHUB test week 2, project 5.4689.02.01. ECN-BEE-2017-014 (2017)

- G. Aranda Almansa. GasHUB – Measurement report of pre-reformer test, February 2017. ECN-BEE-2017-022 (2017)
- G. Aranda Almansa, G. Elzinga, O. Pirgon-Galin. GasHUB – Results of TPR and activity tests of pre-reforming and methanation catalysts. ECN-BEE-2017-090 (2017)

D3.1:

G. Aranda Almansa. GasHUB – results of duration tests (2018). ECN-X—18-024.

D4.1:

L. Boot, P. Schreuder. Roadmap for the development of GasHUB concept.

1.4 Internal communication

The progress of the project was discussed in a number of meetings, summarized in the table below:

Date	Venue	Type of meeting	Participants
26-01-2017	ECN, Petten	Kick-off meeting	ECN, Albemarle
13-10-2017	Albemarle, Amsterdam	Update meeting	ECN, Albemarle
07-02-2018	Albemarle, Amsterdam	Update meeting	ECN, Albemarle

1.5 Structure of this report

This document contains the main results obtained within the project. The report is divided in a number of chapters following a logic structure of WPs. Section 2 presents the results of the short tests of sorbents and catalysts performed within WP2. Section 3 reports the results of complementary microflow testing applied to the pre-reformer and methanation catalysts in WP2. Section 4 summarizes the results of the final duration tests in WP3. Section 5 shows the main findings of the roadmap performed within WP4. The report finalizes with the conclusions and the outlook of the project.

2. Catalyst testing (WP2)

In the framework of WP2 of GasHUB, a number of exploratory short tests were performed at the ESME system using the sorbents and catalysts supplied by Albemarle. The results shed more light on the expected behaviour of the materials, as well as on the activation procedure and activity under different operating conditions, as preparation work for the final duration tests of WP3.

2.1 Testing of ZnO sorbents

First tests were carried out with 2 commercial ZnO sorbents for the removal of H_2S and COS at different temperatures. Both sorbents tested could properly remove H_2S and COS down to detection limits within the range of temperatures studied (150-350°C). The traces of H_2S detected from time to time are due to contamination of the gas sampling and analysis system.

Over the 2 hours of test, the reaction front shifted approximately 100-150 mm. The reason is the decreasing concentration of C_2H_2 and C_2H_4, and the gradual increase in the catalytic activity of the bed material (activation). Due to the high temperature of the second part of the catalyst, thiophene was completely converted.

Figure 2 shows the temperature in the HDS reactor during the test. The decrease of the catalyst bed temperature over time (particularly of T5 and T6) might look as a consequence of catalyst deactivation, but it is actually the consequence of the decreasing concentration of ethylene, acetylene and other unsaturated hydrocarbons in the gas, which leads to less production of heat via exothermic hydrogenation reactions.

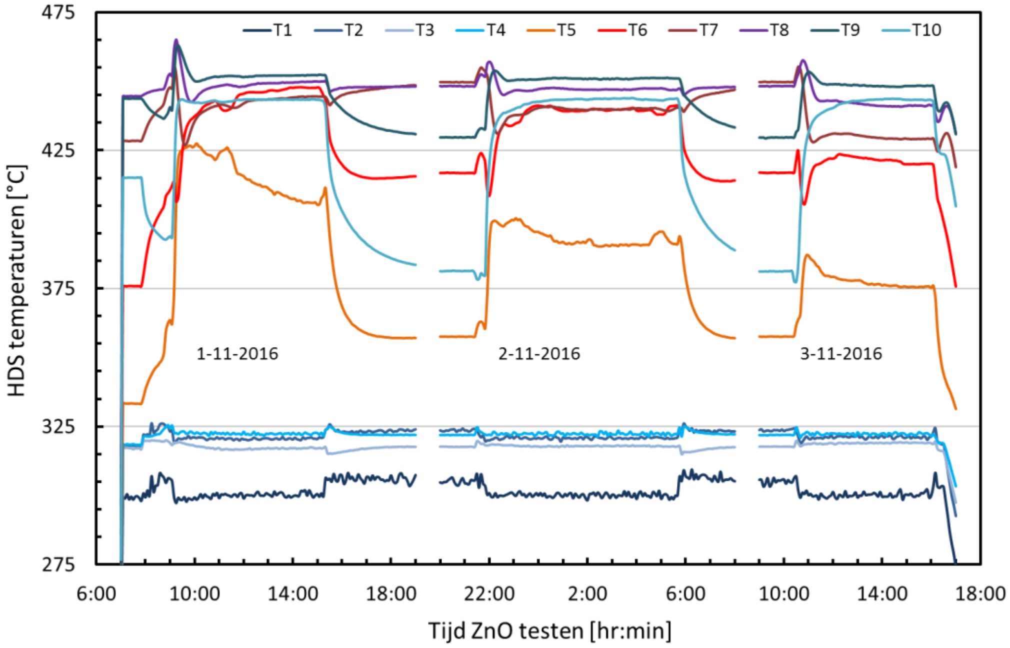

Figure 2. Temperature in HDS reactor during test of ZnO.

The results showed that the gas after the HDS catalyst contains only H_2S and COS, and possibly traces of CH_3SH. Thiophene and thiophene derivatives are completely converted in the catalyst.

The results of the GC-FPD results after the ZnO sorbents tested showed no traces of mercaptans, thiophene or thiophene. Only in one analysis was COS detected. In half of the measurements no H_2S was detected. It is likely that the concentrations are so close to the detection limit that H_2S is not seen in some of the measurements, or that there are false positive measurements due to the contamination of the gas sampling and gas analysis system.

As a conclusion of the test, both ZnO materials can remove COS below detection limits. They can also remove largely H_2S, although it is not clear to which limit. There is no clear relation between the operating temperature of the ZnO sorbent and the remaining traces of H_2S. Higher temperatures than 200°C can be selected, thus confirming the current design value taken in the design of AMBIGO. Longer tests will be needed to get a better insight of the feasible remaining sulphur concentration for the downstream nickel catalysts, and about breakthrough taking place.

2.2 Testing of HDS catalyst

The test described in Section 2.1 was performed using the same HDS catalyst as in the 2014 duration test. The first experiment using the Albemarle HDS catalyst was carried out on 19-21 December 2016, with the objective of determining the room of operating conditions (temperature, gas flow) of this catalyst.

During this experiment, the MILENA gasifier was operated at a temperature of 775°C, close to the expected temperature to be applied in the AMBIGO plant. This temperature leads to a higher concentration of C3-C5 hydrocarbons in the product gas, as well as a different distribution of BTX (more toluene, less benzene).

The 3 heating zones of the HDS reactor were set at 300°C, 300°C and 450°C. The inlet gas flow (0.7 Nm^3/h) resulted in a GHSV ~ 300 h^{-1}. Upon start of the test, the HDS bed temperature increased to 500°C due to reaction of CO and H_2 with the oxygen from the catalyst (reduction), although after 1 hour operation, the temperature stabilized at 450°C. A gas temperature of 280°C above the catalyst bed seems enough for reactions to take place, but a temperature of 310°C is necessary to ensure that 90% of the ethylene is converted to ethane in the top of the bed. Also, 80-90% of the thiophene is converted in the top of the bed.

During this test, the ethylene concentration after the HDS reactor was below or barely above the detection limit. Part of the H_2 in the gas is consumed in hydrogenation reactions of unsaturated hydrocarbons. Some H_2 and CO is consumed in the reduction of the catalyst at the beginning of the operation, from which heat, CO_2 and water is produced. The extent of hydrogenation activity in the top of the bed was observed to be very sensitive to the set temperature of the top part of the HDS reactor. The temperature also influenced largely the extent of conversion of thiophene in the top part of the catalyst: the conversion of thiophene in the top decreased from 90% to 60%, but then got back to 90% upon increase of the temperature setpoint of the upper zone of the HDS reactor. Thiophene was completely converted after the HDS catalyst. Unsaturated C_2-C_5 hydrocarbons were almost completely converted to saturated hydrocarbons in the HDS reactor.

All in all, the results obtained during this test showed that the Albemarle HDS catalyst shows a similar performance as the catalyst previously used in in August 2016 and the 500-h duration test of 2014. The combination of HDS and ZnO reactor can reduce the sulphur concentration well below 1 ppm.

2.3 Testing of HDS + pre-reformer + methanation reactors, January 2017

As follow-up of the HDS test described in Section 2.2, in January 2017, a test was carried out using Albemarle catalysts in the HDS, pre-reformer and methanation catalysts. The main objective of this test was to determine whether the Albemarle pre-reforming catalyst was able to completely convert benzene and toluene into H_2, CO en CH_4 without carbon formation, and whether the pre-reformer catalyst was stable. During the test, 640 g/h steam was added to the product gas, which resulted in a GHSV = 1900 h^{-1} in the pre-reformer and GHSV = 2200 h^{-1} in the methanation reactors.

The first part of the test was successfully performed, and after 3 hours operation the first methanation reactor was put into operation. The catalysts operated under stable conditions for 7 hours. However, after 15 hours operation the unexpected blockage of the steam generator resulted in the feeding of the pre-reformer with dry feed gas (no steam supply). This anomalous operation led to the plugging of the pre-reformer after 1.5 hours, and thus to premature termination of the experiment. Upon post-inspection, a hard layer of carbon was found in the pre-reformer catalyst.

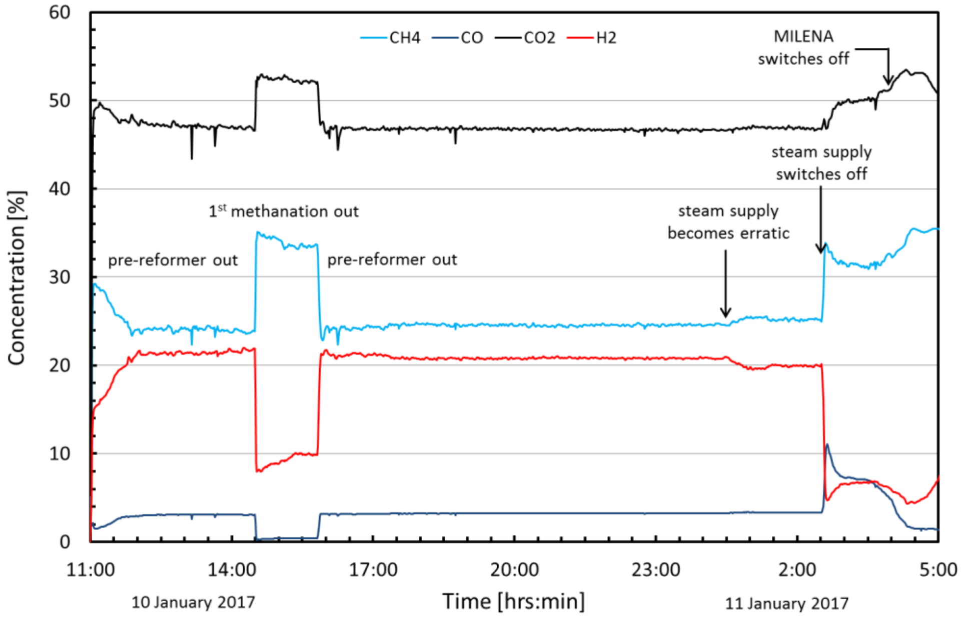

Figure 3. Gas composition after pre-reformer and first methanation reactor during test in January 2017.

In the first micro-GC analyses, benzene and toluene was detected. This was due to the contamination of the gas analysis lines. Gradually, the concentrations decreased down to near the detection limits. Due to the right trends in the temperature of the pre-reformer, the first methanation reactor was put into operation after 3 hours of pre-reformer operation. Figure 3 shows the gas composition measured by the gas monitor. Complementary GC-FID analysis revealed that C2+ hydrocarbons are converted.

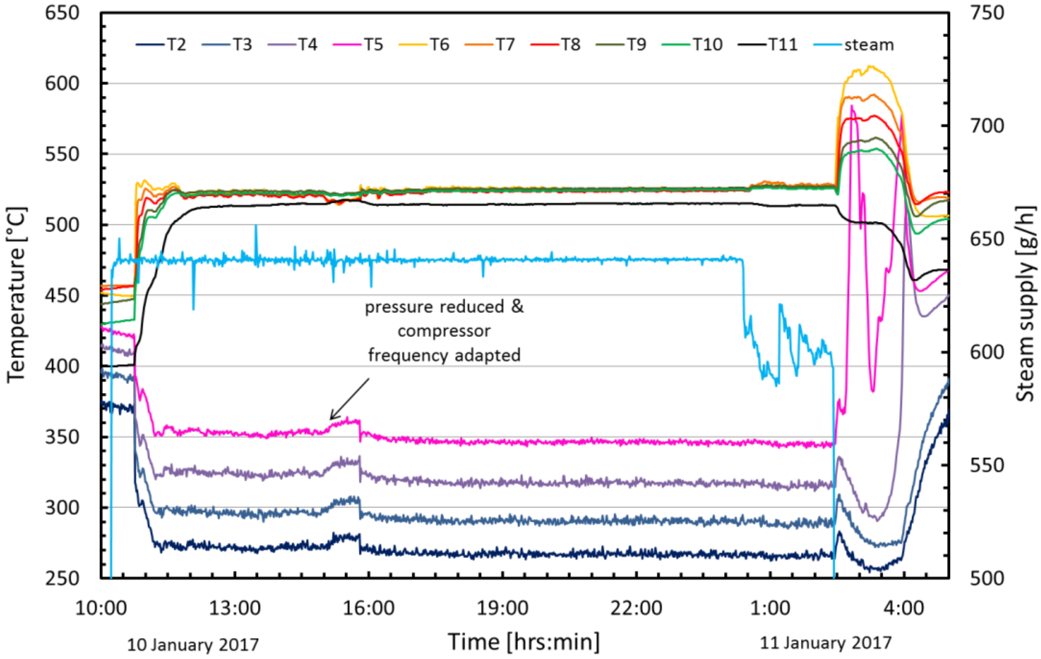

Figure 4. Temperature in pre-reformer and steam flow during test in January 2017.

Figure 4 displays the temperature in the pre-reformer, which was very stable until the shutdown of the steam supply. The first thermocouple in the bed (T6) reaches the maximum temperature, which indicates that the reactions occur very rapidly and that a higher GHSV must be possible. After the stop of the steam supply, the temperature increase up to ~ 600°C. T5 seems to be in contact with solid instead of gas. This solid material might be carbon which is formed under these conditions.

Figure 5 shows the temperature profile in the first methanation reactor. Thermocouples T2-T5 indicate the temperature in the gas, whereas T6-T11 measure the temperature in the catalyst bed. At the beginning of operation, the temperature settings are adjusted to get an inlet gas temperature of 250°C. This results in an intense increase of T6, which indicates that the reactions can only occur above 250°C inlet gas temperature.

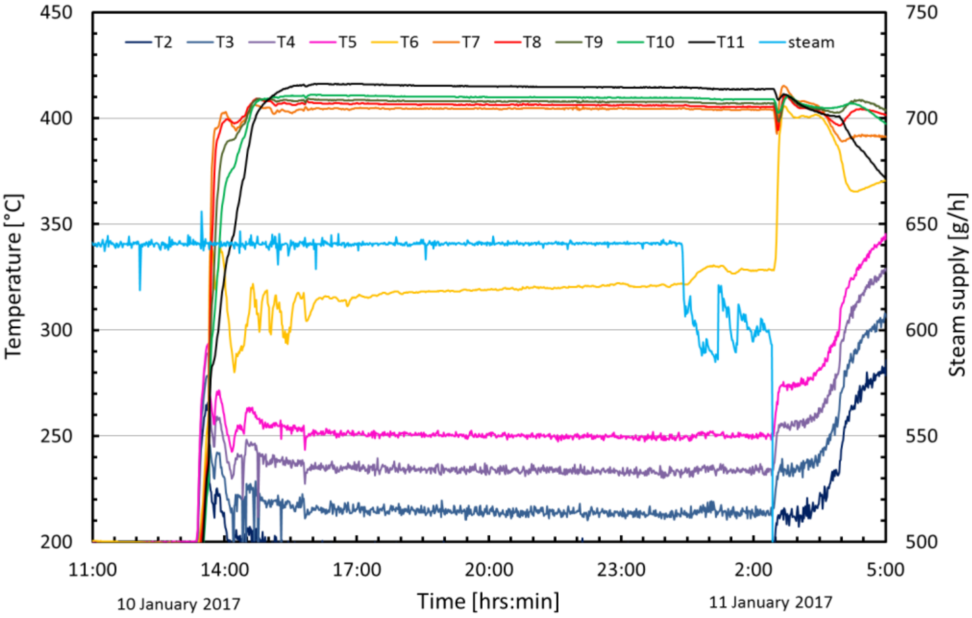

Figure 5. Temperature in first methanation reactor during test in January 2017.

After cooling down of the reactors, the pre-reformer looked completely blocked. In order to be able to open the reactor under safe conditions, the catalyst was flushed with 10% air in N_2 (0.7 NL/min). This led to an increase of the temperature up to 150°C. Upon opening of the reactor, only thermocouples T2 and T3 were above the bed. The height of the bed increased by ~ 50 mm. The top layer (~100 mm) was composed of dust. Thermocouple T5 could not be taken out of the reactor. Just below, approximately 30-50 mm below the initial top of the bed, a hard carbon layer was found which prevented the flow of gas. This hard layer is shown in Figure 6, where the round holes were produced with a hammer and a 6 mm diameter tube. Below this layer, the catalyst was intact, but it was taken out of the reactor anyway, so that the next experiment could be carried out with fresh catalyst. Samples of the carbon and the catalyst were taken for further analysis. The carbon layer might be a polymer formed from benzene or dehydrogenated ethane or methane.

Figure 6. Hard carbon layer found in pre-reformer reactor after test in January 2017.

All in all, the first experiments with the pre-reformer catalyst and the methanation catalyst showed that both catalysts can properly operate at least for 10 hours with MILENA product gas. The temperatures and pressure drop are stable, despite the fact that the steam supply was 5% lower than the amount that was previously estimated as “safe” amount. The unexpected termination of the test due to the shutdown of the steam supply showed the need and importance of safety measures, so that the gas supply to the pre-reformer reactor is stopped if the steam supply is interrupted.

2.4 HDS + pre-reformer + methanation test, February 2017

After loading and activation of the catalyst, a test of the whole ESME train (HDS up to second methanation reactor) was performed in February 2017. The time on stream of the different reactors is summarized in Table 2.

Table 2. Summary of time on stream of the different ESME reactors.

Reactor	Reactor code	Analysis points	Time on stream (h)
HDS	HDS	HDS-5 (inlet), HDS-4 (outlet)	41.3
ZnO bed	R12	HDS-3 (outlet)	39.8
Pre-reformer	R13	SNG 1-4 (outlet)	38.5
Methanation 1	R14	SNG 1-5 (outlet)	20.5
Methanation 2	R15	SNG 1-6 (outlet)	18.4

Despite overall good performance of the catalysts throughout the test (i.e. practically complete conversion of organic S compounds in the HDS, removal of H_2S and COS in the HDS catalyst, and > 99% benzene conversion/100% toluene conversion in the pre-reformer), the test unexpectedly ended after ~38.5 hours of pre-reformer operation. The shutdown was most likely caused by high pressure at the inlet of the OLGA system, which in turn led to shutdown of the MILENA gasifier. Even though at first it was suspected that the high pressure, as well as other minor operational problems were related to the suboptimal operation of OLGA with dust-loaded oil from tests carried out in December 2016, post-inspection revealed that the filtering element of the hot gas filter was broken down. The defect hot gas filter also led to the relatively fast clogging of the Soxhlet filters located between the condenser and the ESME gas compressor, which led to rapid increase in the pressure drop at the inlet of the ESME system. The Soxhlet filters had to be replaced relatively often.

The issues with the pressure drop in the Soxhlet filters caused in turn a limitation in the room to maneuver during the experiment. The adjustment of the gas flow (increase of the booster frequency) could further worsen the issues with pressure drop, and thus the risk of premature system shutdown. Therefore, it was decided not to increase the gas flow despite the fact that the actual gas flow entering ESME was ~ 11 L/min instead of the planned 12.5 L/min, so the steam/carbon ratio at the inlet of the pre-reformer was somewhat higher than the value set in the test plan.

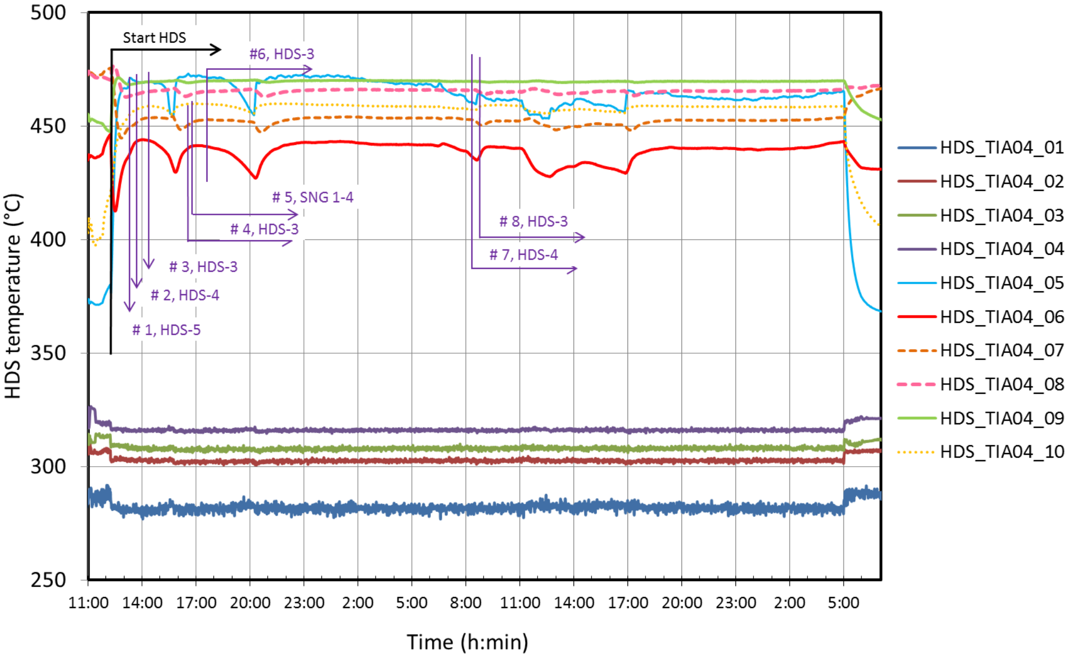

Figure 7. Temperatures of HDS reactor. Gas bags taken for analysis of sulphur compounds and hydrocarbons are indicated in purple.

