21NRM04 BiometCAP

D5: Report on the field-based performance evaluation, of selected industrial gas analyzers and reference instrumentation, using the developed biomethane performance assessment protocol

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Deliverable Cover Sheet

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Glossary

Biogas, on-line measurements, standards, analysers, impurities

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1 Summary

The report gives an overview of the field measurements and field-based performance evaluation of selected industrial gas analyzers and reference instrumentation performed at two biogas production sites in Denmark and one in Finland. The measurements have been performed online at various biogas gas sampling points. The tests are performed according to the protocol developed during the BiometCAP project (recommendation for onsite installation, baseline testing, calibration, results interpretation). The differences and similarities between the measurements with different analyzers and reference instrumentation are given. Finally, valuable observations related to the processes are reported and discussed.

2 Introduction

Biomethane is the final product of a complex biogas upgrading process which includes various steps such as H2O, H2S and VOC removal, CO2 separation and final gas compression and fine filtration. The quality requirements for the final produced biomethane are given in EN16723 standard [1]. Part 1 gives biomethane specifications for injections in natural gas network.

Biogas plants and gas grid operators are often continuously monitoring some compounds such as O2, CO2, H2O (as dew point) and H2S as those impurities are critical to plant´s operation. Non-compliance with the EN16723 standard may normally lead to a shutoff of the plant from the gas grid and a forced flaring of the produced biomethane. Depending on a particular country and raw-biomass origin, additional impurities such as NH3, terpenes and siloxanes can be in focus. These components are of importance for distribution and transmission grids.

The overall upper impurities levels for biomethane with respect to the on-line biomethane conformity assessment are:

NH3 ≤ 3 mg/Nm3; O2 ≤ 0.5 mol%; CO2 ≤ 2 mol%; H2S (+OCS) ≤ 5 mg/Nm3; siloxanes ≤ 1 mg/Nm3; mercaptans ≤ 6 mg/Nm3. Water content (as dew point) shall not exceed – 8 ^{o}C at 70 bar (or 44 ppm at 1 bar).

Wobbe index (calorific value) and relative gas density of the biomethane are defined by the major gas component such as CH4 and have primary interest for fiscal billing of the customers and an overall grid balance in sense of supplied energy.

Measurements of above-mentioned impurities in a CH4 dominated matrix can be challenging because of possible interferences in a particular analyser used and/or the conditions under which the measurements are performed in real-time.

The Report summarizes applications of the developed performance assessment protocol for evaluation of selected industrial analysers and reference instrumentation in real-time (on-line) measurements. The measurements have been performed at two biogas production plants in Denmark and in Finland. The plants have large variations in raw-material suppliers and different upgrading technologies. In addition to measurements on the produced biomethane (product gas) several measurements have been performed at various upgrading stages to understand the fate of the key impurities during biomethane upgrade.

3 Analysers and reference instrumentation used

A review and selection of suitable measurement techniques for biomethane conformity assessment have been done in the A3.1.1 Report [2]. After discussions with biogas plants and considering various practical aspects of on-line gas measurements at the industrial sites and outcomes of the A2.1.3 Report [3], it has been decided to limit the choice of analysers and reference instrumentation to spectroscopy-based analysers. The final selection of the analysers was: Max-iR FTIR commercial analyser (available from TFS, project partner), Pro-CEAS (NH3 laser-based commercial analyser from AP2E, available at VTT), new far-UV analyser (available at DTU) and OGS NH3 (OF-CEAS-based, NH3 analyser available at PTB). All analysers provide on-line measurements capabilities and are suitable for biomethane/biogas on-line measurements. A short description of the analysers is given below.

3.1 Commercial Pro-CEAS NH3 analyser (VTT)

The ProCeas® NH3 analyser by AP2E is a high-end laser infrared spectrometer for low level detection of NH3 in combustion process and pure gases. The device was pre-calibrated by the manufacturer in the concentration range 0-100 ppm. The calibration was verified with the VTT Trace gas generator before and during the field measurements. Entailed specifications of the analyser are given in Table 1.

Table 1: Specification of AP2E ProCeas® NH3 analyser

Concentration range	0-100 ppm
Limit of detection (LOD), 3 sigma, 60 s	0.05 ppm
Response time	< 2 s
Zero drift	none
Max. humidity of sample gas	< 65 %rh
Operating temperature	15 °C – 35 °C

3.2 MAX-iR FTIR analyser (TFS)

MAX-iR is an FTIR-based rack analyser developed by the project partner – Thermo Fisher Scientific, Inc. (TFS). The analyser contains a 9.86 m pathlength gas cell together with a room temperature DTGS detector which allows measurements over 9 orders of concentration (ppb to %) for major and trace gases. The analyser has been optimized for measurements in CH4 matrices. Typical impurities measured: NH3, CO, VOC's, CO2, siloxanes etc. are measurable using this system. The analyser has a spectral database of more than 200 organic/non-organic components. Weight 34 kg. (75 lbs.); dimensions 482.6 x 609.6 x 222.25-mm (19 x 24 x 8.75-inch). The main analyser operating parameters are given in Table 2. Table 3 gives limits of detection for components relevant to biomethane measurements.

Table 2: MAX-iR FTIR Gas Analyzer Operating Parameters

Gas Cell Pressure	1 atm
Gas Cell Temperature	191°C
Resolution	1 cm^{-1} (Cosine apodization)
Analysis Time	60-seconds
Installation Location	The equipment is intended for indoor use in an ordinary location.
Power	208-240VAC, 50/60Hz, 2A 10A Euro Power Cord IEC 320-C13 to Euro CEEE7/7 Plug
PC Interface Connections	*Ethernet Communication to PC:* CAT5E/6 Patch Cord with RJ45 Connector *Serial Communication to PC:* USB Type A-B Cord with USB Type B Connector
Operating Temperature Range	20-30°C
Environmental Humidity	10-90% relative humidity, non-condensing
Altitude	0-2000m
Ingress Protection	The system is designed to meet IP20
Overvoltage Category	Category II - Equipment with plug and socket connector or fixed connection supplied from the electrical system of a building.

Pollution Degree	Pollution Degree 2: Normally only nonconductive pollution occurs. Temporary conductivity caused by condensation is to be expected.
Mains supply voltage fluctuations	±5%

Table 3: Limit of detection for selected gases using MAX-iR (3 times the standard deviation of a blank (nitrogen gas) measurement)

Gas	NH3 (ppm)	CO2 (%)	CO (ppm)	CH4 (%)	H2O (ppm)	Ethylene (ppm)	Propylene (ppm)	Limonene (ppm)	L2 (ppb)	L3 (ppb)	D3 (ppb)	D4 (ppb)	D5 (ppb)
3σ (LOD)	0.058	0.007	0.018	0.002	0.9	0.030	0.118	0.073	6.397	8.835	4.887	4.434	2.763

3.3 Far-UV analyser (DTU)

Far-UV analyser is a new spectroscopy-based multicomponent analyser development at DTU. The analyser consists of a light source, spectrometer and a gas cell. The analyser is capable of on-line measurements of various organic (e.g. VOC's) and non-organic components (e.g. H2O, H2S, NH3 etc.) and can be operated in a wide pressure range. Concentration measurements range depends on the component in question and varies from several ppb to ppm and few percentages.

3.4 Optical feedback-cavity enhance absorption spectroscopy (OF-CEAS) based ammonia analyser to be operated an optical gas standard OGS (PTB)

PTB has upgraded an optical feed-back cavity enhance system to an optical gas standard (OGS) for measuring NH3 in methane/bio-methane. In brief, the spectrometer consists of a V-shaped cavity formed by three high-reflectivity (R > 99.99%) mirrors which allow the laser light to travel more than 10 kilometre inside of a 40 cm long optical cavity, resulting to a FSR ~ 187 MHz. The laser emitting light at around ~1.5µm was used to probe the target NH3 absorption line. The light coming out from the cavity was measured by a photodiode placed behind the exit mirror along one arm of the cavity. The transmitted light is used to calculate the absorption coefficient spectrum. In the presence of an NH3 in CH4 sample in the cavity, the recorded spectrum wis fitted with a Voigt profile (taking into consideration nearby overlapping of ammonia and methane lines) to derive an integrated absorption coefficient (= line area). By means of the line area, the NH3 amount fraction in the sample is calculated. The traceability of the results is address via input parameters such as the measured total gas pressure and temperature that are traceable to respective PTB standards. The line strength of the target NH3 absorption line was measured at PTB using own ultra-high resolution FTIR.

3.5 Application of the protocol

Performance assessment protocol developed in the WP2 has been used for evaluation of the selected gas analysers and reference instrumentation in field environments. Measurement campaigns at two biogas production plants in Denmark (Ribe and Solrød) and one in Finland (Lohja) have been performed.

Planning of the campaigns has been discussed in detail with the biogas plant managers and preparation and implementation of the measurement campaigns have been done according to the Report "R*eview of the requirements for laboratory and field validations of instruments*" [3].

To fulfil safety requirements, all measurements have been done outdoor, in non-ATEX designated areas. The analysers have been placed under a wind-, rain- and fire-resistant tent with a permanently turned on heat-blower, Fig. 1. The blower was keeping the temperature in the tent above +15^{o}C during day and nighttime.

Figure 1: Measurement campaign at Ribe Biogas (Nov. 2024). The opened building door separates ATEX (inside) and non-ATEX (outside) areas where the tent was set up. The biomethane was taken via a PTFE tubing (marked yellow arrow) from the ATEX area to the analysers in the tent through an opening in the wall (marked in red). Several indoor/outdoor gas in-take points were available in the vicinity of the tent.

The analysers have been continuously purged using high-purity N2 from supplied N2-bundles (ten-twelve N2 cylinders 200bar/50L each bundled together). The same N2 was used as a reference calibration gas for the analysers. Keeping warm temperature in the tent with continuous N2 day and overnight purge of the turned-on analysers allowed problem-free and safe operation of multiple-equipment setup over the whole duration of the campaigns for any weather conditions.

The measurements started with blank measurements using N2 at least in the analyser section. Then (by opening a respective connection valve) the biogas/biomethane measurements started. At a biomethane (product gas) pipe connection a regulation valve was typically used to reduce the pressure from about 4 bar to about 1 bar. Few measurements with far-UV analyser were also made at product gas pipe pressures (without any pressure reduction). All product gas measurements were done before receiver stations. The receiver stations do not belong to biogas plant infrastructure and are a part of gas distribution facilities. At the receiver stations the biomethane gas quality (purity) is continuously monitored by accredited GC-based analysers (e.g. EnCal-3000, MEMS-based technology GC), Fig. 2. The gases typically measured at the receiver station are given in the Sec. 2.

Figure 2: Example of multiple EnCal-3000 installation at a gas station.

At the receiver station an odorant is finally added, if the produced biomethane is intended for use in distribution gas net.

At other gas in-take positions along the biomethane upgrading process, the process gas pressure is delivered at a pressure slightly above the ambient pressure and, therefore, no additional pressure reduction was needed. Those additional (to the product gas) gas in-takes were: before and after H2S/VOC removal and after CO2 separation. Few measurements have done on raw biogas before CO2 separation to get a full picture of the biogas upgrade process chain.

The biogas production is an on-going regular process. However, some process changes which can affect quality of the product gas can happen over time. Therefore, it was important to evaluate the performance of the analysers over a long measurement period. Measurements over long-time spans can influence the analyser operation due to for example, contamination of critical (optical) components, possible plugging, pressure and temperature variations either in the biogas/biomethane or in the analyser itself. Therefore, in some measurements, the biomethane flow through the analysers was stopped and then it was switched to N2 to check the baseline. Measurements started again after this control. At the end of the measurement period, the biogas/biomethane flow was stopped and then it was switched to N2 for a final baseline/calibration verification. After the measurements other than the product gas, the whole interface line (line connecting the gas in-take point and the analysers) and the analysers were kept under N2 purge during nighttime to remove any memory effects which can potentially bias the next measurements.

During the biogas/biomethane measurements, the pressure and temperature in the analysers were recorded and all acquired measurement data were corrected for pressure/temperature by respective analyser software.

In the sections below, results of the three measurements campaigns at the different biogas production plants which use different raw materials and CO2 removal techniques are reported and discussed.

4 Measurements at Lohja Biogas in Finland (Oct. 2024)

Gasum’s biogas plant in Lohja is located in the area of the Munkkaa waste management center, west of Helsinki. The plant was commissioned in January 2021. The Lohja biogas plant processes an annual total of

60.000 tones of biowaste and produces about 40 GWh of biogas for transport and industry and 50.000 tons of organic fertilizers per year [4].

The Lohja biogas plant uses biodegradable waste (commercial, household and food industry biowaste) from the Helsinki region as feedstock, which means that the recycled nutrients created in production at the biogas plant meet the criteria for organic fertilizers.

Figure 3: Measurements in non-ATEX area at Lohja Biogas.

4.1 Overview of biogas upgrade in Lohja (GASUM)

The major biogas upgrade stages include H2S and VOC removal by carbon filters and CO2/VOC separation by a membrane technology (Bright Biomethane technology). The plant is CO2 capture/storage ready meaning that a CCS addon unit can easy be integrated withing the plant infrastructure, if there is a commercial interest in the CO2 capture. Currently, separated from the biogas CO2 is emitted into the atmosphere. Product gas pressure is about 4.5 bar and biogas pressure before the membranes (after carbon filters) is about 14 bar. The receiver station is located at about 2 km from the plant.

The measurements have been performed at two locations: 1) at the product gas exit from the plant and 2) before the membranes. Simultaneous on-line measurements at 1) and 2) locations have been performed for long timespans in order to see possible time variations in gas composition.

Fig. shows Pro-CEAS NH3 and MAX-iR FTIR installed in the tent together with VTT’s dynamic gas generator which was used for the Pro-CEAS calibration and validation. An ATEX-approved handheld CH4 leak sensor (SCHUTZ Messtechnik) was used to trace all connection from gas intake to analysers vent. The vent from analysers was placed outside of the tent in the opened air.

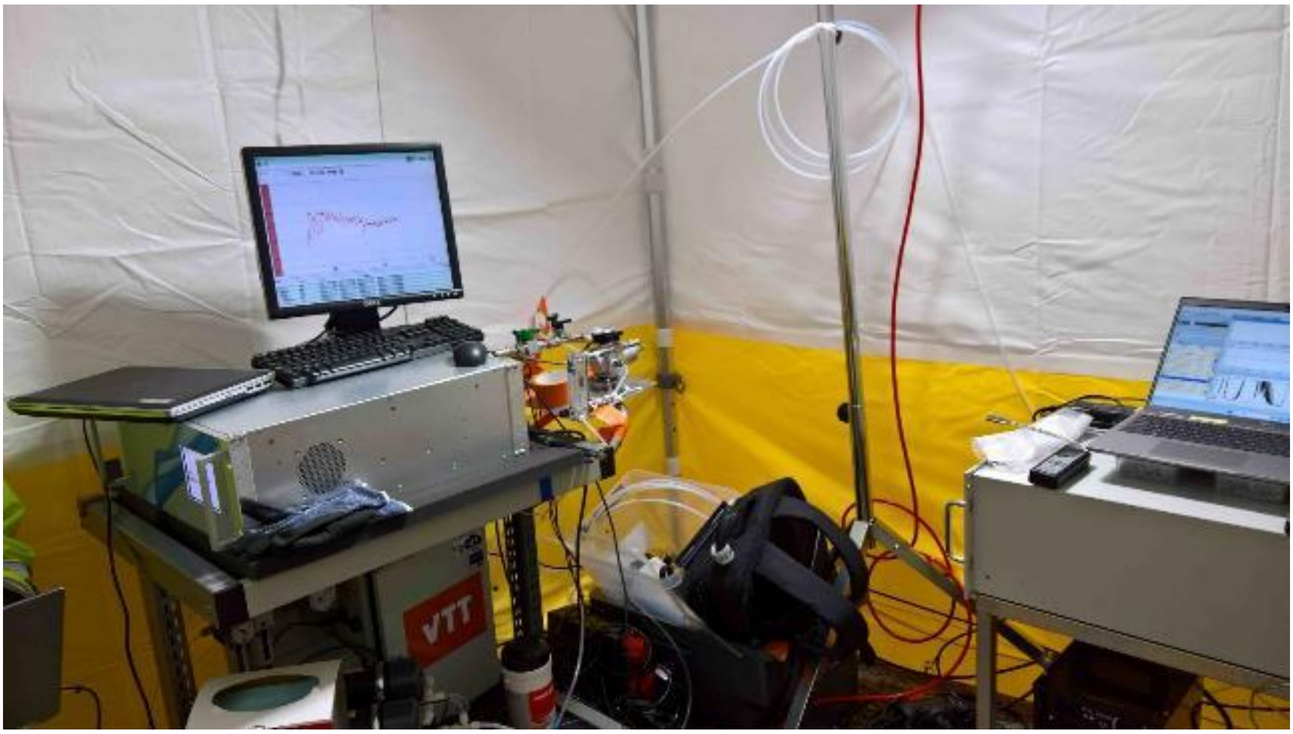

Figure 4: Pro-CEAS NH3 (left) and MAX-iR FTIR (right) analysers in the tent. VTT's dynamic gas generator is under the Pro-CEAS analyser (box with "VTT" red label). The generator was used for Pro-CEAS analyser on-site calibration and validation.