Figure 7 shows the temperature profile of the HDS catalyst. In general, stable operating conditions were achieved throughout the test. GC-FPD analysis was carried out complementary to online micro-GC in order to track the fate of organic S compounds and C1-C5 hydrocarbons along the ESME system (e.g. check whether complete conversion of thiophene was achieved in the HDS reactor, whether the gas entering the pre-reformer was free of H_2S and COS, and whether the HDS catalyst could effectively hydrogenate unsaturated hydrocarbons). Organic S compounds were largely converted by the HDS catalyst: thiophene is converted from feed level to around the detection limit (0.1 ppmv), and mercaptan derivatives were converted to below detection limits (except in one of the analysis, where some methyl-mercaptan was detected). H_2S and COS are also largely adsorbed in the HDS catalyst.

Figure 8 graphically summarizes the fate of the C_1-C_5 hydrocarbons in the first reactors of the ESME system, from the HDS inlet to the outlet of the pre-reformer. For the sake of clarity, the different analyses have been classified in colors as a function of the location in the system (red at the inlet of the HDS reactor, blue at the outlet of the HDS reactor, green at the outlet of the ZnO reactor, and yellow after the pre-reformer). As can be observed, C_2H_4 and C_2H_2 are almost completely converted to C_2H_6, C_3H_6 is largely converted to C_3H_8, the traces of unsaturated C_4 compounds are converted to (iso)C_4H_{10}. The peaks identified at the inlet of the HDS reactor as the sum of 1,3-butadiene + propyne and C_5H_6 cyclo- or pentadienes have disappeared in the gas at the outlet of the HDS reactor. Other compounds such as cyclopentane, 2-methyl-butane, and pentane are produced in the HDS reactor. All these hydrocarbons present in the gas after the HDS and ZnO reactors are eventually converted (just as part of CO and H_2) to CH_4 in the pre-reformer.

In general, stable operation was achieved during the experiment. The variations in the temperature profile of R13 were mainly due to variations in gas flow (due to the increasing pressure drop over the Soxhlet filters). Hints of instability were moreover observed in the temperatures near the catalyst surface in the methanation reactors during the six last hours of the test. These instabilities were probably due to the presence of condensate water drops either in the line of the steam generator, but most likely at the outlet of the R15 reactor (off-gas line).

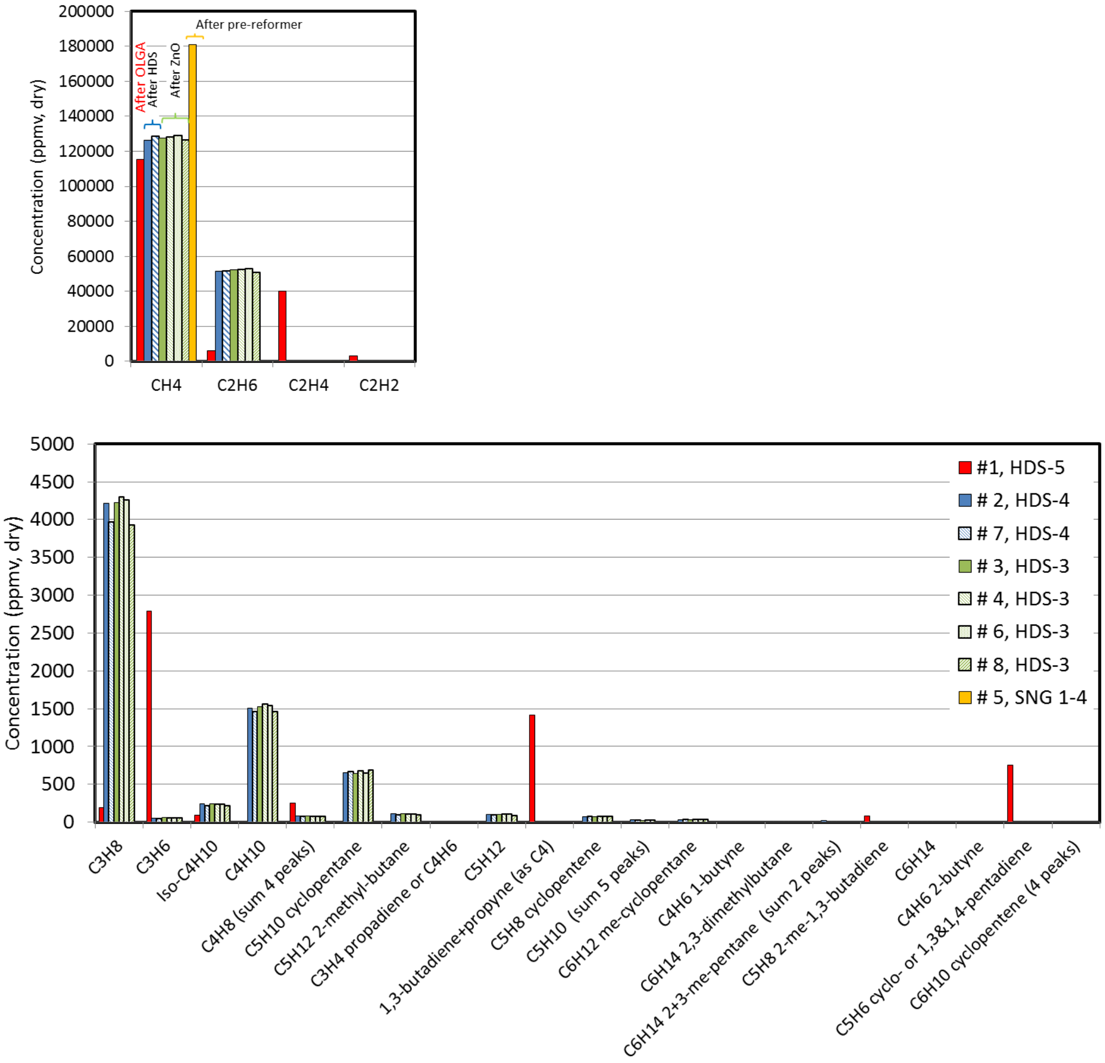

Figure 8. Results of T-GC analysis: concentration of C1-C5 hydrocarbons in the gas along the ESME system (from the inlet of the HDS reactor to the outlet of the pre-reformer): C1-C2 hydrocarbons on the top, C3-C6 hydrocarbons on the bottom. The samples are listed in Figure 7.

From molar balances performed using neon as tracer gas, the molar flows of the most relevant gas compounds for the performance of HDS (ethylene) and pre-reformer (benzene and toluene) have been tracked and plotted in Figure 9. The flows around the HDS reactor (inlet to the pre-reformer) are plotted in blue, whereas the flows after the R13/R15 reactors are plotted in red. This way, the fate of the individual target compounds over the ESME system can be tracked. The variations in molar flows observed in the inlet gas are directly related to variations in the flow (derived from the increase in pressure drop over the Soxhlet filters). Figure 9 shows the complete conversion of ethylene in the HDS reactor (in agreement with the results of GC-FID analysis shown in Figure 8), whereas the pre-reformer effectively converts benzene and toluene. Acceptable closure of carbon balances around the ESME reactors (not shown in this report) was determined. Although the molar flows are not constant (due to varying gas flows entering the system), the gap between inlet and outlet flows not only is very small, but it also keeps constant over time. Therefore, as expected, no carbon issues occurred during the test.

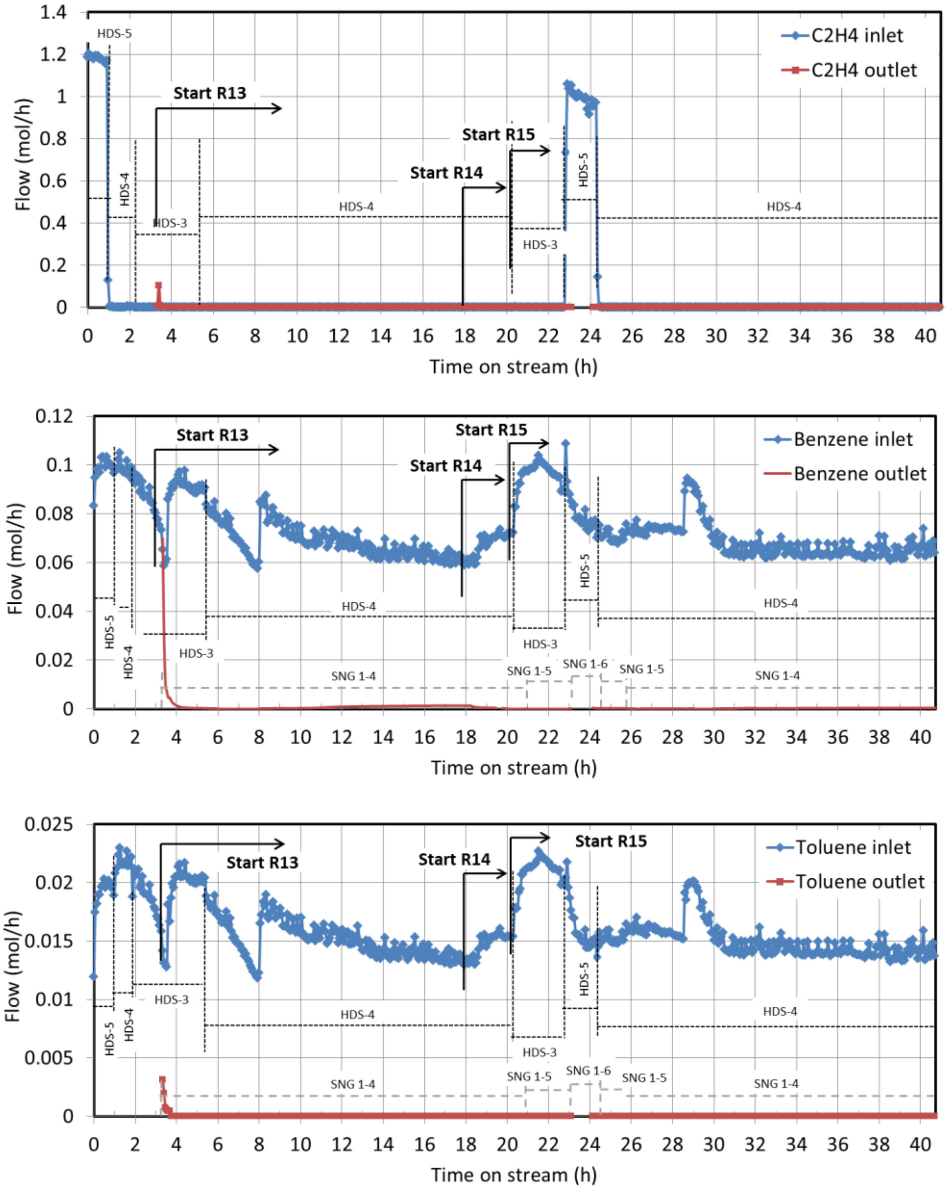

Figure 9. Inlet (HDS reactor) and outlet (after R13/R14/R15) molar flows of C_2H_4, benzene and toluene.

Overall good and stable performance of the catalysts (i.e. practically complete conversion of organic S compounds in the HDS, removal of H_2S and COS in the HDS catalyst, and > 99% benzene conversion/100% toluene conversion in the pre-reformer) was observed throughout the experiment. A dramatic decrease of the CO content from ~30 vol.% to ~ 2 vol.% (converted to H_2 and CH_4 in WGS and methanation reactions, respectively) took place in the pre-reformer. The overall balance between formation (WGS) and consumption (methanation, hydrogenation) reactions in the pre-reformer led to a net increase of the H_2 content from 15 vol.% to ~ 23-24 vol.%. The remaining CO in the gas leaving the pre-reformer is almost completely converted in the methanation reactors (~0.3 vol.% after R14, and below detection limits after R15), whereas the H_2 content after R15 is approximately 9 vol.%.

3. Duration tests of gas upgrading train, WP3

The development work of WP2 resulted in the selection of the final configuration of sorbents and catalysts for the final duration tests of WP3. The objective of the duration test was to demonstrate the long-term performance of the selected materials under real gasification conditions in order to mimic the conditions of the AMBIGO plant[3]. The experiments were performed using the whole system (25 kWth MILENA gasifier, OLGA tar removal and ESME methanation train), using product gas from beech wood gasification. This section summarizes the main results obtained during the final duration tests performed in December 2017-January 2018 (234 hours of HDS operation, and 222 hours of operation of the whole ESME system).

3.1 Overview of duration tests (beech wood gasification)

3.1.1 Experimental setup

The experiments were performed using the whole lab-test rig system (25 kWth MILENA gasifier, OLGA tar removal and the low-pressure test rig ESME methanation train, see Figure 10). This document contains the results obtained during the final duration tests performed in December 2017-January 2018 (234 hours of HDS operation, and 222 hours of operation of the whole ESME system), plus an additional short test using non-woody biomass as gasification feedstock (which results in a product gas with significantly higher sulphur content entering the ESME system).

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[3] The AMBIGO project consists of a 4 MWth bio-SNG plant based on MILENA indirect gasification, OLGA tar removal and ESME methanation system, which will be constructed in Alkmaar. For more information: www.ambigo.nl

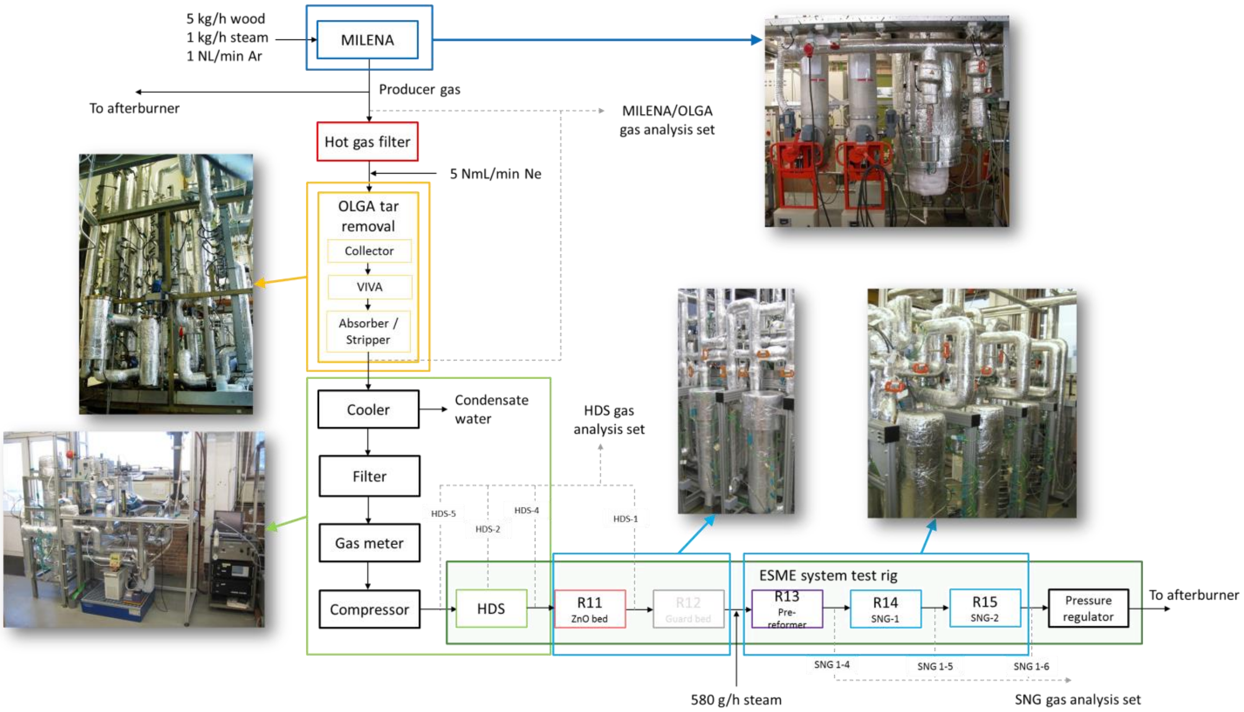

Figure 10. Schematic layout of MILENA/OLGA/ESME lab-scale setup used in the GasHUB duration test, including locations of gas analysis.

3.1.2 Summary of test settings

<u>Settings of MILENA gasifier:</u>

~ 5 kg/h Rettenmayer beech wood.

Olivine as bed material.

< 800°C gasification temperature; ~ 850°C combustor temperature.

<u>Settings of hot gas filter (HGF):</u>

- 400°C set temperature.

<u>Settings of gas cooler:</u>

- 5°C set temperature.

<u>Settings of ESME train:</u>

5.7 bar pressure.

~ 12.5 – 13 L/min inlet gas.

<u>Settings of ESME reactors</u> (see Table 3).

Settings of HDS reactor:

- Filled with HDS catalyst.
  - TIC04_11: 310°C.
  - TIC04_13: 310°C.
  - TIC04_14: 450°C.

Settings of R11, ZnO reactor:

- Filled with ZnO sorbent.
- TIC11_102: 200°C.
- TIC11_103: 250°C.
- TIC11_104: 200°C.

Settings of R13, pre-reformer reactor:

- Filled with pre-reformer catalyst.
- 580 g/h added steam (at 200°C inlet temperature).
- Inlet gas temperature ~ 350°C.
- TI13_103: 300°C.
- TI13_104: 520°C.

Settings of R14, first methanation reactor:

- Filled with methanation catalyst.
- Inlet gas temperature ~ 250°C.
- TIC14_103: 180°C.
- TIC14_104: 390°C.

Settings of R15, second methanation reactor:

- Filled with methanation catalyst.
- Inlet gas temperature ~ 250°C.
- TIC15_103: 240°C.
- TIC15_104: 290°C.

Table 3. Overview of catalyst mass and gas hourly space velocities in the ESME reactors during the duration tests.

Reactor	Mass (g)	Bed height (mm)	GHSV (1/h)
HDS	1769	528	~ 300
R11	1770	409	~ 300
R13	734	310	~ 2000
R14, R15	734	310	~ 2000

There are 3 gas analysis sets (each of them composed of gas monitor and micro-GC), with different gas sampling positions that can be switched: a gas analysis set at MILENA/OLGA (inlet gas entering the ESME system), a gas set around the HDS and ZnO reactors, and a gas set around reactors R13-R15. The 3 gas sets (each composed of online gas analyser and micro-GC) operate simultaneously during the tests. Moreover, gas bags are daily taken around the HDS and ZnO reactors for analysis of S compounds to make sure that the HDS catalyst can completely convert thiophene, to track any breakthrough of sulphur over the HDS catalyst, and that to check that the ZnO sorbent can properly capture H_2S (and COS). In order to avoid contamination of the gas analysis bags, the sampling always starts at the cleanest position (HDS-1 or HDS-4), and then proceeds backwards until the last gas bag, taken at the inlet of the HDS reactor.

3.1.3 Overview of duration tests

The whole endurance experiment of WP3 was split in 2 parts, as shown in the summary Table 4 and Figure 11. The first part of the run, Test 1, was performed in December 2017. The test was completed in January 2018 with the second part, Test 2. In both tests, the reactors were put into operation gradually, as observed in Figure 11. In total, the gasifier was operating for 242.6 hours, the HDS reactor was in operation for 234 hours, and the whole lab ESME system (that is, from MILENA to R15) was in stream for more than 222 hours. During test 1, a gasifier shutdown after 92 hours in operation led to a system stop of approximately 4-6 hours; during test 2, there was a controlled bypass of the ESME system for the replacement of a leaking pressure meter which led to a stop of the HDS reactor for 20 minutes, and of the whole ESME system (up to R15) of approximately 1 hour. All in all, the availability of the lab-ESME system during the overall test (tests 1 + 2) was above 90%.

Table 4. Summary of net time in operation of gasifier and ESME reactors during the WP3 duration test.

	MILENA	HDS	R13	R14	R15 (= whole ESME system)
Time on stream [h:min], net excluding shutdown, test 1	104:02	98:14	95:51	94:37	93:36
Time on stream [h:min], excluding controlled stop, test 2	138:35	135:46	131:43	130:16	128:45
Total duration test (test 1 + test 2)	242:37	234:00	227:34	224:53	**222:21**

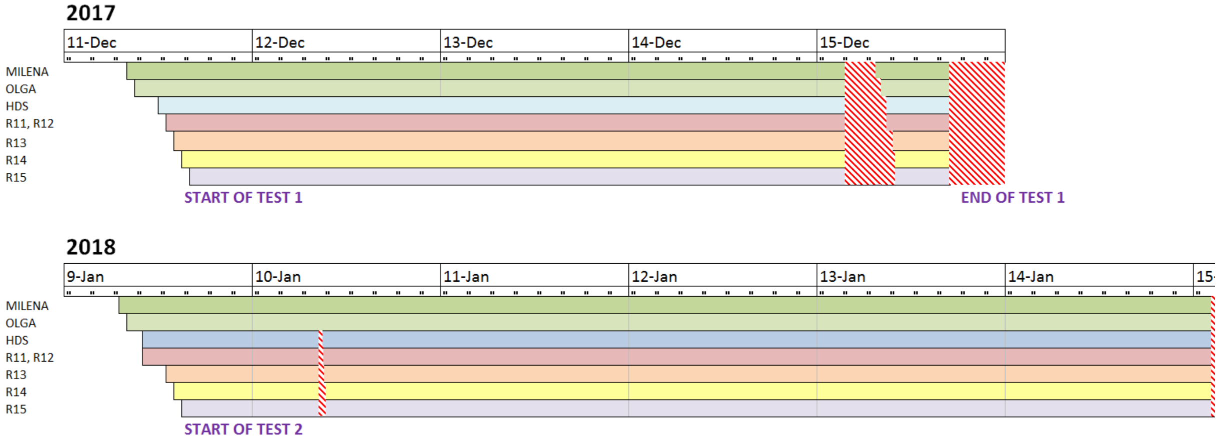

Figure 11. Overview of operation of MILENA, OLGA and ESME reactors during the WP3 duration test.

To clearly understand the information contained in Figure 11, hereby the sequence of start-up of the system is briefly explained:

- The MILENA gasifier is firstly started.
- Once that MILENA runs under stable conditions, the OLGA tar removal is started.
- Once that the OLGA temperatures have reached stable conditions, the ESME system is pressurized to ~ 5.7 bar, and the inlet gas flow is adjusted to 12.5-13 L/min (measured with gas meter and double-checked with Ne concentrations). During this process, all the ESME reactors are set in bypass.
- Once that the ESME pressure and flows are set, the gas flow to the HDS reactor is open (start of HDS operation).

- Once that the HDS is operating under stable conditions (measured with gas analyser and micro-GC), a gas bag is taken at the outlet of the HDS reactor. Once that it is ensured that all thiophenes and mercaptans are converted, the ZnO reactor (R12) is put into operation.
- Once that stable conditions are reached in the ZnO reactor, a gas bag is taken at the outlet. When it is confirmed that H_2S and COS are converted down to sufficiently low levels, the steam generator is switched on, and the pre-reformer R13 is put into operation.
- Once that stable conditions are reached in R13, and it is ensured that all the benzene and toluene are converted in the pre-reformer catalyst (from micro-GC analysis), the methanation reactors R14 and R15 are put into operation.

The above start-up procedure explains in Figure 11 why it takes several hours to start the whole methanation lab-test rig. Once that the system is in operation, the sequence of gas bags analysis around the HDS and the ZnO reactors (going from cleaner to dirtier positions) is daily applied.

3.1.4 Activation of R13-R15 catalysts

The pre-reformer and methanation catalysts (reactors R13, R14 and R15) were activated around 400-450°C prior to the duration test on the 5th (R13 and R14) and 6th December 2017 (R15).

Once activated, the reactors were set back at 250°C and kept flushed with the activation gas until the start of the test. Moreover, between tests 1 and 2, the activation gas (0.5 NL/min H_2 + 4.5 NL/min N_2) was applied to R13/R15 at the set temperatures.

3.2 Results of duration test 1

The first part of the duration test started on the 11th December 2017 (please refer to Figure 11). In total (net time excluding the 4-6 hour shutdown), the gasifier was operating for ~ 104 hours, whereas the whole ESME lab system (that is, up to R15) was in operation for ~ 94 hours. All in all, the system ran under stable conditions. The main events taking place during the experiment (which are indicated in the figures further in this section) are listed below. Please note that the times on stream correspond to that of the MILENA gasifier[4]:

- After ~24 hours on stream, the gasification temperature was reduced from ~850°C to < 800°C (expected temperature in the gasifier of the AMBIGO plant).

- During hours 45-48 of the gasifier operation (corresponding to 04:00-06:30 AM), the gas flow entering the ESME system got unstable due to the plugging of the hot gas filter. However, there was no system shutdown. The issue was solved by switching to another hot gas filter.

- After approximately 40 hours of operation of the ESME system, the set temperatures of reactors R13 and R14 were adjusted (reduced) so that the inlet gas temperatures were ~ 350°C and 250°C, respectively.

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[4] For the sake of clarity, all the figures reported in this section include the 4-6 hour system shutdown.

- Fresh olivine (bed material) was added to the gasifier at approximately hour 76 of the gasifier operation.

- A gasifier shutdown of approximately 4 hours (almost 6 hours if the whole ESME system is considered) took place after more than 90 hours operation of the gasifier. The shutdown was due to a high pressure alarm of the gasifier.

- Eventually, after 108 hours operation, the fuel feeding screw of the MILENA gasifier was broken, which led to a system shutdown. This happened on Friday 15th December 2017. It was then decided to interrupt the duration test, and continue in January 2018. The ESME reactors R13/R14/R15 were maintained until the re-start of the test in January 2018 at the set temperatures under a gas flow of 5 NL/min (10 vol.% H_2 in N_2).

Figure 12 and Figure 13 plot the temperatures of the MILENA gasifier and the composition of the product gas from the gasifier (measured with the online gas analyser). The gasifier started operation at ~850°C (MIL_TI601, riser temperature, in Figure 12). After ~ 24 hours operation, the gasifier temperature was reduced to below 800°C (temperature expected in the AMBIGO plant, thus more relevant for the application of the sorbents and catalysts). The decrease in gasification temperature results in a significant change in the product gas composition (Figure 13), namely an increase in the CH_4 and CO content, and a decrease in the concentrations of H_2 and CO_2 (which indicates a lesser extent of the water-gas shift reaction).

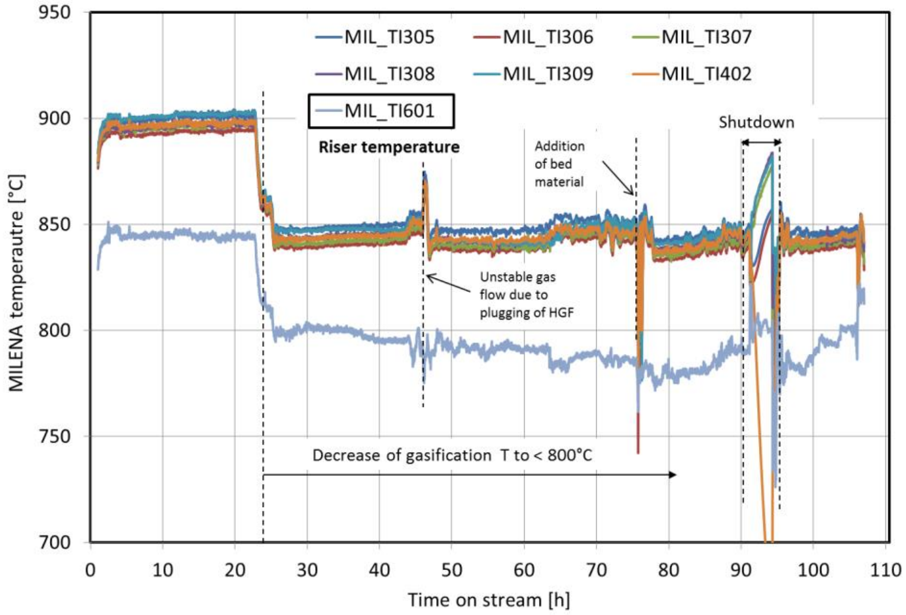


Figure 12. Overview of MILENA gasifier temperatures during duration test 1.

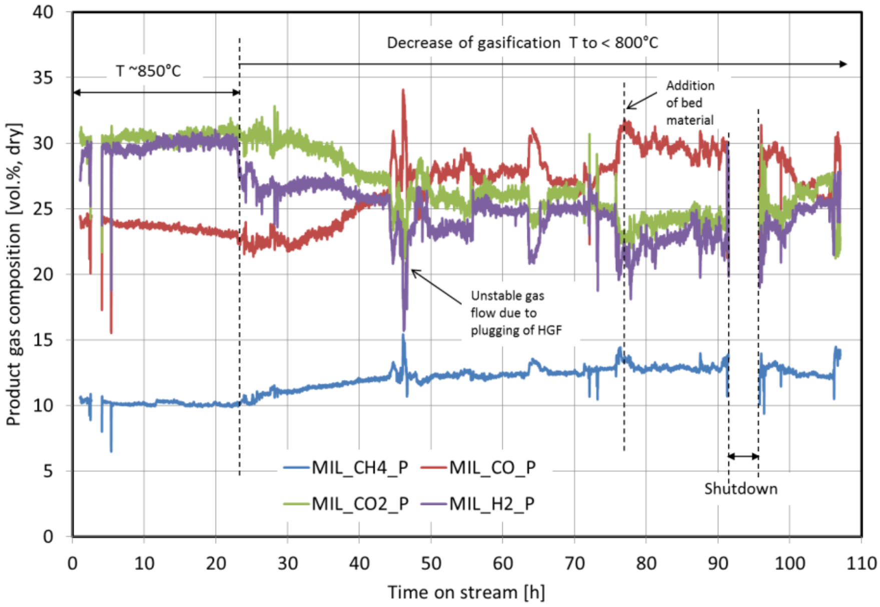


Figure 13. Overview of MILENA product gas composition during duration test 1.

The ESME methanation system operated at 5.7-5.8 bar pressure (Figure 14). Figure 15 displays the temperature profile of the HDS reactor. The inlet gas temperature to the reactor was ~300°C, however the reactions taking place in the HDS catalyst are strongly exothermic, thus the bed temperatures are in the range of 410-450°C. TIA04_05 (purple line in Figure 15) corresponds to the temperature at the top of the catalyst bed, and it is very sensitive to changes in flow and/or composition of the inlet gas. For example, the change in gasification temperature (corresponding to hour ~20 in stream of the HDS reactor onwards) leads to a change in gas composition (seen in Figure 13), which results in an increase of the temperature at the top of the HDS catalyst bed. The changes in gas flow and/or composition resulting from the temporal plugging of the hot gas filter (~ hour 42) and from the addition of bed material (~hour 70 in stream) can be easily seen in the temperature profile of the HDS reactor.

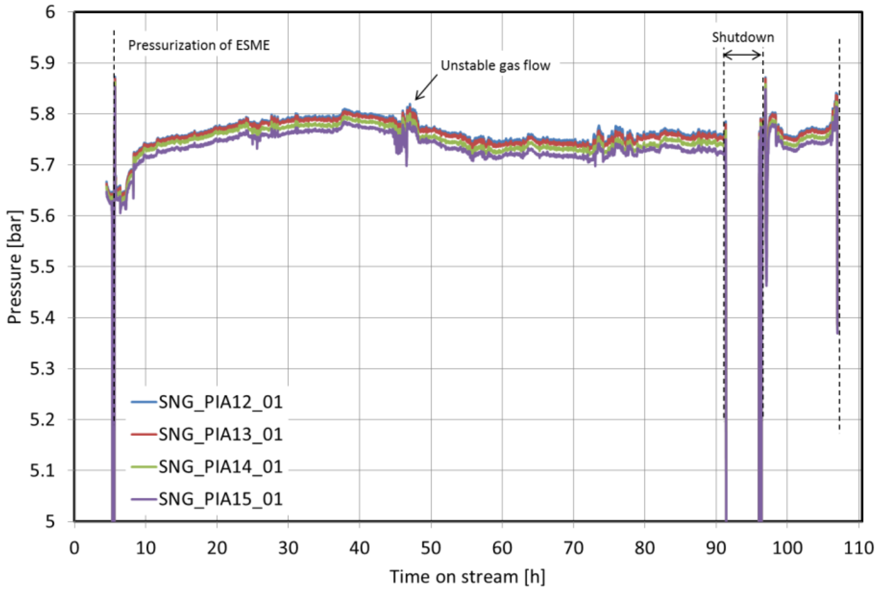


Figure 14. Overview of ESME pressure during duration test (X-axis referring to MILENA gasifier operation).

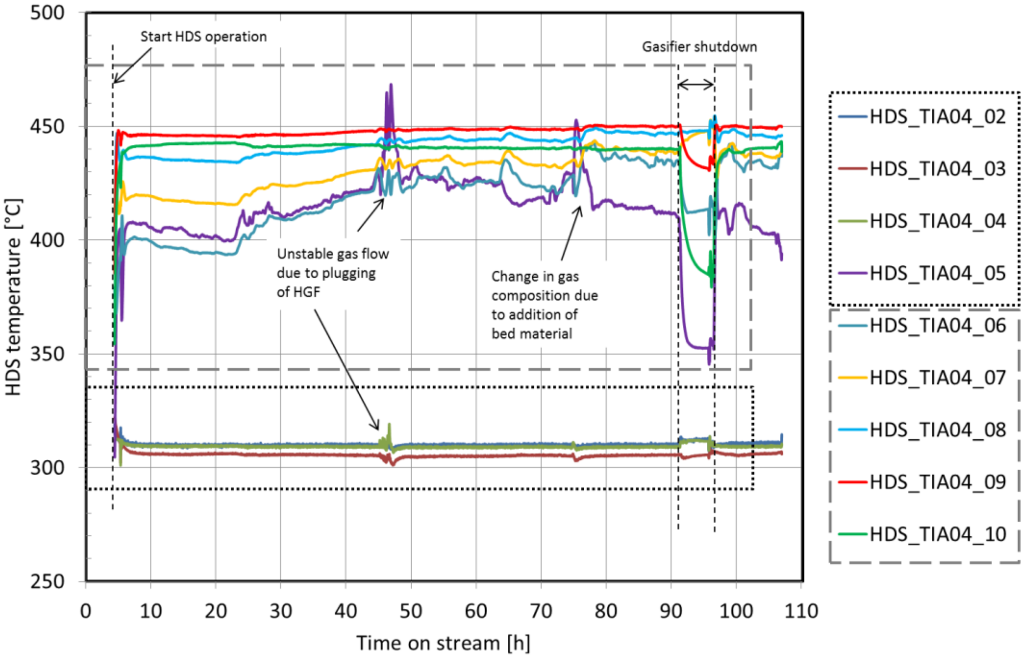


Figure 15. Overview of HDS temperatures during duration test 1 (origin of X-axis referring to MILENA gasifier).

Figure 16 and Figure 17 plot the temperature profiles of the pre-reformer reactor R13, and the first methanation reactor R14, respectively. The main event taking place during the first duration test was the adjustment of the set temperatures of both reactors in order to get an inlet gas temperature (SNG_TI13_05, yellow line) around 350°C in the pre-reformer. The inlet gas temperature in the R14 reactor (SNG_TI14_05, yellow line) was also reduced to ~ 260°C. In the pre-reformer reactor, the overall balance between endothermic reforming reactions and exothermic methanation is an increase of the temperature within the catalyst up to ~530°C. In the case of the methanation catalyst in R14, the temperature in the catalyst increases from 260°C up to approximately 420°C resulting from the methanation reactions taking place within the bed.

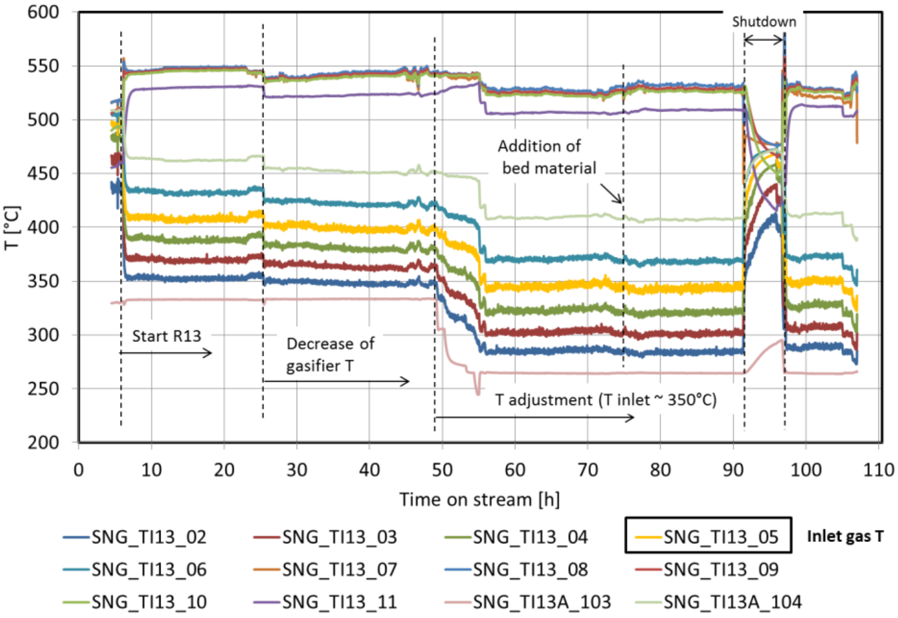


Figure 16. Overview of pre-reformer (R13) temperatures during duration test 1 (origin of X-axis referring to MILENA gasifier).

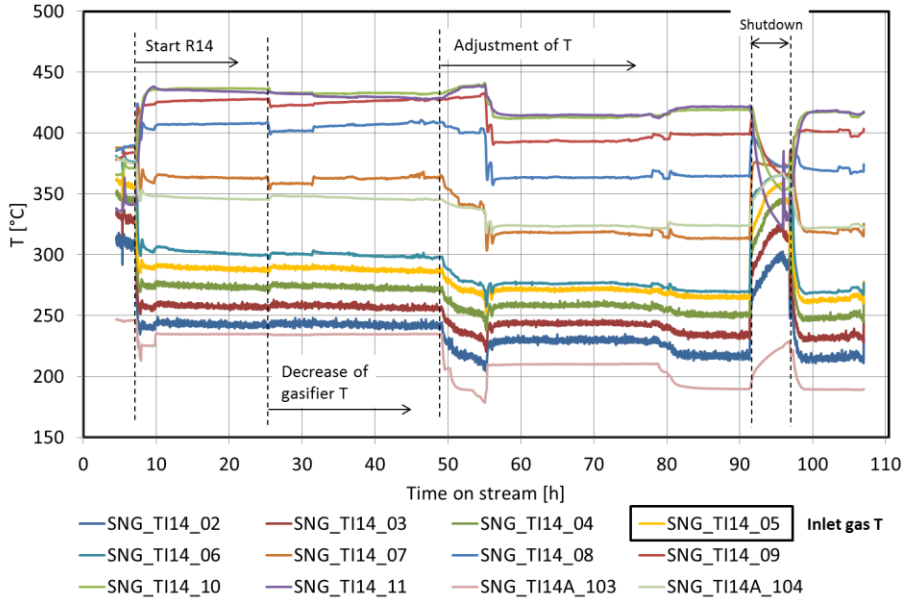


Figure 17. Overview of first methanation reactor (R14) temperatures during duration test 1 (origin of X-axis referring to MILENA gasifier).

Figure 18 displays the bed temperature profile of the second methanation reactor, R15. It is noteworthy that despite the activation procedure applied (described in Section 2.2), the methanation catalyst placed in R15 did not exhibit any activity (that is, no increase in the catalyst bed temperatures above the heater set point, as was observed in the methanation reactor R14). This was also seen in the gas composition, which did not show any change with respect to the outlet composition at R14. It was then decided to gradually increase the temperature to see if the catalyst started to show activity. From hour 75 onwards, when the set temperature was increased to 320°C, signs of catalytic activity started to be observed in the temperature profile (increase of catalyst bed temperature).

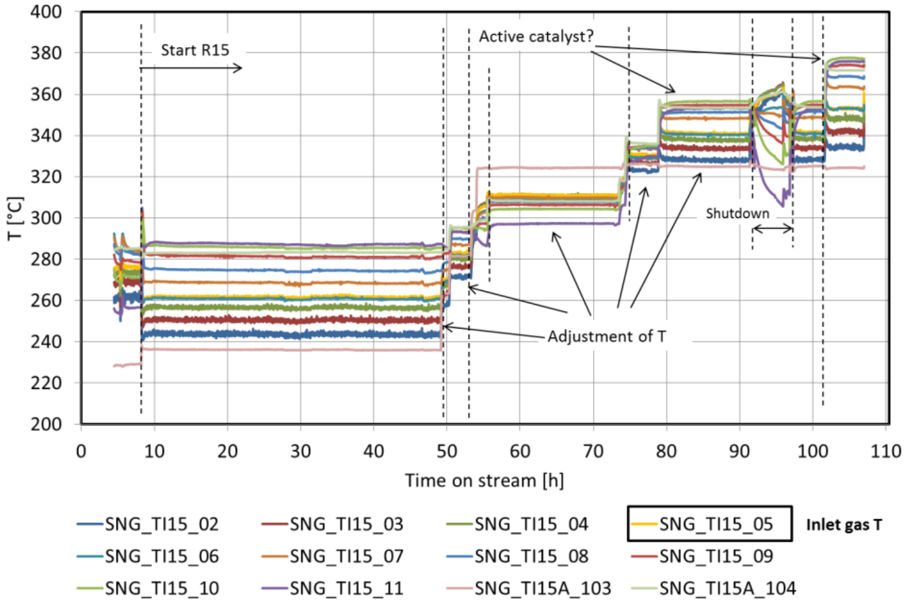


Figure 18. Overview of second methanation reactor (R15) temperatures during duration test 1 (origin of X-axis referring to MILENA gasifier).

The following figures will analyse the evolution of the gas composition along the ESME system. Firstly, Figure 19 and Figure 20 display a first overview of the main compounds (CO, CO_2, CH_4, and H_2) of the gas measured at the HDS gas analysis and the SNG gas analysis, respectively. The concentrations in the figures are measured with an online gas analyser. As explained in Section 1.3, the HDS gas analysis can be switched between different sampling positions located around the HDS and the ZnO reactors:

- HDS-5 (inlet HDS reactor, after gas cooler).
- HDS-2 (at approximately 1/6 within the HDS catalyst bed).
- HDS-4 (outlet HDS reactor).
- HDS-1 (outlet ZnO bed).

The SNG gas analysis can be switched around different sampling positions located around the pre-reformer (R13), and the methanation reactors (R14 and R15):

- SNG 1-4: after pre-reformer R13.
-SNG 1-5: after first methanation reactor R14.
- SNG 1-6: after second methanation reactor R15.

The idea of having 2 different gas analysis sets is to use one of them (the HDS set) for "dirty" gas (that is, containing sulphur, benzene, and toluene), and a dedicated gas analysis set (the SNG set) for clean gas (that is, without benzene and toluene). The reason is that these compounds easily stick to the walls of the gas analysis lines, thus contaminating (and affecting) gas analysis. For this reason, and in order to avoid contamination, the SNG gas analysis set is switched off when dirty gas goes through the system (system in bypass during starting up, for example).

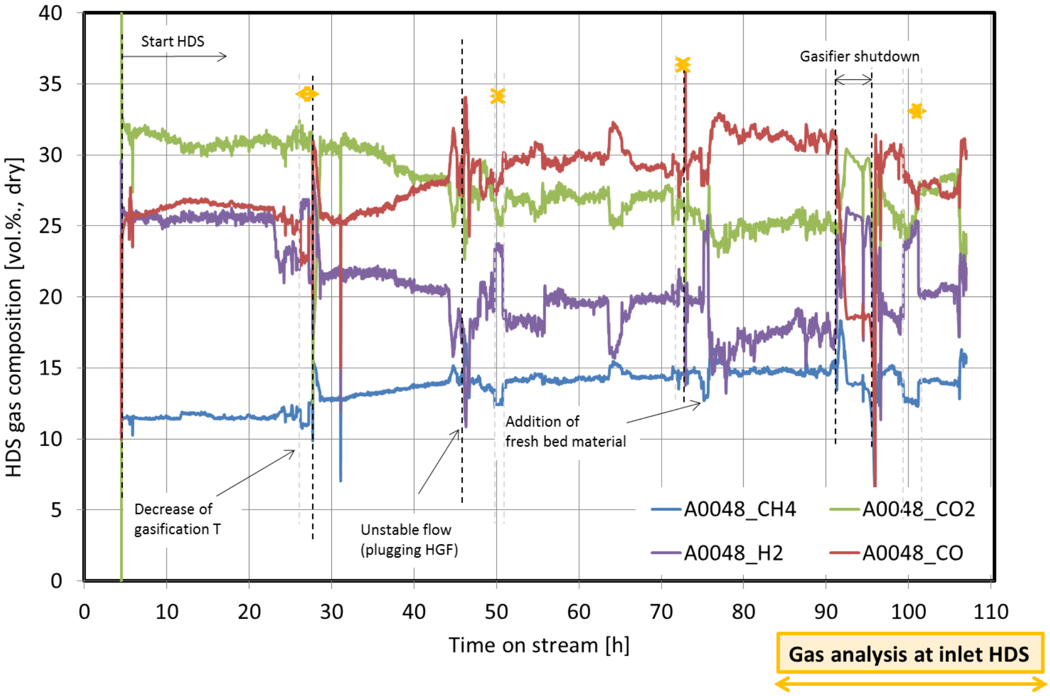


Figure 19. Overview of gas composition measured at the HDS gas analysis set (positions switched around HDS and R11; periods of analysis at the HDS inlet indicated with yellow arrows).