4.2 Measurements on biomethane (product gas, plant exit, before receiver station)

The biomethane was taken into the analysers through about 4.5 m long, Dursan-coated SS-tubing, Fig. 5. At the tent (behind the fence, outdside the tent) the gas flow was spilt into three parallel flows to Pro-CEAS NH3 (VTT), MAX-iR FTIR (TFS) and far-UV (DTU) analysers, Fig. 4 (red line).

Figure 5: Product gas in-take at plant exit. Fence is separating ATEX and non-ATEX areas. The gas was taken to the analysers with a coated SS tubing. The gas flow was separated at three parallel ones at position marked by a red line

An example of the measurements performed on the product gas using the developed protocol is shown in Fig. 6. The measurements started with N2 to establish a baseline, before a gas-intake from the plant was introduced into the analysers. In the middle of the measurements, at about 10:30, a switch of gas to N2 was made to check the baseline. At about 11:03 the product gas on-line measurements are continued. At the end of the measurements (14:40) the gas was switched back to N2. When an analyser shows a return to its “zero” baseline under a flow of N2, it indicates that the analyser performance is not affected by the product gas, and the signal can be considered as produced by the impurities in the analysed gas.

Measurements at 09:31 by plant’s PRONOVA analyser give a concentration of CO2 of 1.99 vol-% which is in very good agreement with our measurements (marked in circle to left) in the Fig. 6. Measurements with Pro-CEAS NH3 and far-UV analysers have shown very low NH3 (< 0.5 ppm) and CS2 (10 ppb) + DMS (300 ppb) concentrations, respectively. To verify the NH3 measurements, the VTT dynamic gas generator was used to introduce known amount of NH3 in the analysers for verification/calibration. On-line measurements of other minor gas components are shown in Fig. 7.

On Fig. 6, CO2 and CH4 concentrations exhibit opposing phase patterns. Minimum in CO2 concentration corresponds to maximum in the CH4 one. The CO2 concentration is oscillating around 2% which is the maximum concentration set as requirement in EN16723 standards. These oscillations are process-related.

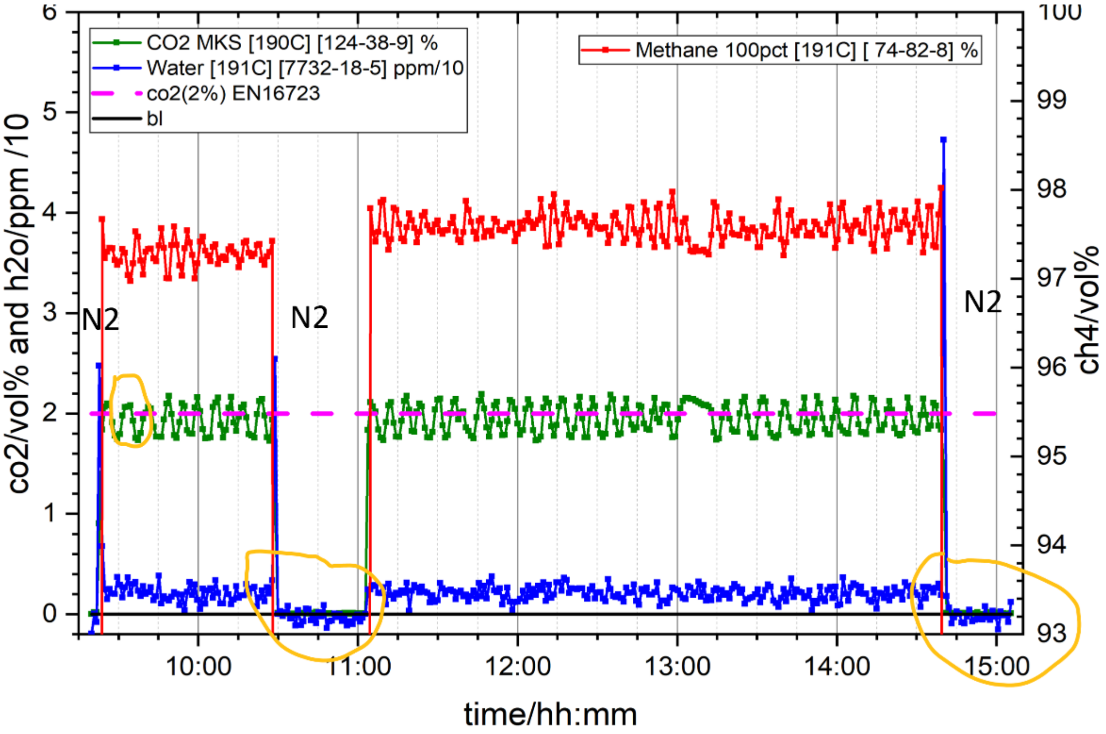

Figure 6: CO2 (olive), H2O (blue, divided by 10) and CH4 (red) on-line measurements by MAX-iR FTIR analyser on product gas. Magenta line shows CO2 concentration according to EN167123 standard. First orange circle shows CO2 concentration measurements in relation to PRONOVA analyser. Other two circles show switch to N2 in the analyser.

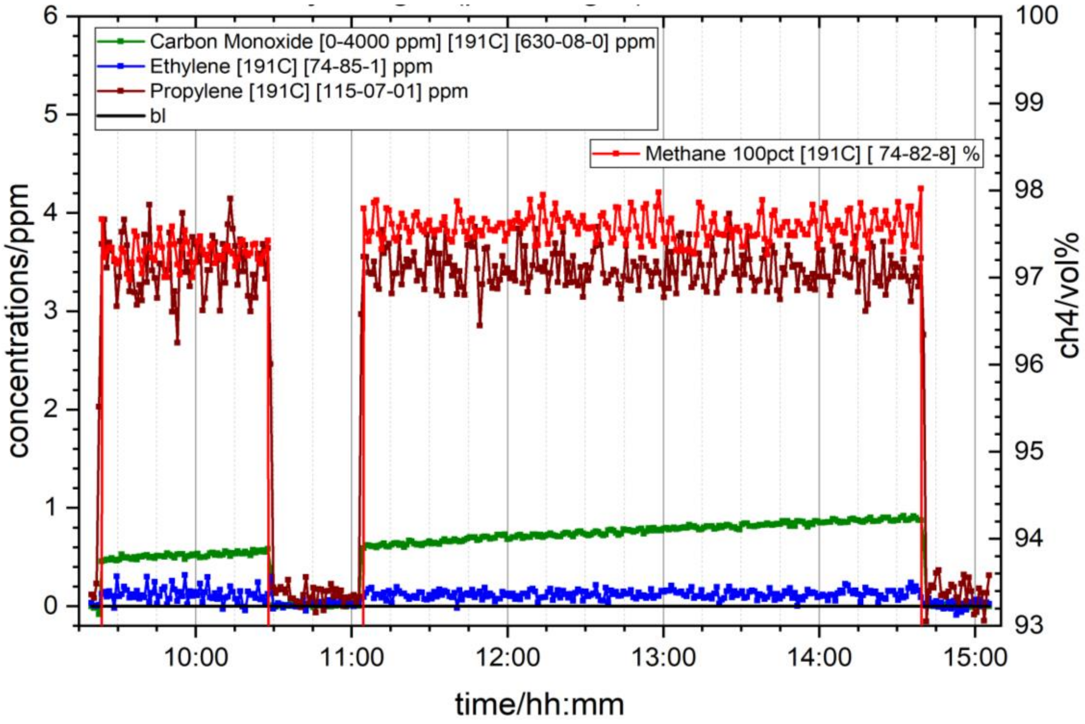

Figure 7: CO (olive), C2H4 (blue) and propylene (wine) on-line measurements by MAX-iR FTIR analyser on product gas. CH4 (red) is given for reference.

4.3 Measurements on biogas (before membrane cascade)

Fig. 8 shows a high-pressure gas intake at about 14 bar, before the CO2 membrane separation cascade. Because the gas in-take position was farther from the tent, an additional PTFE tubing was used together with Dursan-coated SS one. The measurements have been done with pressure reduction from about 14 bar to about 1 bar. Few measurements with far-UV analyser have been done at biogas pressure (i.e. without any pressure reduction).

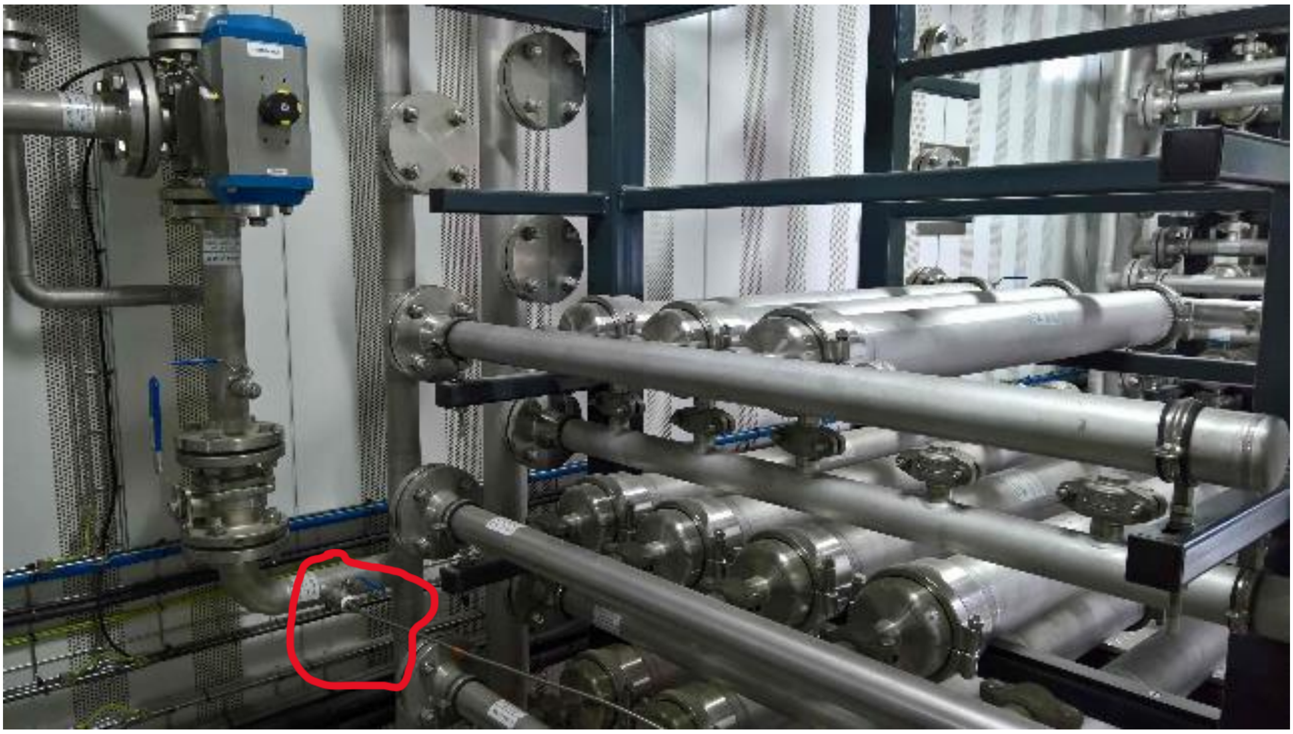

Figure 8: Biogas in-take location prior CO2 membrane separation cascade (to right). Gas in-take marked with a red line.

Results of the measurements with MAX-iR FTIR analyser are shown in Fig. 9 and 10. This biogas is semi-clean and contains about 40% of CO2. The CO2 measurements with MAX-iR FTIR are in agreement with plant's PRONOVA analyser, while the CH4 measurements with MAX-iR FTIR are higher than the PRONOVA data (around 58%). This is because, the MAX-iR FTIR analyser software is not fully optimized for biogas measurements. The Fig.'s 9 and 10 do not show any time patterns either in CO2 or CH4 concentrations. This confirms that the CO2 and CH4 time patterns in the Fig. 6 is related to membrane operation. Measurements with Pro-CEAS NH3 analyser showed very low NH3 (< 0.5 ppm). The far-UV measurements showed much higher CS2 (220 ppb) and DMS (500-800 ppb) concentrations than those for the product gas. This can be explained by the membranes operation which efficiently remove CO2 together with impurities like e,g, H2O, CS2, DMS.

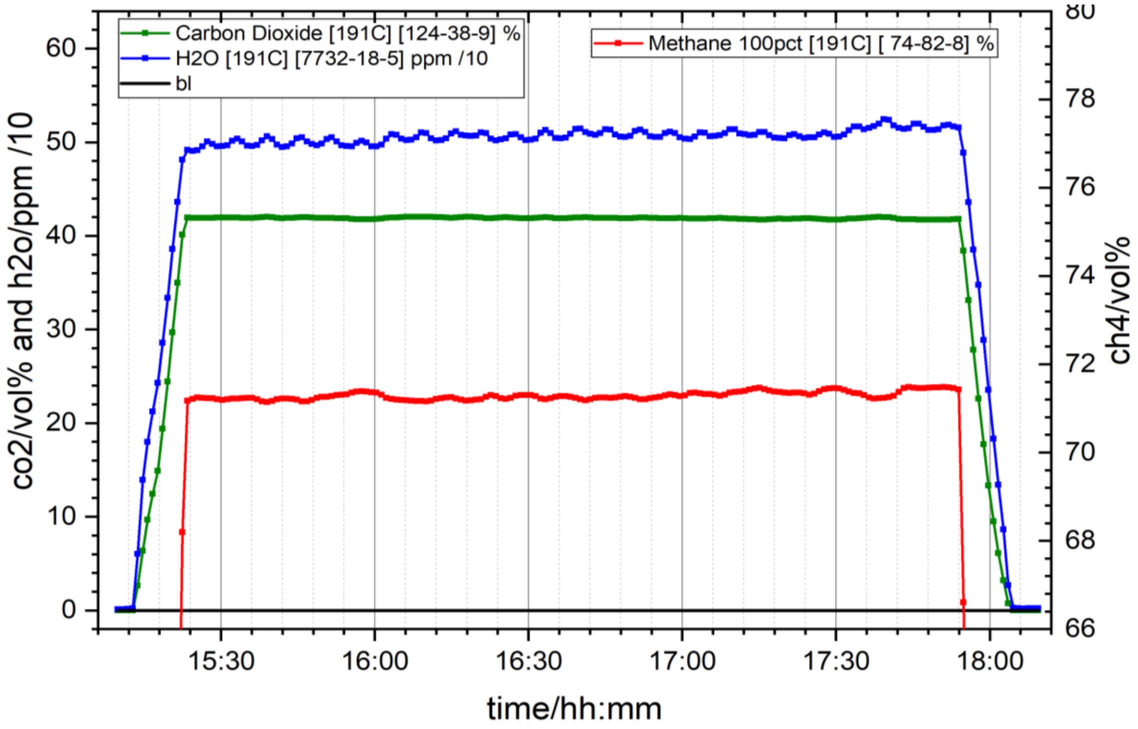

Figure 9 CO2 (olive), H2O (blue, divided by 10) and CH4 (red) on-line measurements by MAX-iR FTIR analyser before membrane cascade.