The gas composition around the HDS reactor (Figure 19) does not differ significantly from the inlet gas measured at the MILENA/OLGA side. The only significant difference is in the H_2 concentration, which is higher at the reactor inlet (marked with yellow arrows in Figure 19). This is because part of the inlet hydrogen in the gas is consumed in hydrogenation reactions. Clearer differences between sampling positions can be observed in the SNG gas analysis (Figure 20). The gas after the pre-reformer (periods marked with yellow arrows in the figure) shows that CO in the gas is largely converted (from 25-30 vol.% down to 3-4 vol.%), whereas the CO_2 concentration significantly increases to ~ 45 vol.%. It is noteworthy that after the adjustment of the pre-reformer temperatures (reduction from ~ 400°C) to get an inlet gas temperature of 350°C (adjustment after ~ 44 hours of operation of the system), the methanation activity is significantly enhanced (CO decreasing from 4 vol.% to 3 vol.%, CH_4 increasing from 22 vol.% to 24 vol.%, whereas H_2 concentration slightly decreases from 25 vol.% to 22 vol.%).This is the result of the overall balance of (H_2-forming) WGS and steam reforming reactions, and (H_2-consuming) methanation reactions.

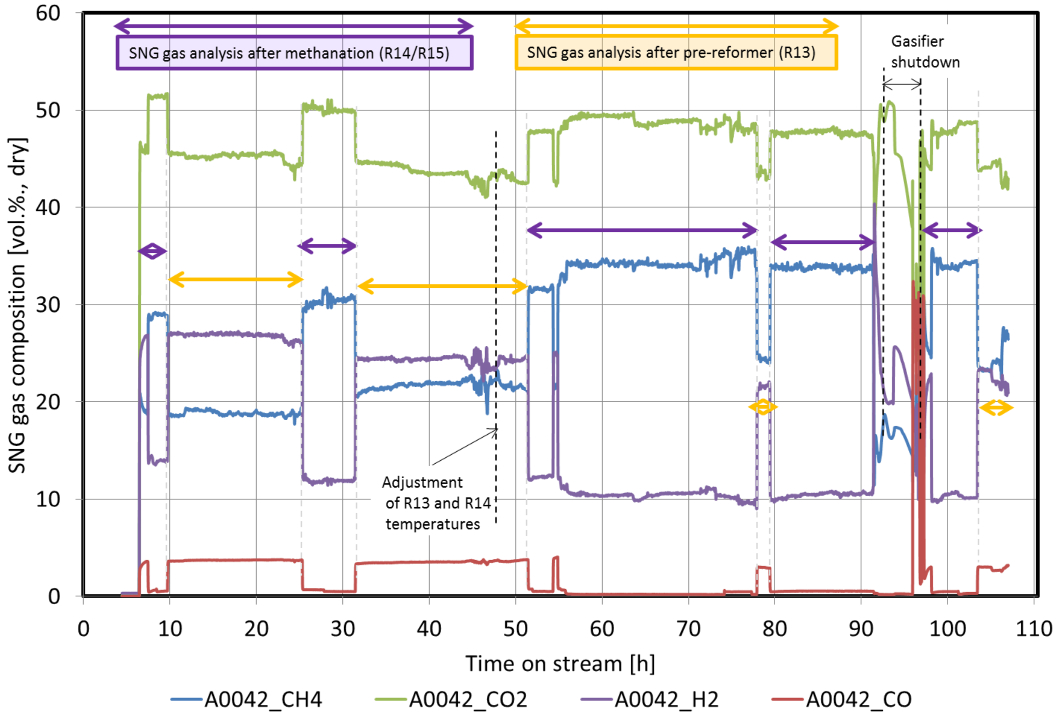


Figure 20. Overview of gas composition measured at the SNG gas analysis set (positions switched after pre-reformer R13, and after methanation reactors R14 and R15).

Further on in the methanation reactor R14 (gas analysis measurement periods indicated with purple arrows in Figure 20), the CH_4 concentration further increases to ~ 35 vol.%, the CO is further converted down to ~ 0.5 – 0.7vol.%, and H_2 is converted down to ~ 10 vol.%. Again, the adjustment (reduction) of the set temperature of R14 around hour 44 leads to a slight improvement of the extent of the methanation reactions (CO content decreasing from 0.7 vol.% to 0.5 vol.%, H_2 content reduced from 12 vol.% to 10 vol.%, and CH_4 concentration increasing from 32 vol.% to nearly 35 vol.%. However, no significant activity was observed in the second methanation catalyst – CO is converted from ~ 0.5 vol.% down to 0.3 vol.%, and the H_2 content remains at ~ 10 vol.%. This was an unexpected result, since all the catalysts were activated following the same procedure. As explained earlier in this section, it was then decided to gradually increase the temperature of R15 to see whether the catalyst became active at some point. At approximately hour 75 of operation, there were hints in the temperature profile of R15 indicating methanation activity of the catalyst. However, there is hardly any difference in the gas composition.

For a better overview of the evolution of the gas composition over the ESME system, Figure 21, Figure 22, Figure 23 and Figure 24 plot the composition of each major compound (CH_4, H_2, CO, and CO_2) at the different gas analysis sets. In the case of CH_4 (Figure 21), the major change in composition takes place in the pre-reformer and methanation reactors. The raw bio-SNG after the methanation reactors contains approximately 35 vol.% methane.

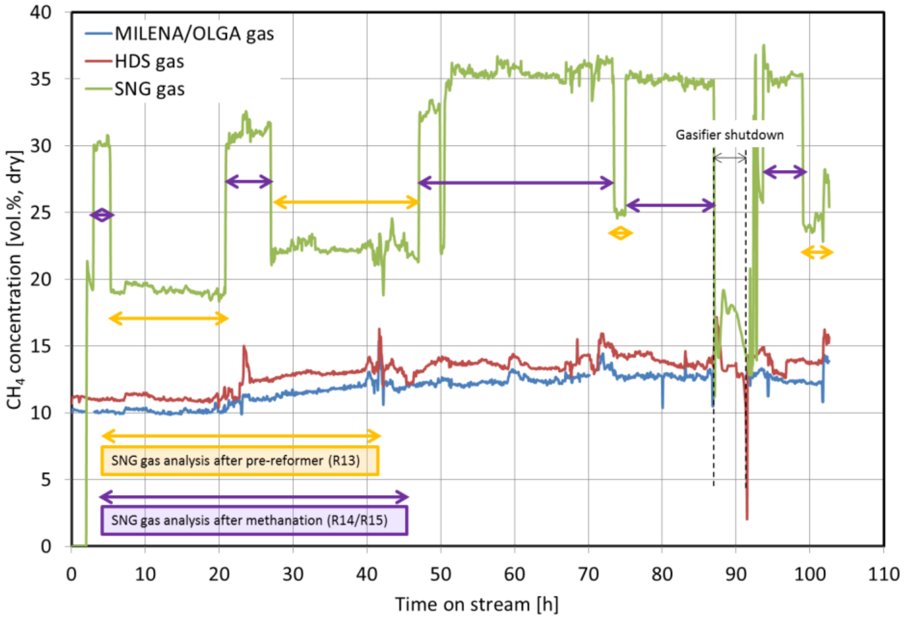


Figure 21. Overview of CH_4 concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

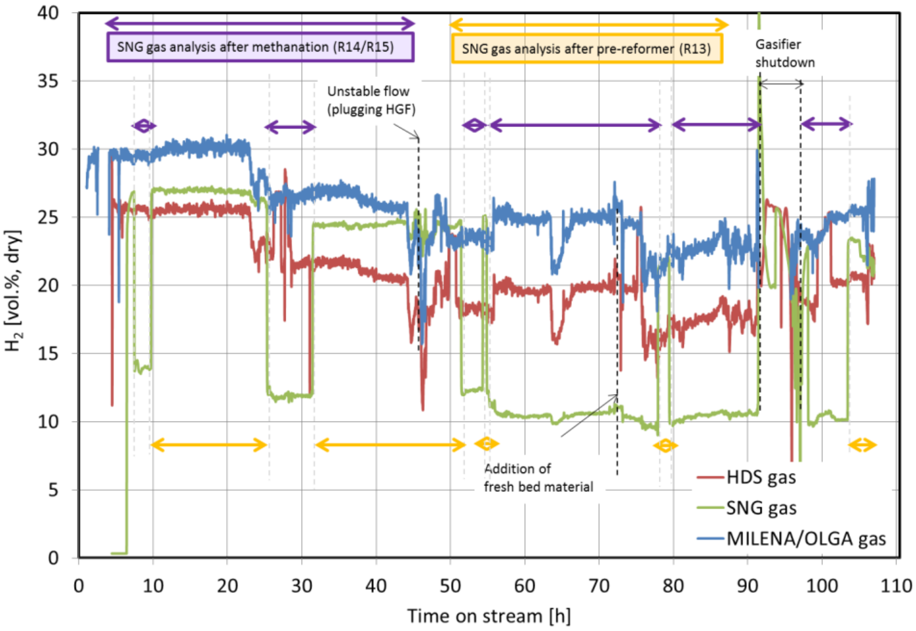


Figure 22. Overview of H_2 concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

In Figure 22 it can be observed that despite changes in the inlet gas composition (deriving from the decrease in the gasification temperature, from hour ~20 onwards), the H_2 concentration decreases by approximately 5 vol.% over the HDS reactor, due to the consumption in hydrogenation reactions. Then, the overall effect in the pre-reformer is a slight increase in H_2 concentration (higher extent of reforming + WGS reactions than consumption via methanation). Finally, the H_2 is largely consumed in the first methanation reactor R14, but does not react further in R15 (not shown). The outlet H_2 concentration after R15 is approximately 10 vol.%, thus the raw bio-SNG still contains a too high content of H_2 for grid injection of SNG.

Figure 23 shows no change of CO_2 concentration (as expected) over the HDS reactor, except for a small increase due to H_2 consumption. On the contrary, the content of CO_2 in the gas increases dramatically over the pre-reformer (which indicates the large extent of the WGS reaction). The CO_2 concentration further increases (although at a lower rate) over the first methanation reactor. No significant change in CO_2 was observed over R15 (Figure 25). Lastly, the main change in CO concentration over the ESME system (Figure 24) takes place in the pre-reformer reactor, where the CO concentration decreases down to 3-4 vol.%, despite changes in the inlet gas composition (CO increasing from 23-24 vol.% to 30 vol.% due to the decrease in gasification temperature).

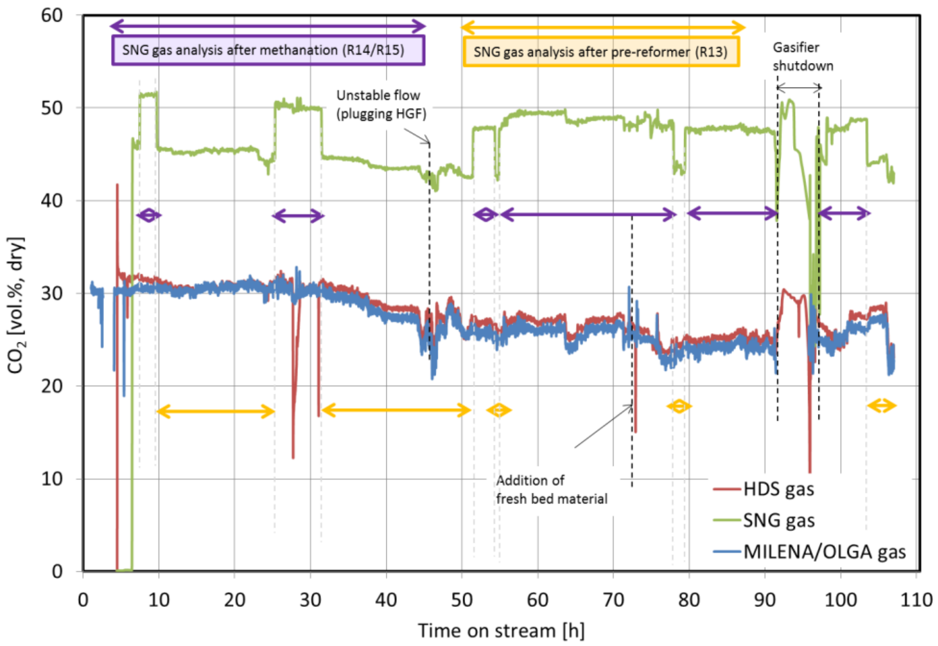


Figure 23. Overview of CO_2 concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

For the sake of clarity and as summary of the above figures, the average values of the main gas compounds (CO, CO_2, H_2 and CH_4) classified per location have been plotted in Figure 24. This gives a graphical evolution of the fate of the main gas compounds over the pre-reformer and the methanation reactors. As can be seen, the largest fraction of CO is converted over the pre-reformer, whereas the increase in CH_4 content takes place over the pre-reformer and the first methanation reactor at similar extent. Besides methanation, a significant amount of CO is converted via WGS to CO_2 at the pre-reformer. This results in an overall increase of the H_2 concentration in the pre-reformer (that is, the production of H_2 via WGS + steam reforming is larger than the hydrogen consumption via methanation).

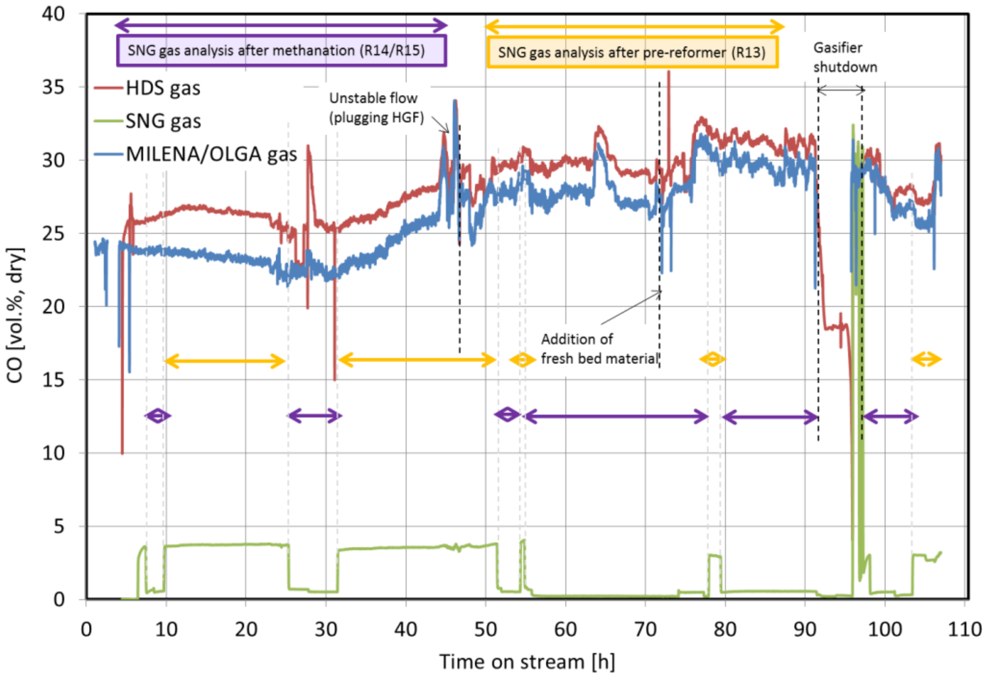


Figure 24. Overview of CO concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

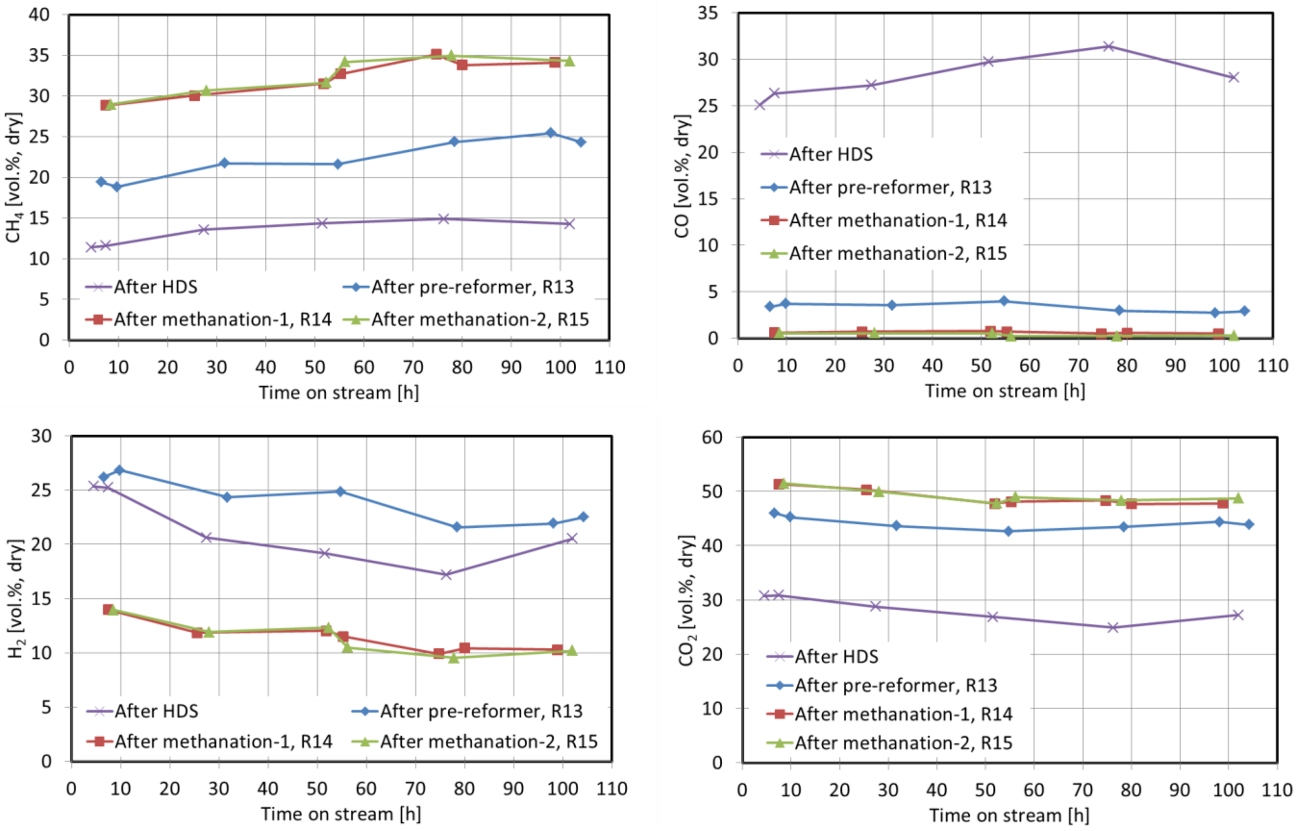
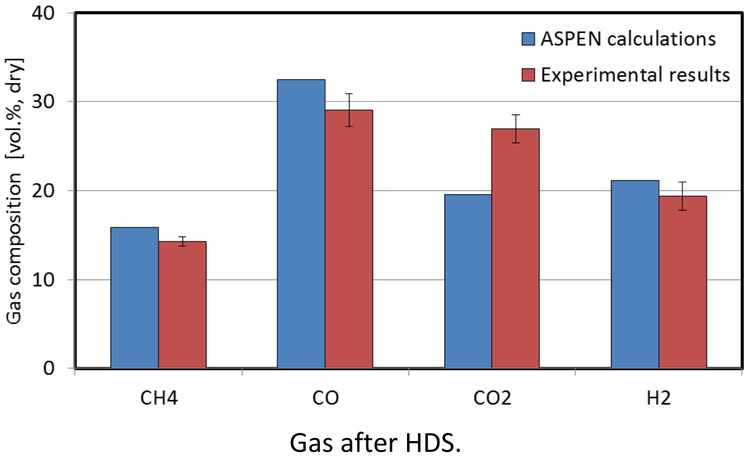
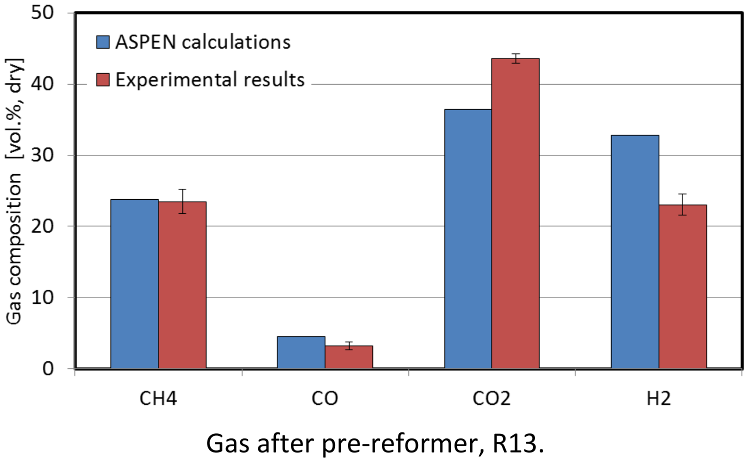


Figure 25. Evolution of CH_4, CO and CO_2 concentration over the ESME reactors (average values measured with online gas monitor)..

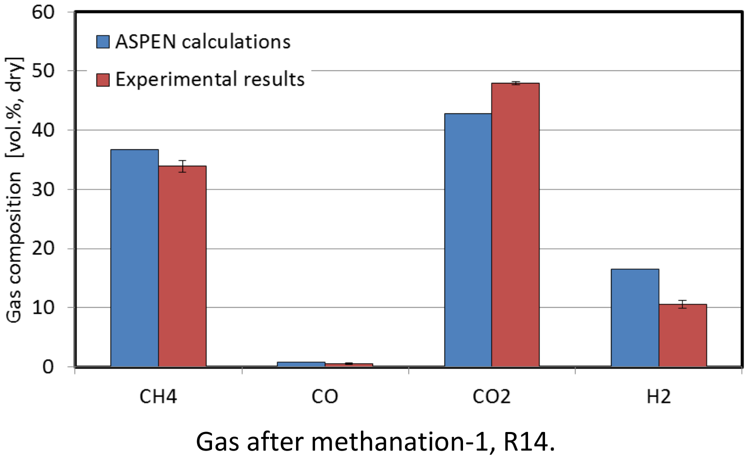
To finalize the analysis of the fate of the main gas compounds over the ESME reactors, Figure 26 compares the experimental results with the values predicted by an Aspen Plus model of the ESME system (results expressed in dry basis for the sake of comparison). As can be observed, there is in general an acceptable agreement between the experimental and the modelled results. The concentrations of CO and CH_4 show a better degree of agreement than H_2 and CO_2 concentrations.



Gas after HDS.



Gas after pre-reformer, R13.



Gas after methanation-1, R14.

Figure 26. Comparison of results of Aspen Plus model and experimental results during test 1 (gas composition expressed in dry basis).

In Figure 27 and Figure 28 it can be observed that benzene and toluene (target compounds to assess the performance of the pre-reformer reactor) are completely converted below detection levels at the pre-reformer (green line zero throughout the test). The peak observed at hour 92 is not due to malfunctioning of the pre-reformer catalyst, but to eventual contamination of the SNG gas analyser with raw gas (during re-start of the system after the 3-hour gasifier shutdown). The peak in benzene and toluene gradually disappears over time (flushing of the gas analysis lines with clean gas). We can conclude that the pre-reformer catalyst performed well throughout this first part of the duration test.

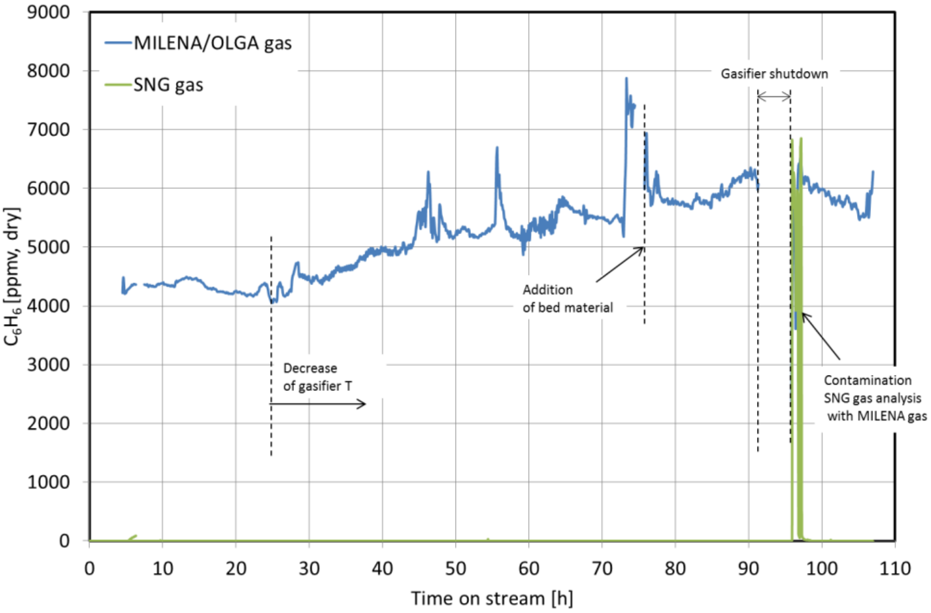


Figure 27. Overview of benzene concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

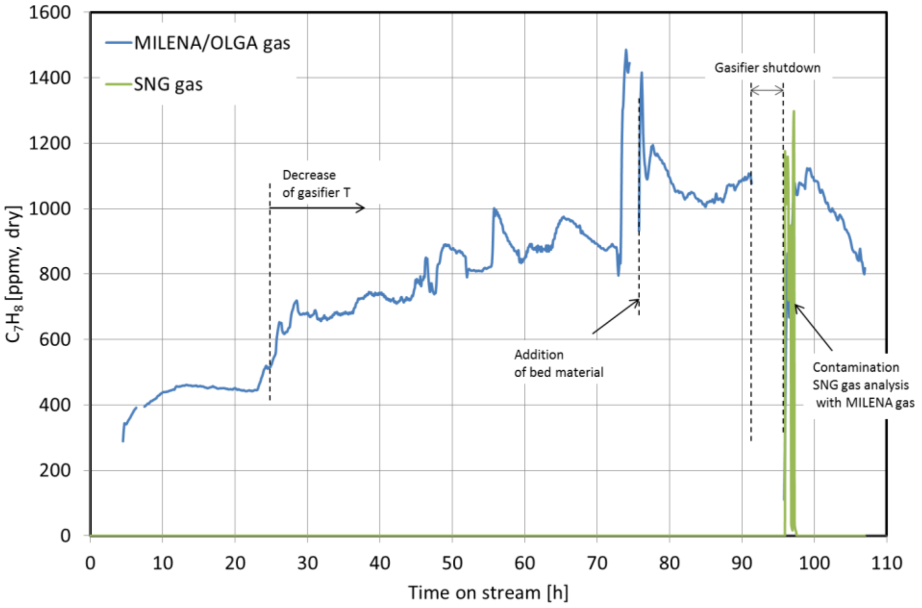


Figure 28. Overview of toluene concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

So far, the gas composition has been analysed. However, over the ESME system there are changes in the total gas flow. This can be seen in Figure 29, where for the sake of clarity the total gas flows (in dry basis, calculated from neon balances over the system) at the HDS gas analysis set (over HDS and ZnO reactors) and at the SNG gas analysis set (around R13, R14, and R15) are compared. As can be observed, the dry gas flow around the HDS is approximately 12 NL/min. In the pre-reformer, the steam reforming reactions lead to an increase in the total dry gas flow to approximately 13-14 NL/min. Afterwards, the methanation reactions taking place in R14 lead to a decrease in the total flow of dry gas to 10-11 NL/min.

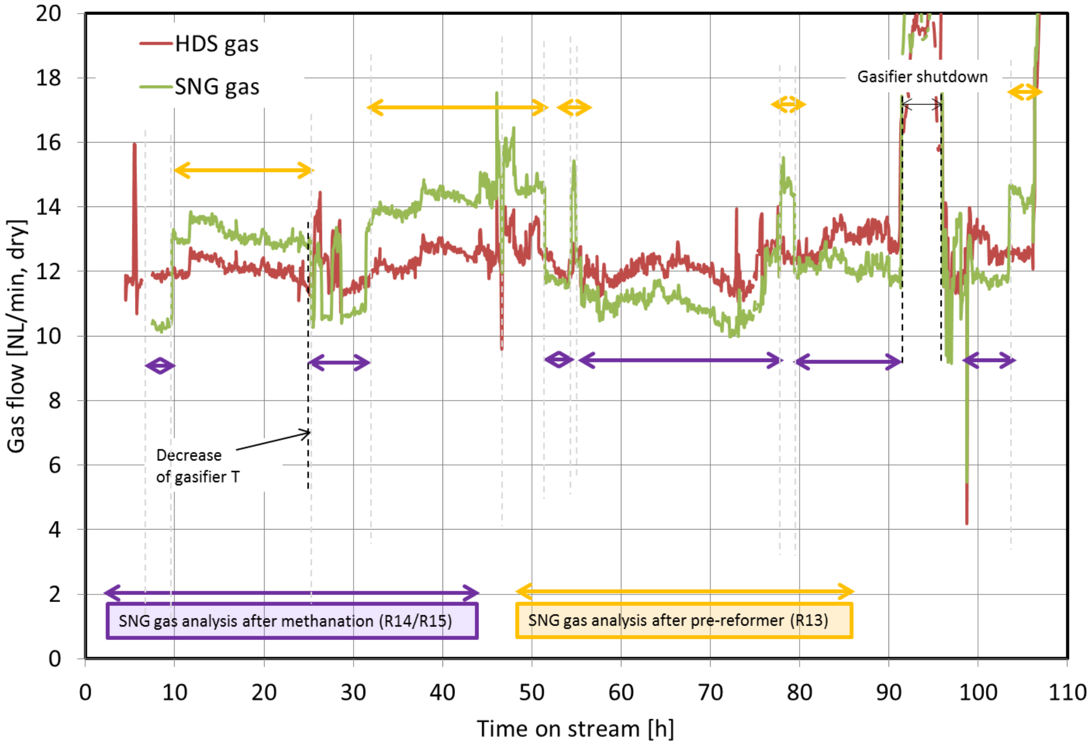


Figure 29. Overview of total gas flow (calculated from balances with neon as tracer gas) around the HDS and the SNG gas analysis sets.

In order to get a better understanding of the evolution of the main gas compounds over ESME, the molar flows of CO and CH_4 (which take into account both changes in gas composition and gas flow) have been plotted in Figure 30. As can be seen, the methane flow in the gas roughly doubles from 4 mol/h to 8 mol/h over the pre-reformer, whereas CO is converted and reduced from 8-9 mol/h to approximately 1.5 mol/h. It is noteworthy that the adjustment of the set temperature in hour 44 of the test had a positive effect on the extent of the methanation reactions, since in the period 50-85 hours on stream the methane flow increases from 4.5 mol/h to 10-11 mol/h. During this same period, maximum values of CO conversion (around 98-99%, calculated as the CO at the outlet of the methanation reactor R15 divided by the CO contained in the inlet OLGA gas) were observed. CO conversion plots (Figure 31) showed that approximately 85% of the CO is converted at the pre-reformer (value increasing up to 90% after adjusting the inlet gas temperature at R13), whereas CO is further converted up to 97% (99% after temperature adjustment) in R14. No catalytic activity was observed in R15, which results in incomplete conversion of CO after the second methanation reactor.

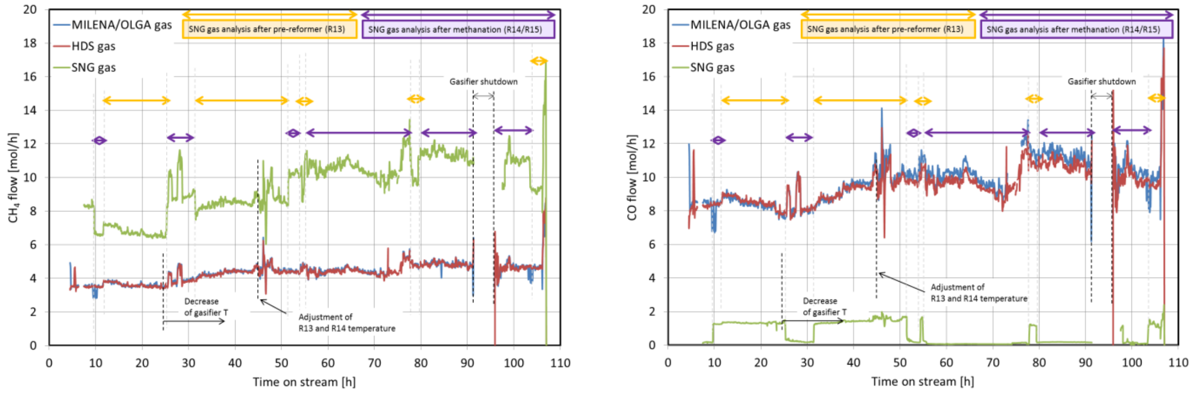


Figure 30. Overview of molar flows of methane (left) and CO right around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (around pre-reformer R13 and methanation reactors R14 and R15).

Figure 32 plots the molar ratio of added steam/carbon (measured in the gas around the HDS gas set) as well as the ratio of added steam with respect to the dry gas flow entering the HDS reactor. As can be seen, during test 1, approximately 1.2 mol/mol added steam/carbon were maintained in the ESME system. This is equivalent to approximately 800 g added steam/Nm^3 dry gas entering the HDS reactor. The latter amount is slightly lower than the minimum value previously calculated in Aspen in order to avoid carbon formation in the pre-reformer reactor. The addition of fresh bed material in the gasifier at hour 70 of operation results in an increase of the gas flow around the ESME system (Figure 29), and therefore, a corresponding slight decrease in the steam/carbon ratio from 1.2 mol/mol to 1.1 mol/mol. However, no signs of deactivation due to coking were detected at this time scale.

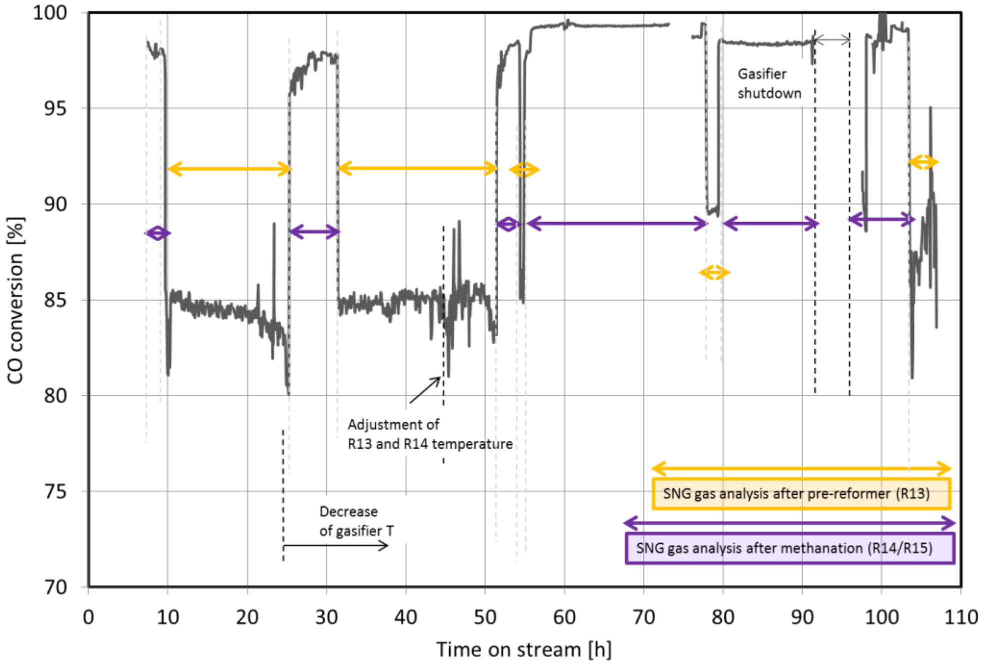


Figure 31. Overview of CO conversion over reactors R13-R15 during test 1.

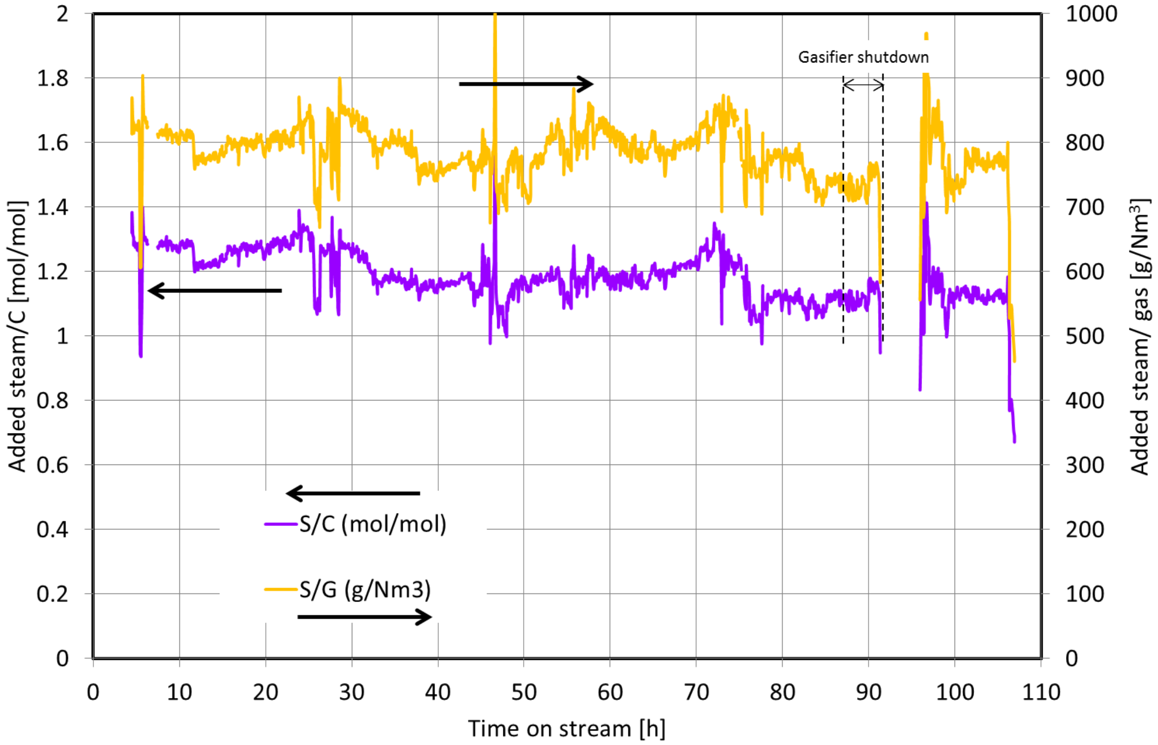


Figure 32. Overview of (added) steam/carbon and (added) steam/HDS dry gas ratios during test 1.

A reduction in gasification temperature from 850°C to below 800°C leads to an increase in the concentration of the inlet H_2S from 60 ppmv to 100-120 ppmv, whereas COS is not so significantly affected by the temperature of the gasifier. H_2S was completely removed from the gas down to detection limits either after the HDS reactor (due to the capture of H_2S and COS by the catalyst), or after the ZnO bed (once that H_2S breakthrough over the HDS reactor takes place). H_2S breakthrough was observed after the HDS catalyst, at the moment from which the H_2S concentration at the outlet of the HDS reactor starts to gradually increase up to 40 ppmv (that is, ~ 40% of the inlet gas concentration). Even so, both micro-GC analysis and GC-FPD applied to gas bags (results not shown in this report) revealed that the ZnO bed is able to capture the slipping H_2S down to sufficiently low values for the application at AMBIGO. The breakthrough of COS occurs some time later.

Other relevant compounds to assess the performance of the HDS reactor are ethylene and acetylene. As can be observed in Figure 33, ethylene is nearly completely converted at the outlet of the HDS reactor (values measured by micro-GC around 0.001 vol.%). Acetylene was converted below detection limits throughout the test. Figure 34 goes deeper into the conversion of ethylene within the HDS catalyst. Average values of ethylene at 3 different locations (inlet HDS, approximately 1/6 within the catalyst bed, and outlet HDS) have been plotted. As can be seen, although ethylene conversion takes mainly place at the first part of the catalyst, after 70 hours in operation, there is a slight decrease in the ethylene conversion taking place on the top of the catalyst.

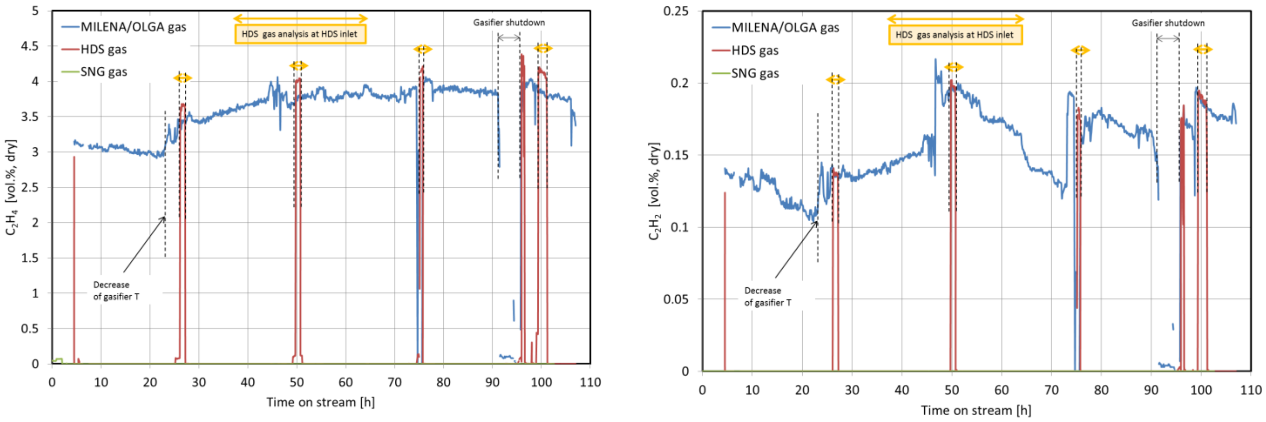


Figure 33. Overview of ethylene (left) and acetylene (right) concentration in gas around ESME: MILENA/OLGA absorber (inlet gas), HDS gas analyser (around HDS and R11) and SNG gas analyser (after pre-reformer R13 and after methanation reactors R14 and R15).

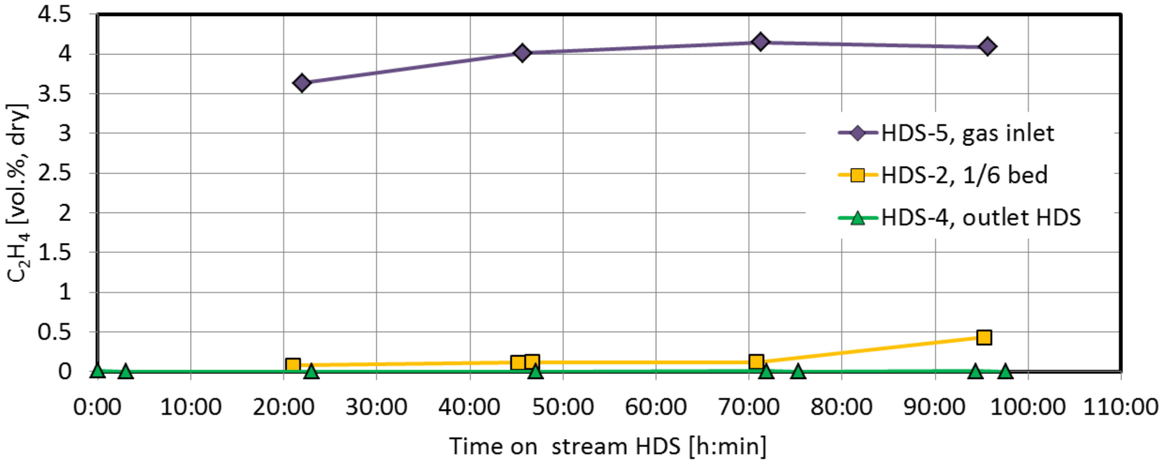


Figure 34. Ethylene concentration at different locations of the HDS reactor: inlet, ~ 1/6 of catalyst bed (HDS-2) and outlet (HDS-4). Average values from each measurement period expressed at the starting time of each period.