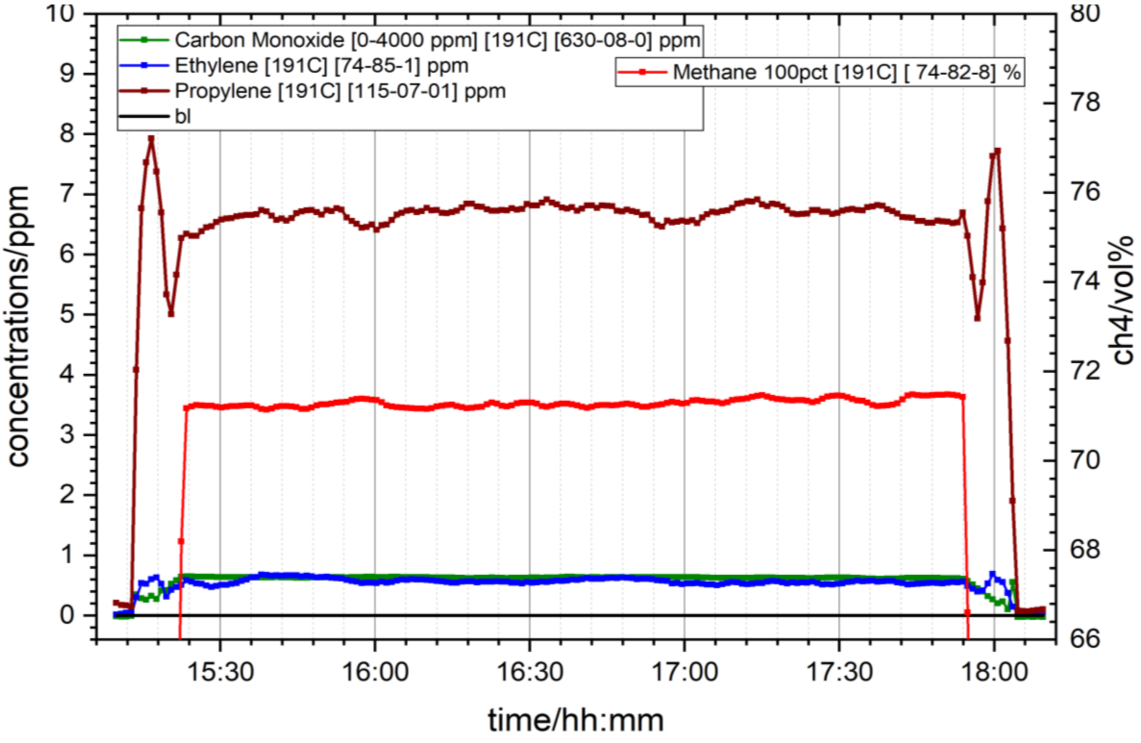

Figure 10 CO (olive), C2H4 (blue) and propylene (wine) on-line measurements by MAX-iR FTIR analyser before membrane cascade. CH4 (red) is given for reference

5 Measurements at Ribe Biogas in Denmark (Nov. 2024)

Ribe Biogas is the oldest biogas production plant in Denmark [5]. It was put into operation in 1990 and was at that time the world's largest thermophilic biogas plant. The company is owned by RBMF (83%) and NGF Nature Energy (Shell) (17%).

Ribe Biogas has undergone major modernization and expansion in the period 2015-2020. The expansion was further expanded in production combined with an upgrade of the gas that was put into operation in July 2018. The last part of modernization was completed in 2022 and consisted of a new intake system for various agricultural-based biomass and an expansion of the odor treatment system. The plant currently processes approx. 420.000 tons of biomass annually, of which approx. 30.000 tons are from industry. Approx. 20 000 000 m³ of biomethane is produced, which is sold via a gas distribution network connected to the entire European Gas Network.

5.1 Overview of biogas upgrade in Ribe

Produced biogas is first treated in an amine-based adsorber-stripper system (AMMOGAS technology) which separates CO2 and H2S from the raw-biogas. Then the gas is passing through a carbon filter (VOC removal) and compressed to about 5 bar, followed by a passage through a fine filter (H2O and fine particles). Produced biomethane is odorized at the receiver station located at the plant area.

A long PTFE tubing (Ø 6 mm) was used to reach all gas intake positions and keep the same integrity with the measurements at all gas intake positions. An ATEX-approved handheld CH4 leak sensor (SCHUTZ Messtechnik) was used to control all connections from gas intake to analysers vent. The vent from analysers was placed outside of the tent in the opened air. Fig. 11 shows installation of the far-UV, MAX-iR FTIR and OF-CEAS/OGS in the tent.

Figure 11: Far-UV (left), MAX-iR (middle) and OF-CEAS/OGS (right) analysers in the tent in Ribe.

5.2 Measurements on biomethane (product gas, plant exit, before receiver station)

The biomethane gas intake point at Ribe Biogas is shown in Fig. 12. The gas pressure was about 5 bar. A Ø6 mm PTFE tubing was used to connect the valve and the analysers inlet in the tent. The gas flow was split in parallel through all analysers.

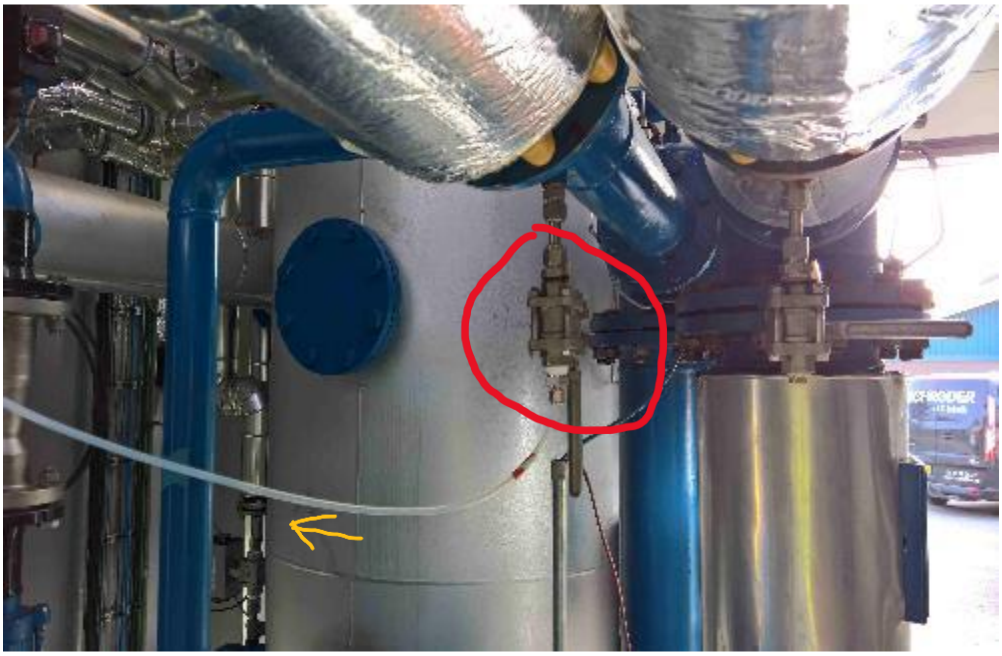

Figure 12: Product gas in-take point before receiver station and gas flow direction to the tent (red line and yellow arrow, respectively).

Examples of the results of the measurements on the product gas at Ribe are shown below.

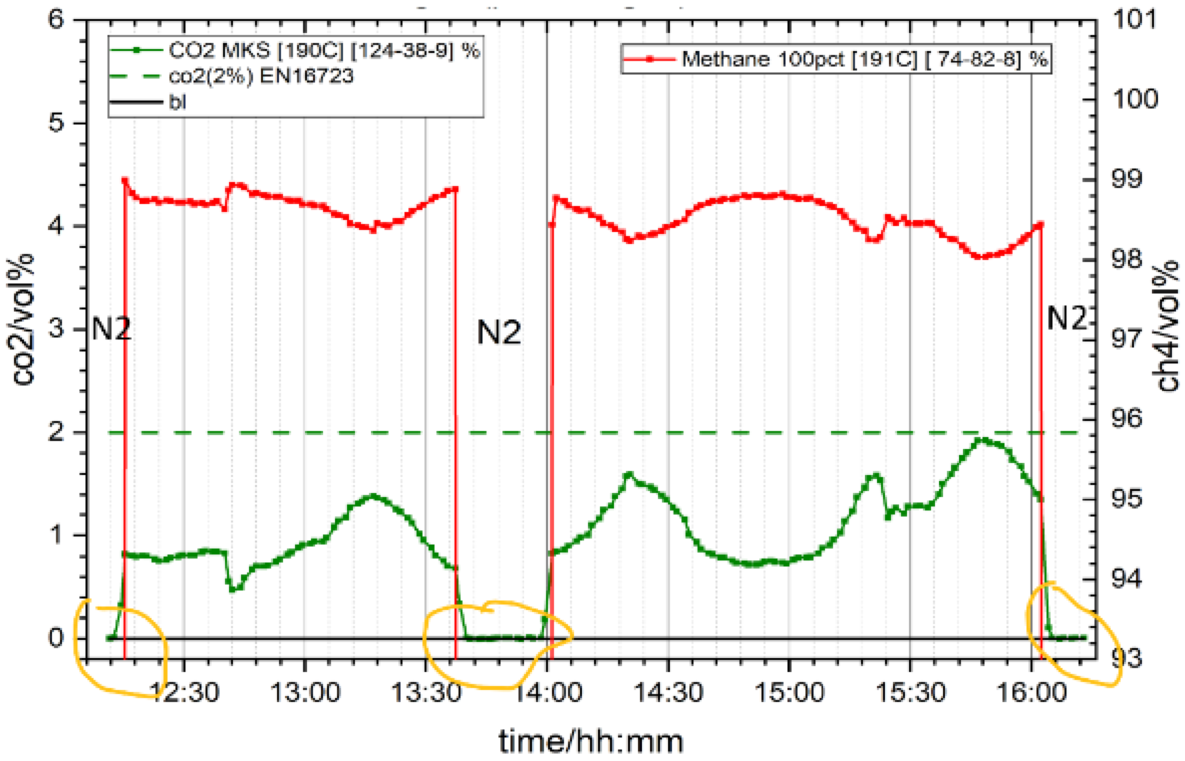

Figure 13: CO2 (olive) and CH4 (red) on-line measurements with MAX-iR FTIR analyser with use of the protocol. CO2 upper limit given by EN16723 standard (dash line).

The developed performance assessment protocol (WP2) was used while performing the measurements. The measurements started with N2 as a reference gas in all analysers to establish the baseline. Then the in-take valve (Fig. 12) was opened, and the measurements have been continued. After about 2 hours of the continues measurements, the in-take valve was closed and the measurements continued with N2 gas to check the response time and the baseline of the analysers (marked as “N2” in the Fig.’s 13-15 below by orange lines). After that, the measurements on the product gas have been continued and at the end the product gas intake was stopped and a switch to N2 reference gas was made. As one can see from the Fig’s 13-15, the baseline goes to zero with switch to N2. This can ensure that there is no analyser contamination which can potentially biased the measurements and can cause a memory effect.

There are clear CO2 and CH4 time variations as one can see in the Fig. 13. This is due to the non-uniform removal of CO2 in the amine adsorber which is in turn due to the non-uniform MEA distribution: high CO2 capture (i.e. low CO2 in the gas) corresponds to high CH4 concentration in the gas. These oscillations are in the range of about ± 0.5 %.

Water is a common impurity in all industrial gases, and it is known that reliable low-level water measurements require an appropriate interface between the gas sampling point and the analysers. As one can see from the Fig. 14, it takes about 30 min to achieve a stable H2O signal. Another observation from the Fig. 14 is that D3 and limonene concentrations do not depend on CO2 and CH4 variations as in the Fig. 13 and are subject of process variations: after monotonic increase in 12:30- 15:10 time span, both D3/limonene start to decrease and then to increase again.

Ethylene and propylene are not affected by the process in the amine adsorber, Fig. 15. At around 15:30, the propylene concentration is decreasing in the same way as the D3 one (Fig. 14) that indicate on the same (biological) origine of both. CO appears from time-to-time and not correlated to any of other major or minor components.

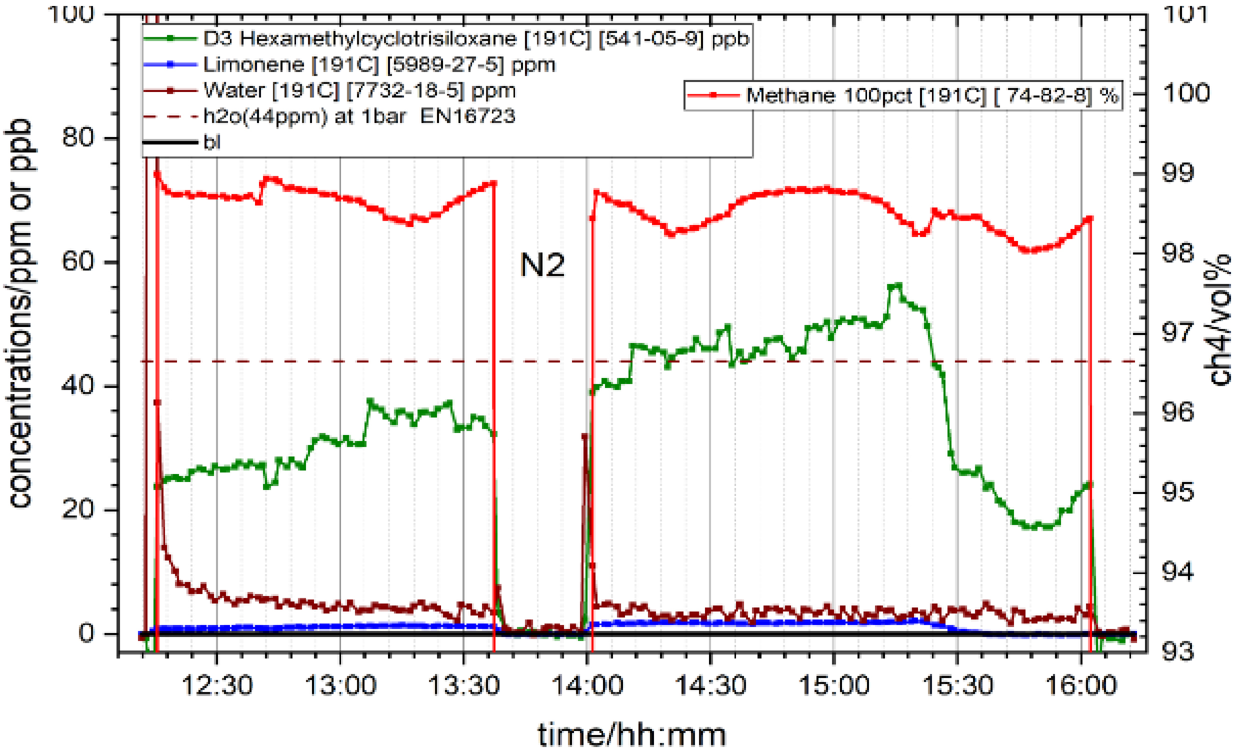

Figure 14: D3 (olive), limonene (blue), H2O (wine) and CH4 (red) on-line measurements with MAX-iR FTIR analyser with use of the protocol. H2O upper limit given by EN16723 standard (dash wine line).