Complementary to micro-GC analysis, GC-FPD analysis for the analysis of sulphur gas compounds was performed to gas bags which were daily sampled around the HDS reactor and the ZnO reactor (R11). The objective was to determine whether complete conversion of organic sulphur compounds was achieved and maintained by the HDS catalyst, and whether the ZnO sorbent was able to properly remove H_2S and COS over time from the gas before entering the nickel catalysts. The target analytes included, besides H_2S and COS, other organic compounds such as thiophene (and thiophene derivatives), mercaptan derivatives, among others. The inlet gas from the OLGA tar removal unit contains thiophene (and thiophene derivatives), as well as mercaptans, at ppmv level. These compounds are not removed in the cooler, and enter thus the HDS reactor (HDS-5 position, inlet HDS). Ethylmercaptan, isopropyl mercaptan and thiophene derivatives (ethyl- and methyl-thiophene) are removed at the top of the HDS catalyst bed (decrease of concentration below detection limits at the HDS-2 position). Methylmercaptan is largely removed at the top of the catalyst, but not completely. Approximately 50-60% of thiophene is also converted in the top of the catalyst bed (above the position of HDS-2). Further in the bed, the remnants of all organic sulphur compounds (except for COS) are converted below detection limits. GC-FPD analyses detected a slip of H_2S from the beginning of the test. This slip increased gradually over time, until exceeding the upper limit of the measurement range. Similarly to H_2S, the slip of COS over the HDS reactor gradually increases. However, COS is captured down to below detection limit in the ZnO reactor (position HDS-1), whereas H_2S is captured down to sufficiently low values.

3.3 Results of duration test 2

The second part of the duration test started on the 9th January 2018. In total, the gasifier was operating without interruption for ~ 138.5 hours. After ~ 25 hours of gasifier operation, a leaking pressure meter at the neon feeding line (near the hot gas filter), which had to be replaced, led to a controlled bypass of ESME, with a maximum duration of ~ 1 hour. MILENA was not stopped. Except for this minor event, the whole ESME system was in operation during almost 130 hours. Stable operation was observed in general in the whole system. The test was stopped on the 15th January 2018 at around 2:00 AM, due to a high pressure alarm at the gasifier[5]. The main events taking place during the experiment (indicated in the figures of the results section, 4.2) are summarized here:

- After 24 hours of MILENA operation: reduction of gasification temperature (from 820°C to approximately 790°C), and controlled bypass of ESME during 0.3 hours (HDS) to 1 hour (R15).

- After approximately 72 hours of gasifier operation: peak observed in system temperature (from gasifier up to R13).

- At hour 120 of gasifier operation, signs of transitory instability were observed in temperature profiles. This event matched with a transient decrease in the gas flow entering at ESME, which indicates that probably there was some clogging at the hot gas filter or the Soxhlet filter.

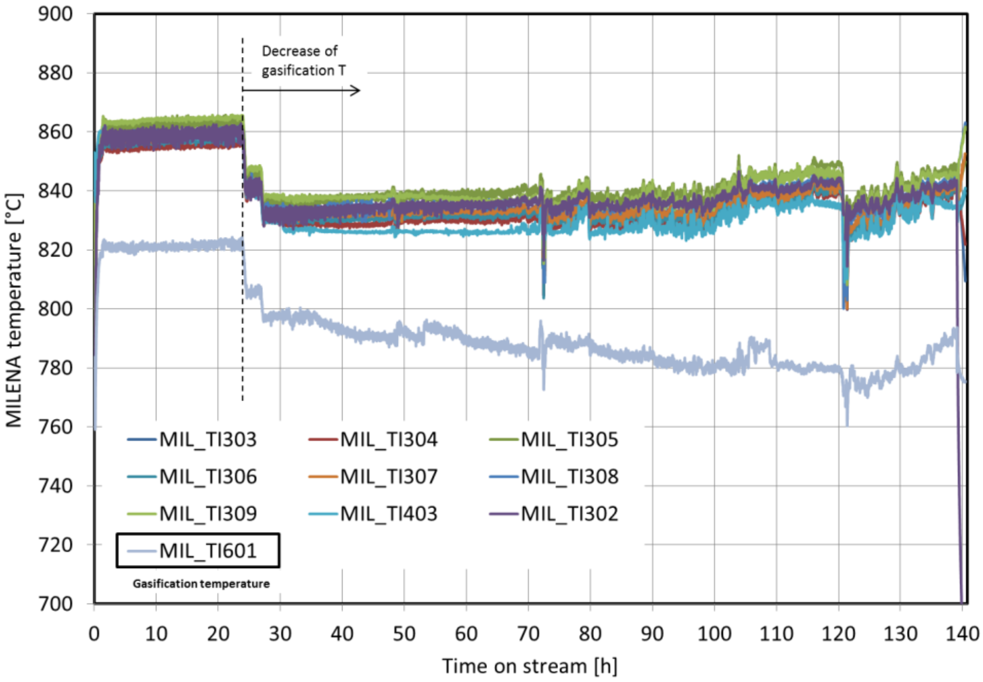


Figure 35. Overview of MILENA gasifier temperatures during duration test 2.

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[5] During post-inspection, it was found out that the insulation material at the top of the gasifier had broken down. Most likely, this was the cause of the high-pressure alarm, and thus, of the system shutdown.

Figure 35 displays the temperatures in the gasifier. TI_601 is the temperature measured at the riser (thus, the gasification temperature), whereas the rest of temperatures are measured at the bubbling fluidized combustor side. As can be seen, after 25 hours operation, the set temperatures at the gasifier (operating at 820°C) were reduced to get a gasification temperature of ~790°C (temperature expected at the AMBIGO plant). The combustion temperature was meanwhile approximately 830-840°C. The decrease in gasification temperature resulted in a modification of the MILENA product gas composition (plotted in Figure 36), namely an increase of the CO concentration, a corresponding decrease of CO_2 content, and a slight increase of the methane concentration.

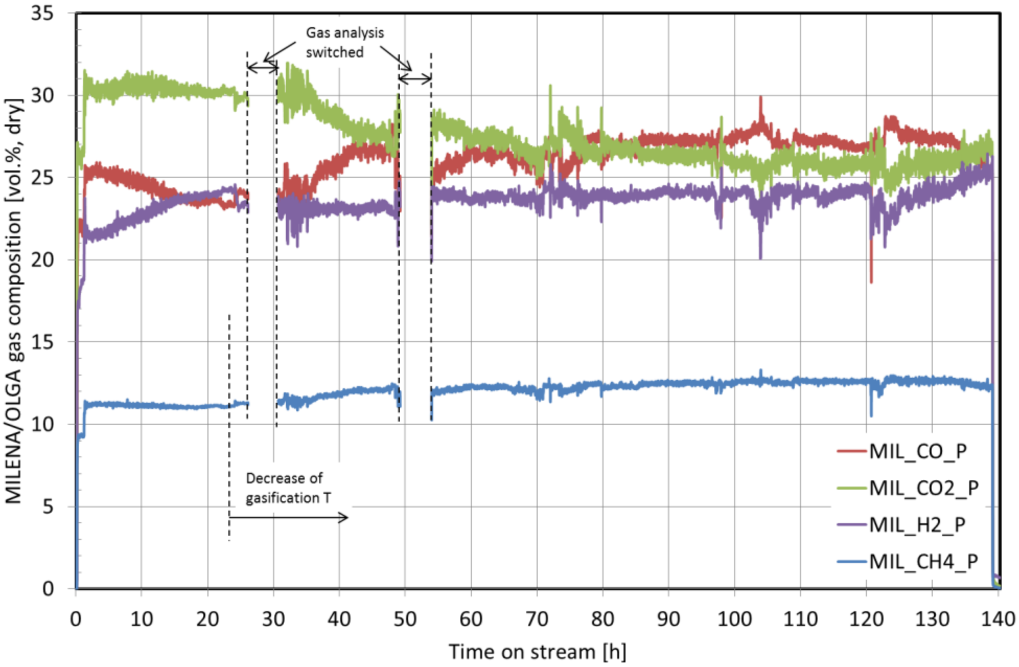

Figure 36. Overview of MILENA product gas composition (measured with online gas analyser, dry basis) during duration test 2. The gaps correspond to a transient switch of the gas analysis set to a different lab setup.

Figure 37 plots the pressure over the ESME system (in the figure shown from the position after R12 up to after the second methanation reactor R15). As can be observed, the system pressure was kept at 5.7 bar during most of the experiment. At hour 70, some transient instability is observed, but in general, stable operation was maintained throughout the test.

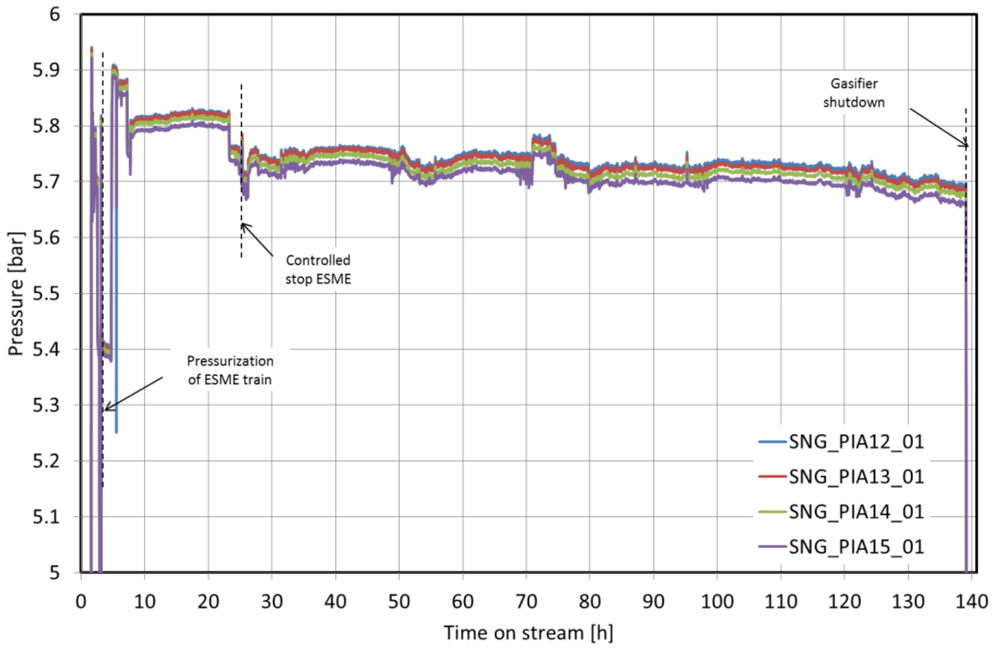

Figure 37. Overview of pressures around ESME system during duration test 2.

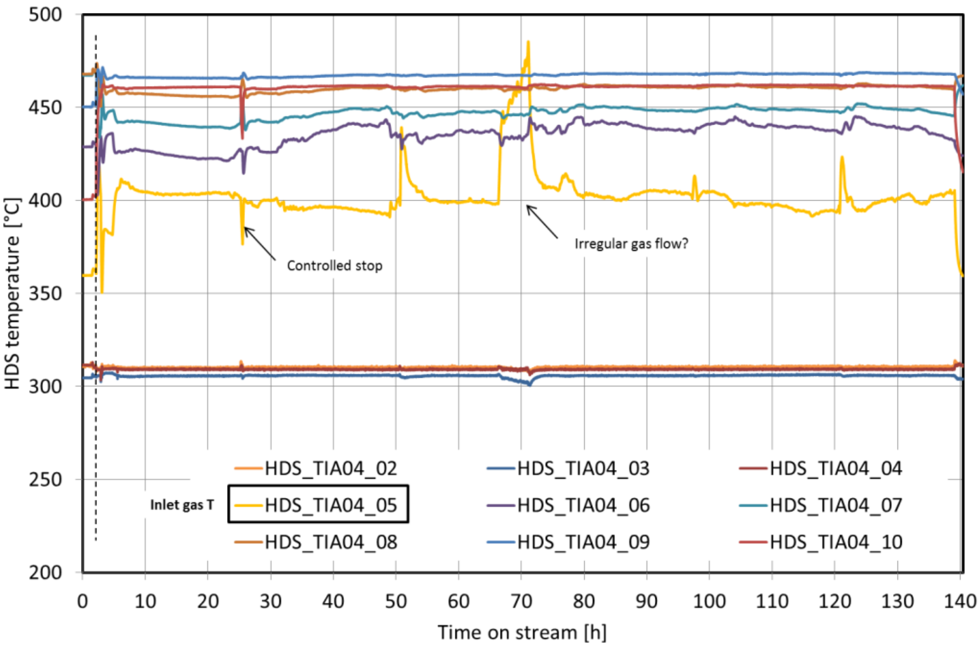

Figure 38. Overview of HDS temperature profile during duration test 2.

The temperature profile of the HDS reactor during the test is plotted in Figure 38. In general, stable operation was achieved throughout the experiment. As already commented in Section 3.2, the temperature at the top of the catalyst (HDS_TIA4_05) is very sensitive to changes in flow and/or composition of the inlet gas. A number of events leading to unstable flow, the most important of which takes place at hour 70 of HDS operation, can be identified over the test. The event at hour 70 matches with the peaks observed at the gasification temperature. Therefore, it is likely that some transient increase in product gas flow took place in the gasifier, which led to instability at the entrance of the HDS reactor and in the rest of the ESME reactors (visible in the temperature profiles of the ESME reactors).

Figure 39 displays the overview of temperature profile at the pre-reformer reactor, R13. In general, stable operation of the reactor was observed. The temperature at the inlet of the catalyst (TI13_05, plotted in yellow) was maintained at ~350°C throughout the experiment. The temperature within the catalyst bed increased up to ~530°C, similarly as what was observed during test 1 (Figure 16). No signs of deactivation were observed in the catalyst throughout the test. A number of minor fluctuations in the catalyst temperature (apart from the controlled bypass of the ESME system, hour 25) are observed scattered along the experiments. These changes match with the fluctuations of the inlet temperature at the HDS catalyst (TIA04_05 in Figure 38), and at the inlet temperature of the methanation reactors (Figure 40 and Figure 41), and are most likely due to transient variations in gas flow. It is noteworthy that after approximately 35 hours operation, TI13_08, thermocouple located in the catalyst bed (blue line), starts to slightly deviate (increase) from the rest of the bed temperatures TI13_7, TI13_09 and TI13_10. This might be an indication of increased methanation activity of the catalyst, which might be in consistency with the trends observed in the (increasing over time) methane concentration in the pre-reformer outlet gas (Figure 42).

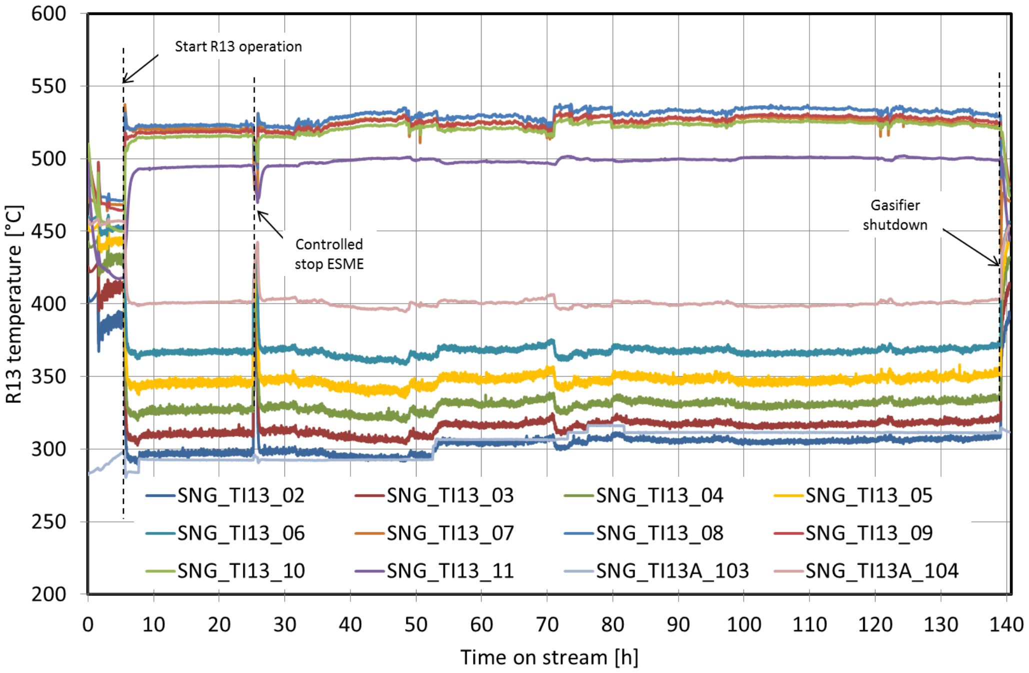

Figure 39. Overview of pre-reformer (R13) temperature profile during duration test 2. The inlet gas temperature is TI13_05 (yellow line).

Figure 40 and Figure 41 show, as in the rest of the ESME reactors, stable operation in reactors R14 and R15 throughout the experiment. It is noteworthy that during the second duration experiment, the methanation catalyst located at R15 exhibited methanation activity (when comparing the temperature profiles of tests 1 and 2 in Figure 18 and Figure 41, respectively). Unlike in the first test, during the second part of the test in January, an increase of the catalyst bed temperatures is observed upon start of operation. This was accompanied by a visible change in gas composition over R15. The temperature at the inlet of the catalyst bed (TI15_05, yellow line) was kept at ~250°C throughout the experiment. The only explanation possible to the increase of activity of the R15 catalyst with respect to test 1 is the activation period applied between the end of the first part of the duration test in December 2017 and the start of the second part of January 2018, when 10 vol.% H_2 in N_2 was flushed through reactors R13-R15 at the set temperatures of the reactors. On the other hand, no signs of deactivation of the methanation catalyst were observed during the test.

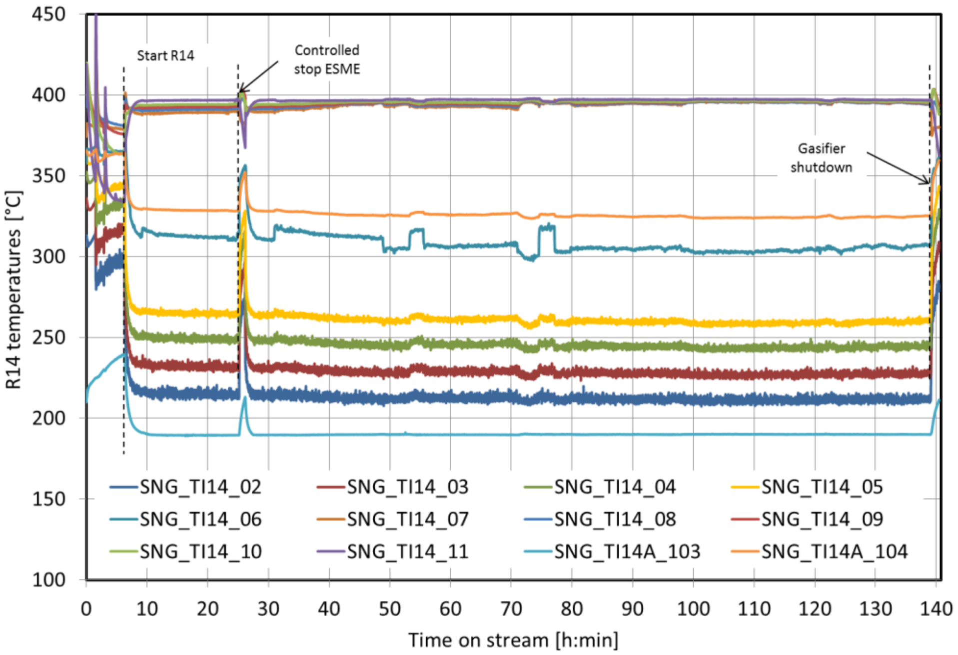

Figure 40. Overview of first methanation reactor (R14) temperature profile during duration test 2. The inlet gas temperature is TI14_05 (yellow line).

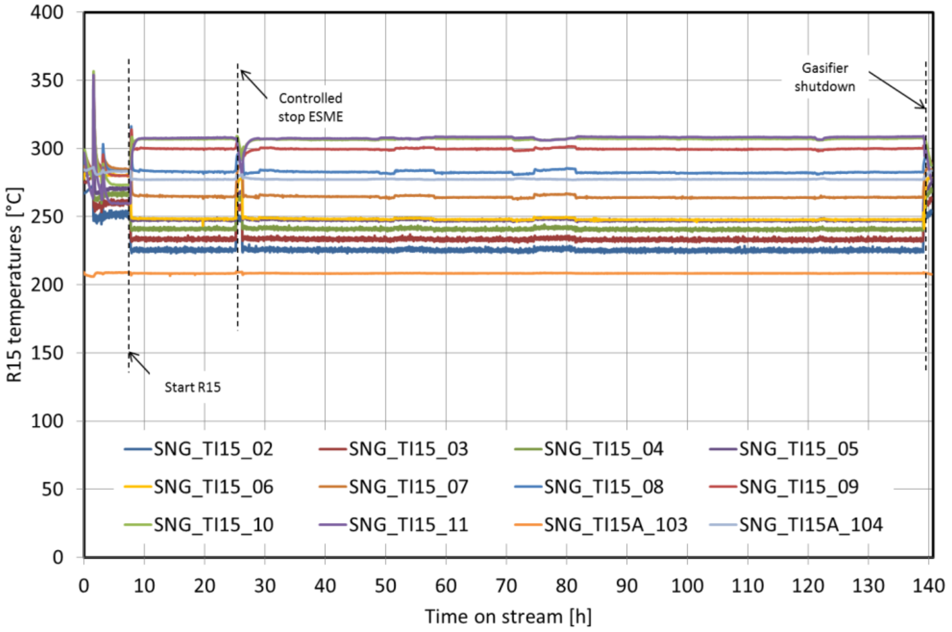

Figure 41. Overview of second methanation reactor (R15) temperature profile during duration test 2. The inlet gas temperature is TI15_06.

Figure 42- Figure 44 plot the changes of gas composition over the ESME system. Figure 42 shows an overview of the main gas compounds (measured by online gas monitor at the SNG gas analysis set). In this gas set, the gas sampling position can be switched: after the pre-reformer (position SNG 1-4),

after the first methanation reactor (position SNG 1-5) and after the second methanation reactor (position SNG 1-6). When comparing the gas composition measured over time after the second methanation reactor (periods marked with red arrows in Figure 42), it can be seen that the methane concentration progressively increases over time up to approximately the half of the test, after which it remains approximately constant. There is also a slight increase in the methane content after the pre-reformer. It is uncertain to assess if this phenomenon is a combined effect of the change in the inlet gas composition, and changes in the catalyst activity, and what the relative weight of each factor is in the overall effect observed.