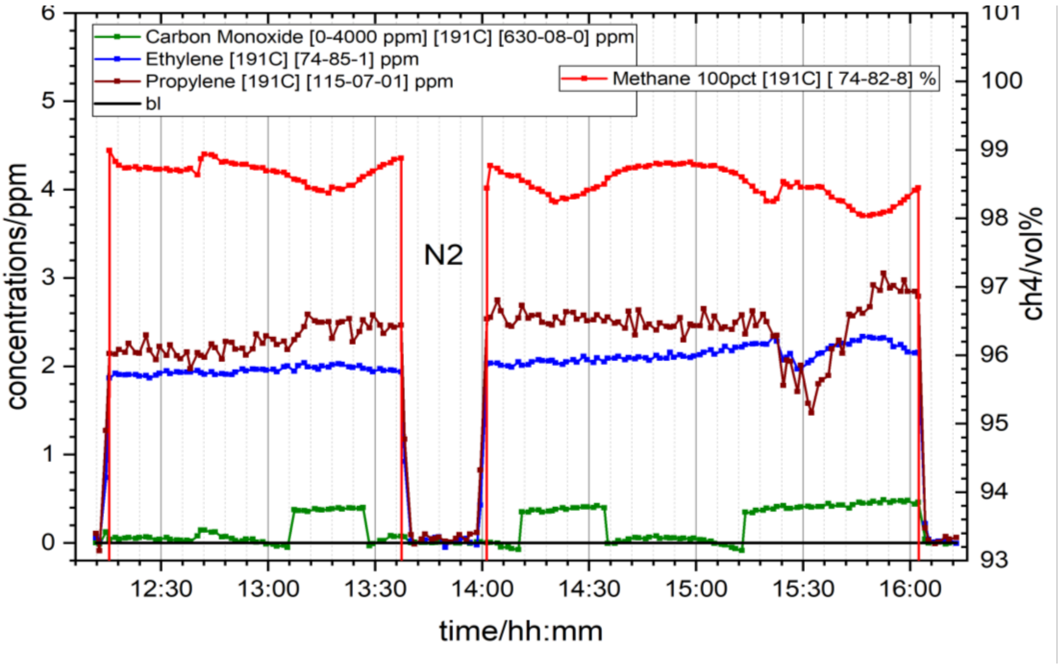

Figure 15: CO (olive), C2H4 (blue), propylene (wine) and CH4 (red) on-line measurements with MAX-iR FTIR analyser with use of the protocol.

One of the ways to verify the performance of an (sampling line + on-line analyser) combination, in addition to steps described in the protocol, is a comparison with available (on-line) data from the receiver station. These data, however, are not normally in a free access and a permission to use those are normally required. Fig. 16 shows a comparison of the CO2/CH4 measurements by MAX-iR FTIR analyser versus CO2/CH4 measurements at the receiver station (GC, EnCal 3000).

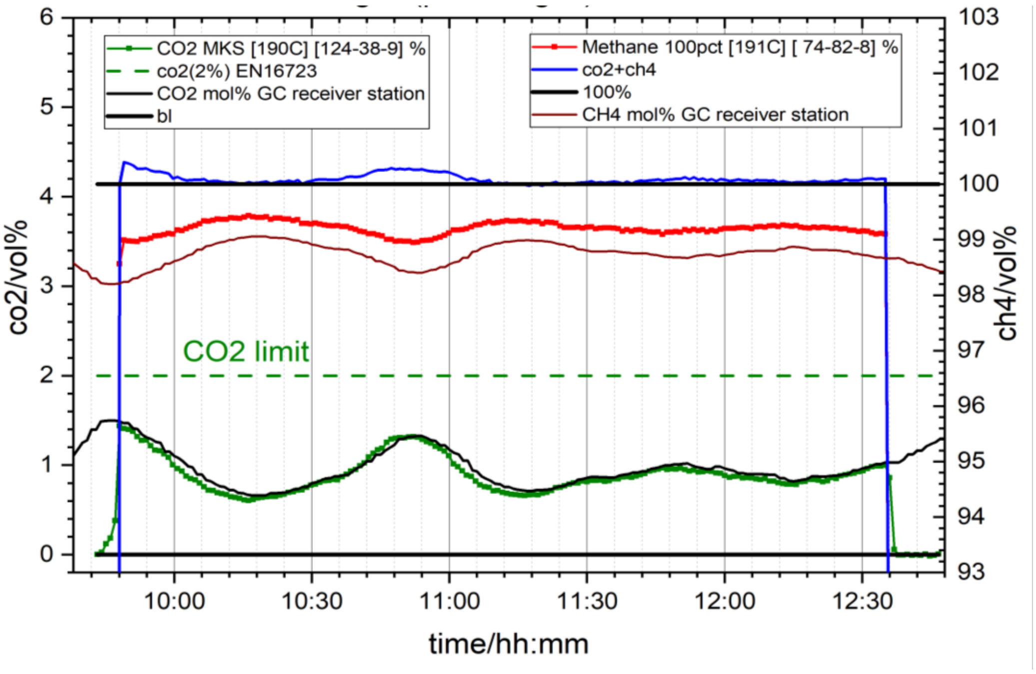

Figure 16: CO2 (olive) and CH4 (red) on-line measurements with MAX-iR FTIR in comparison with receiver station gas analysis (EnCal 3000): CO2 (black) and CH4 (wine). Total as CH4+CO2 (FTIR) (blue). CO2 upper limit (dash olive).

As one can see from the Fig. 16, the CO2 measurements by two completely different analysers are in a very good agreement which can be considered as very good result, taking into account a difference in response time of both analysers and the length of the sampling line. The CH4 measurements by the MAX-iR FTIR are about 0.4 % above the EnCal 3000 (GC) data. The sum of CH4+CO2 from MAX-iR FTIR data plotted (blue line) is close to 100 % (note that O2 is found at concentration of around 0.18 % - see Fig. 20 below).

In all measurements, the OF-CEAS/OGS measurement of NH3 concentration in product gas varied between 10 - 500 ppb which is in a full compliance with the EN16723 standard. Fig. 17 shows typical NH3 variations in the product gas which correlate with the CH4 variations. *This indicates that the CO2 removal in the amine adsorber "defines" an overall NH3 time patterns in the product gas and the downstream gas upgrade process chain does not smooth NH3 time patterns, rather significantly decrease NH3 content in the product gas. This should be kept in minds if some malfunction of the amine adsorber can happen.*

Fig. 18 and 19 show time variations of other minor species such as D3 siloxane, H2O, CO, C2H4, propylene and limonene (MAX-iR FTIR measurements). Fig. 20 shows the far-UV measurements of O2, CS2, DMS and benzene. The O2 measurements at the receiver station are given for a comparison. The far-UV and GC O2 measurements show the same time patterns and are in a good agreement (- 0.01 % difference). As one can see form the Fig. 19 and 20, an increase in limonene concentration correlates with DMS/benzene increase, while CS2 concentration does not change with time at all. This relates to a change in a raw material feedstock.

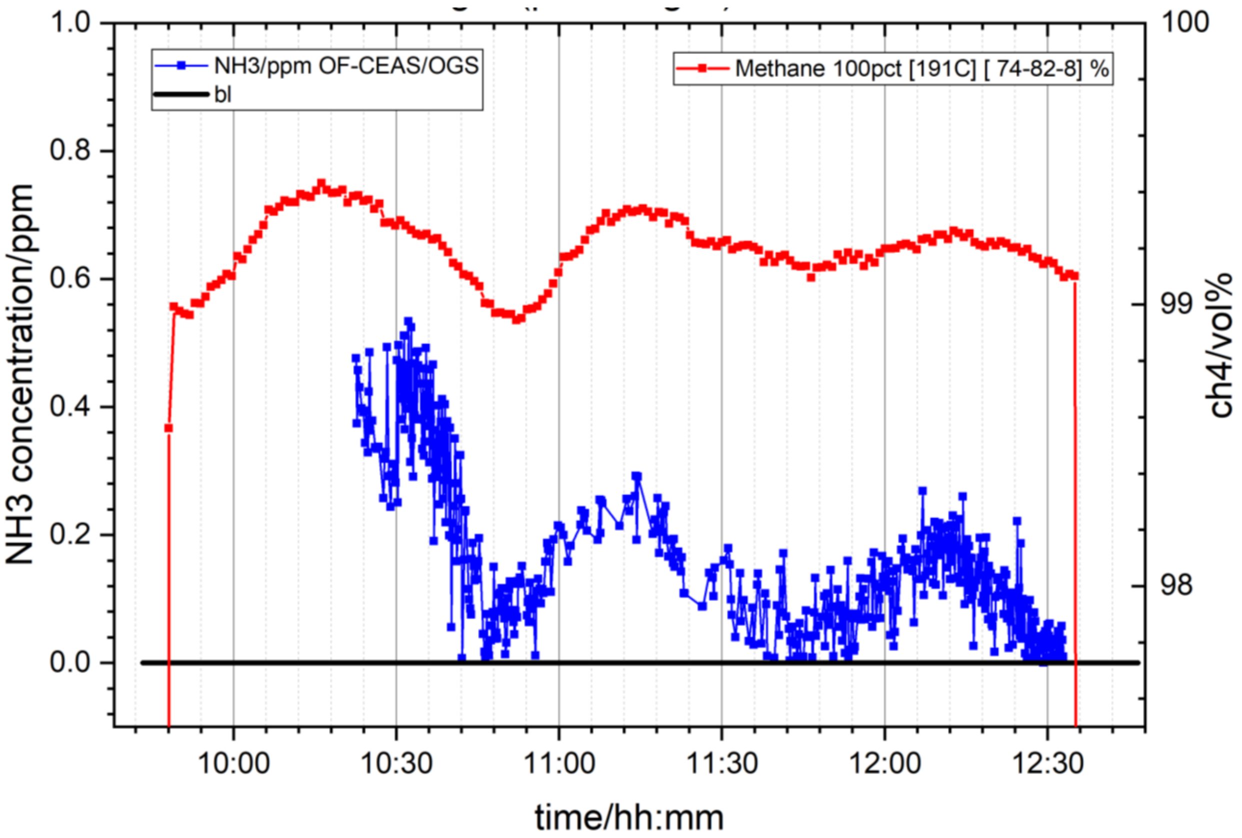

Figure 17: OF-CEAS/OGS based measurement of NH_3 in biomethane in product gas (blue) and CH4 (red, MAX-iR FTIR).

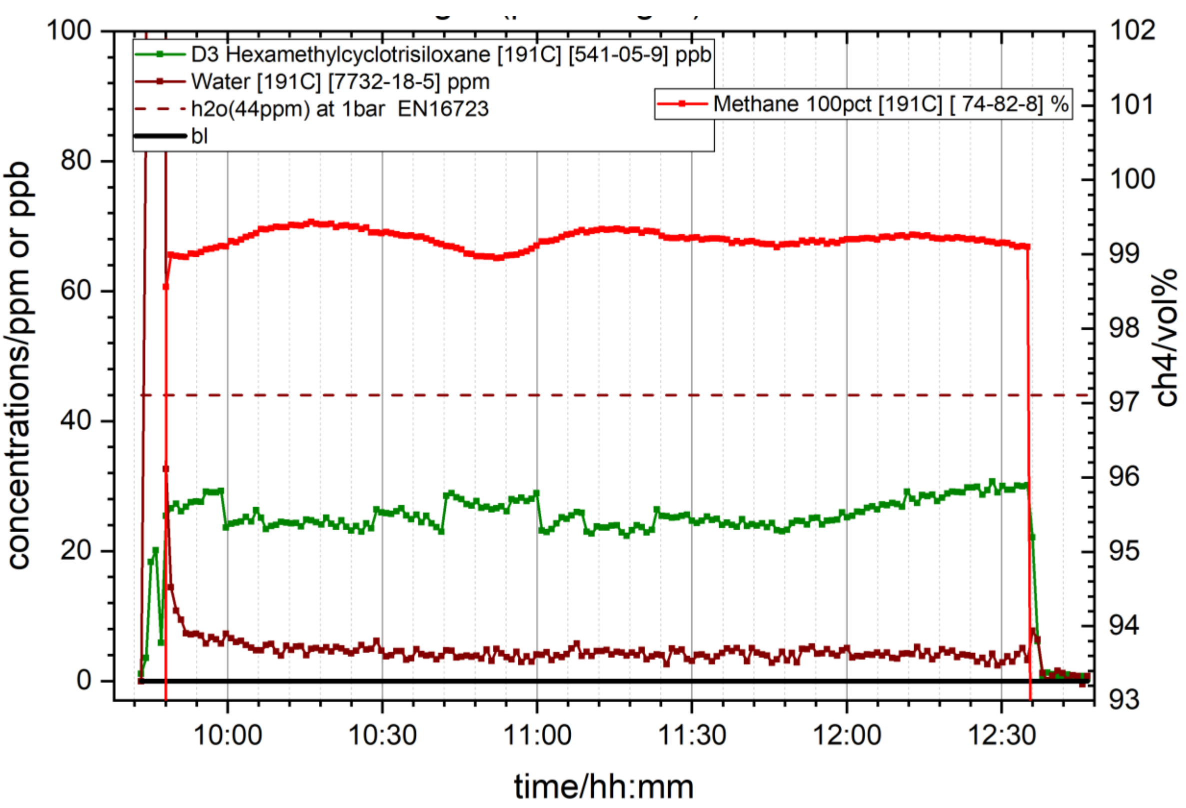

Figure 18: D3 siloxane (olive), H_2O (wine) and CH_4 (red) measurements on the product gas with MAX-iR FTIR. Upper H_2O limit (EN16723) (dash wine).

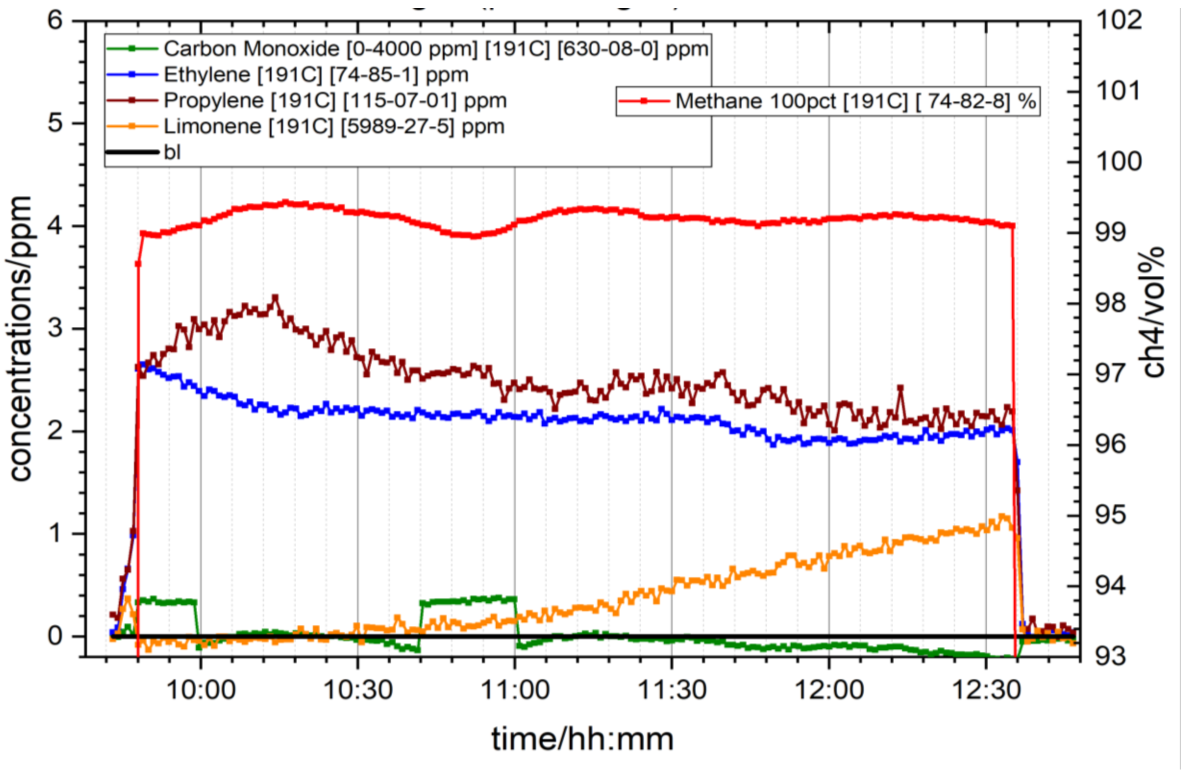

Figure 19: Left: CO (olive), C_2H_4 (blue), propylene (wine) and limonene (orange) on-line measurements by MAX-iR FTIR analyser on the product gas. Right: CH_4 (red) is given for reference.