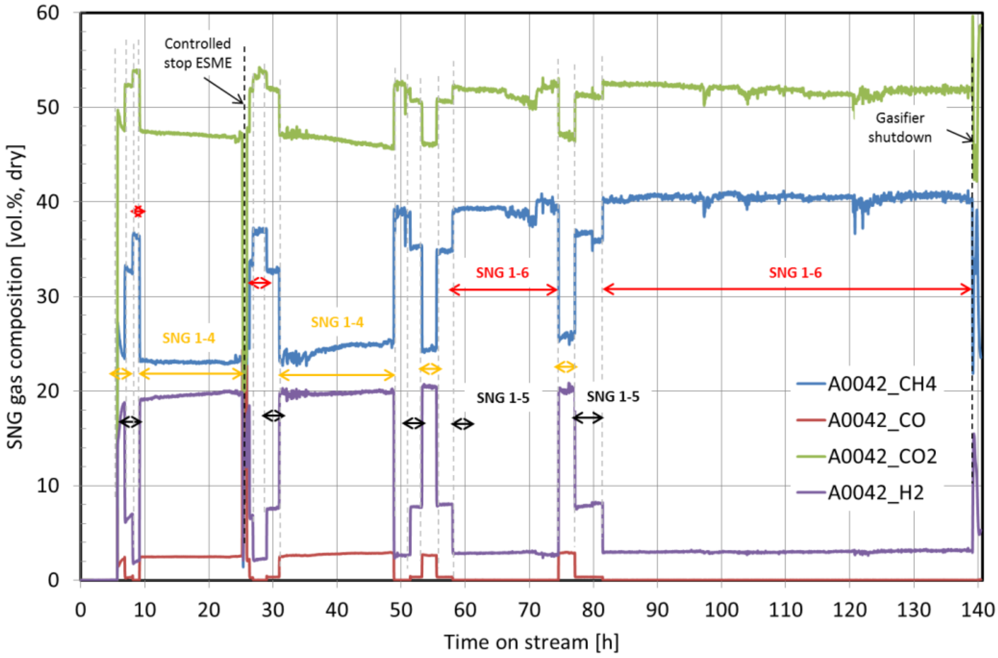

Figure 42. Overview of gas composition measured with online gas analyser at the SNG gas set (after pre-reformer, position SNG 1-4; after first methanation reactor, position SNG 1-5; and after second methanation reactor, position 1-6) during test 2.

Figure 43 plots the overview of the main compounds of the gas over the HDS gas analysis set. The analysis positions of this gas set can be switched around the HDS reactor (position HDS-5, gas inlet; position HDS-2, within the catalyst bed; position HDS-4, after the HDS; and position HDS-1, located after the ZnO reactor). In Figure 43, the periods where the gas analysis was located at the entrance of the HDS reactor are indicated by black arrows. It can be clearly observed how hydrogen is being consumed within the reactor in hydrogenation reactions.

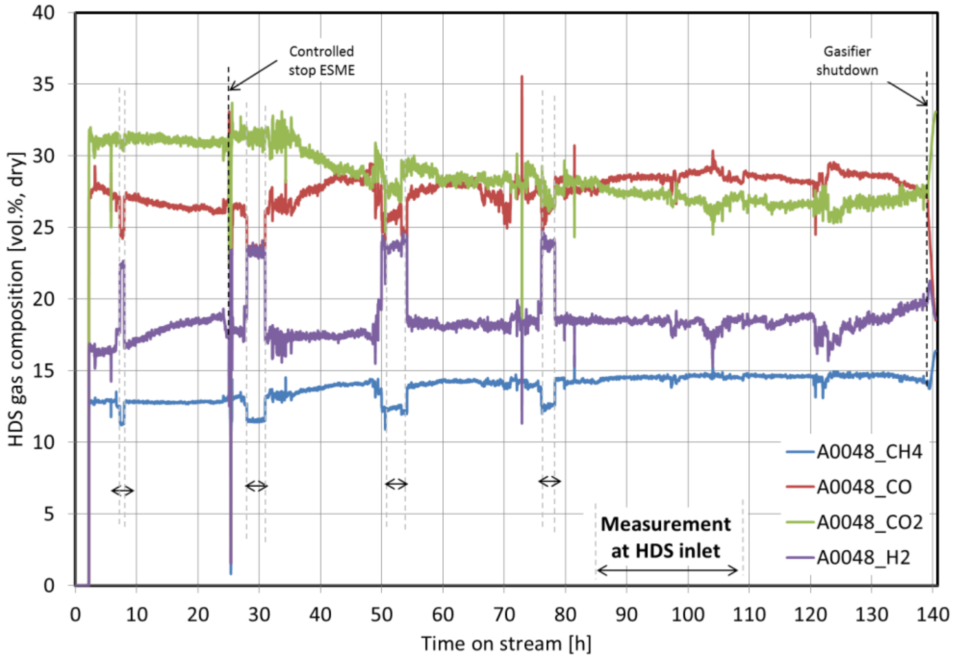

Figure 43. Overview of gas composition measured with online gas analyser at the HDS gas set (around the HDS and ZnO reactors) during duration test 2. The arrows indicate analysis position at the inlet of the HDS reactor.

Figure 44 plot the evolution of the main gas compounds between the outlet of R13 and the outlet of R15 along the duration of the experiment (that is, over the methanation reactors). For that, average values of the measurement periods at each analysis position (expressed at the beginning of each period) have been taken. As can be seen, R14 takes care of the conversion of a larger fraction of CO and H_2 compared to R15. The CO concentration is dramatically reduced from ~ 2.5 vol.% to 0.3 vol.% over R14, whereas the rest of the CO is converted in R15. The H_2 concentration is reduced from 20 vol.% to 8 vol.% in R14, and further consumed down to 3 vol.% in R13. From these trends it can be clearly seen the positive effect of the activation of the methanation catalyst at R15. It is noteworthy the increasing trends over time of CH_4, and the corresponding decreasing trends of CO_2. Since the gas composition remains approximately constant during the second half of the test (see Figure 36), but the methane content is still increasing during the second half, then it might be inferred that there is a progressive increase of the catalytic activity of the pre-reforming and methanation catalysts over test 2[6].

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[6] Another possibility is that the lower gasification temperature results in a product gas with increased concentration of CH_4, CO, BTX and C_2 hydrocarbons. This would have led in turn to a change in S/C ratio which would promote methanation.

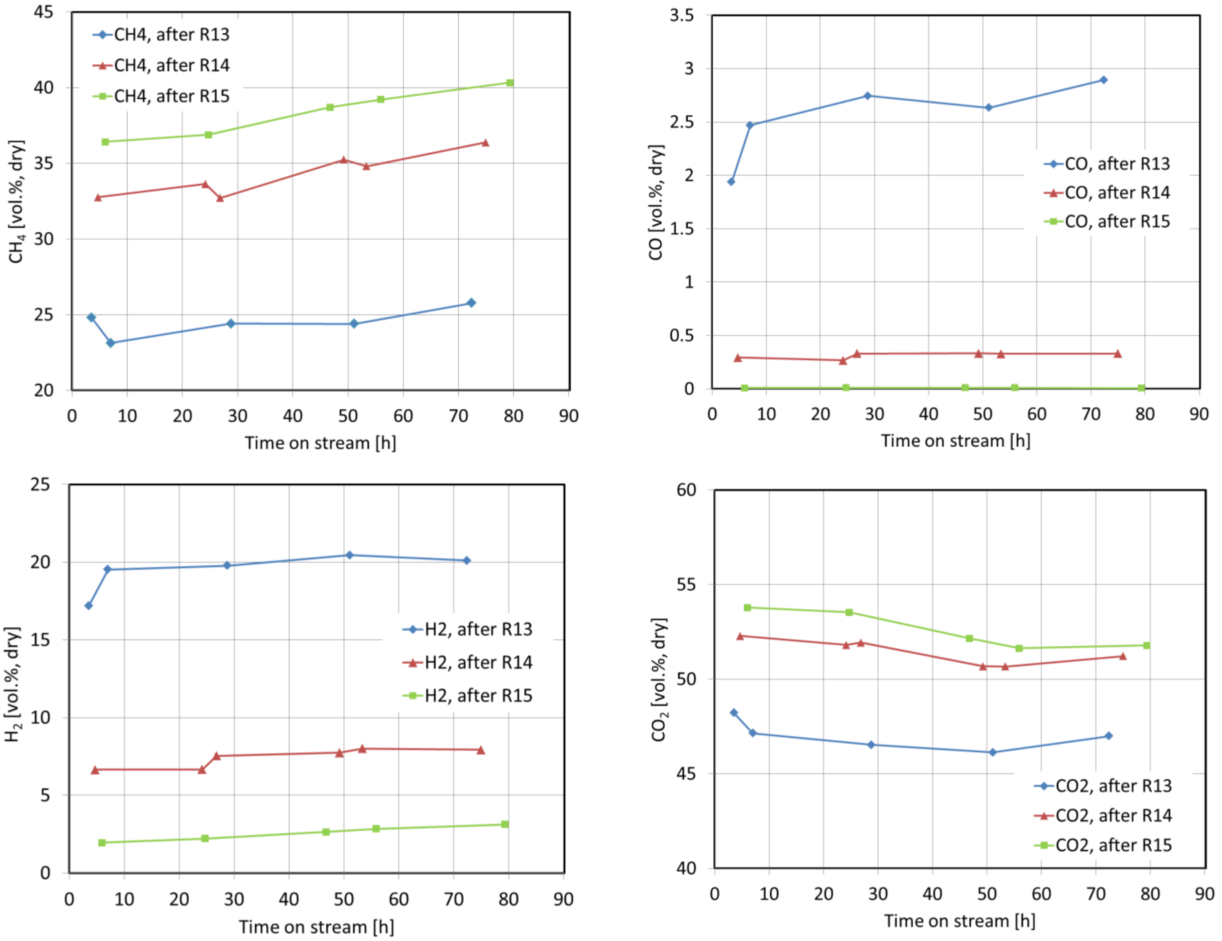

Figure 44. Average concentrations (measured with online gas monitor) of H_2, CO, CH_4 and CO_2 after reactors R13, R14 and R15 during duration test 2 (origin of X-axis at start of HDS operation).

The trends of ethylene over the system are plotted in Figure 45. As can be seen, the HDS catalyst converts ethylene almost completely (down to 0.001 vol.%, according to micro-GC analysis). Acetylene (not plotted) was completely converted below detection levels throughout the experiment. When switching the gas sampling position to HDS-2 (located approximately 1/6 within the HDS bed), it was shown that the bulk of ethylene conversion takes place in the top of the HDS catalyst: at HDS-2, ethylene is already converted down to 0.5-0.6 vol.%; the rest of ethylene is converted over the rest of the catalyst.

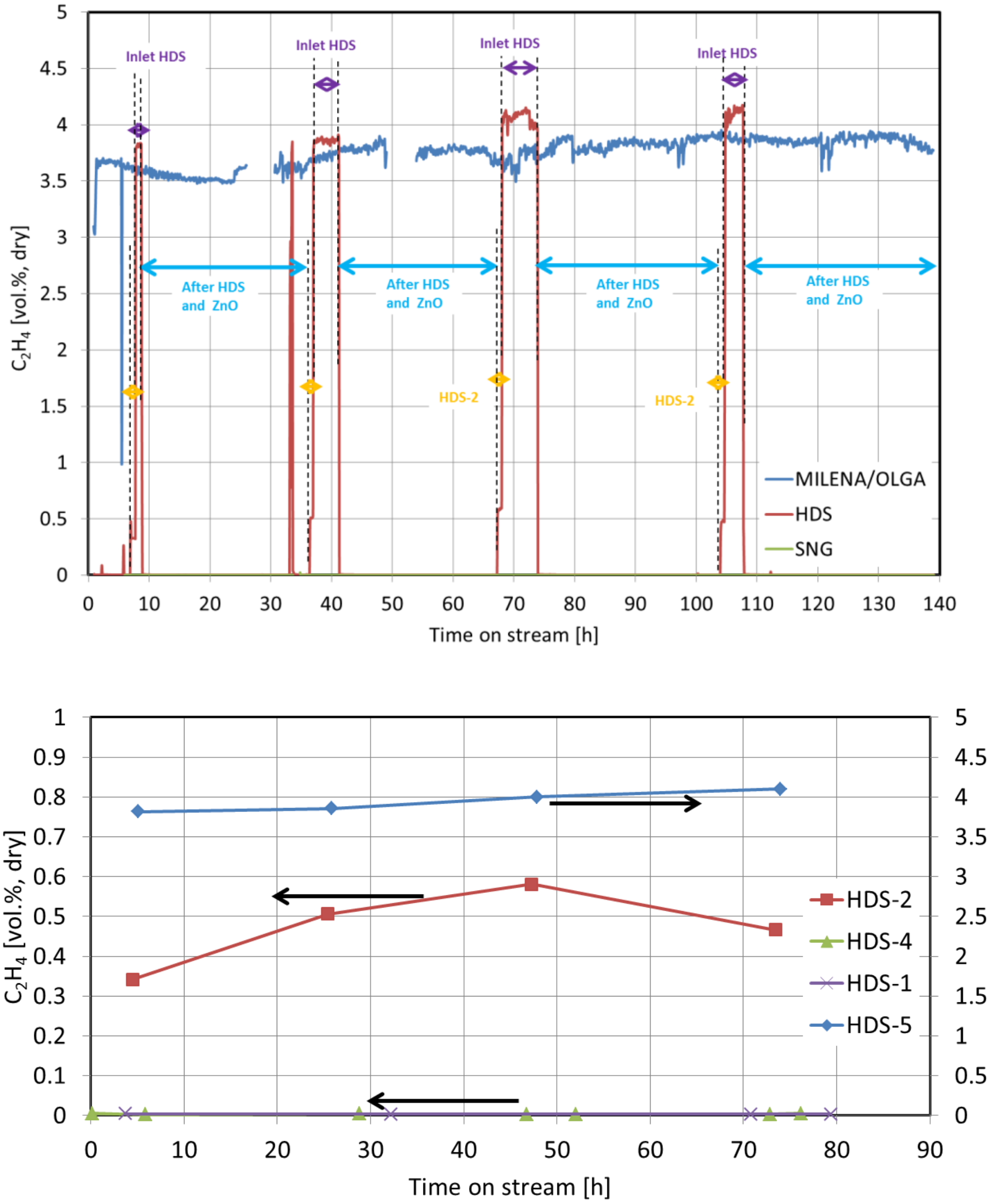

Figure 45. Evolution of ethylene concentration over the ESME system during test 2 (top), and average concentration values at each measurement location (bottom): HDS-5 (inlet HDS); HDS-2 (~ 16% within HDS bed); HDS-4 (outlet HDS); HDS-1 (outlet ZnO bed).

Figure 46 plots the concentration of benzene and toluene at the inlet MILENA gas (blue line) and over the SNG gas analysis set (green line). As can be seen, the pre-reformer catalyst was able to convert BTX down to below detection limits throughout the experiment. Figure 47 focuses on the overall CO conversion. The conversion was obtained from molar balances performed around the ESME system (neon was added as tracer gas), and was calculated with respect to the CO measured in the HDS gas set (inlet to the R13 reactor). As can be seen, the bulk of CO, approximately 88-90%, is converted over the pre-reformer reactor. Then, CO is further converted down to ~99% in the first methanation reactor. The remaining traces of CO are finally converted in the second methanation reactor.

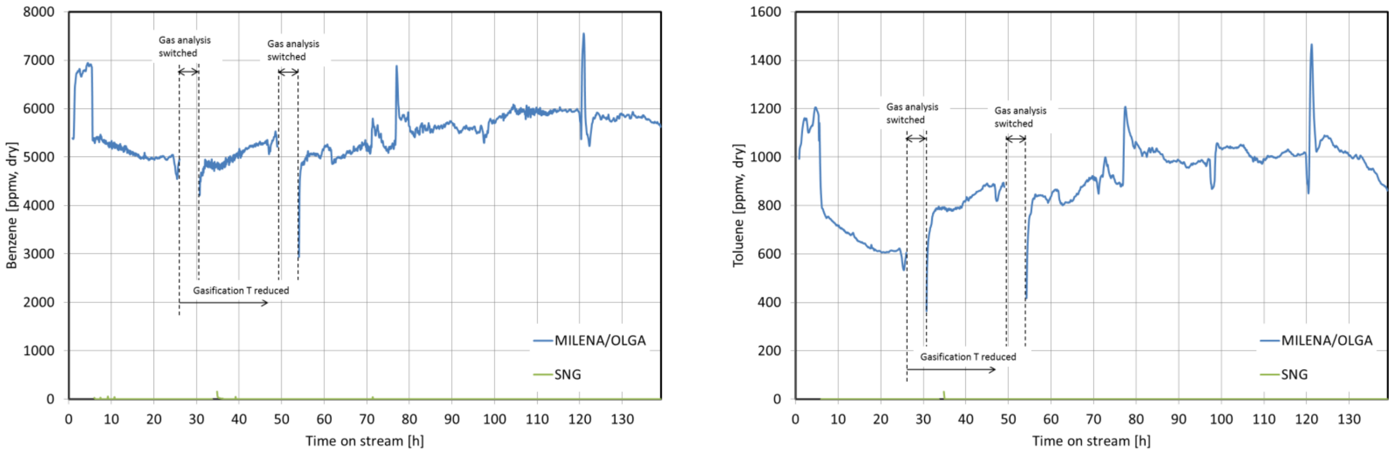

Figure 46. Evolution of benzene and toluene concentration over the ESME system: MILENA/OLGA gas and SNG gas analysis (over R13-R15) during test 2.

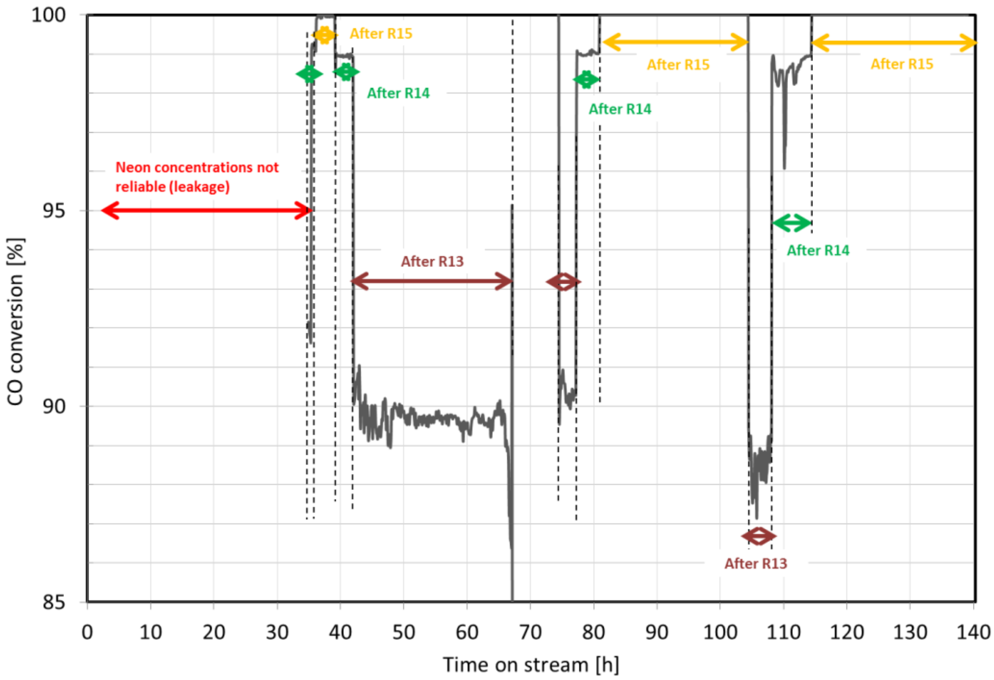

Figure 47. Overview of CO conversion around the pre-reformer R13, and the methanation reactors R14 and R15 during test 2.

Figure 48 shows that over the second part of the test, ~ 1.2 mol/mol added of steam/carbon (which is equivalent to approximately 800 g steam/Nm^3 gas entering the ESME system) was kept at the inlet of R13. These values were of the same order of those observed during the first part of the test (Figure 32), but most likely above the theoretical carbon formation boundary, since no apparent signs of deactivation were observed during the test.

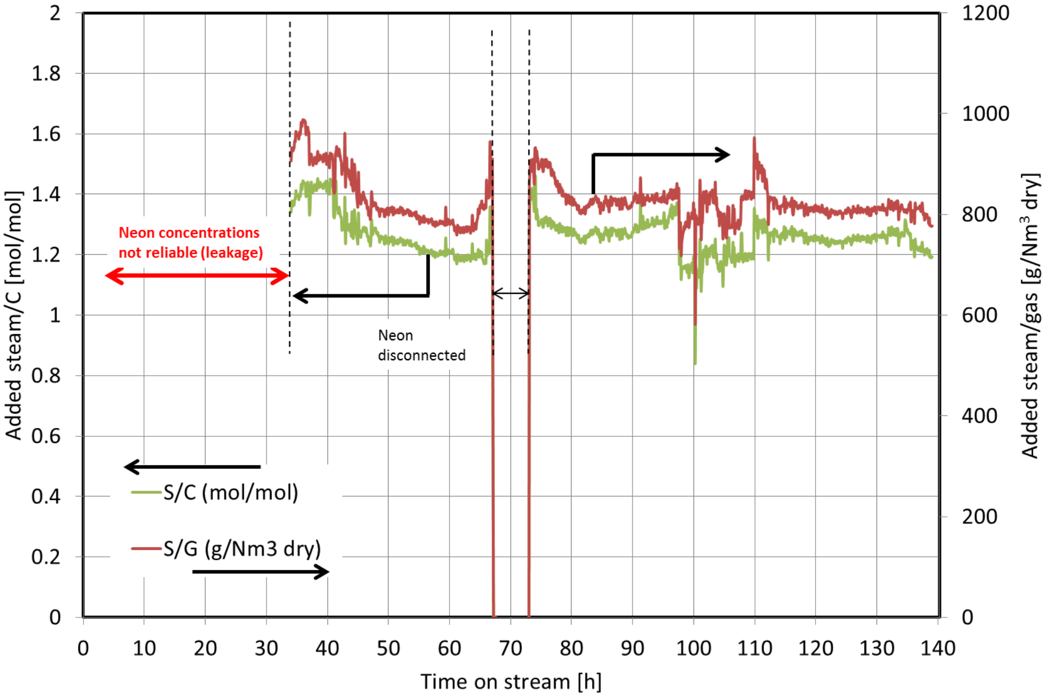

Figure 48. Overview of steam/carbon and (added) steam/gas (around HDS, dry basis) during test 2.