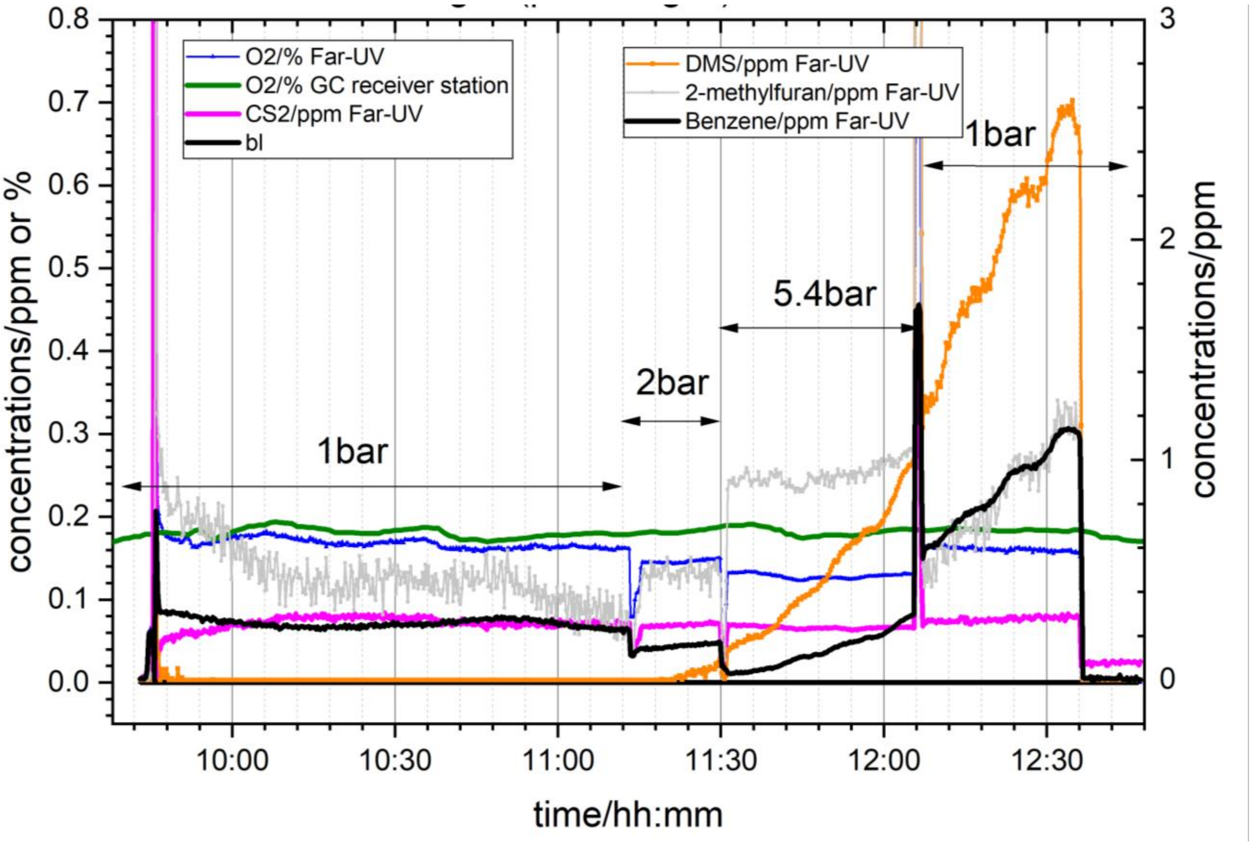

Figure 20: Left: O2 (blue), CS2 (magenta), DMS (orange). Right: 2-methylfuran (grey) and benzene (black) on-line measurements with far-UV analyser. O2 data from the receiver station (olive). Product gas intake pressure 5.4 bar. Numbers and arrows indicate working pressure in the far-UV analyser.

5.3 Measurements on biogas (after amine adsorber, before VOC removal)

Measurements on the “semi-clean” biogas before VOC removal do not considerably differ from the measurements after the VOC removal, therefore they are omitted here.

5.4 Measurements on biogas (after VOC removal)

Measurement location for biogas intake after carbon filter (VOC filter) is shown in Fig. 21. This filter is located downstream, after CO2 separation in the amine CO2 adsorber. There is no additional gas cleaning in between. The gas is cold (about 20 ^{o}C) and contains typically 1-2 % of water.

Figure 21: Biogas in-take location after VOC filter (red line). Arrow shows direction of the gas flow to the tent.

All three analysers have shown significant amount of NH3 in the gas. A time-series of parallel measurements with MAX-iR FTIR, far-UV and OF-CEAS/OGS analysers is shown in Fig. 22. The MAX-IR FTIR collects averaged over about 1 min data set. The far-UV and OF-CEAS/OGS analysers can perform fast data collection, under 1 s acquisition time for a data set.

The measurement series in the Fig. 22 was done using the developed protocol. The measurements started and finished with N2 gas to control the baseline. As it can be seen on Fig. 22, response time for CO2 with the far-UV analyser is much faster than for NH3. This is a general observation when a wet gas is taken into the analysers via a non-heated sampling line.

As one can see from the Fig. 22, CO2 and NH3 time-profiles has opposite phase correlations. Measurements of CO2 concentration by MAX-iR FTIR and far-UV analysers are in a good agreement.

The MAX-iR FTIR analyser has a slower response time compared to the far-UV and OF-CEAS/OGS ones. The far-UV and OF-CEAS/OGS analysers show more detailed NH3 concentration time variation, while the MAX-iR FTIR one gives an overall smoothed NH3 behaviour. An increase in datasets rate for the far-UV analyser (or by other words – reducing acquisition time per one data set, e.g. from 8 s to 1 s) does not add additional information into the obtained NH3 data, Fig. 22. In opposite, reduced acquisition time decrease S/N ratio in the raw data and therefore increase a “noisiness” in the CO2 concentrations.

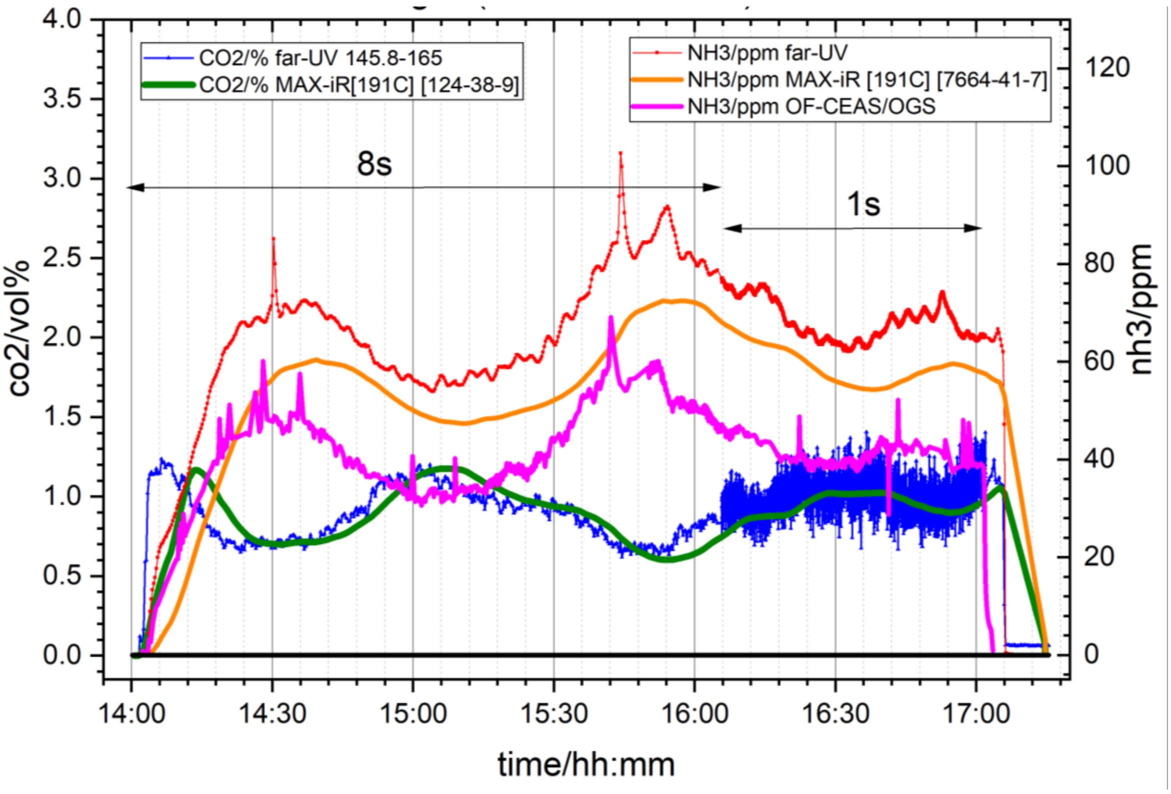

Figure 22: Left: CO2 MAX-iR FTIR (olive) and far-UV (blue) on-line measurements. Right: NH3 MAX-iR FTIR (orange), far-UV (red) and OF-CEAS/OGS (magenta) on-line measurements. Acquisition time per one dataset for far-UV analyser marked arrows with numbers.

The NH3 measurements for all three analysers show the same time patterns. However, there is a bias in overall concentration measurements: the MAX-iR gives about – 8 ppm difference, while the OF-CEAS/OGS gives about – 23 ppm lower than the far-UV ones in the NH3 concentration. This difference is not yet fully understood. The measured water concentration by MAX-iR FTIR (0.47 %) is also lower than the one measured by the far-UV analyser (0.9 %), Fig. 25. Therefore, the difference in NH3 concentrations between MAX-iR FTIR and far-UV may be explained by NH3 trapping by (condensed) water probably before the analyser or by a NH3 chemical conversion inside (the analyser's measurement volume is heated to 190 ^{o}C, while the far-UV one has no heating). The same NH3 condensation may happen in the OF-CEAS/OGS branch.

Fig. 23 shows time variations of CO, C2H4 (ethylene), propylene and limonene in the measurements after the VOC filter. CO2 and CH4 concentrations are shown in Fig. 24. This Fig. is similar to the Fig. 13 and shows opposite phase CH4/CO2 time variations. In Fig. 25 and 26 time-variations of other trace gases are shown. None of these variations are correlated with either with CO2 or CH4. Benzene and 2-methylfuran concentrations are higher after VOC filter than those in the product gas because their removal in the followed compression and fine filtering steps.

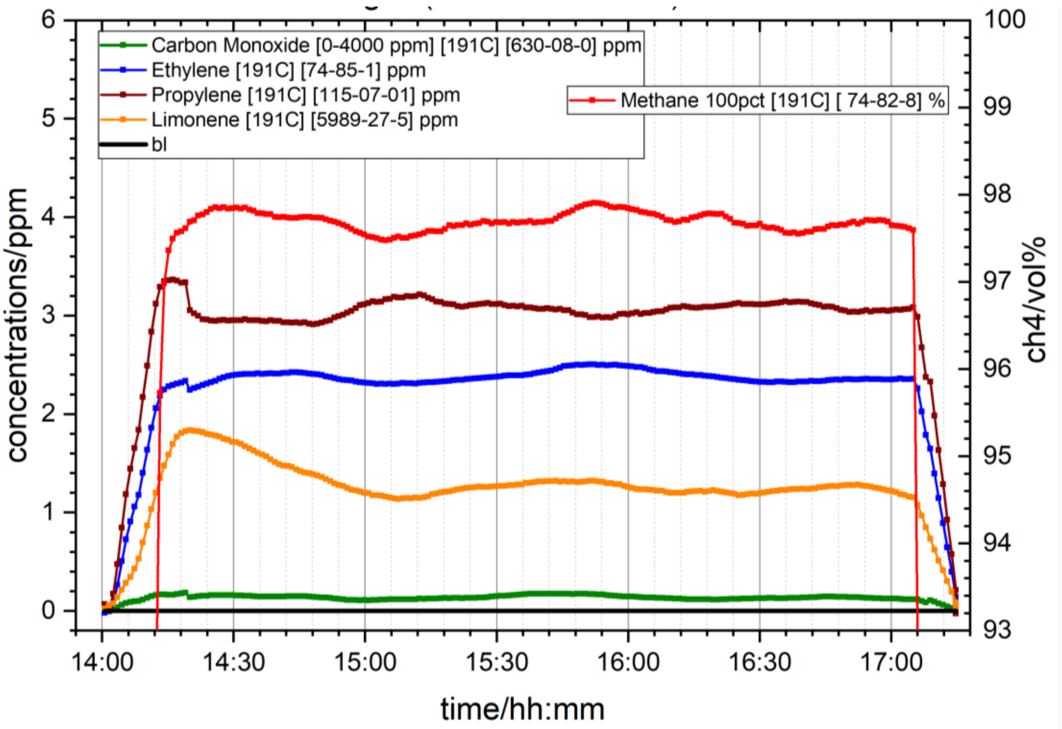

Figure 23: Left: CO (olive), C2H4 (blue), propylene (wine) and limonene (orange) on-line measurements by MAX-iR FTIR analyser after VOC filter. Right: CH4 (red) is given for reference

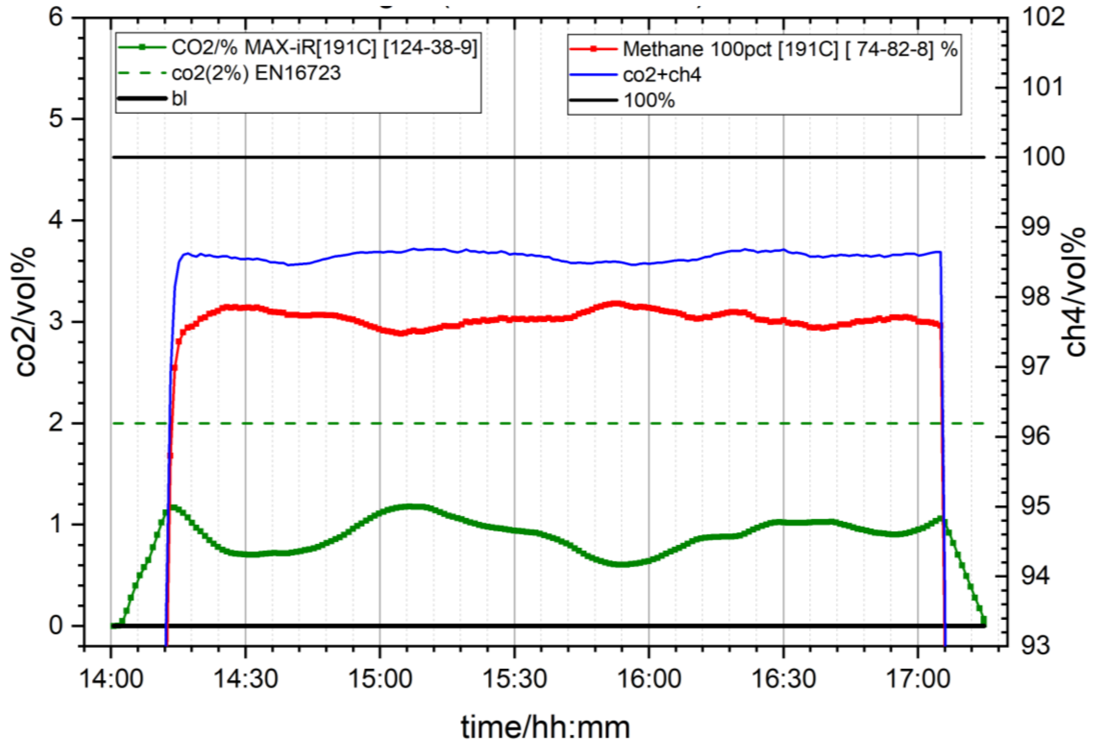

Figure 24: CO2 (olive) and CH4 (red) on-line measurements by MAX-iR FTIR analyser after VOC filter. Sum of CO2+CH4 (blue).

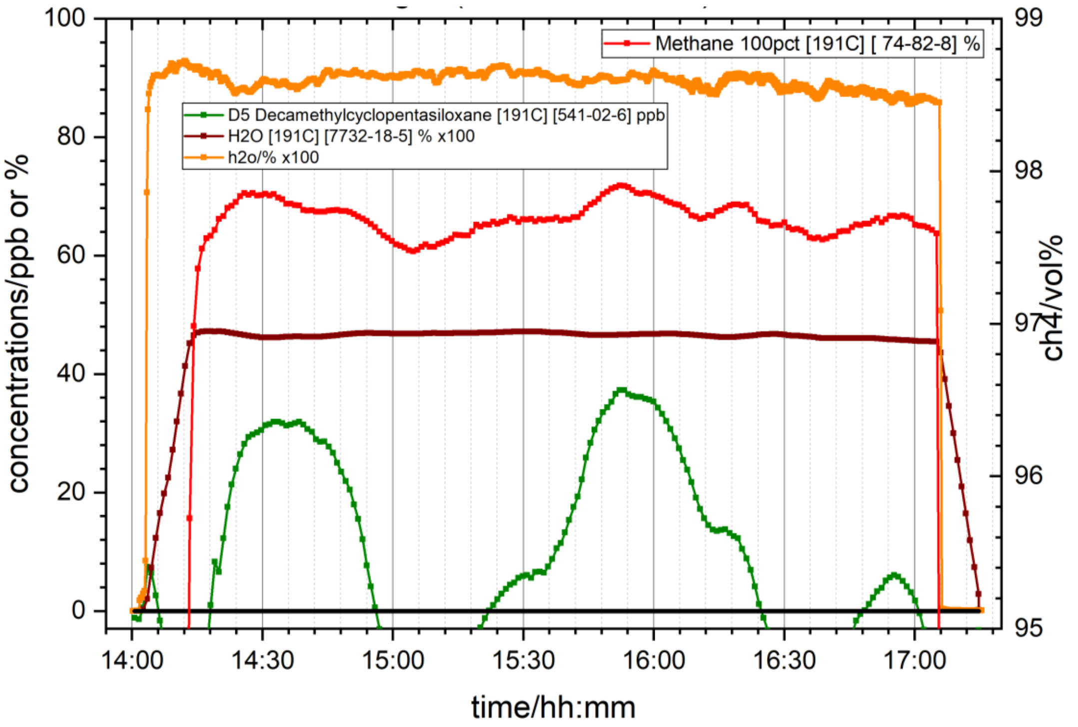

Figure 25: D5 siloxane (olive), H2O (wine, x100) and CH4 (red) on-line measurements by MAX-iR FTIR analyser after VOC filter. Far-UV on-line H2O (orange, x100)

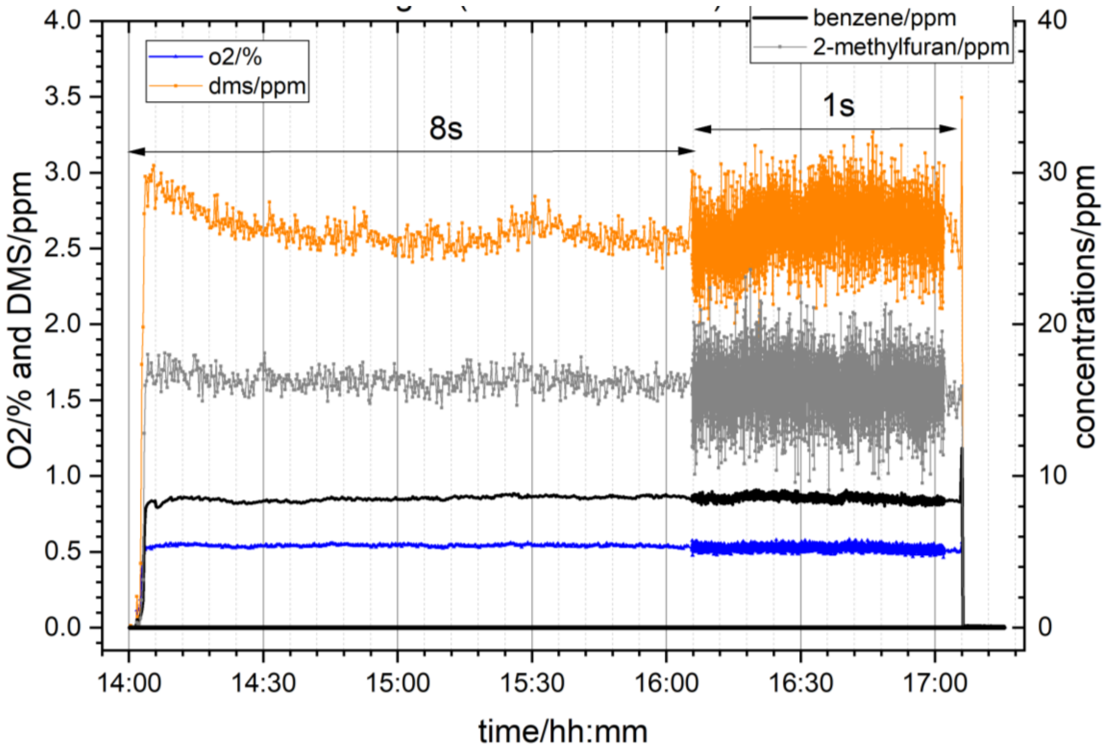

Figure 26: Left: O2 (blue), DMS (orange). Right: 2-methylfuran (grey) and benzene (black) on-line measurements with far-UV analyser. Acquisition time per one dataset for far-UV analyser marked arrows with numbers.

5.5 Measurements on raw biogas (after first gas cooler, before amine absorber)

Few measurements have been on a raw biogas taken after the first gas cooler (removes an excess of water in the raw biogas after the digestor) and before the amine scrubber, Fig. 27. The measurements have beam done according to the Protocol (WP2).

This raw biogas contains water and high amounts of CO2, CH4, VOC's and various S-compounds. The gas was taken into the analyser through unheated PTFE tubing exposed to the ambient air at about + 2.3 °C. This temperature works as a set point for water dew point for the wet raw biogas and defines saturated water concentration which is 0.69 vol % at + 2 °C (NIST). Results of the far-UV analyser measurements are shown in Fig. 28 and 29.

Figure 27: Raw-biogas in-take location before amine adsorber and gas flow direction (red circle and yellow arrow, respectively).

As one can see from the Fig. 28, the measured water concentration is about 0.7 vol% which is in a good agreement with the theoretical value of 0.69 %. The NH3 concentration pattern follows the H2O concentration pattern with some time delay, in a similar way, as it is shown in Fig. 22.

The gas in-take has been stopped at 16:28 and the whole PTFE sampling line and the far-UV analyser have been purged by N2. Non-soluble compounds (e.g. CO2 and H2S) are quickly removed, while removal of H2O and NH3 take more time, Fig. 28-29. In Fig. 29, time-depended concentrations for light hydrocarbon (C2H4), VOC (propylene, benzene) and DMS are shown.

The NH3 concentration measured in the raw biogas on different days lies between 12 and 25 ppm and there are no visible time correlations with the CO2 concentration as e.g. shown in the Fig. 24. Moreover, that NH3 concentration in raw biogas is below the one measured after the VOC filter, Fig. 22. This means that *the major contribution to the NH3 in the "semi-clean" biogas comes from the amine adsorber as one of the products of MEA decomposition*. *That NH3 (together with H2O) is removed from the biogas in the final compression and fine gas cleaning stages. The final NH3 concentration in the biomethane is < 0.5 ppm, Fig. 17. The drain water is acidic and shall be treated in a proper way. Some other corrosion-related issues on the plant's infrastructure may be observed with time.*

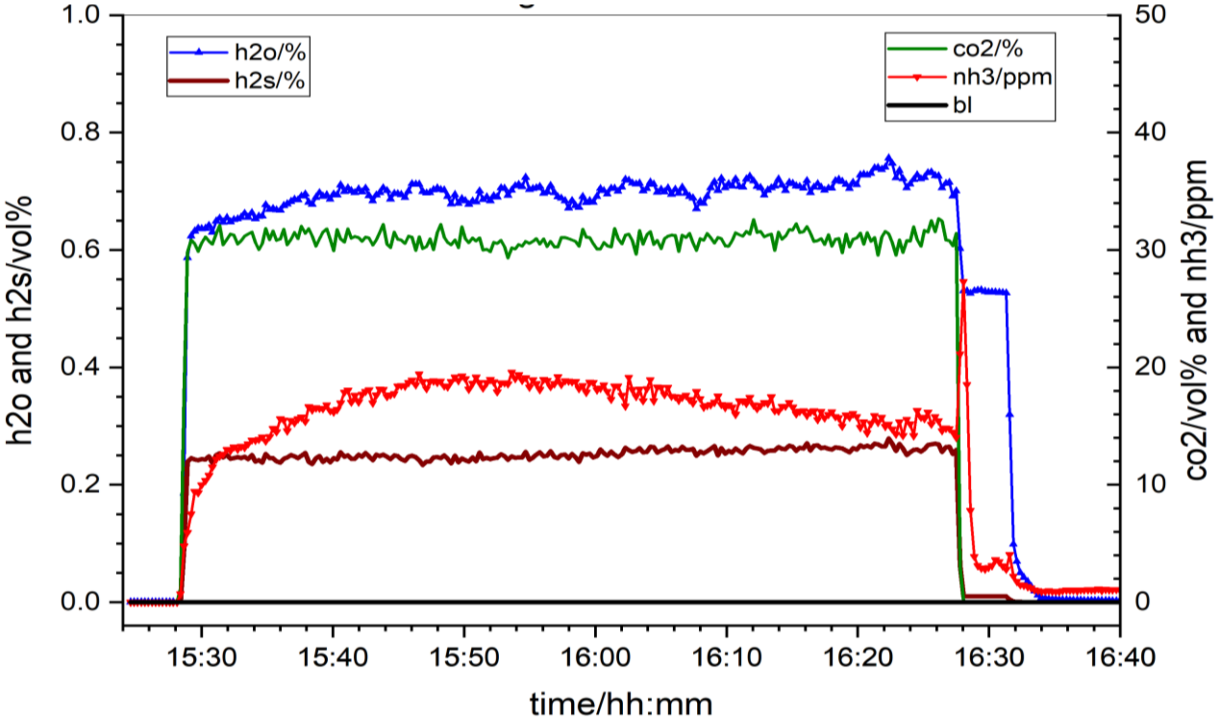

Figure 28: H2O (blue), H2S (wine), CO2 (olive) and NH3 (red) on-line measurements with far-UV analyser on raw-biogas before amine adsorber at gas in-take position shown in Fig. 27.

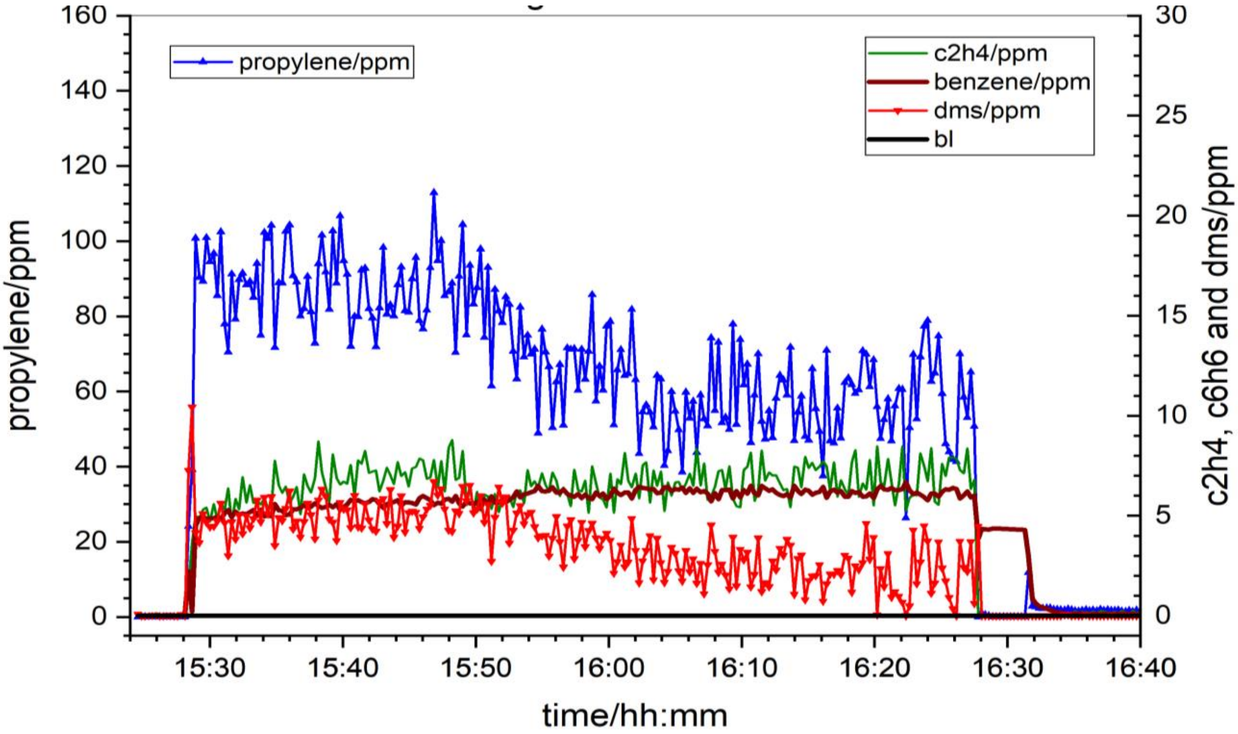

Figure 29: Propylene (blue), C2H4 (olive), benzene (wine) and DMS (red) on-line measurements with far-UV analyser on raw-biogas before amine adsorber at gas in-take position shown in Fig. 27.

6 Measurements at Solrød Bioenergy in Denmark (Dec. 2024)

Solrød Biogas is a biogas plant located west from Copenhagen [6]. It was put in operation in 2015. The plant produces biomethane which partly delivers to the gas net (3.500.000 m3, equivalent of 19 GWh) and to a nearby electricity (29 GWh) and heat (39 GWh) production facilities (13.000.000 m3), Fig. 30. The plant is also producing about 220.000 tons of fertilizers.

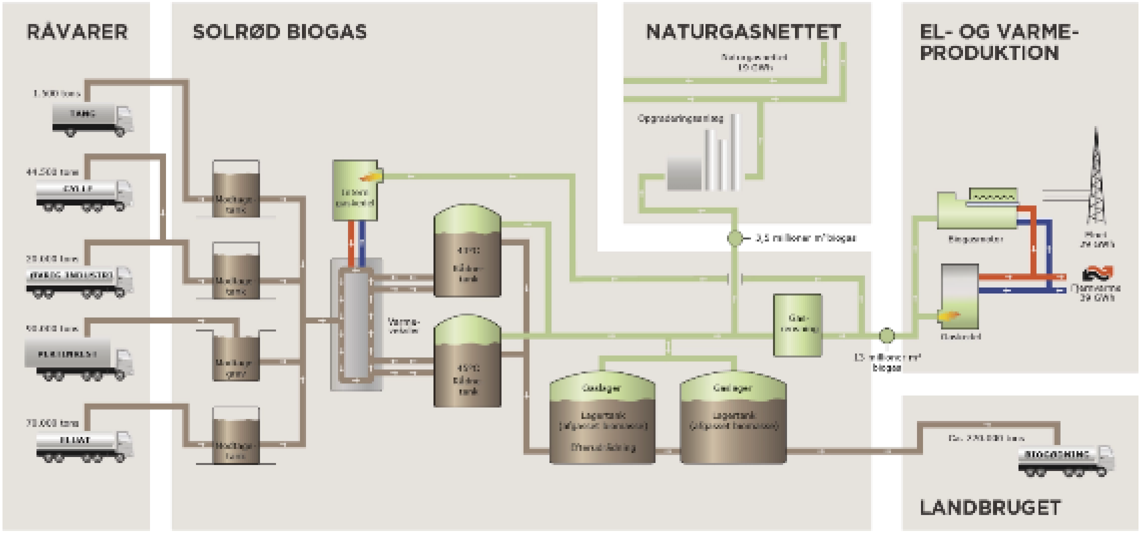

Figure 30: An overall biomethane production chain at Solrød Bioenergy [6].