As already mentioned in Section 3.2, H_2S breakthrough was observed at the outlet of the HDS reactor. The H_2S concentration at the outlet of the HDS catalyst increased from 20 ppmv (start of test 2) up to ~ 100 ppmv, which means that the outlet and inlet H_2S are approximately equal. It thus seems that the adsorption capacity of the HDS catalyst was saturated. From that moment onwards, the analysis position was switched after the ZnO sorbent (most relevant position, to follow whether the sorbent was able to capture the slipping H_2S from the HDS reactor). The ZnO sorbent could properly capture H_2S and COS. Also the COS concentration at the outlet of the HDS catalyst, as H_2S, increases over time, in such a way that the outlet COS concentration roughly doubles that at the inlet. This is due to the equilibrium reaction taking place at the HDS catalyst ($H_2S + CO_2 \leftrightarrow COS + H_2O$).

Again, thiophene derivatives and mercaptans derivatives are largely converted in the top part of the HDS catalyst bed (HDS-2 position), the rest being converted below detection limits in the rest of the bed. Approximately 30-40% of the thiophenes are converted above the HDS-2 position, although in the rest of the bed, thiophenes can be completely converted (values below detection limits at HDS-4). It is interesting to compare the values of sulphur compounds in the HDS-2 position with those obtained during the first part of the duration test. It can be observed that a lower fraction of mercaptan derivatives is converted above the HDS-2 position during test 2. This suggests a gradual shift in the reaction front in the HDS catalyst. After the HDS reactor, there is H_2S and COS (whose breakthrough started in test 1), as well as traces of methylmercaptan (compound which was not observed in test 1). On the other hand, the ZnO bed is able to capture the COS below detection limits, whereas H_2S is reduced sufficiently low for the application in the AMBIGO plant.

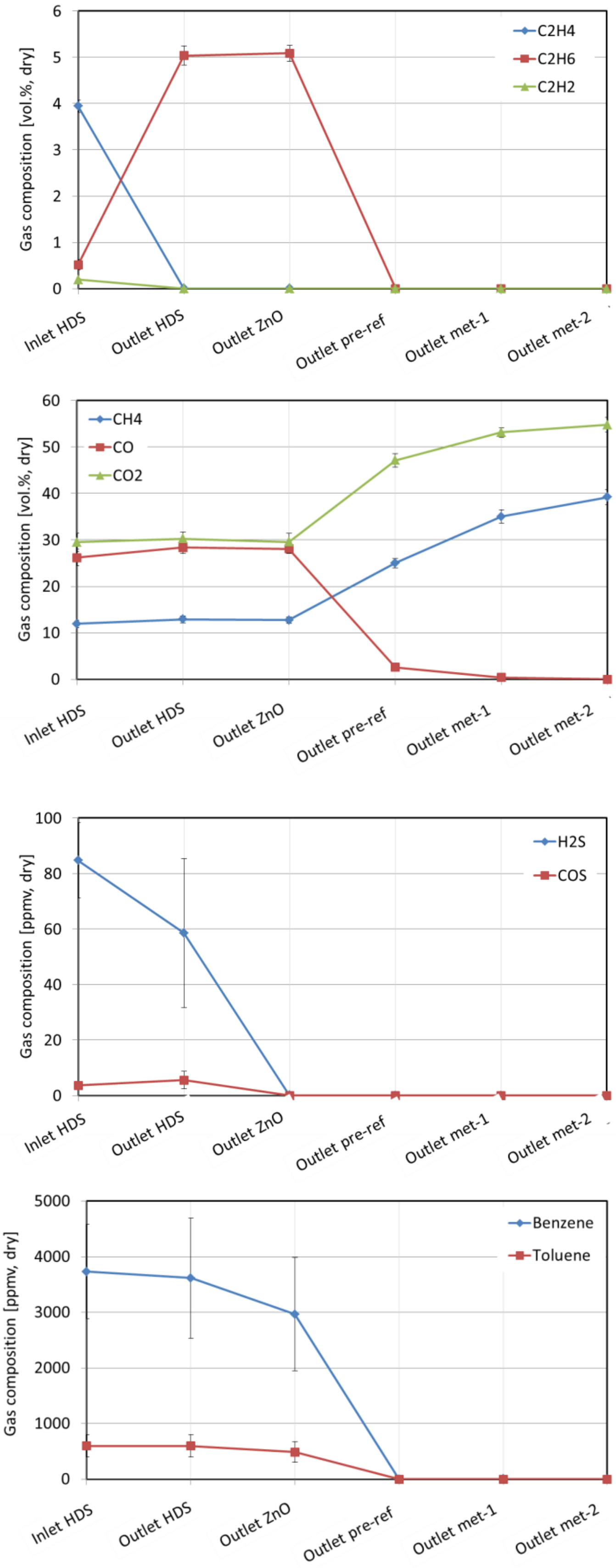

Figure 49. Evolution of gas compounds along the ESME system.

4. GasHUB development roadmap, WP4

4.1 Introduction

As part of deliverable D4.1 within WP4 of GasHUB, Albemarle analysed various routes towards commercialization of a potential GasHUB module, its optimization and other relevant considerations for the development of the GasHUB concept. The results of the duration tests carried out in WP3 were used as a foundation for the analysis, and the place in the integral value chain as laid out in the project plan, with the intended end products as outputs was taken as a central theme to review the various routes in the roadmap.

4.2 GasHUB routes – initial considerations

When evaluating at the economic outlook of GasHUB applications a distinction needs to be made between production of green gas, hydrogen, chemicals and biofuels – or possible combinations that may be described as co-generation. The routes considered in the roadmap are depicted in Figure 50.

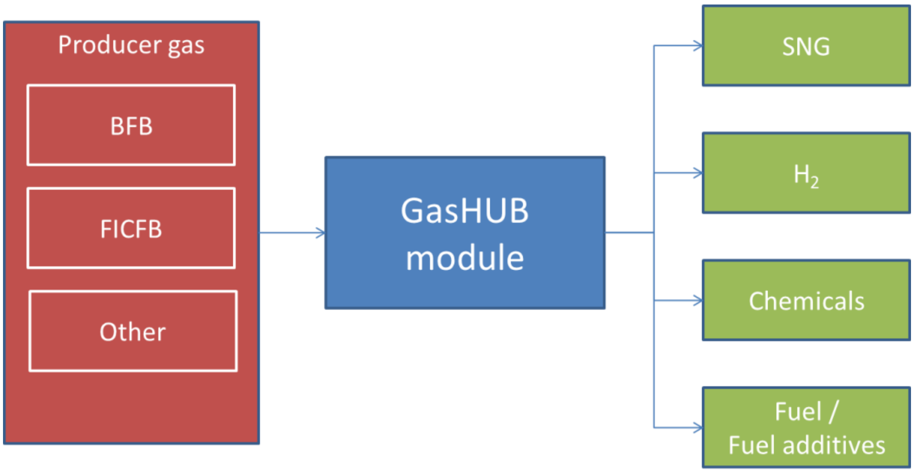

Figure 50. GasHUB module at the crossroads of the feed-to-product routes.

Of each the 4 potential product categories mentioned above (leaving combinations aside for the moment) a brief analysis and outlook will be presented below as a setup for a techno-economic analysis (TEA), but first some initial assumptions will be listed.

1. **Biobased feedstock availability** and logistics/transport and supply contracts will be essential for a successful commercial development project. Without this, and without ensuring this in a very early stage of the development, it is not recommended to engage in a commercialization project. If already some development work has been done, but the requirement of a guaranteed and economical feed supply has not been fulfilled, it is better to put the project on hold or to shelve the technology until this issue has been solved.

2. For evaluation of different routes to products, the gas composition needs to be a "given" even though gas compositions are not constant or equal. There are gasification technology-feed biomass combinations which will give differences (like in in contaminant content) and they can also lead to different requirements for the PFD or the absorbents/catalysts employed. Gas composition cases can be studied for a certain gasification technology and given feed. For the current evaluations, the MILENA indirect gasification technology and the producer gas composition that is currently known can be used as starting point.

3. Technical requirements will have an influence on the economic outlook but at the same time, technically everything is possible, as all challenges can be solved and issues resolved. That does not guarantee a commercial success as has been shown in countless examples. **Regulations and incentives** will have to continue to go in the positive direction, for example, as is currently still the case in driving the development of more environmentally friendly or less environmentally damaging technologies. Different policies (e.g. emission tax/credits) or world scale disruptions (e.g. shale gas) may change priorities as well, or change the preferred feed-product combination, thus **flexibility** on this aspect needs to be kept as a priority. Unfortunately, this hedging of opportunities also dilutes resources and increases the development time.

For each route / GasHUB configuration case there has to be a definition of "In" and "Out" for each case, which will lead to a current estimate of the possibility of using commercial or semi-commercial catalysts and absorbents (which may be preferred as it will not add extra development time for new materials and functionality), and to suggestions for connecting with the right partners as needed. Then, based on the current technical state-of-the-art, the various PFD configurations required can be looked at. When the cases are reviewed, the priorities/ranking can be determined based on current technical readiness (shorter time to revenue is always preferred) and current economic situation. As this can change over time, at set times the priority/ranking needs to be reviewed to see if the case receiving the highest fraction of resources is still the most favourable.

Key aspects/parameters are (as mentioned partly above) listed here:

1. **Raw materials** (biomass) availability will determine the feasibility of a commercial development. Also its characteristics (composition, aggregation state) will govern the GasHUB feed composition and technical specs, as in the feed CO:H_2 and the feed contaminants, and therefore the economic viability. The development of scenarios or even a Roadmap per type of biomass could be helpful to look at this aspect.

2. The result of the above studies will determine the **process conditions** and demands and will constitute the next hurdle in the feasibility evaluation, both technical and economic. Defining a mass and energy balance for the configuration is vital here. A next perspective on the economic viability can then be obtained.

3. **Product** demand (although sometimes volatile) will also control the flexibility requirements, for example by the product gas CO:H_2 ratio and the product specifications. Constantly feeding and updating the product economics will from this side provide visibility on the economic sustainability (again with the option of developing and updating various scenarios going forward).

A last key question in the overall assessment: what problem has been solved with the GasHUB unit or configuration that has been developed? Additional to the continuously updated TEA above, there is a clear sustainability requirement if the basis of this development is to provide an improvement of the overall environment, for example by being carbon-neutral or by establishing an overall net CO_2 negative process. Doing a life cycle analysis (LCA) that describes the cost and environmental impacts will provide this qualification- ECN has performed LCA's in other projects and that effort can be extended and updated for GasHUB.

4.3 Description of GasHUB routes

As a roadmap per product, several milestones and associated timelines (in brackets) can be listed for the selected example cases:

A. Example case 1: Bio-SNG

This case (as it is the objective of the "ESME" development) has currently the most advanced state of development, and was thus the selected route for the WP3 duration tests. The GasHUB configuration in this case consists of a HDS/Absorbent/Pre-reforming/Methanation setup. Milestones that can be envisioned towards commercialization and propagation of the technology are:

1. Demonstration of feasibility of the ESME technology next scale level in the AMBIGO plant – meaning at a larger scale but also with the full PFD in place and producing the desired SNG composition and specifications. This will indicate whether the current catalysts and absorbents are performing satisfactorily [*2020/2021*].

2. Licensing and construction of the first industrial scale SNG plant based on the gasification technology. This phase will be dependent on the findings analysed in previous sections if the demo unit shows significant shortcomings or optimization opportunities, a step back needs to be taken and it could be that a second demo unit, with all the connected development work, is more appropriate for a next step [*2021+*].

3. Establishing a further user base of industrial scale gasification based SNG units [*2025+ if no parallel license project is developed concurring with the 1st license*].

B. Example case 2: hydrogen

Hydrogen can be viewed upon as a chemical product, but as it is one of the components of the product gas it also takes a special position. Furthermore, various technologies are available for hydrogen production that are similar to producing methane. The GasHUB configuration (to be tested) would be HDS/absorbent/(Pre)reforming/WGS. Conceivable milestones are:

1. Similar to the current ESME bench/pilot scale unit, a similar design must be constructed and tested to be able to define the PFD for the demo phase. Several catalysts that are available today may provide a suitable performance if steam reforming (or autothermal reforming) in one of its forms is the right technology. The classical technologies to purify the reforming product (WGS) could be needed, but also SE-technology that is known to ECN may be advantageous and effective here. [*2018-2020*].

2. The construction of a demonstration unit would be a logical next step here, followed by a commercialization track as for the SNG technology. Without solid information on the winning technology further milestones should be defined later [*2020+*].

C. Example case 3: Chemicals

This case is less well-defined so far as there is a range of chemical products that might qualify for this category. Generally, in the petrochemical arena, light olefins and aromatics are listed here, but also oxygenates could be thought of. A stepwise pathway going through methanol (followed by a Methanol-to-Olefins MTO type setup) or ethanol (that would be dehydrated subsequently) could be alternative routes to olefins. Some ideas for obtaining aromatics either by a direct route (isolation and separation from the product gas instead of converting BTX in the ESME pre-reformer) or by an aromatization reaction have already been put forward (see for example, results from the Blue Bird TKI project, TEBE115001). Oxygenates, which either can be the final chemicals produced or serve as intermediates for olefins, are described below as they can also be regarded as fuels or fuel additives. Various GasHUB configurations can be conceived, but those are different for each chemical product to be obtained. Therefore, devising a GasHUB-for-Chemicals configuration could be the start of a next project, building on the results already obtained in other projects such as the Blue Bird project mentioned above. Milestones of this route might be:

1. Definition of the most preferred chemical to work on. Despite the need for flexibility that has been mentioned before, the variety of chemicals and the required process development is too wide to enable working on all potential products so a choice needs to be made based on current insights and already available technology and/or catalysts [*2018*].

2. After making this selection, further lab, pilot and demo phases can be defined as in the previous cases [*2019+*].

D. Example case 4: Fuel/fuel additives

Biobased fuels are defined here as transportation fuels ranging from naphtha boiling range up to the diesel range and the fuel-enhancing additives that fall in the right boiling range or molecular weight size. Established technologies exist to get to these molecules, but the difference here is the use of product gas. It may turn out that for example the application of Fischer-Tropsch (FT) technology and catalysts to make diesel range product proves to be too expensive and therefore not viable for the gasification route because of the need for too deep purification. Methanol generation and subsequent production of DME might be a more workable pathway, for which catalysts exist already as well. A last option which is already under development by Albemarle is the production of alcohols (methanol to pentanol range, depending on the catalyst and PFD). This is in fact similar to the chain-length growth type of process as FT, but the chains in this case are terminated by alcohol functional groups. An advantage is that the syngas can be relatively unpolished. The design process for the GasHUB configuration that is needed for this case consists of similar steps as described in Case C for chemicals. However, because of the different markets and outlook, cases C and D should only be combined for the same molecules, if they can be used as a chemical and as a fuel/fuel additive, like the alcohols.

The envisioned milestones for this route are:

1. The first milestone is again the choice for the most preferred fuel-range product based on current technical readiness and economics. If the synthesis of mixed alcohols is the best choice (for example if the option of producing chemicals is taken into account here as a combined route), this case can tag along with the already ongoing development of the mixed alcohols process [*2018*].

2. Further to this – the next phase may be reached sooner if pilot results or equipment that is already in use today can be used [*2019+*].

Constantly, while moving to the next milestone for each of the cases described above, the following aspects need to be monitored and updated to make sure further development work remains justified (see Figure 51 for some positive and negative drivers):

- Techno-economic analysis of the current scale of execution, including the feed availability (per region) and product demand (per region) for the envisioned next step.

- Update and extension of the LCA made in the Blue Bird TKI project, TEBE115001with the current and most up-to-date insights.

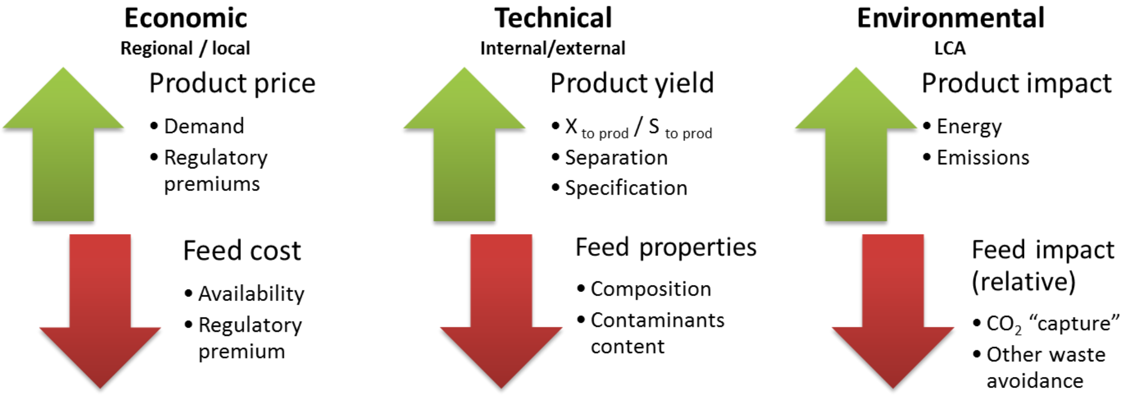

Figure 51. Contributing and suppressing factors that influence the evaluation of a certain route at any time.

4.4 Conclusions and path forward

This chapter has outlined the development path of a number of routes in view of the gas upgrading train envisioned in the GasHUB project. In conclusion, some remarks can be made regarding the current preferred configuration, also based on the results from WP2 and WP3 of the GasHUB project:

1. The ESME configuration that is envisioned for the AMBIGO plant for bio-SNG production is currently the furthest advanced and this (without a full TEA and LCA of all other cases) seems to be the preferred configuration to work on at this moment in view of time-to-market. Commercial catalysts have been proven to be viable for use under the applied conditions in the GasHUB project test work so the next step in the scale-up process can be taken. No showstoppers or red flags have been identified during the current project by the test results.

2. If commercial availability of the catalysts is a major factor in the ranking, the order of preference at this time could be A (SNG) > B (H_2) > C (Chemicals) ~ D (Fuels-Fuel additives). For routes C and D however, it is necessary to make the indicated analysis and this could, if economics or LCA weigh in, change the ranking.

As a closing remark, the roadmaps pictured in advance in this section for each case in will certainly be different from the likely or actual roadmaps (the route that led to the end result, as recorded and reviewed in hindsight). Several decades of process development at Albemarle have provided this insight. Nevertheless, the outlined routes above will hopefully provide a guideline towards the envisioned end goal: the development of a process that will be beneficial to all stakeholders. For Albemarle, this will entail the establishment of the commercial production, marketing and operation of the required catalysts and absorbents, at a scale which will give the required return on investment.

4.5 References

- Somayeh Farzad, Mohsen Ali Mandegari, Johann F. Görgens, *Biofuel Research Journal*, 12 (2016) 483-495
- Vineet Singh Sikarwar, Ming Zhao, Paul S. Fennell, Nilay Shah, Edward J. Anthony, *Progress in Energy and Combustion Science*, 61 (2017) 189-248

5. Conclusions and outlook

The GasHUB project (reference TEBE 116178) focuses on the testing and optimization of sorbents and catalysts for the development of a robust, flexible gas upgrading train for the conversion of biomass (via gasification) into a range of energy carriers (such as biofuels, green gas and hydrogen) and chemicals. The gas upgrading includes the conversion and removal of sulphur contaminants and the conversion of higher hydrocarbons into syngas. All in all, the tests performed have resulted in extensive knowledge gained on the performance of sorbents and catalysts, in terms of activation procedures, window of operating conditions, long-term performance, and effect of the type of gasification feedstock.

The first exploratory short tests performed within WP2 revealed proper performance of sorbents and catalysts. The tested ZnO materials can remove COS below detection limits, and also largely H_2S. Higher temperatures than 200°C can be selected, thus confirming the current design value taken in the design of AMBIGO. The Albemarle HDS catalyst is sufficiently active. Overall good and stable performance of the catalysts (i.e. practically complete conversion of organic S compounds in the HDS, removal of H_2S and COS in the HDS catalyst, and > 99% benzene conversion/100% toluene conversion in the pre-reformer) was observed during the first short experiment with the whole ESME train.

Complementary TPR and activity tests were carried out within WP2 to shed more light on activation procedure and window of operating conditions. This is relevant information in view of shutdown/re-start procedures at the AMBIGO plant. The activity tests showed that the pre-reformer catalyst and methanation catalyst are sufficiently active (in terms of methane production, CO conversion, and CO_2 production) as well.

The knowledge gained within WP2 resulted in the selection of the final configuration (sorbents and catalysts) for the final duration test of WP3. The objective was to demonstrate the long-term performance of the selected materials under relevant gasification conditions in view of the operation of the AMBIGO plant. The total duration test (whole ESME system on stream for 222 hours), was split in 2 periods (94 hours in December 2017 and 128 hours in January 2018), with overall availability above 90%. All in all, stable operating conditions were achieved in the gasifier, the tar removal unit and the methanation train throughout the endurance experiments. Total conversion of CO was observed during test 2 after R15. The raw bio-SNG gas at the outlet of the second methanation reactor contained approximately 40 vol.% CH_4, 3 vol.% H_2 and ~ 50 vol.% CO_2. The HDS reactor showed all in all satisfactory operation, with complete conversion of organic sulphur compounds and of unsaturated hydrocarbons. The ZnO bed was able to reduce the H_2S concentration down to the accuracy limits of the current detection equipment, which can be considered as an acceptable value for the AMBIGO plant. In the HDS catalyst, thiophene derivatives and mercaptans derivatives were observed to be largely converted in the top part of the HDS catalyst bed, the rest being converted below detection limits in the rest of the bed. No signs of deactivation due to carbon deposition were observed in R13-R15 throughout the test.

The research work was complemented with a business case roadmap for the development of the GasHUB gas upgrading train. A number of routes have been thus selected and described, as well as background considerations relevant to the deployment of bio-based routes in general. The analysis indicates that the bio-SNG route is at this stage the furthest advanced one. If commercial availability of the catalysts is a major selection factor, the current order of preference of routes is SNG > H_2 > Chemicals ~ Fuels/Fuel additives. For the latter (chemicals and fuels), the inclusion of economics or LCA as selection factors will influence the ranking. Complementary and in parallel with the progress in milestones of each route, the drivers and risks need to be constantly monitored. Relevant factors identified in the analysis include the availability of biomass feedstock, the process scale, and process flexibility.

The knowledge gained within the GasHUB project on the sorbents and catalysts (activation procedure, window of operating conditions, long-term performance) will be firstly applied in the AMBIGO project.