Compared to Lohja and Ribe plants, there is a wide diversity in the raw materials suppliers at Solrød Bioenergy. The plant has very mixed composition of the raw materials which consist of about 1) 1.500 tons of seaweed (algae that often lives and grows in salt water), 2) 44.500 tons of manure (a mixture of liquid waste from agricultural production of cattle and pigs), 3) 90.000 toms of residual products from pectin and carrageenan production at CP Kelco (contain mostly carbohydrates and some protein and fat), 4) 70.000 tons of eluate (or whey) from Chr. Hansen (a residual product from the production of lactic acid bacteria) and 5) 20.000 tons of other diverse blended biowaste (e.g. household biowaste).

Figure 31: Measurements at Solrød Bioenergy. CO2 separation towers are in the middle and to the left. Tent location is in the middle.

6.1 Overview of biogas upgrade in Solrød

There are two independent biogas upgrade stages: the gas which is delivered to a gas engine (electricity production) and a gas boiler (heart production) is only cleaned from H2S while the gas for the gas net undergoers more complex cleaning (or upgrade). On the first step, H2S is removed by carbon filters. On the second stage the same type of the filters is used to remove VOC's from the gas. Finally, CO2 separation is made in a pressurized CO2-water scrubber (MALMBERG technology).

The measurements were conducted at various stages of the biogas upgrading, and on the biogas used for gas net. The same length PTFE tubing (Ø 6 mm) as it was used at Ribe Biogas, was used to reach all gas intake positions and keep the same integrity with the Ribe measurements. An ATEX-approved handheld CH4 leak sensor (SCHUTZ Messtechnik) was used to trace all connections from gas intake to analysers vent. The vent from analysers was placed outside of the tent in the opened air. Fig. 31 shows measurement location at Solrød Bioenergy biogas plant. Measurements have been performed with use MAX-iR FTIR and far-UV analysers.

6.2 Measurements on biomethane (product gas, plant exit, before receiver station)

Measurement location on the product gas is shown in Fig. 31. The gas is atambient temperature) and at around 5 bar pressure. Far-UV spectral data are dominated by CO2, H2O, O2, BTEX (o-xylene) and terpenes (p-cymene) components. The data are very consistent and for further analysis, references data for some components are required.

During measurements at various gas in-take locations, it was noted that *there is a minor effect of the H2S and VOC filters on the far-UV data: the far-UV spectra are "loaded" with various VOC's (BTEX + terpenes). The far-UV measurements on the product gas show significant reduction in VOC's but still presence of BTEX components (toluene, m-xylene and p-xylene).* In the further discussion only MAX-iR FTIR data are presented.

On-line measurements on the product gas are shown in Fig. 32. The CO2 concentration exhibit no time variations (contrary to what was observed at the Ribe and the Lohja biogas plants). The CO2 concentration is below CO2 limit given by EN16723 standard. The product gas contains light VOC's and various siloxanes at higher concentrations than those in Ribe (Fig. 19, 33), see Fig. 33 and 34 below.

Figure 31: Product gas intake position before receiver station at Solrød Bioenergy (red, pressure around 5 bar). Flow direction is given by yellow arrow.

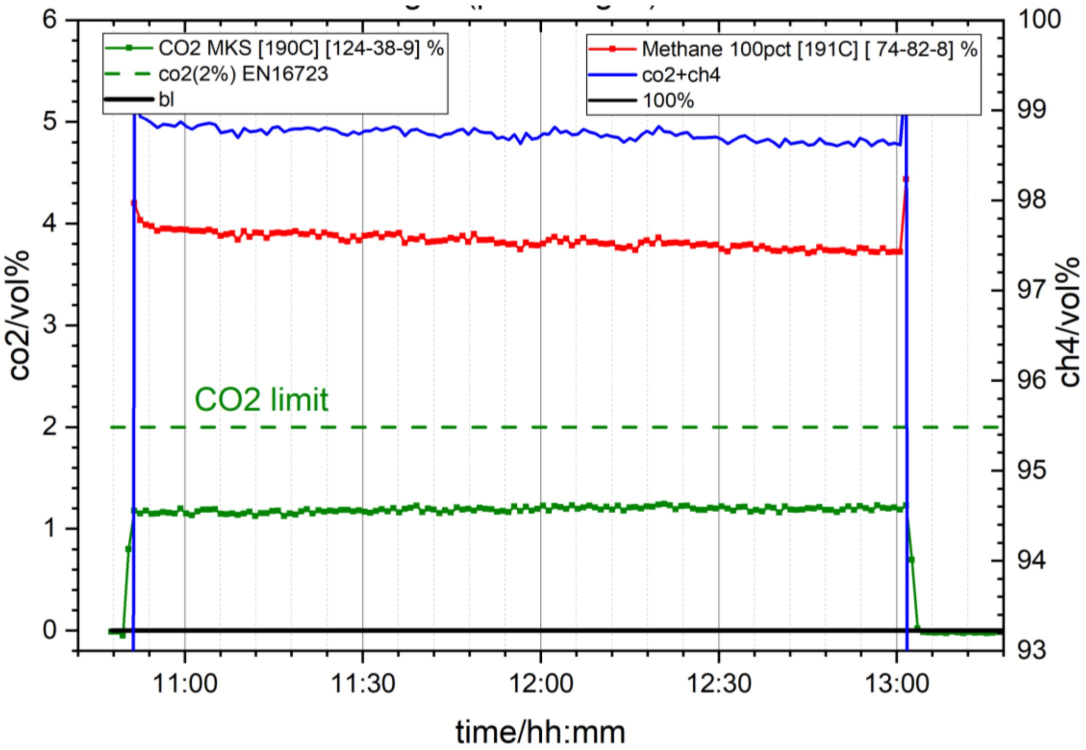

Figure 32: CO2 (olive) and CH4 (red) on-line measurements by MAX-iR FTIR analyser on product gas. Sum of CO2+CH4 (blue).

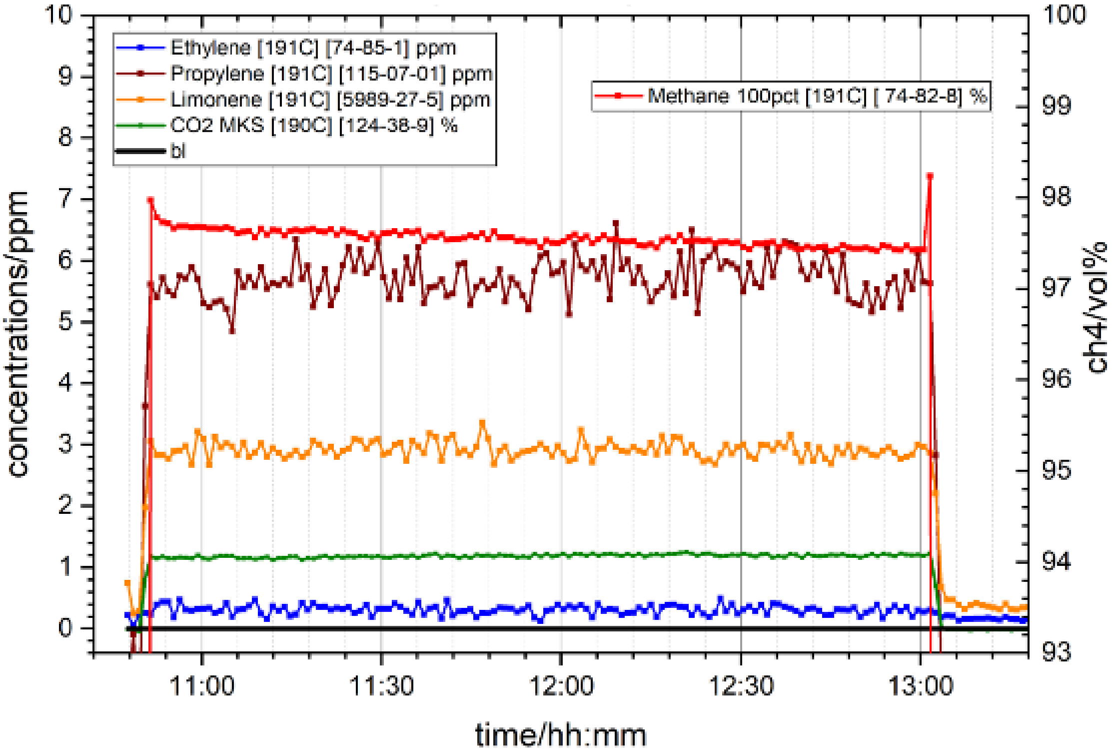

Figure 33: CO2 (olive), C2H4 (blue), propylene (wine) and limonene (orange) on-line measurements by MAX-iR FTIR analyser on product gas. Right: CH4 (red) is given for reference

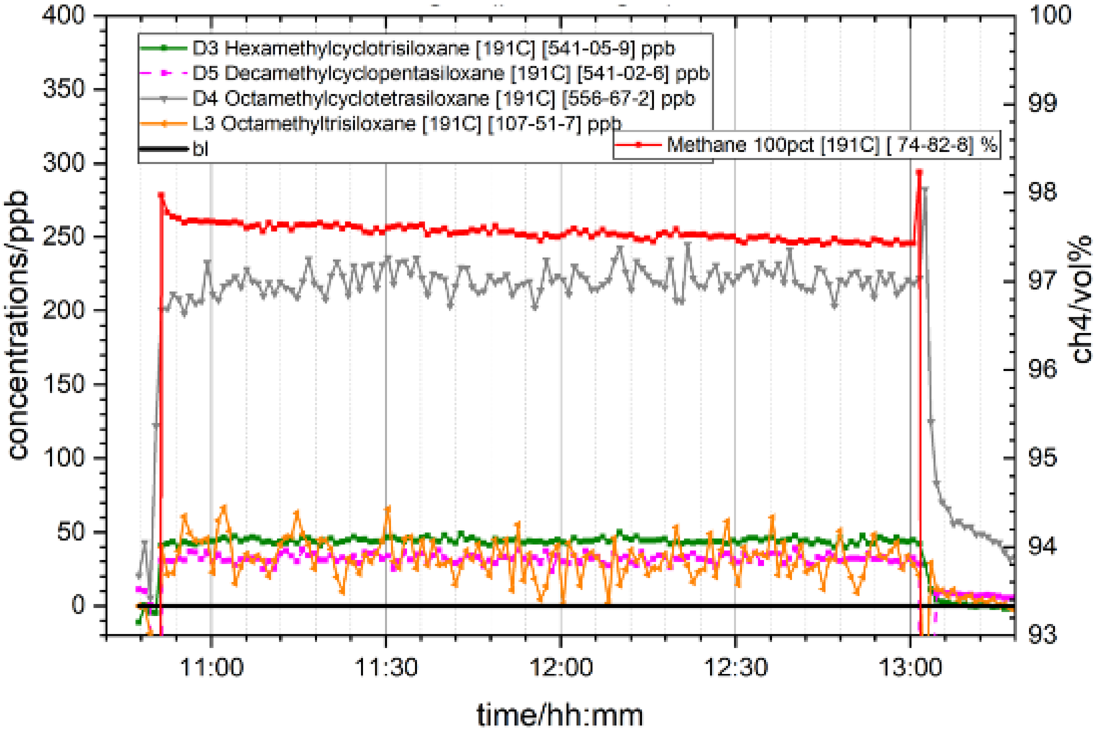

Figure 34: D3 (olive), D5 (magenta), D4 (grey) and L3 (orange) siloxanes on-line measurements by MAX-iR FTIR analyser on product gas. Right: CH4 (red) is given for reference

The concentration profiles shown on Fig, 32-34 exhibit no time variations and therefore a traditional gas sampling in bags or gas cylinders can be recommended for further advanced lab-analysis.

6.3 Measurements on biogas (after VOC removal)

Figure 35: Biogas intake position after VOC filter (red, pressure a bit above 1 bar). Flow direction is given by yellow line.

Gas intake measurement location after VOC filter (before CO2 removal) is shown in Fig. 35. The gas is at ambient temperature and kept at a bit overpressure.

The gas contains high concentration of CO2, Fig. 36 and higher concentrations of light VOC's (ethylene, propylene and limonene) compared to the product gas. Fig. 37. This is also in agreement with far-UV measurements. The observation is also true for siloxanes, Fig. 38.

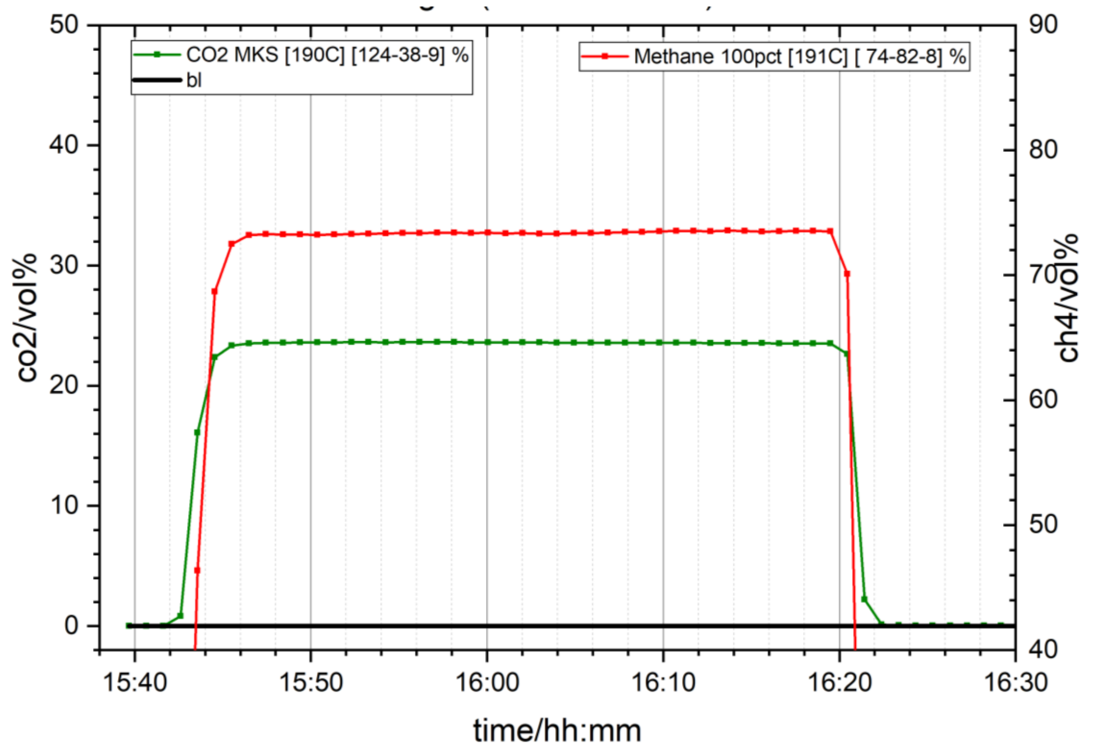

Figure 36: CO2 (olive) and CH4 (red) on-line measurements by MAX-iR FTIR analyser after VOC filter.

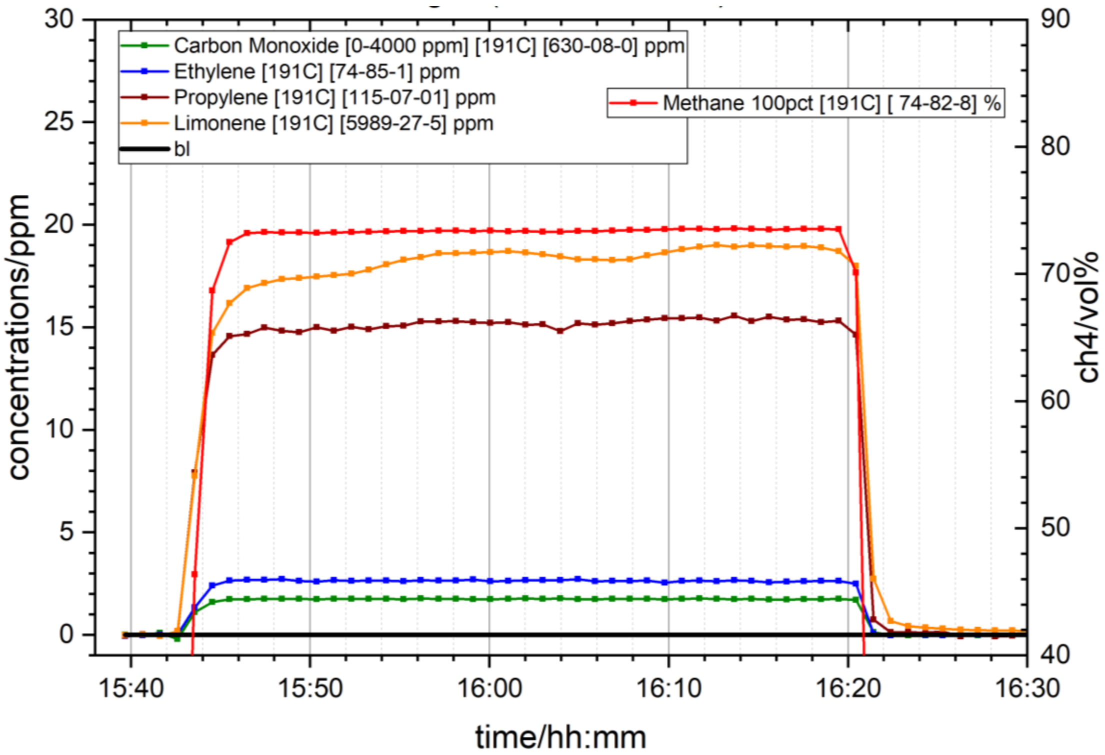

Figure 37: CO (olive), C2H4 (blue), propylene (wine) and limonene (orange) on-line measurements by MAX-iR FTIR analyser after VOC filter. Right: CH4 (red) is given for reference

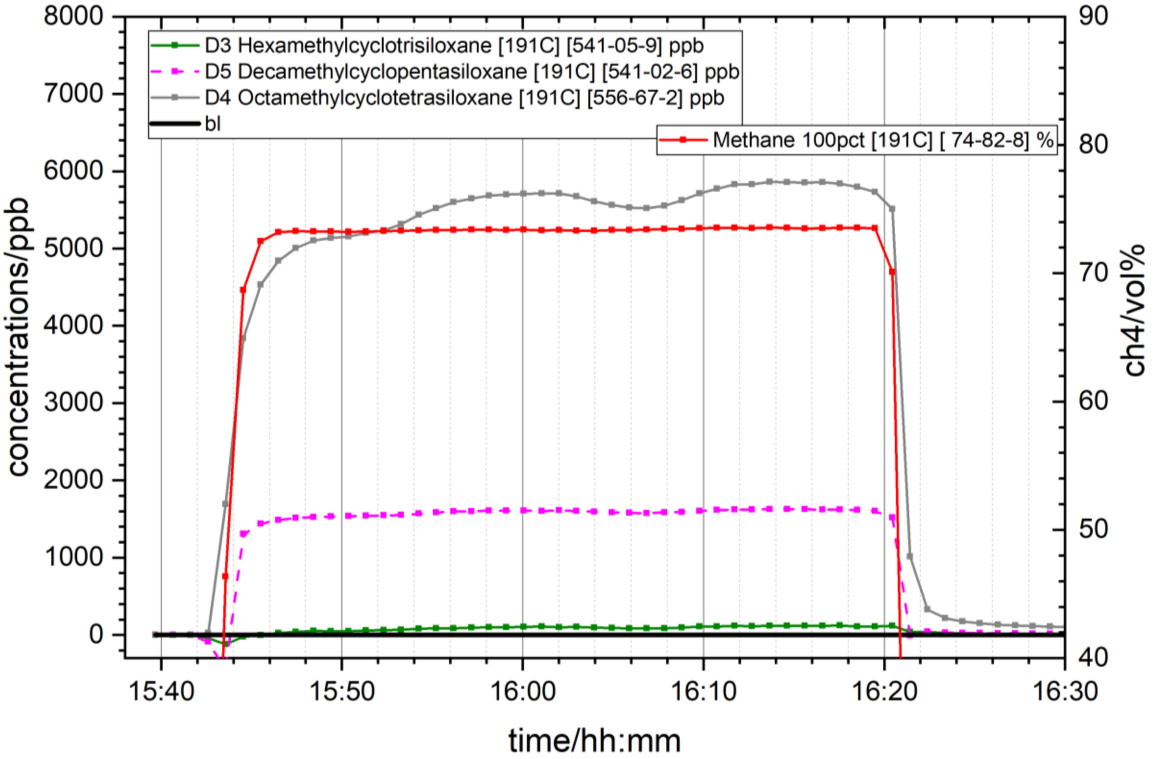

Figure 38: D3 (olive), D5 (magenta), D4 (grey) siloxanes on-line measurements by MAX-iR FTIR analyser after VOC filter. Right: CH4 (red) is given for reference

6.4 Measurements on biogas (after H2S removal)

Measurements performed after the H2S filter, Fig. 39 have been found to be in the same order of magnitude than the ones after the VOC filter and they are not reported here.

Figure 39: Biogas intake position after H2S filter and before VOC filter (red, pressure a bit above 1 bar). Flow direction is shown by yellow arrow.

6.5 Measurements on raw biogas (before H2S removal)

The location for the measurements performed at the raw-biogas intake point is shown in Fig. 40 and the results are shown in Fig. 41 to 43.

Figure 40: Raw biogas intake position (red, pressure a bit above 1 bar, temperature about +5.5°C). Flow directions are given by yellow arrows.

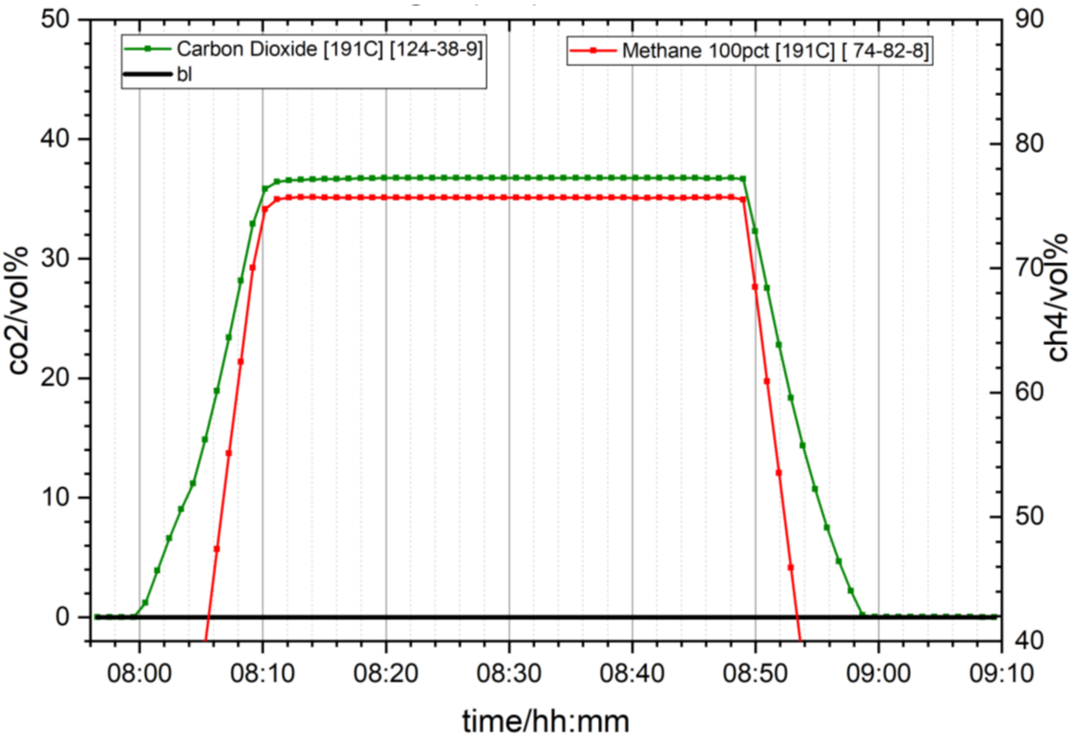

Figure 41: CO2 (olive) and CH4 (red) on-line measurements by MAX-iR FTIR analyser on raw biogas.

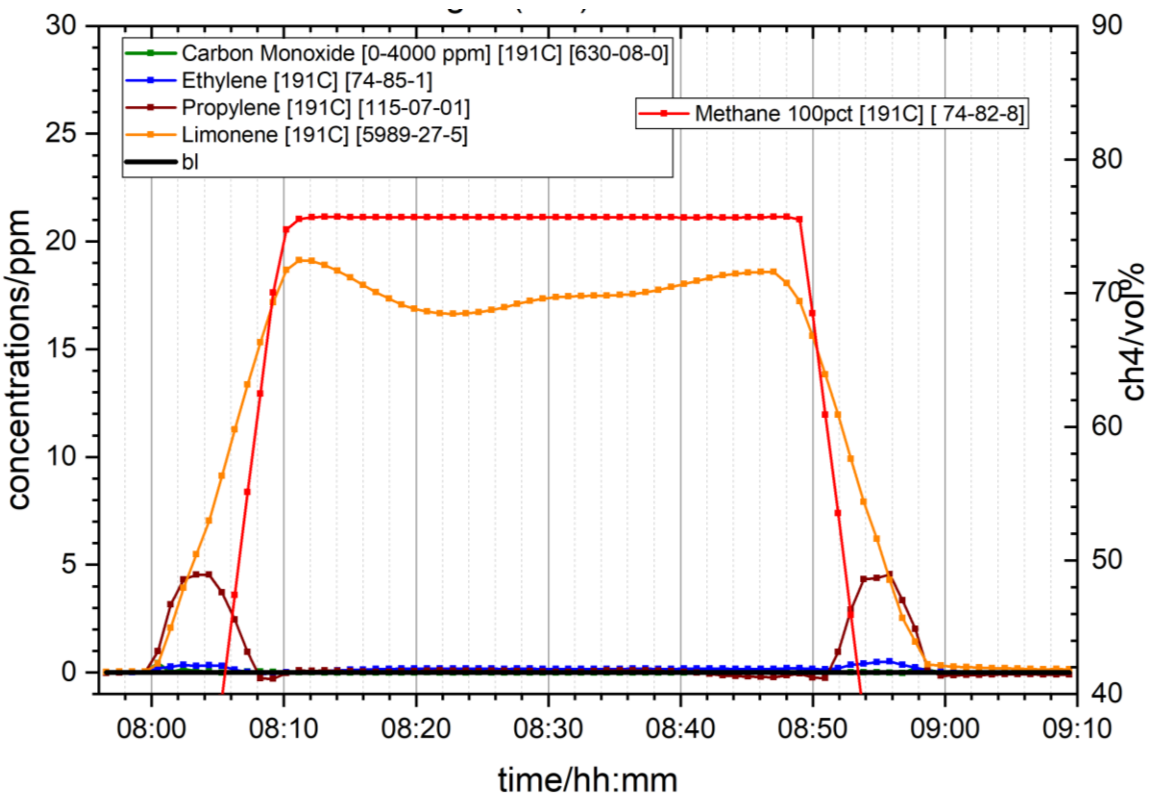

Figure 42: CO (olive), C2H4 (blue), propylene (wine) and limonene (orange) on-line measurements by MAX-iR FTIR analyser on raw biogas. Right: CH4 (red) is given for reference.

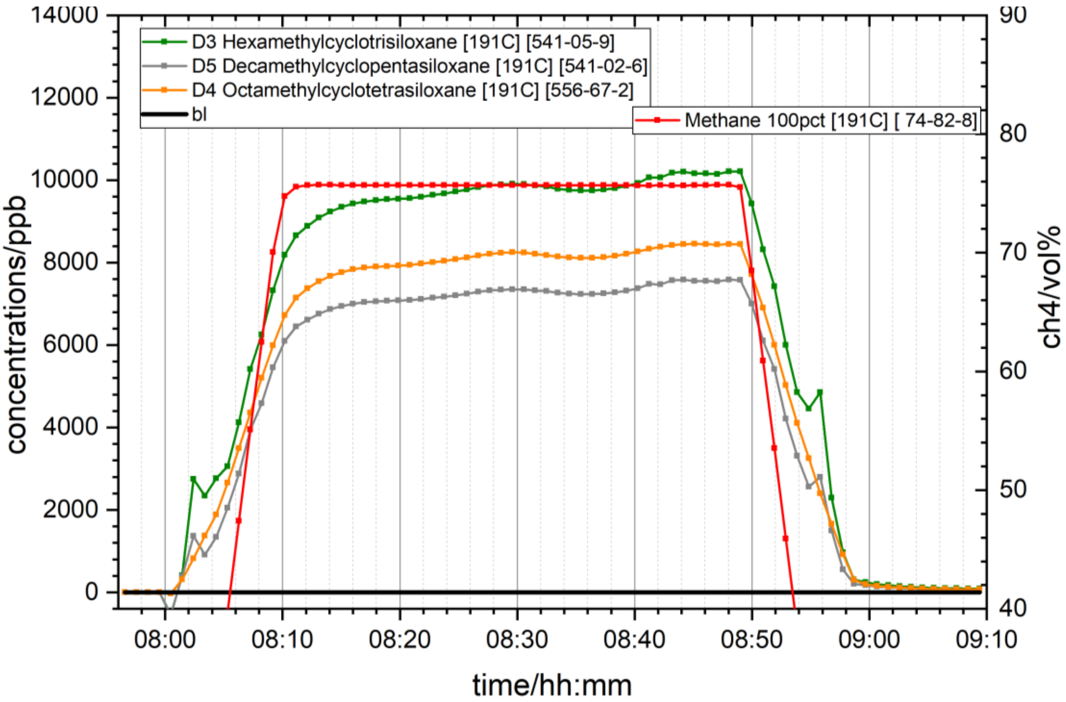

Figure 43: D3 (olive), D5 (grey), D4 (orange) siloxanes on-line measurements by MAX-iR FTIR analyser in raw biogas. Right: CH4 (red) is given for reference

The limonene concentration in the raw biogas (Fig. 42) is similar to the limonene concentration after the VOC filter (Fig. 37). This is in agreement with far-UV measurements mentioned above. Siloxanes concentration, in the raw biogas, Fig. 43, was found to be much higher than after the VOC filter, Fig. 38. It can be concluded that the *H2S/VOC filters remove efficiently the siloxanes, while the VOC's are removed together with the CO2 in the high-pressure CO2-water scrubber.* The product gas has no signatures of NH3 but still contains several VOC's compounds and siloxanes.

7 Conclusions

The report describes on-line measurements performed at three biogas plants in Denmark (two sites) and one in Finland using several analysers. The tests are performed according to the protocol developed during the BiometCAP project (recommendation for onsite installation, baseline testing, calibration, results interpretation). These biogas plants use different CO2 separation techniques and have various raw materials feedstocks, both leading to large variations in the product gas (biomethane).

Moreover, the report also provides valuable observations related to operation specific biogas production plants. The observations can be used by the plant's personnel for further process control and optimization.

The main conclusions of the work are:

- ☐ There are broad variations in minor gas components.
- ☐ The product gas on-line measurements are in agreement with the receiver station measurements.
- ☐ The biomethane is compliant with the EN16723 standard.
- ☐ Process data analysis can be relevant to amine-based CO2 capture in CCUS area.
- ☐ *On-line gas analysis is a must when there are in-process variations.*
- ☐ Off-line gas analysis can only be used for a representative gas analysis.
- ☐ Off-line gas analysis is recommended, if there are no process-related variations in gas composition.

8 References

[1] *EN16723-1:2016 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network, part 1: Specifications for biomethane for injection in the natural gas network,* Bruxelles, Belgium: European Committe on Standardisation, 2016

[2] *Review and selection of suitable measurement techniques for biomethane conformity assessment*, Report under A3.1.1 BiometCAP project.

[3] *Review of the requirements for laboratory and field validations of instruments*, Report under A2.1.3 BiometCAP project.

[4] Lohja Biogas Plant: Lohja biogas plant | Gasum

[5] Ribe Biogas Plant: Ribe BioGas A/S - Grøn energi gennem 40 år - Ribe Biogas A/S

[6] Solrød Bioenergy: Solrød Biogas - forvandler restprodukter til grøn energi